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Formation of carbyne complexes in reactions of laser-ablated Os atoms with halomethanes: characterization by C-H(X) and Os-H(X) stretching absorptions and computed structures[†]

Han-Gook Cho^a and Lester Andrews*^{a,b}

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Reactions of laser-ablated Os atoms with halomethanes have been investigated. Small carbyne complexes are produced in reactions of Os atoms with fluoromethanes and identified through matrix infrared spectra and vibrational frequencies computed by density functional theory. The preference for the carbon–osmium triple bond is traced to the low energy of the Os carbyne products. The C–H and C–X stretching absorptions of the carbyne complexes are observed on the high frequency sides of the corresponding precursor bands, which result from the high s character in the C–H bond and interaction between the C–X and C–Os stretching modes, respectively. The calculated Os complex structures show a large variation with the ligands and electronic states, similar to the analogous Ru complex structures. The present report also compares previous Fe, Ru, and Os results and supports the general trend that the higher oxidation state complexes become more stable on going down the family group column.

Introduction

Interest in carbene and carbyne complexes has grown remarkably since their first introduction in the 1970's.¹ Increasing applications in various syntheses, particularly C–H insertion and metathesis catalytic properties provide the driving force for the progress in high oxidation state complex chemistry.^{2,3} Numerous synthetic routes are also introduced to generate osmium high oxidation state complexes,^{2–5} which often show distinctive structures and various catalytic and ligand effects.⁶ Hydrogen transfer from carbonto-osmium atom is directly observed in a recent time-resolved infrared study.⁷

More recently, simple Fe and Ru high oxidation state complexes were produced in reactions of laser-ablated Fe and Ru atoms with halomethanes, introducing a new way to effectively provide the Fe and Ru derivatives and allowing for examination of their structural and photochemical properties.⁸ Both methylidenes and methylidynes were observed with Ru, but no Fe carbynes were identified from the reactions with small alkanes and fluoroalkanes.⁸ Exclusive formation of Os methylidynes in reactions of Os with CH_4 , C_2H_6 and CH_3X have also been reported, showing a high preference for the triple bond between carbon and the third row transition metal,⁹ parallel to the W and Re systems.^{10,11}

The elusive carbyne C–H stretching absorptions¹² are clearly observed at ~200 cm⁻¹ on the blue side of the corresponding precursor absorption from the Ru and Os carbynes^{8,9} as well as the Re, W and Mo methylidynes.^{10,11} A general trend of increasing methylidyne C–H stretching frequency with the s

character in the C–H bond has also been reported.^{10,11a,b} The carbyne C–X stretching frequencies of the halogenated derivatives are exceptionally high (C–F and C–Cl stretching frequencies higher than 1500 and 1200 cm⁻¹), resulting from X–C–M antisymmetric stretching character.^{10,11c} The small group 8 metal complexes also show unusual, low symmetry structures including the highly distorted methylidynes^{8,9} similar to the structures of the corresponding Re carbynes¹¹ and unusual inclination of the C–Cl bond toward the metal center in the Fe insertion complexes.^{8a} The non-bonding electrons evidently play an important role in the distinct structures of the group 8 metal complexes,^{8,9} while the distorted structures of the small Re methylidynes¹⁰ are traced to the Jahn–Teller effect.¹³

Here, we report the IR spectra of isotopic products from reactions of laser-ablated Os atoms with halomethanes. The carbyne products, the only identified product from the reactions, reaffirm the preference of the carbon–osmium triple bond, and the interesting methylidyne C–H(X) stretching absorptions are also observed on the blue sides of the corresponding precursor bands. DFT computations substantiate the stability of the carbyne products and reveal unique structures for the products along with the structural effects of the lone electron pair on the metal center.

Experimental computational methods

Laser ablated Os (Metallium, Inc.) atoms were reacted with CH_2F_2 , CD_2F_2 , ¹⁴ CH_2FCl , CH_2Cl_2 , CD_2Cl_2 , ¹³ CH_2Cl_2 , $CHCl_3$, $CDCl_3$, ¹³ $CHCl_3$, CF_3Cl , ¹³ CF_3Cl , ¹⁴ CF_2Cl_2 , $CFCl_3$, CCl_4 (Dupont) and ¹³ CCl_4 in excess argon during condensation at 10 K using a closed-cycle refrigerator (Air Products HC-2). These methods have been described in detail elsewhere. ¹⁵ Reagent gas mixtures ranged 0.5–1.0% in argon. After reaction, infrared spectra were recorded at a resolution of 0.5 cm⁻¹ using a Nicolet 550 spectrometer (lower limit near 410 cm⁻¹) with an MCT-B detector. Samples were later irradiated for 20 min periods by a

^aDepartment of Chemistry, University of Incheon, 177 Dohwa-dong, Nam-ku, Incheon, 402-749, South Korea

^bDepartment of Chemistry, University of Virginia, P. O. Box 400319, Charlottesville, Virginia, 22904-4319, USA. E-mail: lsa@virginia.edu † Electronic supplementary information (ESI) available: Additional calculated and observed fundamental frequencies. See DOI: 10.1039/b811805a

mercury arc street lamp (175 W) with the globe removed and a combination of optical filters, and subsequently annealed to allow further reagent diffusion.¹⁵

In order to support the assignment of new experimental frequencies and correlate with related work,8-11 density functional theory (DFT) calculations were carried out using the Gaussian 03 package,¹⁶ the B3LYP density functional,¹⁷ the 6-311++G(3df,3pd) basis sets for C, H, F, Cl¹⁸ and SDD pseudopotential and basis set¹⁹ for Os to provide a consistent set of vibrational frequencies for the reaction products. Geometries were fully relaxed during optimization, and the optimized geometry was confirmed by vibrational analysis. The BPW9120 functional was also employed to complement the B3LYP results. The vibrational frequencies were calculated analytically, and the zero-point energy is included in the calculation of the binding energies. Previous investigations have shown the DFT calculated harmonic frequencies are usually slightly higher than observed frequencies,^{8-11,21,22} depending on the mode anharmonicity, and they provide useful predictions for the infrared spectra of new molecules.

Results and discussion

Reactions of osmium with halomethane isotopic modifications were carried out, and the matrix infrared spectra of new products will be compared with frequencies calculated by density functional theory.

$Os + CH_2X_2$

Previous studies show that reactions of metal atoms with small alkanes and halomethanes generate small metal complexes (insertion, carbene, and carbyne products) as primary reaction products.^{8,22} Fig. 1 shows the CH₂F₂, CD₂F₂ and CH₂FCl reaction product spectra in the C–H stretching and low frequency regions. The much stronger product absorptions in the CH₂FCl spectra indicate that substitution of F with Cl increases the reaction yield considerably. Only one group of absorptions marked "y" (y for methylidyne) are observed, which decrease and increase reversibly on visible ($\lambda > 420$ nm) and UV (240 < $\lambda < 380$ nm) irradiations. No significant changes were observed on annealing. The observed frequencies are listed in Table 1 and compared with DFT computed frequencies for the simple carbyne products in Tables S1 and S2.[†]

The experimental evidence favours 1 : 1 metal-precursor reaction products. In the case of similar experiments with Mo, natural Mo isotopic splittings were resolved, which indicates a single Mo atom contribution to the important Mo-C stretching mode in question.¹⁰ Since Os is more difficult to evaporate than Mo, it is straightforward to conclude that a single Os atom



Fig. 1 IR spectra in the selected regions of 3130–3090 and 630–500 cm⁻¹ for laser-ablated Os atoms co-deposited with CH_2F_2 isotopomers and CH_2FCl in excess argon at 10 K and their variation. (a) Os + 0.5% CH_2F_2 in Ar co-deposited for 1 h. (b) As (a) after visible ($\lambda > 420$ nm) photolysis. (c) As (b) after UV (240 < $\lambda < 380$ nm) photolysis. (d) As (c) after visible photolysis. (e) As (d) after UV photolysis. (f) As (e) after annealing to 28 K. (g) Os + 0.5% CD_2F_2 in Ar co-deposited for 1 h. (h) As (g) after visible photolysis. (i) As (h) after UV photolysis. (j) As (i) after visible photolysis. (k) As (j) after UV photolysis. (l) As (k) after annealing to 28 K. (m) Os + 0.5% CH_2FCl in Ar co-deposited for 1 h. (n) As (m) after visible photolysis. (o) As (n) after UV photolysis. (p) As (o) after visible photolysis. (o) As (n) after UV photolysis. (p) As (o) after visible photolysis. (q) As (p) after UV photolysis. (r) As (q) after annealing to 28 K, "y" denotes the product absorption. P and c designate the precursor and absorptions common to this precursor with different metal atoms, respectively.

contributes to these primary reaction products. Relatively dilute, 0.2 and 0.5%, reagent concentrations were employed here, and doubling the reagent concentration only increased the product absorptions by one third. Furthermore, no significant absorption growth was observed on annealing. Hence, we also conclude that a single reagent molecule is involved in these primary reaction products. Higher stoichiometry products have been limited to the CH_4 and CH_3X reagents and favoured in group 4 metal reactions,

Table 1Frequencies of product absorptions observed from reactions of CH_2X_2 isotopomers with Os in excess argon"

Group	CH_2F_2	CD_2F_2	CH ₂ FCl	CD ₂ FCl	¹³ CH ₂ FCl	CH_2Cl_2	CD_2Cl_2	$^{13}\mathrm{CH}_{2}\mathrm{Cl}_{2}$	Description
у	3113.7 	 	3107.3 666.9 612.1 568.7	2351.6 	3095.9 — 611.8 565.0	3101.3 657.7 	2335.7 	3090.1 655.8 — 577.5, 574.5	C–H stretch HCOsH bend Os–F stretch HCOs bend

^a All frequencies are in cm⁻¹. Stronger absorptions in a set are bold. Description gives major coordinate and "y" stands for carbyne (methylidyne) products.

and such absorptions increase substantially on annealing,²² in contrast to the osmium reaction products observed here.

The sharp y absorption in the C-H stretching region at 3113.7 cm^{-1} in the CH₂F₂ spectra has its counterpart at 3107.3 cm^{-1} in the CH₂FCl spectra while its D counterpart is covered by residual CO₂ absorptions. The C-H stretching absorptions whose frequencies are about 200 cm⁻¹ higher than the corresponding precursor bands strongly suggest that the products contain a C-Os triple bond, which in turn increases the s character in the C-H bond, parallel to the previous results of carbyne C-H stretching bands.8-12 The y absorption at 605.9 cm-1 has its D and CH₂FCl counterparts at 601.5 and 612.1 cm⁻¹ and is assigned to the OsF2 anti-symmetric stretching mode of the carbyne complex $(HC \equiv O_{S}HF_{2})$ on the basis of the frequency and small shifts. The OsF₂ symmetric stretching absorption, expected at about 10 cm⁻¹ on the blue side, is believed to be covered by a common feature in the spectra. We are not aware of infrared spectra of binary osmium fluorides, but the matrix-isolated OsO₃F₂ molecule exhibits Os-F stretching modes in this region at 619 and 646 cm⁻¹.²³

Another y absorption at 521.5 cm⁻¹ has its CH₂FCl counterpart at 568.7 cm⁻¹, but its D counterpart is unfortunately beyond our observation range. It is assigned to the HCOs bending mode due to the frequency and sizable shifts (Tables S1 and S2†). Other absorptions are computed to be much weaker. The good agreement with the strongest DFT predicted frequencies substantiates formation of the Os carbynes, HC=OsHF₂ and HC=OsHFCl. Analogous reversible photochemistry was observed for the Ru analogues and their methylidene partners,^{8b} but the Os methylidene complexes were not detected here most likely owing to masking by common absorptions in the precursor. It is of course possible for this reversible photochemistry to involve another transient species that is not observed here.

Fig. 2 shows the methylene chloride spectra in the C-H and C-D stretching and low frequency regions. Only y absorptions are observed again, which are almost depleted and recover reversibly in the alternating cycles of visible and UV irradiations. The sharp y absorption at 3101.3 cm⁻¹ shows D and ¹³C shifts of -765.6 and -11.2 cm⁻¹ (H : D and 12 : 13 ratios of 1.328 and 1.004). The C-H stretching absorptions at about 200 cm⁻¹ on the blue side of the corresponding precursor absorption is again strong evidence that the carbyne complex (HC≡OsHCl₂) is formed (Table S3[†]). The y absorption at 657.7 cm⁻¹ has its ¹³C counterparts at 655.8 cm⁻¹ (12:13 ratios of 1.003) and is assigned to the HCOsH symmetric in-plane bending mode without observation of the D counterpart. Another y absorption at 577.7 cm⁻¹ with its ¹³C counterpart at 574.5 cm^{-1} (12 : 13 ratio of 1.006 compared with the calculated ratio of 1.006) is assigned to the HCOs bending mode without observation of the D counterpart.

It is interesting to compare the trend in C–H stretching frequencies in the above methylidyne complex series. These frequencies increase from 3101.3 to 3107.3 to 3113.7 cm⁻¹ with increasing fluorine substitution, which parallels an increase in s character in the C–H bond calculated by NBO analysis, as described previously,^{10,16} namely 48.19, 48.61 and 49.46%, respectively. Such correlations were also found in Re and group 6 methylidyne complexes.^{10,11} Lower C–H stretching frequencies and smaller s characters were reported for the HC≡RuHFCl and HC≡RuHCl₂ counterparts,^{8b} but the HC≡RuHF₂ counterpart had higher s character (49.95%) and a lower frequency, which is out of line. The



Fig. 2 IR spectra in selected regions of 3125–3075, 2360–2310, and 670–560 cm⁻¹ for laser-ablated Os atoms co-deposited with methylene chloride isotopomers in excess argon at 10 K and their variations. (a) Os + 0.5% CH₂Cl₂ in Ar co-deposited for 1 h. (b) As (a) after visible photolysis. (c) As (b) after UV photolysis. (d) As (c) after visible photolysis. (e) As (d) after UV photolysis. (f) As (e) after annealing to 28 K. (g) Os + 0.5% CD₂Cl₂ in Ar co-deposited for 1 h. (h) As (g) after visible photolysis. (i) As (h) after UV photolysis. (j) As (i) after annealing to 28 K. (k) Os + 0.5% CD₂Cl₂ in Ar co-deposited for 1 h. (l) As (g) after visible photolysis. (i) As (h) after UV photolysis. (j) As (i) after annealing to 28 K. (k) Os + 0.5% 13 CH₂Cl₂ in Ar co-deposited for 1 h. (l) As (k) after visible photolysis. (m) As (l) after UV photolysis. (n) As (m) after annealing to 28 K, "y" denotes a product absorption. CO₂ and c designate the residual CO₂ and absorptions common with different metals.

present HC=OsHF₂ observation suggests that the C–H stretching frequency for HC=RuHF₂ should be higher even than the osmium counterpart.

The reversible photochemistry described above for the $HC\equivOsHCl_2$ product is parallel to that observed for the $CH_2=RuCl_2$ and $HC\equivRuHCl_2$ counterparts,^{8b} but the 6 kcal mol⁻¹ higher energy photochemical partner methylidene complex $CH_2=OsCl_2$ is not detected here because its strongest chromophore, the anti-symmetric $OsCl_2$ stretching mode (Table S2 continued†), falls below our instrumental limit of about 410 cm⁻¹. We are however, confident that the analogous photochemical reactions take place with Os and Ru, but the relative yield of the highest oxidation state product is probably higher with Os.

$$Os + CH_2Cl_2 \rightarrow CH_2Cl \text{-}OsCl^* \rightarrow CH_2 = OsCl_2 \leftrightarrow HC \equiv OsHCl_2$$

Os + CHCl₃

Fig. 3 illustrates the CHCl₃ spectra in the C–H and C–D stretching and HCOs bending regions, and Table 2 lists the observed frequencies. The product absorptions (all labelled y) increase about 40% on visible irradiation, are almost depleted on UV irradiation, and partly recover on the following visible irradiation. The y absorption at 3091.5 cm⁻¹ has its D and ¹³C counterparts at 2326.8 and 3080.7 cm⁻¹ (H : D and 12 : 13 ratios of 1.329 and 1.0035), whose high frequency and isotopic shifts strongly suggest formation of a complex with a carbon–osmium triple bond (HC≡OsCl₃). (The c absorptions are common to

 Table 2
 Frequencies of product absorptions observed from reactions of CHCl₃ isotopomers with Os in excess argon^a

Group	CHCl ₃	CDCl ₃	¹³ CHCl ₃	Description
у	3091.5 596.3	2326.8	3080.7 591.3	A' C–H stretch A' HCOs bend

^{*a*} All frequencies are in cm⁻¹. Description gives major coordinate, "y" stands for carbyne (methylidyne) products.



Fig. 3 IR spectra in the regions of 3110-3050, 2335-2315, and 605-585 cm⁻¹ for laser-ablated Os atoms co-deposited with chloroform isotopomers in excess argon at 10 K and their variations. (a) Os + 0.5% CHCl₃ in Ar co-deposited for 1 h. (b) As (a) after visible photolysis. (c) As (b) after UV photolysis. (d) As (c) after visible photolysis. (e) As (d) after annealing to 28 K. (f) Os + 0.5% CDCl₃ in Ar co-deposited for 1 h. (g) As (f) after visible photolysis. (h) As (g) after UV photolysis. (i) As (h) after annealing to 28 K. (j) Os + 0.5% ¹³CHCl₃ in Ar co-deposited for 1 h. (k) As (j) after visible photolysis. (l) As (k) after UV photolysis. (m) as (l) after visible photolysis. (n) As (m) after annealing to 28 K, "y" denotes a product absorption. P and c indicate the precursor and common absorptions, respectively.

CHCl₃ experiments with other metals). Another y absorption at 595.6 cm⁻¹ has its ¹³C counterpart at 591.3 cm⁻¹ and is assigned to the in-plane HCOs bending mode. Other absorptions from HC=OsCl₃ are either too weak to observe, covered by precursor bands, or beyond our observation range (Table S4[†]). Again, a reversible photochemical process with the methylidene is implicated, analogous to the Ru case,^{8b} but we cannot detect the likely methyldene partner.

$Os + CX_4 (X = F \text{ or } Cl)$

Fig. 4 shows the CF₃Cl spectra in the C-F and OsFCl₂ stretching regions, and Table 3 gives the observed absorptions. The y absorptions increase slightly, 50%, and 50% upon visible, UV, and full arc ($\lambda > 220$ nm) irradiations, respectively. The v absorption at 1580.9 cm⁻¹ with the ¹³C counterpart at 1532.7 cm⁻¹ (12 : 13 ratio of 1.031) is designated to the C-F stretching mode of FC=OsCl₃ on the basis of the unusually high frequency and sizable ¹³C shift. Mode analysis shows that the unusually high frequency is due to the fact that the C-F stretching mode is essentially the F-C-Os anti-symmetric stretching mode with considerable carbon motion, parallel to the previous results.^{8,10,11} The strong coupling between the C-F and C-Os motions is another evidence for formation of the carbyne tetrahalide: the frequency of a C-Os single or double bond would be too low to yield meaningful coupling with the C-F stretching mode. In the low frequency region, the y absorption and its ¹³C counterpart at 615.6 and 615.4 cm⁻¹ are assigned to the antisymmetric OsFCl₂ stretching modes on the basis of the frequencies and negligible ¹³C shift. A weak y absorption is observed at



Fig. 4 IR spectra in the regions of 1620–1500, 1235–1215, and 625–575 cm⁻¹ for laser-ablated Os atoms co-deposited with CF₃Cl and ¹³CF₃Cl in excess argon at 10 K and their variations. (a) Os + 0.5% CF₃Cl in Ar co-deposited for 1 h. (b) As (a) after visible photolysis. (c) As (b) after UV photolysis. (d) As (c) after full arc ($\lambda > 220$ nm) photolysis. (e) As (d) after annealing to 28 K. (f) Os + 0.5% ¹³CF₃Cl in Ar co-deposited for 1 h. (g) As (f) after visible photolysis. (h) As (g) after UV photolysis. (i) As (h) after full arc photolysis. (j) As (i) after annealing to 28 K, "y" denotes a product absorption and P indicates a product absorption.

Table 3 Frequencies of product absorptions observed from reactions of CX4 isotopomers with Os in excess argon^a

Group	CF ₃ Cl	¹³ CF ₃ Cl	CF_2Cl_2	CFCl ₃	CCl ₄
у	$\frac{1580.9 \text{ FC}}{} \text{CsF}_2\text{Cl}(\text{T})$	$1532.7 F^{13}C \equiv OsF_2Cl(T) 1231.0, 1224.2 Cl^{13}C \equiv OsF_3(T)$	1571.6 FC≡OsFCl ₂ (T) 1279.2, 1271.3 ClC≡OsF ₂ Cl(T)	1551.2 FC≡OsCl ₃ (T) 1283.0 ClC≡OsFCl ₂ (T)	
	$\frac{-}{615.6} \text{ FC} \equiv \text{OsF}_2\text{Cl}(\text{T})$	$\frac{-}{615.4} \text{ FC} \equiv \text{OsF}_2\text{Cl}(\text{T})$	$597.9 \text{ FC}=OsFCl_2(T)$ 606.5 ClC=OsF Cl(T)	_	
	$585.7 \text{ FC} \equiv \text{OsF}_2\text{Cl}(\text{T})$	_	$600.3 \text{ ClC} = \text{OsF}_2\text{Cl}(T)$ $621.3 \text{ ClC} = \text{OsF}_2\text{Cl}(T)$	$\frac{-}{608.2 \text{ ClC}} \equiv \text{OsFCl}_2(\text{T})$	

^{*a*} All frequencies are in cm⁻¹. Description gives major coordinate, "y" stands for carbyne (methylidyne) products.

585.7 cm⁻¹, but the ¹³C counterpart is believed to be overlapped by a common band. It is assigned to the OsFCl₂ symmetric stretching mode. The good agreement with DFT frequencies (Table S5†) substantiates the formation of FC \equiv OsF₂Cl.

Another product absorption marked "y", which is much weaker than the C–F stretching absorptions of FC=OsF₂Cl, is observed at 1224.2 cm⁻¹ in the ¹³CF₃Cl spectra. Assuming that its ¹²C counterpart expected at about 1272 cm⁻¹ is covered by a precursor band, it is tentatively assigned to the ¹³C–Cl stretching mode of Cl¹³C=OsF₃, a structural isomer of FC=OsF₂Cl. While FC=OsF₂Cl is only slightly (4.3 kcal mol⁻¹) more stable than ClC=OsF₃, the small energy difference only is seemingly not enough to explain primary formation of FC=OsF₂Cl. This, therefore, suggests that the C–Cl insertion followed by Cl migration is easier than the F counterpart, and it is also consistent with the considerable increase in reaction yield by substitution of F with Cl.

Fig. 5 illustrates the CF₂Cl₂ and CFCl₃ spectra in the C–F and C–Cl stretching and low frequency regions, where two groups of absorptions "y" and "y" are observed. The y absorptions in the CF₂Cl₂ spectra increase about 10%, 30% and 10% upon visible, UV, and full arc irradiations, whereas the y' absorptions increase about 30% and slightly more on visible and full arc irradiations but stay almost the same on UV irradiation. The y absorptions at 1571.6 cm⁻¹ most probably arise from the C–F stretching mode of FC=OsFCl₂ on the basis of the unusually high frequency and intensity, and the one at 597.9 cm⁻¹ is believed from the Os–F stretching mode (Table S6†). The y' absorptions at 1279.2 and 1271.3 cm⁻¹ are assigned to the C–Cl stretching mode of ClC=OsF₂Cl, the structural isomer of FC=OsFCl₂, on the basis of the exceptionally high frequency and high absorption

intensity. The y' absorptions at 621.3 and 606.5 cm⁻¹ are assigned to the A" and A' OsF₂ stretching modes (Table S6†). The isomers are again energetically comparable: FC=OsFCl₂ is 5.6 kcal mol⁻¹ more stable than ClC=OsF₂Cl.

The y absorptions in the CFCl₃ spectra increase about 10, 50 and 10% on visible, UV, and full arc irradiations, whereas the y' absorptions increase about 20, 200 and 30% on the series of irradiations. Parallel to the case of CF₂Cl₂, The y and y' absorptions at 1551.2 and 1283.0 cm⁻¹ in the CFCl₃ spectra are assigned to the C–F and C–Cl stretching modes of FC≡OsCl₃ and ClC≡OsFCl₂ on the basis of the high frequencies similar to those of the halogenated carbyne complexes^{8,10,11} and consistency with the DFT values. Another y' absorption at 608.2 cm⁻¹ is assigned to the Os–F stretching mode of ClC≡OsFCl₂. The FC≡OsCl₃(S) product is only 2.6 kcal mol⁻¹ lower in energy than ClC≡OsFCl₂(T).

Fig. 6 shows the CCl₄ and ¹³CCl₄ spectra in the C–Cl stretching region. The y absorptions increase about 5, 15 and 5% in visible, UV, and full arc irradiations, whereas the y* absorptions increase distinctly less on the same irradiation sequence. The y absorption at 1346.3 cm⁻¹ has ¹³C counterpart at 1298.4 cm⁻¹ (12 : 13 ratio of 1.037) is assigned to the C–Cl stretching mode of ClC=OsCl₃(S) on the basis of the characteristic high frequency and sizable ¹³C shift, which are consistent with the DFT values (Table S7†). The large ¹³C shift is due to the anti-symmetric Cl–C–Os stretching nature of this normal mode. As reported for the analogous ClC=WCl₃ molecule,¹⁰ the Cl 35–37 isotopic splitting for a single Cl atom is small (1.7 cm⁻¹) and not resolved from the major bands although there is an unresolved red shoulder that could contain this isotopic splitting. Unfortunately,

CF₂Cl₂ 0.04 (i) (h) (g) Absorbance CFC1, (d) (c) (b) **人**(a) 1260 630 1300 590 1600 1560 Wavenumbers (cm⁻¹)

Fig. 5 IR spectra in the regions 1600-1525, 1300-1260 and 630-590 cm⁻¹ for laser-ablated Os atoms co-deposited with CFCl₃ and CF₂Cl₂ in excess argon at 10 K and their variations. (a) Os + 0.5% HFCl₃ in Ar co-deposited for 1 h. (b) As (a) after visible photolysis. (c) As (b) after UV photolysis. (d) As (c) after full arc photolysis. (e) As (d) after annealing to 28 K. (f) Os + 0.5% CF₂Cl₂ in Ar co-deposited for 1 h. (g) As (f) after visible photolysis. (h) As (g) after UV photolysis. (i) As (h) after full arc photolysis. (j) As (i) after annealing to 28 K, "y" and "y'" denote the product absorptions groups and w and c designate the residual water and common absorptions.



Fig. 6 IR spectra in the region 1450–1150 cm⁻¹ for laser-ablated Os atoms co-deposited with CCl₄ and ¹³CCl₄ in excess argon at 10 K and their variations. (a) Os + 0.5% CCl₄ in Ar co-deposited for 1 h. (b) As (a) after visible photolysis. (c) As (b) after UV photolysis. (d) As (c) after full arc photolysis. (e) As (d) after annealing to 28 K. (f) Os + 0.5% ¹³CCl₄ in Ar co-deposited for 1 h. (g) As (f) after visible photolysis. (h) As (g) after UV photolysis. (i) As (h) after full arc photolysis. (j) as (i) after annealing to 28 K, "y" and "y*" denote the product absorption groups and c designates a common absorption.

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the strongest other $ClC \equiv OsCl_3$ band is beyond our observation range.

The y* absorption at 1295.6 cm⁻¹ (50.7 cm⁻¹ lower than the y absorption) in the CCl₄ spectra shows a 13 C shift of -46.2 cm⁻¹ (12: 13 ratio of 1.039). While the C-Cl stretching frequency is unusually high like those of other small transition metal carbynes,^{8,10,11} the large frequency differences between the y and y* absorptions in the isotopomer spectra (different 12:13 frequency ratios) virtually preclude the possibility that the weaker y* absorptions arise from ClC≡OsCl₃(S) in a different matrix site. Other plausible products (e.g. CCl_3 -OsCl and CCl_2 =OsCl₂) would not show an absorption in this high frequency region: normally the C-Cl, Os-Cl, and C-Os stretching frequencies are much lower (<900 cm⁻¹). Therefore, we cautiously suggest the possibility that the v* absorption arises from $ClC \equiv OsCl_3$ in the triplet state, which is only 1.7 kcal mol⁻¹ higher in energy than the singlet ground state. The observed frequency and its ¹³C shift are in excellent agreement with the predicted values of 1311.7 and -47.5 cm⁻¹ for the triplet state as shown in Table S7.†

The structures of ClC=OsCl₃ in the singlet and triplet states are significantly different as shown in Fig. 7. While both structures have C_s symmetry, the singlet structure has one short and two long Os–Cl bonds and the two Cl atoms are relatively close to each other (<ClOSCl = 85.2° and r(Cl–Cl) = 3.116 Å). In contrast, the triplet structure has one long and two short Os–Cl bonds and the

Fig. 7 Optimized molecular structures of Os carbyne complexes in the ground electronic states. The structures are calculated with B3LYP/6-311++G(3df,3pd) and the SDD core potential and basis set are used for Os. In HC=OsHX₂, C, Os and two halogen atoms form a near

and angles are in Å and °, respectively.

planar structure and the hydrogen atom is located above it. Also notice

that FC=OsF₂Cl and ClC=OsFCl₂ have C_1 structures. The bond lengths

two Cl atoms are farther from one another (<ClOsCl = 138.8° and *r*(Cl–Cl) = 4.290 Å). In consideration of the van der Waals radius of Ar (1.88 Å), it is possible that an argon atom can be trapped between the two chlorine atoms. Therefore, the difference in the molecular structures with the Os–Cl bonds long enough to hold an Ar atom in between may be preserved in the matrix cages, resulting in the observed y and y* absorptions from the two close lying singlet and triplet electronic states.

Os carbyne structures

Fig. 7 reveals that the Os carbyne structure varies significantly with the ligands and electronic states. $HC \equiv OsHX_2$ (X = F or Cl) in its singlet ground state shows a highly distorted structure. The H, C, Os and two halogen atoms form a near planar structure and the remaining hydrogen atom bonded to the Os atom is located straight above it. $HC \equiv OsCl_3$ has a C_s structure with one long Os– Cl bond and two short Os–Cl bonds, instead of a C_{3v} structure, similar to the structure of $HC \equiv OsH_3$ reported previously.⁹ The carbyne tetra halides ($XC \equiv OsX_3$) also show distorted structures. For the carbynes with a $OsCl_3$ or OsF_3 group, one Os–X bond is shorter than the remaining two Os–X bonds in the singlet state, which are relatively close to each other. On the other hand, in the triplet state one Os–X bond is longer than the other two Os–X bonds, which are farther apart than those in the singlet state.

While the Re carbynes, whose low symmetry structures are traced to the Jahn–Teller effect due to the unpaired electron,¹¹ the Ru and Os carbynes in the singlet ground state also have similarly distorted structures. The lone electron pair on the metal center apparently plays a crucial role in determining the structure.^{8,9} Fig. 8 illustrates the HOMO's of HC=OsHF₂(¹A'), CIC=OsCl₃(¹A'), and CIC=OsCl₃(³A''). Clearly there is a nodal plane between the two F atoms in HC=OsHF₂, pushing them apart and thereby forming a near planar structure with H, C and Os atoms. In the CIC=OsCl₃ singlet state, the lone electron pair provides bonding character between the remaining chlorine atoms and anti-bonding character between the remaining chlorine atom and two chlorine atoms, resulting in the small Cl–Os–Cl bond angle. In the triplet state, on the other hand, the anti-bonding character between ther mapart.

Comparison of Fe, Ru and Os complexes

The previous¹⁻³ and present results reveal that the primary products of group 8 metal reactions with small alkanes and halomethanes vary greatly with going down the family group column. Parallel to the previous early transition metal studies,^{1,2} the tendency that the higher oxidation state complexes are more favoured in reactions of heavier metals with small alkanes and halomethanes is evident with group 8 metals.³ Fe forms both the insertion and carbene products with di-, tri-, and tetrahalomethanes, whereas it provides only the insertion products in reactions of small alkanes and methyl fluoride. Ru generates carbynes along with carbene or insertion complexes in reactions with halomethanes while it still produces an insertion product in reactions with small alkanes. On the other hand, only carbyne products are identified from the reactions of Os with small alkanes and halomethanes, showing the high preference of carbonosmium triple bond.





Fig. 8 The HOMO's of $HC\equiv OsHF_2(^1A')$, $CIC\equiv OsCl_3(^1A')$, and $CIC\equiv OsCl_3(^3A'')$. Notice the anti-bonding character between the two F atoms in $HC\equiv OsHF_2$, spreading them apart. The significant difference between the singlet and triplet structures of $CIC\equiv OsCl_3$ can also be traced to the HOMO's. The nodal planes bisecting the two Os–Cl bonds in the triplet state spread the two Cl atoms apart, but the two Cl atoms are much closer in the singlet state.

Fig. 9 illustrates, as an example, the energies of the plausible group 8 metal reaction products with methylene chloride in the ground electronic states relative to the reactant $(M + CH_2Cl_2)$ energies. Attempts to locate a stable Fe carbyne species result in the Fe insertion or methylidene structure depending on the electronic state: we were unable to locate a stable methylidyne on the singlet or triplet potential energy surface for this system. This indicates that the Fe methylidyne complex is not a stable energy minimum. In contrast, the Ru carbene and carbyne complexes are more stable than the insertion product, and the Os carbyne product has the lowest energy among the three probable complexes. The previous studies also suggest that a higher oxidation state complex is perhaps more stable in the matrix than predicted, due to the more polarized bonds (particularly the carbon-metal bond).^{8,10,11,22} Finally, our experimental and computational results with group 8 metal atoms are consistent with those from analogous group 6 and 7 studies.10,11,22



Fig. 9 The energies of the plausible reaction products from reactions of group 8 metals with CH_2Cl_2 . Attempts to optimize the Fe carbyne structure gave the insertion or methylidene structure depending on the electronic state (see ref. 8a).

The computed group 8 metal complex structures show unusual distortions as illustrated in Fig. 10. The C–Cl bond in the Fe insertion complex is inclined to the metal center while the C–H and C–F bonds of the corresponding products do not show similar distortion.^{8a} Most probably, the inclination originates



ClC≡OsCl₃(³A")

Fig. 10 Optimized molecular structures with B3LYP/6–311++G-(3df,3pd)/SDD for the plausible products from group 8 transition metals and CH_2Cl_2 . Notice their unusual structures, particularly the C–Cl distortion in CH_2Cl –FeCl, allene-type structure of CH_2 =FeCl₂, and near planar structure of the carbyne complexes with a hydrogen atom placed right above (see ref. 8a).

from the interaction between the lone electron pair of the electron-rich chlorine atom and the metal center. The allenetype carbene structures and the near planar carbyne structure with the hydrogen atom right above is believed to be related to the non-bonding extra electrons on the metal center. Fig. 11 shows the MO's believed responsible for the distorted molecular structures. While the unpaired electrons in CH₂Cl–FeCl(Q) occupy the Fe d orbitals, one of the lone electron pairs on the Cl atom bonded to the carbon atom interacts with the metal center, leading to inclination of the C–Cl bond toward the Fe atom.^{8a} The carbene complex HOMO's reveal that the planar structure of the CMCl₂ moiety results from the anti-bonding character between the two chlorine atoms. Similarly the near planar structure



Fig. 11 MO's responsible for the distinct structures of the group 8 transition metal complexes. The MO (31st α -spin) of CH₂Cl–FeCl(Q) corresponds to the lone electron pair on the Cl atom showing the interaction between the chlorine and iron atoms, distorting the C–Cl bond. The HOMO's of the carbene and carbyne complexes reveal that the non-bonding electrons provide anti-bonding character between the chlorine atoms.

consisting of the C, Ru and two Cl atoms in the carbyne complex is also caused by the extra lone electron pair on the metal center.^{8b}

Our recent studies show that groups 9–12 transition metals do not form a carbyne complex in reactions with small alkanes and halomethanes,²⁴ which is consistent with the computational results that the high oxidation state complexes become gradually less favoured on moving from group 8–12. Previous investigations have also shown that higher oxidation-state complexes are more favoured with moving from group 3–6.²² Only the carbyne products are identified from reactions of Re and Os with small alkanes and halomethanes, revealing the stability of the carbyne product relative to the insertion and carbene complexes.^{9,11} All of these previous and the present results^{8–10,11,22} lead to a conclusion that Re and Os are indeed at the apex in terms of the preference for the high oxidation-state complexes in reactions of transition-metal atoms and small alkanes and halomethanes.

This trend is also illustrated in the $CH_2=MHF$ methylidene structures calculated for the group 8 metals and illustrated in Fig. 12. Although these intermediate molecules are not observed in our spectra, they are physically stable and their computed structures illustrate the trend of increased α -H-transfer from the carbon to the metal center, which accompanies formation of the higher oxidation state complexes.

Fig. 12 Molecular structures for the methylidene complexes CH_2 =MHF computed with B3LYP/6-311++G(3df,3pd) and SDD for Ru and Os.

Conclusions

The matrix IR spectra show that the Os carbyne products are predominantly formed in reactions with di-, tri-, tetra-halomethanes, in line with the previous results of Os reactions with methane, methyl halides, and ethane,9 re-confirming the high preference for the carbon-osmium triple bond. The carbyne C-H stretching frequencies are observed at about 200 cm⁻¹ on the blue side of the corresponding precursor absorption, due to the higher s character in the bond. Vibrational analyses show that the carbyne C-X stretching mode coupled with the C=Os stretching mode, resulting in the unusually high frequencies. DFT calculations reveal low symmetry structures for the small Os carbynes, and the extra electrons evidently play an important role in the structures, in line with the previously investigated Fe and Ru products.8 The two sets of product absorptions in the Os + CCl₄ spectra suggest that both singlet and triplet ClC=OsCl₃ with similar energies are trapped in an argon matrix, due to the large differences in structure and long Os-Cl bonds.

The dominant formation of the Os carbynes, along with the previous results of group 8 metals,^{8,9} reveal the tendency that higher oxidation state complex is more favoured on going down the column,²⁵ parallel to the previously investigated early transition metal systems.^{10,22} DFT calculations also reproduce the tendency that stability of the carbyne product relative to the corresponding insertion and methylidene complexes increases with going down the column. The present and previous results lead to a conclusion that Re and Os, the group 7 and 8 third row elements, have the highest preference to form a carbyne complex in reaction with small alkanes and halomethanes. The group 8 metal complexes also show interesting photochemistry including photoreversibility and highly distorted structures including unusual inclination of the C–Cl bond in the Fe insertion complexes.

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