

Photochemistry of Os(η^6 -arene) complexes in low-temperature matrices: an infrared spectroscopic study of C–H bond activation

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Received 3 February 1995; in revised form 12 April 1995

Abstract

The photochemistry of a series of Os(η^6 -arene) complexes has been investigated in argon, methane and dinitrogen matrices with IR and UV/vis detection. The coordinatively unsaturated complex, Os(η^6 -C₆H₃Me₃)(CO), may be formed by photolysis of either Os(η^6 -C₆H₃Me₃)(CO)(H)₂ or Os(η^6 -C₆H₃Me₃)(CO)(CH₃)(H) in argon matrices. Irradiation of Os(η^6 -C₆H₃Me₃)(CO)(H)₂ in nitrogen matrices yields Os(η^6 -C₆H₃Me₃)(CO)(N₂). Activation of methane C–H bonds occurs on photolysis of either Os(η^6 -C₆H₃Me₃)(CO)(H)₂ or Os(η^6 -C₆H₃Me₃)(CO)₂ in methane matrices. The formation of Os(η^6 -C₆H₃Me₃)(CO)(CH₃)(H) is established by comparison of a complete IR spectrum with that of an authentic sample in the matrix. These studies provide extremely strong evidence that insertion into alkane C–H bonds is preceded by formation of the 16-electron intermediate Os(η^6 -C₆H₃Me₃)(CO). Vinyl hydride complexes Os(η^6 -C₆H₃Me₃)(L)(C₂H₃)(H) (L = CO, C₂H₄) and Os(η^6 -C₆H₆)(CO)(C₂H₃)(H) are formed on photolysis of the ethene complexes, Os(η^6 -C₆H₃Me₃)(L)(C₂H₄) and Os(η^6 -C₆H₆)(CO)(C₂H₄). The vinyl hydride products are established by comparison of the spectra from C₂H₄ and C₂D₄ complexes, and observation of OsH(D) and vinyl vibrations, as well as characteristic ν (CO) modes. The photoproducts of Os(η^6 -C₆H₃Me₃)(CO)(CH₂=CHMe) are probably *cis* and *trans* isomers of the propenyl hydride Os(η^6 -C₆H₃Me₃)(CO)(CH=CHMe)H.

Keywords: Osmium; Matrix isolation; Infrared spectroscopy; Photochemistry; Arene; Vinyl

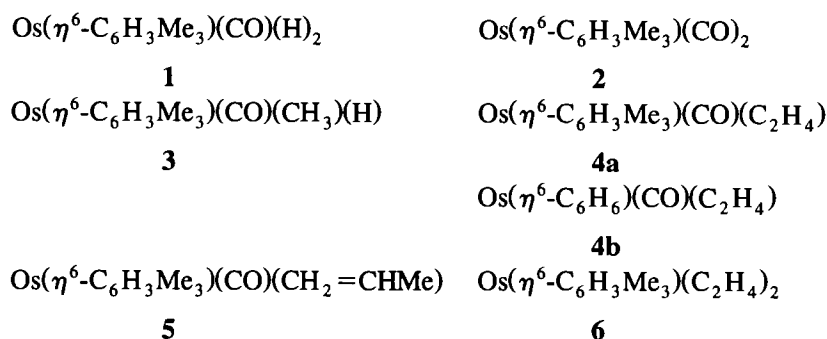
1. Introduction

The photochemistry of d⁸ complexes, M(η^5 -C₅R₅)(L)(L') (M = Rh, Ir; R = H, Me; L, L' = CO, C₂H₄, PMe₃) and Ir(η^5 -C₅H₅)(CO)(H)₂, in low-temperature matrices has proved a rich source of information about 16-electron fragments, M(η^5 -C₅R₅)(L), dinitrogen complexes, M(η^5 -C₅R₅)(L)(N₂), methane activation products M(η^5 -C₅R₅)(L)(CH₃)H, vinyl hydride complexes, M(η^5 -C₅R₅)(L)(C₂H₃)H, and about C–F bond activation [1–10]. These studies have provided key evidence that alkane activation reactions proceed in two steps: first CO, C₂H₄ or H₂ is dissociated from the starting complex generating a 16-electron fragment; subsequently, this fragment reacts with alkane to form the metal alkyl hydride product [4,8–10]. The matrix experiments have not only extended the range of com-

pounds which react with methane by oxidative addition, but also shown the limits of reactivity. Thus Rh(η^5 -C₅H₅)CO and Rh(η^5 -C₅H₅)(PMe₃) react but Rh(η^5 -C₅H₅)(C₂H₄) does not [4,8,10]. Matrix isolation also alerted us to the isomerisation of metal ethene complexes to metal vinyl hydride complexes, although the products subsequently proved amenable to study by NMR spectroscopy [5,7,8]. More recently, we have established both C–F bond activation of coordinated hexafluorobenzene, and C–H activation of methane at Rh(η^5 -C₅H₅)(PMe₃) by IR spectroscopy without the benefit of CO as a reporter ligand [4,6].

The synthesis of a family of Os(η^6 -arene) complexes containing carbonyl, ethene, alkyl, and hydride ligands [11–14] provides an excellent opportunity to develop new C–H activation chemistry and to investigate the mechanisms of these reactions by matrix isolation. In this paper we describe the photochemistry of a group of Os(η^6 -arene)(L₁)(L₂) (arene = 1,3,5-trimethylbenzene

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Scheme 1. The precursor complexes.

Table 1
IR data for some $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)$ complexes in argon matrices excluding 2120–1880 cm^{-1} region, $[\text{Os}] = \text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)$ ($\bar{\nu}/\text{cm}^{-1}$)

[Os](CO)L		[Os](C ₂ H ₄) ₂	[Os](CO)(X)H		Assignment
L = C ₂ H ₄	L = CO		X = H	X = CH ₃	
4a	2	6	1	3	
3034 w	3030 w	3028 m			$\nu(\text{CH}_2)$, ethene
2991 w	2990 w		2999 w	2999 w	$\nu(\text{CH})$, ring
2973 m	2975 w		2990 w		$\nu(\text{CH}_2)$, ethene
			2980 w	2982 w	$\nu(\text{CH}_3)$, ring
2966 m		2966 m			$\nu(\text{CH}_2)$, ethene
				2951 w	$\nu(\text{CH}_3)$
2933 w	2930 w	2925 m	2929 w	2932 w	$\nu(\text{CH}_3)$, ring
				2909 w	$\nu(\text{CH}_3)$
1525 w			1529 w	1525 w	$\nu(\text{CC})$, ring
1506 w		1508 w	1511 w	1508 w	
1460 w	1456 m	1465 m	1455 m	1455 m	
1453 m	1454 m	1455 m	1452 m	1452 m	$\delta(\text{CH}_3)$, ring
1444 m	1446 m	1444 m	1445 m	1447 m	$\delta(\text{CH}_3)$, ring
				1424 w	
1386 m	1387 m	1385 m	1387 m	1385 m	
1380 m	1382 m	1380 m	1381 m	1380 m	$\delta(\text{CH}_3)$, ring
1298 m	1299 w	1298 w	1299 m	1299 m	$\delta(\text{CH}_3)$, ring
				1222 m	$\delta(\text{CH}_3)$
1119 s		1154 s			$\nu(\text{CC})\text{-}\delta(\text{CH}_2)$
		1138 m			$\nu(\text{CC})\text{-}\delta(\text{CH}_2)$
1041 m	1039 m	1038 m	1041 m	1040 m	$\delta(\text{CH}_3)$, ring
1035 s			1039 m	1036 m	
1003 w	1007 w	1000 w	1003 w	1001 w	$\delta(\text{CH})$, ring
997 w	997 w				
980 w	981 w	986 w	986 w	979 w	$\delta(\text{CH})$, ring
971 w		975 w			$\rho(\text{CH}_2)$
954 w					$\rho(\text{CH}_2)$
861 w	885 w	872 w	857 w	840 w	
848 w	833 w		848 w	835 w	
			814 m	824 w	$\delta(\text{CH}_3)$
			811 s		$\delta(\text{OsH}_2)$
796 w		798 w			$\rho(\text{CH}_2)$
		784 m			
				780 m	$\delta(\text{OsH})$
			728 s		$\delta(\text{OsH}_2)$
			723 m		
				704 m	$\delta(\text{OsH})$
639 w	741 w		652 w	645 w	
595 m	615 w		605 m	583 m	$\delta(\text{OsCO})$ or $\delta(\text{OsH}_2)$
	574 w				
			559 w		$\delta(\text{OsH}_2)$
550 m	565 w		537 m	539 m	$\delta(\text{OsCO}) + \nu(\text{OsC})$
513 w			521 w	531 w	$\nu(\text{OsC})$
				515 m	$\nu(\text{OsCH}_3)$
460 m					$\nu(\text{OsC}_2)$

(mesitylene), benzene) and $\text{Os}(\eta^6\text{-arene})(\text{L})(\text{X})(\text{Y})$ complexes isolated in low-temperature matrices (Scheme 1). There is a clear parallel between the d^8 , $\text{M}^{(0)}(\eta^5\text{-C}_5\text{R}_5)\text{L}_2$ ($\text{M} = \text{Rh}, \text{Ir}$) and the d^8 , $\text{Os}^{(0)}(\eta^6\text{-arene})\text{L}_2$ compounds. The osmium complexes have the advantage over the rhodium and iridium complexes that a much more complete series of compounds is available, all of which can be sublimed and isolated in low-temperature matrices. Apart from our own preliminary communication of these results and related solution photochemistry [14], there has been one other study of C–H activation by $\text{Os}(\eta^6\text{-arene})(\text{carbonyl})$ complexes [15]. In the latter, Graham et al. show that photolysis of $\text{Os}(\eta^6\text{-C}_6\text{Me}_6)(\text{CO})(\text{H})_2$ in alkanes yields the alkyl hydride complexes, $\text{Os}(\eta^6\text{-C}_6\text{Me}_6)(\text{CO})(\text{R})(\text{H})$, and free hexamethylbenzene. Oxidative addition of arenes, but not of alkanes, has been observed at $\text{Os}(\eta^6\text{-arene})(\text{tri-alkylphosphine})$ and related ruthenium complexes [16].

2. Results

2.1. Photochemistry of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{H})_2$ (**1**) in argon and dihydrogen-doped argon matrices

IR data for the regions 3100–2120 and 1880–400 cm^{-1} for the $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)$ precursor complexes are listed in Table 1 with assignments. IR data for the $\nu(\text{CO})$ and $\nu(\text{OsH})$ region for complexes **1–3** are given

in Table 2. The IR spectrum of **1** isolated in an argon matrix shows an intense, split $\nu(\text{CO})$ mode at 1972, 1967 cm^{-1} . Two medium intensity bands are observed for **1** at 2078, 2059 and 2056 cm^{-1} which are assigned to the $\nu(\text{OsH})$ modes (Fig. 1(a)). A trace of free CO is present in the matrix (2148, 2138 cm^{-1}). Four prominent $\delta(\text{CH}_3)$ modes of coordinated mesitylene are observed at 1452, 1381, 1299 and 1041 cm^{-1} . These bands are found in similar positions in all the $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)$ complexes discussed here. The carbonyl and hydride bands in the IR and Raman spectra of solutions of **1** have already been assigned in detail by Polzer et al. [12]. Bands in the matrix spectra at 811, 728 and 559 cm^{-1} , with no counterparts in the spectra of **2** and **4**, are assigned as $\delta(\text{OsH}_2)$ modes in agreement with Ref. [12]. The band at 605 cm^{-1} was also assigned as an OsH_2 deformation in Ref. [12], although the comparison with the spectra of **2** and **4** suggests that it may be an OsCO deformation mode.

The UV/vis spectrum of **1**, a white complex, shows bands at 344, 296 and 268 nm in an argon matrix. Irradiation of the matrix with wavelengths $\lambda > 280$ nm has a negligible effect on the spectrum. However, broad band UV irradiation ($\lambda > 200$ nm, 120 min) reduces the intensities of the starting material bands by 40%, and four split $\nu(\text{CO})$ product bands appear at ca. 1989, 1946, 1919 and 1889 cm^{-1} (Table 2). There is very little photogenerated CO. Further periods (180 min, Fig. 1(b), and 420 min) of broad band irradiation increase

Table 2

IR data in the 2120–1880 cm^{-1} region for $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{H})_2$, **1**, $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}_3)(\text{H})$, **3**, and $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})_2$, **2**, in matrices and their photoproducts ($\bar{\nu}/\text{cm}^{-1}$)

Precursor/matrix								Assignment
1/Ar	1/N ₂	1/ ¹⁴ N ₂ / ¹⁵ N ₂	1/CH ₄	2/Ar	2/CH ₄	3/Ar	3/CH ₄	
	2108	2108						$\nu(\text{NN})$, 8
			2085 ^a		2085	2086	2090	$\nu(\text{OsH})$, 3
						2084	2080	$\nu(\text{OsH})$, 3
2078	2088	2086	2081					$\nu(\text{OsH})$, 1
2059	2080	2079	2057					$\nu(\text{OsH})$, 1
2056								$\nu(\text{OsH})$, 1
		2042						$\nu(\text{NN})$, 8-¹⁵N₂
1989				1989	1981	1989		$\nu_s(\text{CO})$, 2
					1976			$\nu_s(\text{CO})$, 2
1972	1967	1968	1971					$\nu(\text{CO})$, 1
1967	1964	1966	1967					$\nu(\text{CO})$, 1
			1961		1959	1962	1965	$\nu(\text{CO})$, 3
			1950		1951		1949	$\nu(\text{CO})$, 3
1946	1941	1941				1946		$\nu(\text{CO})$, Z
1943	1937					1943		$\nu(\text{CO})$, Z
							1933	photoproduct ^b
							1925	photoproduct ^b
1919			1909	1917	1909	1920		$\nu_s(\text{CO})$, 2
1917					1902			$\nu_s(\text{CO})$, 2
	1917	1917						$\nu(\text{CO})$, 8-¹⁴N₂
		1915						$\nu(\text{CO})$, 8-¹⁵N₂
1889						1885		$\nu(\text{CO})$, 7

^a Partially obscured by $\nu(\text{OsH})$ of **1**. ^b Product not identified.

the intensities of all four product bands at the expense of 1.

When the experiment is repeated with an argon matrix doped with 10% H₂, the product distribution is changed substantially. There is an increase in the amount of CO released, a decrease in the product bands at 1989, 1919 and 1889 cm⁻¹, but no change in the 1946 cm⁻¹ product. Neither in pure argon nor in the H₂/Ar matrix was there any conclusive evidence for regeneration of 1 on long-wavelength photolysis.

2.2. Photochemistry of 1 in dinitrogen matrices

The IR spectrum of 1 isolated in a dinitrogen matrix at 20 K shows a $\nu(\text{CO})$ band at 1967 cm⁻¹ and a band around 2080 cm⁻¹ with complex structure due to the $\nu(\text{OsH})$ modes. Brief UV photolysis ($\lambda > 200$ nm, 5 min) consumes ca. 15% of 1, and generates product bands at 2108 cm⁻¹ and 1917 cm⁻¹. A weak, split $\nu(\text{CO})$ band is also observed at 1941 cm⁻¹. Further periods of UV photolysis ($\lambda > 200$ nm, 45 and 105 min) reduce the intensities of the bands of 1, while the product bands at 2108 and 1917 cm⁻¹ grow further (Fig. 2(a), Table 2).

Irradiation of 1 in a mixed 55% ¹⁴N₂:45% ¹⁵N₂ matrix results in the appearance of two bands in the $\nu(\text{NN})$ stretching region, at 2108 cm⁻¹ and 2042 cm⁻¹, together with a single $\nu(\text{CO})$ band at 1917 cm⁻¹ (Fig.

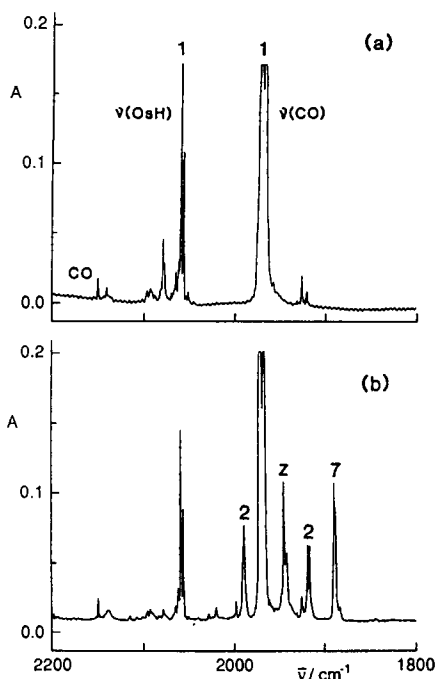


Fig. 1. (a) IR spectrum in the CO and OsH stretching regions of Os($\eta^6\text{-C}_6\text{H}_3\text{Me}_3$)(CO)(H)₂, 1, in an argon matrix at 20 K; (b) IR spectrum after UV irradiation ($\lambda > 200$ nm, 300 min) showing formation of Os($\eta^6\text{-C}_6\text{H}_3\text{Me}_3$)(CO)₂, 2, Os($\eta^6\text{-C}_6\text{H}_3\text{Me}_3$)(CO), 7 and Z.

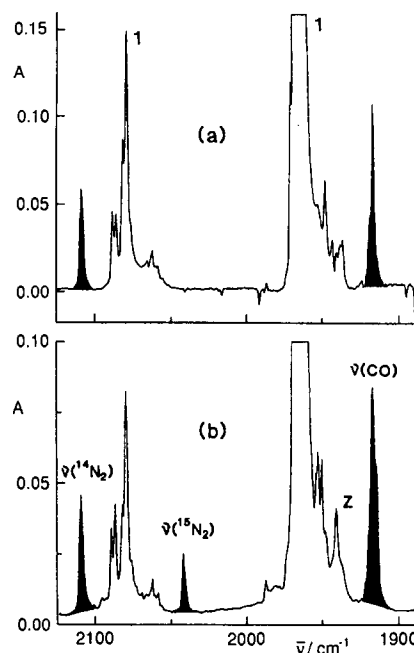


Fig. 2. IR spectra after photolysis of 1 in nitrogen matrices (a) after UV irradiation ($\lambda > 200$ nm, 45 min) of a ¹⁴N₂ matrix showing formation of Os($\eta^6\text{-C}_6\text{H}_3\text{Me}_3$)(CO)(N₂), 8 (bands shown in black); (b) after irradiation ($200 < \lambda < 360$ nm, 45 min) of a ¹⁴N₂:¹⁵N₂ (55:45) matrix showing formation of both the ¹⁴N₂ and ¹⁵N₂ isotopomers of 8, shown in black.

2(b)). The shift from 2108 cm⁻¹ to 2042 cm⁻¹ of 66 cm⁻¹ is appreciably smaller than the calculated isotopic shift of 71.3 cm⁻¹ for an isolated NN oscillator. A close examination of the $\nu(\text{CO})$ product band in Fig. 2(b) shows a shoulder at 1915 cm⁻¹ not present in the spectrum in ¹⁴N₂ (Fig. 2(a)), indicating that isotopic substitution does affect the CO-stretching mode slightly.

2.3. Photochemistry of 1 in methane and methane-doped argon matrices

Complex 1 shows broad $\nu(\text{OsH})$ and split $\nu(\text{CO})$ bands at ca. 2081 and 1971 cm⁻¹ when isolated in a methane matrix at 12 K. UV irradiation ($220 < \lambda < 360$ nm, 104 min) results in the loss of ca. 15% of 1, and $\nu(\text{CO})$ bands of product appear at 1961 and 1950 cm⁻¹. After further irradiation ($220 < \lambda < 360$ nm, 620 min) the bands of 1 are diminished by 50%, and the $\nu(\text{CO})$ bands at 1961 and 1950 cm⁻¹ have grown (Table 2). Virtually no photogenerated CO is detected in the matrix; the product bands found at 1946 and 1889 cm⁻¹ in argon have no counterpart in methane. A total of twelve new product bands are clearly observed in the region 1250–500 cm⁻¹. The existence of stable, sublimable Os($\eta^6\text{-C}_6\text{H}_3\text{Me}_3$)(CO)(CH₃)(H), 3, provides a good opportunity to test for C–H activation of methane. The comparison between the IR spectrum of the photoproduct of 1 in a methane matrix and the IR spectrum of 3,

deposited directly into a methane matrix, is illustrated in Fig. 3. Although the $\nu(\text{OsH})$ band of **3** is obscured by the $\nu(\text{OsH})$ bands of **1**, the excellent agreement of other bands of the photoproduct and authentic **3** (ca. 12 bands within 1 cm^{-1} of each other) provides unequivocal evidence that irradiation of **1** in solid methane results in formation of **3**.

When a similar experiment is performed in which **1** is isolated in an argon matrix doped with 5% methane, product bands are found at 1988, 1943 and 1916 cm^{-1} as in pure argon, but the 1889 cm^{-1} band was already absent at this concentration of methane. When the bands of **1** are subtracted out, the resulting difference spectrum reveals the bands of **3** at 1960, 1222, 1041 and 1001 cm^{-1} , once more in excellent agreement with direct deposition.

2.4. Photochemistry of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})_2$, **2**, in argon and methane matrices

The principal components of the $\nu(\text{CO})$ bands of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})_2$, **2**, are found at 1989 and 1917 cm^{-1} in an argon matrix. This yellow complex (λ_{max}

265 and 312 nm in Ar matrix) shows *no* net photochemistry in argon matrices at 20 K. UV photolysis with $\lambda > 285\text{ nm}$ (60 min), $220 < \lambda < 360\text{ nm}$ (120 min), and $\lambda > 200\text{ nm}$ (675 min) failed to induce any observable reaction. Such photostability was observed in the matrix photochemistry of $\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ in argon matrices [10], and was attributed to efficient in-cage recombination of photogenerated $\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})$ and CO.

The IR spectrum of **2** isolated in a methane matrix at 12 K shows very split symmetric and antisymmetric $\nu(\text{CO})$ modes at ca. 1981 and 1909 cm^{-1} . Weak $\nu(\text{CO})$ bands due to carbonyl-containing impurities are observed at 2070, 2031 and 2003 cm^{-1} . After photolysis with $\lambda > 280\text{ nm}$ (145 min), the bands of **2** drop to 70–75% of their original intensity. Product bands are observed at 2136 cm^{-1} (CO) and at 1959 and 1951 cm^{-1} , characteristic of the matrix-split $\nu(\text{CO})$ band of **3**. A weak, broad band at 2085 cm^{-1} is identified as the $\nu(\text{OsH})$ mode of **3** (Fig. 4, Table 2). An inspection of the ‘‘fingerprint region’’ ($1250\text{--}400\text{ cm}^{-1}$) reveals nine further bands which lie within 4 cm^{-1} of the bands of an authentic sample of **3** isolated in a methane matrix.

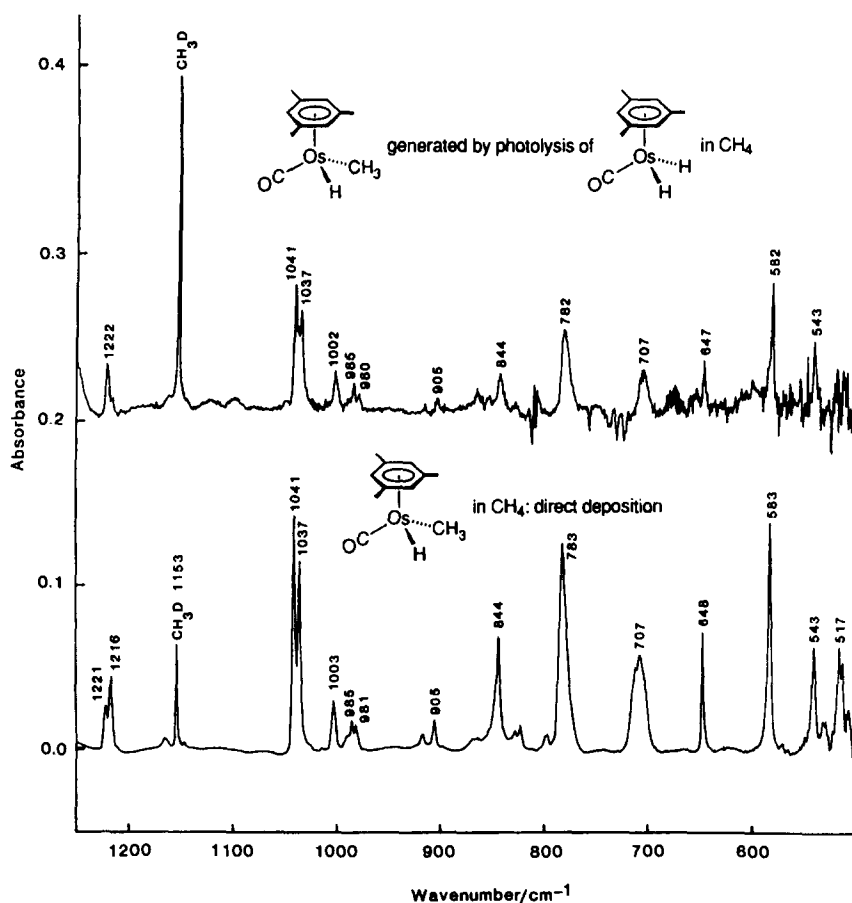


Fig. 3. Above: IR spectrum in the region below 1250 cm^{-1} obtained following irradiation ($\lambda > 200\text{ nm}$, 620 min) of **1** in a methane matrix. The residual bands of **1** have been subtracted from the spectrum completely. Below: IR spectrum of an authentic sample of **3** deposited directly into the methane matrix. The correspondence of the two spectra demonstrates that irradiation of **1** in solid methane yields **3**.

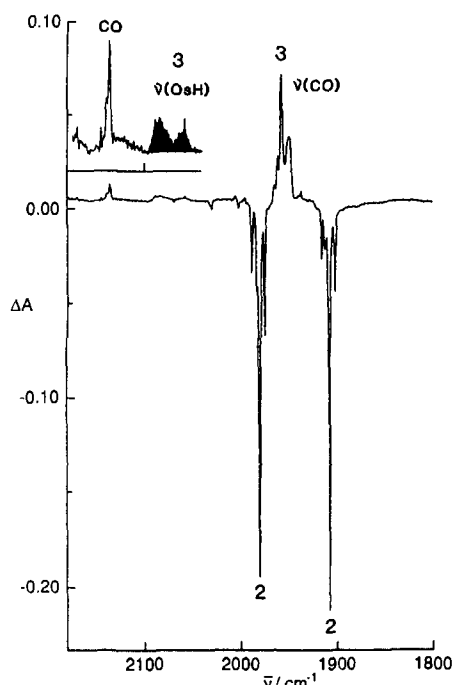


Fig. 4. IR difference spectrum after irradiation ($\lambda > 280$ nm, 145 min) of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})_2$, **2**, in a methane matrix showing formation of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}_3)\text{H}$, **3**, and loss of **2**. The inset shows a 7-times expansion of the high frequency region with the $\nu(\text{OsH})$ bands of **3** shown in black.

This comparison confirms beyond reasonable doubt that **2** is converted to **3** on photolysis in methane matrices.

2.5. Photochemistry of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}_3)\text{H}$, **3**, in argon and methane matrices

$\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}_3)\text{H}$, **3**, shows a single, intense $\nu(\text{CO})$ band at 1962 cm^{-1} and a medium intensity, split $\nu(\text{OsH})$ band at ca. 2085 cm^{-1} in an argon matrix. A small amount of free CO is present in the matrix. Assignments of IR bands in Tables 1 and 2 are based on comparisons between the related osmium complexes and comparisons of the metal methyl vibrations to the spectrum of iodomethane [18]. UV photolysis ($\lambda > 200$ nm, 195 min) consumes 20% of **3**, and $\nu(\text{CO})$ bands of product are observed at 1989, 1946, 1920 and 1885 cm^{-1} (Table 2). Free methane is readily identified by characteristic bands at 2910 and 1305 cm^{-1} , but there is no detectable photo-generated CO. Long wavelength photolysis ($\lambda > 416$ nm, 120 min) has a negligible effect, but further UV photolysis (either $220 < \lambda < 360$ nm or $\lambda > 200$ nm) increases the loss of **3**, with a concomitant increase in the intensities of the four product bands. A comparison with the spectra from irradiation of **1** in argon matrices shows that all four product $\nu(\text{CO})$ bands are common to the photoproducts of **3** and **1**.

The spectrum of **3** isolated in a methane matrix was

used to compare with those of the photoproducts of **1** and **2** in methane (Table 2). On photolysis ($\lambda > 200$ nm), CO is released, but new, unidentified carbonyl bands are also observed at 1933 and 1925 cm^{-1} .

2.6. Assignments of photoproducts of **1** and **3**

At this stage it is possible to make some further deductions about the photoproducts of **1** and **3**. The photoproducts observed in Ar matrices for the two precursors appear to be identical. The bands at 1989 and 1919 cm^{-1} are assigned to $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})_2$, **2**, by comparison to the spectrum of an authentic sample in an argon matrix. The bands at 1889 cm^{-1} and 1946 cm^{-1} must belong to two different species, since the latter persists in nitrogen and methane-doped argon matrices, while the former does not. Expulsion of H_2 from **1** is expected to cause a substantial shift to lower wavenumber because of the reduction in oxidation state. The 1889 cm^{-1} band does indeed lie 80 cm^{-1} below the $\nu(\text{CO})$ band of **1**, and is assigned to $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})$, **7** (cf. $\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{H})_2$, $\nu(\text{CO}) = 2022\text{ cm}^{-1}$, and its photoproduct $\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})$, $\nu(\text{CO}) = 1954\text{ cm}^{-1}$ [9]). The slight difference between the position of the band of **7** when generated from **1**, and its position when generated from **3**, reflects the perturbation by expelled H_2 or CH_4 . Identification of the product (labelled **Z**) associated with the band at 1946 cm^{-1} is postponed until the Discussion [17].

The principal photoproduct of **1** in nitrogen matrices is $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{N}_2)$, **8**, with $\nu(\text{NN})$ at 2108 and $\nu(\text{CO})$ at 1917 cm^{-1} . There is some mixing between the $\nu(\text{CO})$ and $\nu(^{15}\text{N}^{15}\text{N})$ modes of $^{15}\text{N}_2$ labelled **8**, with the result that the carbonyl band is shifted 2 cm^{-1} to lower wavenumber, and the dinitrogen band is at slightly higher wavenumber than expected. The weak feature at 1941 cm^{-1} corresponds to the band observed at 1946 cm^{-1} in argon matrices and is assigned as **Z**. The photoproduct of **1** in methane matrices has already been demonstrated to be the methyl hydride, **3**.

2.7. Photochemistry of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{C}_2\text{H}_4)$, **4a**, and $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{C}_2\text{D}_4)$, **4a-d**, in argon matrices

The IR spectrum of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{C}_2\text{H}_4)$, **4a**, in an argon matrix exhibits an intense $\nu(\text{CO})$ band at 1937 cm^{-1} , and a band at 1119 cm^{-1} due to the coupled $\nu(\text{CC})-\delta(\text{CH}_2)$ mode characteristic of the ethene ligand (Table 3). The UV/vis spectrum of **4a** in solid Ar shows maxima at 288 and 332 nm with a long tail extending into the visible, making it pale yellow. IR spectra after UV photolysis ($220 < \lambda < 360$ nm, 30, 90, 250 and 850 min) are represented by difference spectroscopy in Fig. 5. The $\nu(\text{CO})$ mode of **4a** decreases

Table 3

CO-stretching bands and IR bands due to coordinated ethene of $\text{Os}(\eta^6\text{-arene})(\text{CO})\text{L}$ (arene = mesitylene, benzene; L = C_2H_4 , C_2D_4) in Ar matrices ($\bar{\nu}/\text{cm}^{-1}$)

4a	4a-d ₄	4b	4b-d ₄	Assignment
3034 w	2287 m	3042 w	2293 m	$\nu(\text{CH})$
2973 m	2188 m	2983 m	2196 m	$\nu(\text{CH})$
2966 m	2157 m	2979 m	2168 m	$\nu(\text{CH})$
1937 vs	1934 vs	1943 vs	1942 vs	$\nu(\text{CO})$
1934 sh				
	1235 m		1244 w	$\nu(\text{CC}) + \delta(\text{CH}_2)$
	1063 w	1435 ^a	1064 w	$\delta(\text{CH}_2)$
1119 s	926 m	1128 m	929 m	$\nu(\text{CC}) - \nu(\text{CH}_2)$
971 w	782 w	972 w	780 w	$\rho(\text{CH}_2)$
954 w	712 w	955 w	711 w	$\rho(\text{CH}_2)$
796 m	579 w	788 ^a	577 w	$\rho(\text{CH}_2)$
569 w	540	552 vw	508 vw	$\nu(\text{OsC})$

^a Approximate, obscured by benzene ligand band.

steadily with photolysis time, and the ultimate conversion exceeds 75%. An intense, split $\nu(\text{CO})$ product band is detected with its principal component at 1978 cm^{-1} , to higher frequency of the starting material indicative of an Os(II) product (Table 4). At no time during the experiment is a band at 1889 cm^{-1} , assignable to **7**, formed, nor are there bands due to “free” ethene or “free” CO. A second product band is observed at 2060 cm^{-1} , which is consistent with a $\nu(\text{OsH})$ mode, (cf. the matrix IR spectra of **1** and **3**). The photoproduct has no distinct UV/vis absorption bands.

A matrix with almost twice the concentration of **4a** shows changes in the IR spectra in the carbonyl region on photolysis entirely analogous to those observed in the more dilute experiments. The vibrational signature

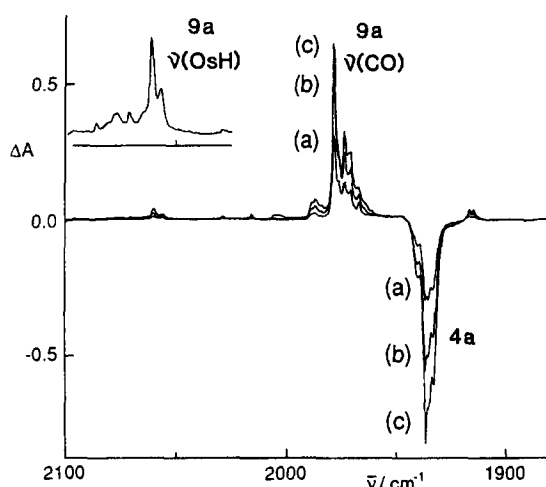


Fig. 5. IR difference spectra after irradiation ($\lambda > 200$ nm) of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{C}_2\text{H}_4)$, **4a**, in an argon matrix showing the depletion of the $\nu(\text{CO})$ band of **4a** and growth of the $\nu(\text{CO})$ band of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{C}_2\text{H}_3)\text{H}$, **9a**, after irradiation ($220 < \lambda < 360$ nm) for (a) 30, (b) 90, (c) 250 min. The $\nu(\text{OsH})$ band of **9a** is shown as inset with 30-times ordinate expansion measured after the second period of photolysis.

Table 4

IR data for $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{C}_2\text{H}_3)\text{H}$, **9**, and $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{C}_2\text{D}_3)\text{D}$, **9a-d₄** ($\bar{\nu}/\text{cm}^{-1}$), formed by photolysis of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{ethene})(\text{CO})$, **4a** and **4a-d₄** in matrices: assignments are listed for the protio compound

Photoproduct/matrix				Assignment
9a/Ar	9a-d ₄ /Ar	9a/N ₂	9a/CH ₄	
2060	1493 ^a	2061	2083 br	$\nu(\text{OsH})$
2057	1477			
1978	1979	1970	1975	
1974	1974	1965	1966	$\nu(\text{CO})$
1971		1963	1961	
		1961	1956	
1565	1512 ^a	1560		$\nu(\text{CC})$, vinyl
		1558		
1372	1044	1372	^b	$\delta(\text{CH}_2)$, vinyl
1298	1298	1301	^b	$\delta(\text{CH}_3)$, ring
1257	990	1266	^b	$\delta(\text{CH})$, vinyl
		1257		
1042	1041	1043	1038	$\delta(\text{CH}_3)$, ring
1009				$\rho(\text{CH})$, vinyl
887	705	887	880	$\delta(\text{OsH})$
880		874		
840	839			
798				
775	616	780	780	$\delta(\text{OsH})$
798		777		
720		713		
649	650	649		$\nu(\text{OsC})$, carbonyl
583	585	585	584	$\delta(\text{OsC})$, carbonyl

^a The $\nu(\text{OsD})$ and $\nu(\text{CC})$ modes are likely to mix considerably.

^b Obscured by methane absorptions.

of a metal vinyl group is immediately recognisable from the product spectrum in the 1600–1200 cm^{-1} region ($\nu(\text{CC})$, $\delta(\text{CH}_2)$ and $\delta(\text{CH})$ vibrations at 1565, 1372 and 1257 cm^{-1} ; Table 4) by comparison with the spectra of $\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{L})(\text{C}_2\text{H}_3)\text{H}$ (L = CO, PMe_3 ; M = Rh, Ir) [5,7]. We conclude that the photoproduct is $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}=\text{CH}_2)\text{H}$, **9a**.

The IR spectrum in an argon matrix of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{C}_2\text{D}_4)$, **4a-d₄** (ethene ligand deuterated to > 98%), shows an intense $\nu(\text{CO})$ band at 1934 cm^{-1} , shifted 3 cm^{-1} to low wavenumber compared to **4a**. Comparison of the spectra of **4a** and **4a-d₄** leads to an assignment of most modes of coordinated ethene (Table 3). UV irradiation ($\lambda > 200$ nm, 30 min) consumes 25% of **4a-d₄**, and an intense product $\nu(\text{CO})$ band (absorbance 0.8) is formed at 1979 cm^{-1} . Even with 20-fold scale expansion, no bands are observed in the $\nu(\text{OsH})$ region. Further irradiation with wavelengths $\lambda > 200$ nm increases the conversion of **4a-d₄** to the photoproduct, with the final yield exceeding 60%. The absence of free C_2D_4 and of the $\nu(\text{CO})$ mode of **7** demonstrates that ethene is not released in the reaction. In the region 1600–900 cm^{-1} the $\nu(\text{CC})$ band characteristic of **9a** at 1565 cm^{-1} is shifted to lower frequency upon deuteration. The product bands observed at 1512

and 1493 cm^{-1} are assigned to the $\nu(\text{CC})$ and $\nu(\text{OsD})$ stretches respectively of the $\text{Os}(\text{C}_2\text{D}_3)\text{D}$ group, although mixing of these modes is probable. The $\delta(\text{CH}_2)$ and $\delta(\text{CH})$ modes of **9a**, at 1372 and 1257 cm^{-1} , are also shifted to lower frequencies upon deuteration, viz. to 1044 and 990 cm^{-1} respectively. Two further bands of **9a**, detected at 887 and 775 cm^{-1} , are shifted to 705 and 616 cm^{-1} upon deuteration (Table 4). These bands are too low to be associated with $\text{CH}(\text{D})$ vibrations, and are assigned as $\delta(\text{OsH}/\text{OsD})$ bending modes. Thus, the matrix photochemistry of **4a–d**₄ provides convincing evidence for insertion into the C–D bond of coordinated ethene to form $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{C}_2\text{D}_3)\text{D}$.

2.8. Photochemistry of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{C}_2\text{H}_4)$, **4a**, in nitrogen and methane matrices

The IR spectrum of **4a** isolated in a nitrogen matrix shows a $\nu(\text{CO})$ band split into three components of roughly equal intensity, at 1931 , 1928 , and 1927 cm^{-1} . Irradiation ($\lambda > 200\text{ nm}$, 45 min) reduces the intensities of the bands of **4a** by 35%. Product bands are observed for **9a** (Table 4) and a small amount of liberated CO, but no “free” ethene is detected. In addition, weak, unassigned bands are observed at 2106 , 2092 , 2079 and 1998 cm^{-1} . Since the intensities of these bands are similar to the intensity of the $\nu(\text{OsH})$ band of **9a**, they represent minor pathways.

The IR spectrum of **4a** isolated in a methane matrix shows an intense, split $\nu(\text{CO})$ band with major components at 1934 and 1920 cm^{-1} . UV irradiation ($220 < \lambda < 360\text{ nm}$, 50 min) consumes 50% of **4a**, and a split $\nu(\text{CO})$ band is produced with a major component at 1956 cm^{-1} (Table 4). A broad, weak band is observed at 2083 cm^{-1} . Since solid methane absorbs strongly between 1580 and 1250 cm^{-1} , detection of any vinyl modes of the product is precluded. This spectroscopic evidence is consistent with formation of either **9a** or **3**. However, there is no detectable free ethene (952 cm^{-1}) as would be expected if the product is **3**. When the experiment is repeated with **4a–d**₄ in CH_4 , no product band is observed in the $\nu(\text{OsH})$ region. All the observations indicate that the major product is **9a**, but the formation of small amounts of **3** cannot be ruled out.

2.9. Photochemistry of $\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})(\text{C}_2\text{H}_4)$, **4b**, and $\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})(\text{C}_2\text{D}_4)$, **4b–d**₄, in argon matrices

The IR spectrum of the benzene complex $\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})(\text{C}_2\text{H}_4)$, **4b**, isolated in an argon matrix shows an intense $\nu(\text{CO})$ band at 1943 cm^{-1} , to slightly higher frequency of **4a**. The $\nu(\text{CC})$ – $\delta(\text{CH}_2)$ mode of the coordinated ethene is observed as a split band at 1128 , 1126 cm^{-1} (Table 3). Photolysis ($220 < \lambda < 360\text{ nm}$, 150 min) consumes 20% of **4b**, and a $\nu(\text{CO})$ band

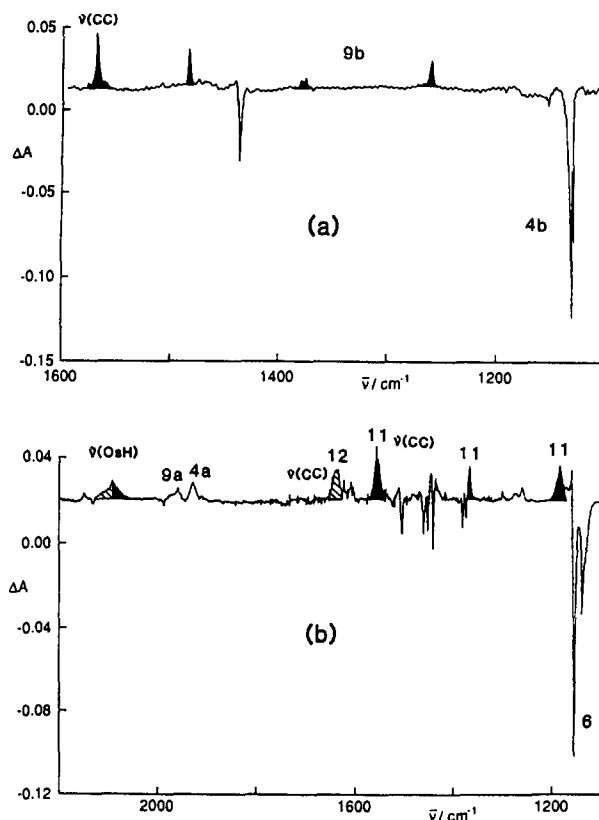


Fig. 6. (a) IR difference spectra after irradiation ($\lambda > 200\text{ nm}$, 270 min) of $\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})(\text{C}_2\text{H}_4)$, **4b**, in an argon matrix showing formation of the characteristic vinyl modes of **9b** and the depletion of the bands of **4b**. The assignment of the vinyl bands is given in Table 5. (b) IR difference spectra after irradiation ($\lambda > 200\text{ nm}$, 695 min) of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{C}_2\text{H}_4)_2$, **6**, in an argon matrix showing the growth of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3\text{H})$, **11**, (bands shown in black), and of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{C}=\text{CH}_2)(\text{H})_2$, **12**, (bands shaded). In addition, the presence of CO impurity results in the formation of traces of **4a** and **9a**. Notice the difference in the wavenumber scales of a and b.

of the product is observed 43 cm^{-1} to higher wavenumber of the starting material at 1986 cm^{-1} in an exactly similar manner to the mesitylene complex, **4a**. After further periods of irradiation the conversion reaches 60%. A new, split band is observed in the $\nu(\text{OsH})$ region at 2059 cm^{-1} . Changes in the IR spectrum at lower frequencies (Fig. 6(a), Table 5) show the characteristic bands of a metal vinyl group. There is no detectable free ethene in the matrix. We conclude that irradiation of **4b** in argon matrices yields $\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})(\text{C}_2\text{H}_3)\text{H}$, **9b**.

The IR spectrum of **4b–d**₄ (> 98% deuteration) isolated in an argon matrix shows an intense $\nu(\text{CO})$ band at 1942 cm^{-1} . Ethene modes are listed and assigned in Table 3. Upon UV photolysis ($\lambda > 200\text{ nm}$, 300 min) the bands of **4b–d**₄ decrease in intensity and an intense $\nu(\text{CO})$ band is formed at 1987 cm^{-1} , demonstrating the formation of **9b–d**₄. No free C_2D_4 is seen in the matrix. Deuteration affects the bands of the

Table 5

IR data for $\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})(\text{C}_2\text{H}_3)\text{H}$, **9b**, and $\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})(\text{C}_2\text{D}_3)\text{D}$, **9b-d₄** formed by photolysis of $\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})(\text{ethene})$, **4b**, in argon matrices ($\bar{\nu}/\text{cm}^{-1}$): assignments are listed for the proto compound

9b	9b-d₄	Assignment
2059	1481 ^a	$\nu(\text{OsH})$
2057	1474	
1986	1987	$\nu(\text{CO})$
1567	1507 ^a	$\nu(\text{CC})$, vinyl
	1496	
1483	1481	$\nu(\text{CC})$, benzene
1376	1044	$\delta(\text{CH}_2)$, vinyl
1256	989	$\delta(\text{CH})$, vinyl
886	702	$\delta(\text{OsH})$
788		$\delta(\text{OsH})$
680	679	$\nu(\text{OsC})$, carbonyl
	571	$\delta(\text{OsC})$, carbonyl

^a The $\nu(\text{OsH})$ and $\nu(\text{CC})$ modes are likely to mix considerably.

osmium vinyl hydride group in a similar manner to **4a** (Table 5).

2.10. Photochemistry of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}_2=\text{CHMe})$, **5**, in argon matrices

The IR spectrum of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}_2=\text{CHMe})$, **5**, shows a split $\nu(\text{CO})$ band (1932, 1931, 1928 cm^{-1}). We presume that there are contributions to this spectrum from conformers with the propene methyl group pointing either towards or away from the ring. UV photolysis (295–376 nm) depletes the bands of **5** progressively (reaching 50% conversion after 8 h irradiation) and gives way to a product band at 1977 cm^{-1} with a series of shoulders stretching down to 1963 cm^{-1} . Additionally, very weak bands are formed at 2077, 2044 and 2013 cm^{-1} and a trace of CO is released (2138 cm^{-1}). In the low frequency region propene should be revealed by a very intense band at 908 cm^{-1} [19], but none is observed. The analogy with the photochemistry of **4**, the shift of the $\nu(\text{CO})$ band of 30 cm^{-1} to high wavenumber of the precursor and the product band in the $\nu(\text{OsH})$ region (2077 cm^{-1}) all point to the formation of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}=\text{CHMe})\text{H}$, **10**, as has been observed in solution [20]. This product could be formed with osmium *cis* or *trans* to the methyl groups, and with the propenyl group in different rotational conformations. A further possible product with similar vibrational characteristics would be $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\eta^1\text{-CH}_2\text{-CH}=\text{CH}_2)\text{H}$. For comparison, we consulted spectra of halopropenes recorded in the gas phase [21]. The principal difference between their spectra lies in the region 1350–1200 cm^{-1} : *cis*-1-chloropropene 1322 cm^{-1} (vs), *trans*-1-chloropropene, 1247 cm^{-1} (vs), *cis*-1-bromopropene 1312 cm^{-1} (vs), *trans*-1-bromopropene 1225 cm^{-1} (vs), 3-bromopropene (allyl bromide) 1213 cm^{-1} (vs). Product **10** shows features at 1322, 1301 and 1217

cm^{-1} consistent with formation of both *cis*- and *trans*-**10**. The η^1 -allyl complex (see above) could also be present.

The release of some CO on photolysis of **5** indicates that a small amount of non-carbonyl product is formed. Since one candidate for such a product, $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\eta^3\text{-exo-allyl})\text{H}$, is available [22], we isolated this complex in an argon matrix. Its $\nu(\text{OsH})$ band appears at 2035 cm^{-1} . The only other bands of reasonable intensity which lie away from mesitylene vibrations are at 925, 910 and 851 cm^{-1} , the latter being by far the most intense. Since there is no sign of the 851 cm^{-1} band in the product spectrum we conclude that $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\eta^3\text{-exo-allyl})\text{H}$ is not formed. (The *endo* isomer remains a possibility, although unlikely.)

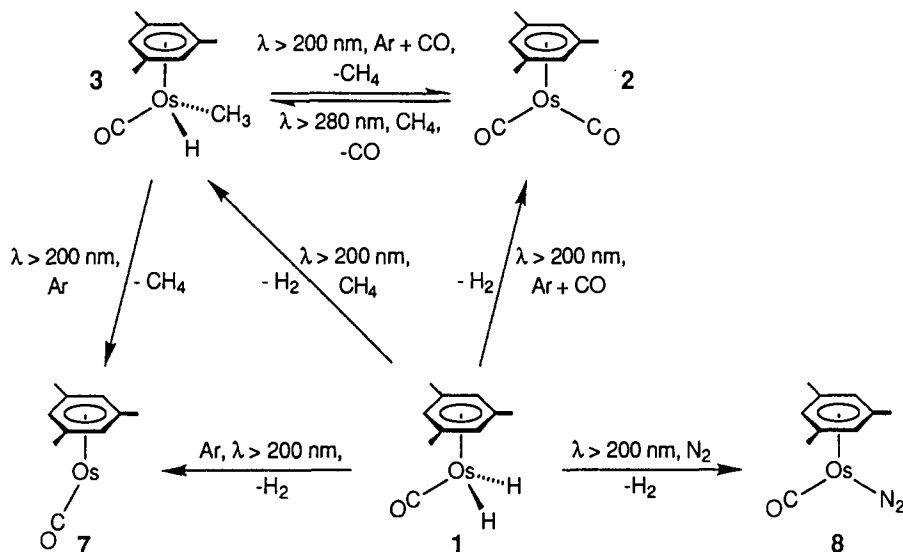
2.11. Photochemistry of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{C}_2\text{H}_4)_2$, **6**, in argon matrices

The IR spectrum of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{C}_2\text{H}_4)_2$, **6**, isolated in an argon matrix shows two bands at 1154 and 1138 cm^{-1} , characteristic of the two $\nu(\text{CC})$ – $\delta(\text{CH}_2)$ modes of a bis(ethene) complex. After irradiation ($\lambda > 200$ nm, 110 min), the intensities of the bands of **6** decrease by 30% (Fig. 6(b)). Product bands are observed at 2093 (broad, weak), 1557, 1370 and 1264 cm^{-1} which are readily assigned to a $\nu(\text{OsH})$ stretch and $\nu(\text{CC})$, $\delta(\text{CH}_2)$ and $\delta(\text{CH})$ vibrations of a vinyl group. These spectra provide good evidence, therefore, for the formation of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{H}$, **11** (Table 6). A small amount of free ethene is detected in the matrix at 952 cm^{-1} . In addition, a trace of CO in the matrix results in weak $\nu(\text{CO})$ peaks from **4a** and **9** at 1930 and 1960 cm^{-1} respectively. Further irradiation ($\lambda > 200$ nm, 585 min) reduces the amount of starting material still further, and more free ethene is generated, yet the intensities of the bands of the osmium vinyl group do not increase noticeably. The $\nu(\text{OsH})$ band at 2093 cm^{-1} and a band at 1640 cm^{-1} increase in intensity (Fig. 6(b)). The similarity to the matrix photochemistry of $\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4)_2$ is evident [7]; the vinylic C–H activation of one ethene ligand to form **11**

Table 6

IR data for the photoproducts of **6** in argon matrices, $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{H}$, **11**, and $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CCH}_2)(\text{H})_2$, **12** ($\bar{\nu}/\text{cm}^{-1}$)

11	12	Assignment
2093	2093	$\nu(\text{OsH})$
	1640	$\nu(\text{CC})$, vinylidene
1557		$\nu(\text{CC})$, vinyl
1370		$\delta(\text{CH}_2)$, vinyl
1264		$\delta(\text{CH})$, vinyl
1186		$\nu(\text{CC})$ – $\delta(\text{CH}_2)$, ethene
861		$\delta(\text{OsH})$
772		$\delta(\text{OsH})$
688		



Scheme 2. Matrix photochemistry of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{H})_2$, **1**, $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})_2$, **2**, and $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}_3)(\text{H})$, **3**.

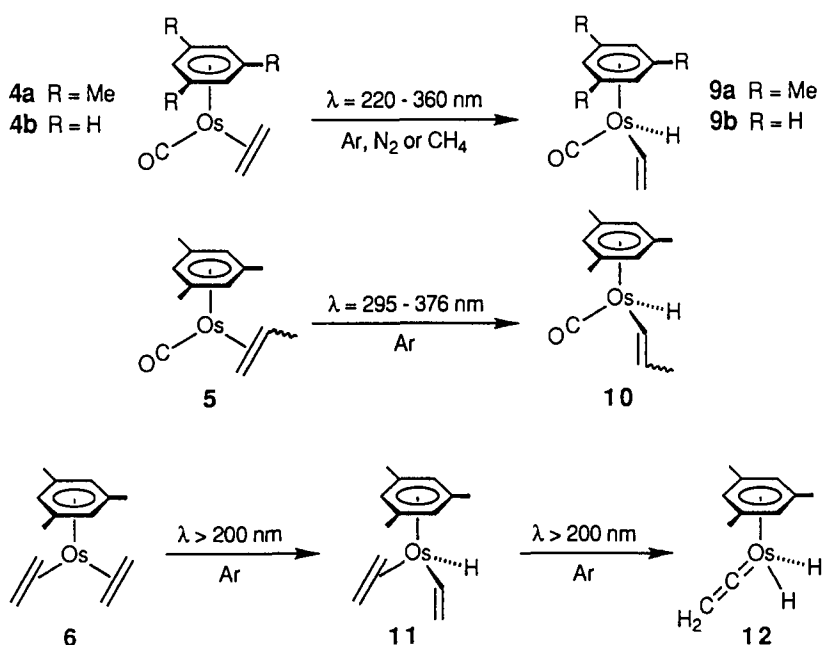
is almost certainly followed by formation of the vinylidene dihydride complex $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{C}=\text{CH}_2)(\text{H})_2$, **12**. The band at 1640 cm^{-1} which is assigned as $\nu(\text{CC})$ of the vinylidene group occurs 41 cm^{-1} below that of the $\text{Ir}(\eta^5\text{-C}_5\text{H}_5)$ analogue.

3. Discussion

3.1. Overview

The photochemistry of some $\text{Os}(\eta^6\text{-arene})$ complexes in matrices has revealed a web of reactions linking

carbonyl dihydride (**1**), carbonyl methyl hydride (**3**), dicarbonyl (**2**), carbonyl dinitrogen (**8**), carbonyl ethene (**4**) and carbonyl vinyl hydride (**9**) complexes (Schemes 2 and 3). All these species satisfy the 18-electron rule; in addition the 16-electron $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})$ can be detected. Since the CO-stretching bands carry information about the effects of different ligands, we list their principal values and the resulting force constants in Table 7. The primary photoprocesses on irradiation of **1** and **3** in argon matrices are reductive elimination of H_2 and CH_4 respectively to form $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})$, **7**, with $\nu(\text{CO})$ at 1889 cm^{-1} . Some $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})_2$, **2**, is also formed by reaction with a little carbon monoxide impurity present in the argon



Scheme 3. Matrix photochemistry of ethene and propene complexes, **4–6**.

Table 7
Energy-factored CO stretching force constants for $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{CO}$ complexes in Ar matrices

Complex	$\nu(\text{CO})^a$ (cm^{-1})	Stretching force constant (N m^{-1})
1	1970	1568
2	1989 (sym)	1541 ^b
	1917 (antisym)	
3	1962	1555
4a	1937	1516
4b	1943	1525
5	1928	1502
7	1889	1441
8	1917 ^c	1484
9	1978	1580
10	1977	1579

^a Principal component, or average value. ^b Interaction force constant = 57 N m^{-1} . ^c In nitrogen matrix.

matrix. A third carbonyl product, **Z**, with $\nu(\text{CO})$ at 1946 cm^{-1} is also observed (see below). The photoejection of CO does not appear to be a significant reaction, since only very small quantities of free CO are present. The cage effect imposed by the matrix completely suppresses loss of arene, a reaction which has complicated both our [14] and Graham's [15] investigations of solution chemistry of $\text{Os}(\eta^6\text{-arene})$ complexes. When the matrix is doped with H_2 , formation of **2** is almost eliminated and formation of **7** is reduced, but **Z** is still formed. Under these conditions more CO is released, indicating that CO is probably recombining in the cage in pure argon matrices. Upon irradiation of **1** in nitrogen matrices, $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})$ is replaced by the new dinitrogen complex $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{N}_2)$, **8**, but **Z** is still formed.

3.2. Reaction with methane

Irradiation of **1** in methane matrices also leads to photodissociation of H_2 , but $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})$ is replaced by the C–H activation product **3**. Even in argon matrices doped with 5% methane, **3** is formed from **1** with no trace of **7**, but under these conditions **Z** is still formed. Irradiation of **2** in methane matrices results in photodissociation of CO and also yields **3**. Changes in the $\nu(\text{CO})$ region are very similar in nature to those described previously for $\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})$ complexes [8–10]. In the osmium case, however, conclusive proof for the formation of $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}_3)(\text{H})$, **3**, is found in the comparison of spectra of **3** formed photochemically from either **1** or **2** in methane matrices with an authentic sample of **3** deposited directly into methane. The proposed mechanism for C–H activation of methane, by photodissociation of H_2 or CO from a half-sandwich complex and subsequent insertion of the 16-electron intermediate into methane, now rests on a much more secure foundation.

By now, there is evidence for the formation of metal methane complexes (i.e. coordination without C–H bond cleavage) from several different sources. Methane complexes have been formed in matrices by photolysis of d^6 metal carbonyls in solid methane [23,24], by deposition of metal atoms in methane [25,26], by similar deposition of RhH_2 [27] and by photolysis of cobalt methyl hydride in a hydrogen-doped argon matrix [28]. In solution, striking evidence for methane complexes has come from isotopic exchange of $\text{L}_n\text{M}(\text{CH}_3)\text{D}$ [29–32]. In the gas phase the ion $[\text{Mn}(\text{CO})_5(\text{CH}_4)]^+$ has been observed [33]. Calculations on oxidative addition reactions (e.g. of $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)\text{CO}$) have also provided evidence for a potential minimum corresponding to a methane complex on the pathway to oxidative addition [34–40]. Closely related experimental evidence has come from studies of the reactivity of other alkanes [41].

It might have been expected that a methane complex would be formed prior to the metal methyl hydride on irradiation of complexes such as **1** and **2** in methane matrices. Analogous evidence is indeed forthcoming in the reactions of metal atoms, most strikingly in the photochemical interconversion of $\text{Co}(\text{CH}_4)$ and $\text{CoH}(\text{CH}_3)$ [28]. Neither in the present osmium complexes nor in the half-sandwich complexes studied previously (see introduction) can stepwise conversion first to a methane complex and then to a metal methyl hydride be demonstrated. Any evidence for methane complexes in these systems is at best inconclusive [9]. (We have also attempted to form methane complexes or metal methyl hydrides by photolysis of precursors in methane-doped matrices followed by annealing, but without success.) The most plausible explanation of the photolysis reaction is that the excess energy released following light absorption by **1** or **2** is sufficient to carry the methane complex over the potential barrier to the methyl hydride before the system returns to thermal equilibrium (a 300 nm photon has an energy of ca. 400 kJ mol^{-1} , far exceeding the metal–CO bond energy). Similarly, excess energy is released on photolysis of the methyl hydride, **3**. If that energy is dissipated rapidly, **3** is regenerated within the cage. If the energy is dissipated slowly, the methane diffuses out of the cage and the 16-electron fragment, **7**, is observed. We point to three results which are consistent with our postulates. Firstly, the most recent calculations place the methane complex $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{CH}_4)$ 32 kJ mol^{-1} below $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO}) + \text{CH}_4]$ and 23 kJ mol^{-1} below the transition state to formation of the methyl hydride. Thus there is no point on the trajectory with energy above the starting $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)\text{CO} + \text{CH}_4]$ [39]. Secondly, the experimental determination of the barrier (ΔH^\ddagger) to conversion of $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{cyclohexane})$ to the oxidative addition product is 19 kJ mol^{-1} , consistent with theory [41]. Thirdly, we note that $\text{Co}(\text{CH}_3)\text{H}$ is sensitive to relatively low energy radiation ($\lambda > 400$

nm) [28], whereas $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}_3)(\text{H})$ reacts only on high energy irradiation ($\lambda > 200$ nm), yielding $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})$, but no methane complex.

3.3. Identity of **Z**

The assignment of the product **Z**, with $\nu(\text{CO})$ at 1946 cm^{-1} in argon matrices, is less certain. Increasing the dilution of **1** or **3** in the argon matrix by a factor of three has only a marginal effect on the relative intensity of the $\nu(\text{CO})$ band of **Z**. Moreover, the sharpness of the IR bands of both the starting material and products indicates good isolation. Complex **Z** therefore appears to be mononuclear. The band of **Z** formed from **1** is coincident with that formed from **3**, representing a shift to low frequency relative to the precursor of 26 cm^{-1} for **1** and 16 cm^{-1} for **3**. The persistence of **Z** in dinitrogen matrices weighs against 16-electron species, whether formed by hydrogen migration from metal to ring, or arene decoordination. An 18-electron dihydrogen complex, $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\eta^2\text{-H}_2)$, would appear to be an alternative but the $\nu(\text{CO})$ bands of known dihydrogen complexes $\text{ML}_n(\text{H}_2)$ are close to the corresponding dinitrogen complexes $\text{ML}_n(\text{N}_2)$ [42–44], whereas the $\nu(\text{CO})$ mode of **Z** is ca. 30 cm^{-1} to high frequency of that of **8**. We would also need to postulate an $\eta^2\text{-CH}_4$ with a coincident $\nu(\text{CO})$ band formed from **3**, which seems implausible. A cyclometallated complex with an 18-electron configuration could be formed by insertion into the C–H bond of a ring methyl group (c.f. ‘tucked-in’ $\text{C}_5\text{Me}_4\text{CH}_2$ complexes derived from $\eta^5\text{-C}_5\text{Me}_5$ [45,46]). However, the evidence from preliminary experiments on $\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})(\text{H})_2$ indicates that a product analogous to **Z** is formed although there are no methyl groups on the ring [17]. A 17-electron species offers a more satisfactory alternative for **Z**. Loss of a hydrogen atom from **1** or a methyl radical from **3** would yield the same radical species $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})\text{H}$ which is expected to be stable with respect to dinitrogen or dihydrogen and have a $\nu(\text{CO})$ band to lower frequency of those of **1** and **3**, but above those of **7** and **8**. Loss of hydrogen atoms is not usually observed from dihydride complexes [47], but has been observed from monohydride complexes, $\text{Re}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}$, $\text{Mn}(\text{CO})_5\text{H}$ and from $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{H}$ [48–50]. In the latter case, the $\nu(\text{CO})$ band of $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})$ in Ar matrices lies 17 cm^{-1} below that of $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{H}$ [50]. However, loss of CH_3 from **3** is less likely.

Related photochemistry was observed with $\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{H}_2$ in argon matrices [9]. The lowest frequency product band was assigned to the unsaturated $\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})$. A dihydrogen complex or the 16-electron migration product, $\text{Ir}(\eta^5\text{-C}_5\text{H}_6)(\text{CO})\text{H}$, were suggested for the higher frequency band. A related

species observed in methane matrices was suggested to be an $\eta^2\text{-CH}_4$ complex or migration product, $\text{Ir}(\eta^4\text{-C}_5\text{H}_6)(\text{CO})\text{Me}$. The arguments above suggest that radical species could also be considered. Unfortunately, proof of the structure of **Z** and its analogues is still lacking.

3.4 Vinylic C–H bond activation

Irradiation of **4a** in argon matrices leads not to ethene or CO loss, but to the formation of a vinylic C–H activation product $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{C}_2\text{H}_3)(\text{H})$, **9a**. An analogous $\text{Os}(\eta^6\text{-C}_6\text{H}_6)$ species is formed from **4b**. These vinyl hydride complexes are characterised by OsH stretching modes and the three conspicuous vibrations of a vinyl group, established unambiguously by investigation of the C_2D_4 analogues of **4a** and **4b** (Scheme 3). The vinyl hydride, **9a**, remains the major product of **4a** even in reactive methane matrices, showing that the reaction is best described as an intramolecular isomerisation. This behaviour contrasts with that of $\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{C}_2\text{H}_4)$, which yields a 50:50 mixture of methyl hydride and vinyl hydride complexes on photolysis in a methane matrix [5]. The bis(ethene) complex, $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{C}_2\text{H}_4)_2$, **6**, undergoes a similar photoreaction to **4a** in the first stage, but proceeds in a second step to form the vinylidene complex, $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{C}=\text{CH}_2)(\text{H})_2$ (Scheme 3). This reaction is exactly analogous to that of $\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4)_2$ [7]. The matrix photochemistry of the propene complex $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}_2=\text{CHMe})$, **5**, is harder to establish unambiguously. Activation of the alkene C–H bond occurs, but it is not possible through IR spectroscopy to rule out accompanying hydrogen migration to form an allyl hydride complex, $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\eta^1\text{-CH}_2\text{-CH}=\text{CH}_2)\text{H}$. However, taken together with the evidence of NMR spectroscopy in solution [20], it seems likely that the only products are the *cis*- and *trans*-propenyl complexes, $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})(\text{CH}=\text{CHMe})\text{H}$. In contrast, matrix photolysis of $\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHMe})$ yields the η^3 -allyl hydride, $\text{Fe}(\text{CO})_3(\eta^3\text{-CH}_2\text{CHCH}_2)\text{H}$, via $\text{Fe}(\text{CO})_3(\text{CH}_2=\text{CHMe})$ [51].

We have also studied the reactivity of several of the $\text{Os}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)$ complexes in solution with NMR spectroscopy following low temperature photolysis. Preliminary results on the formation of **9a** from **4a** and the formation of aryl hydride complexes from **1** have been reported already [14]. Taken together with Graham’s demonstration of alkane activation by $\text{Os}(\eta^6\text{-C}_6\text{Me}_6)(\text{CO})$ complexes [15], it is evident that the matrix photochemistry and solution photochemistry are extremely similar, but the matrix suppresses the loss of arene.

4. Experimental

Samples of complexes **1–6** were synthesised by published methods [11–14] and purified by sublimation prior to use. The matrix isolation apparatus has been described previously [8]. In brief, the matrices were deposited on a CsI window (experiments with IR detection only) or a BaF₂ window (experiments with combined IR and UV/vis detection) cooled by a closed-cycle refrigerator. Matrices were deposited continuously at 20 K (argon, dinitrogen), 25 K (CH₄), 12 K (Ar + H₂) 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: **1** 314–318 K, **2** 311 K, **3** 310–318 K, **4a** 318–333 K, **4b** 314 K, **5** 324–330 K, **6** 333 K. After deposition the matrices were cooled to 12 K. IR spectra were recorded on a Mattson Sirius or Mattson RS FTIR spectrometer at 1 cm⁻¹ resolution. UV/vis spectra were measured with a Perkin Elmer Lambda 7G spectrometer at 2 nm resolution. Matrices were irradiated with the water-filtered output of a Philips HPK 125 W medium-pressure mercury arc with appropriate interference and cut-off filters.

Acknowledgements

We are pleased to acknowledge the support of NATO, SERC, the EC Commission, the Royal Society, British Gas and Deutsche Forschungsgemeinschaft (SFB 347).

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