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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**

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Table S1: Calculated Fundamental Frequencies of $\text{HC}\equiv\text{OsHF}_2$ Isotopomers in the Ground $^1\text{A}'$ state^a

Approximate Description	$\text{HC}\equiv\text{OsHF}_2$			$\text{DC}\equiv\text{OsDF}_2$				
	^b obs	^c BPW91	^d B3LYP	^d int	^b obs	^c BPW91	^d B3LYP	^d int
A' C-H str.	3113.7	3216.0	3274.4	64	Covered ^e	2397.0	2440.4	41
A' OsH str.		2319.3	2346.8	1		1645.3	1664.8	0
A' C≡Os str.		1104.8	1126.2	6		1051.2	1071.7	4
A' HCOs bend		935.7	966.4	2		730.7	756.3	1
A' COsH bend	Covered ^e	680.2	697.6	52		489.6	500.7	26
A' OsF ₂ str.	616sh	602.4	615.2	66	Covered ^e	602.4	615.2	65
A' OsF ₂ wag		210.6	216.9	1		201.2	207.4	1
A' OsF ₂ scis		153.2	154.8	4		153.0	154.6	4
A'' OsF ₂ str.	605.9	592.1	605.6	103	601.5	588.7	601.8	159
A'' HCOs bend	521.5	532.3	561.8	150		401.1	424.3	56
A'' OsF ₂ rock		161.1	166.9	1		154.3	158.8	0
A'' OsH bend		97.2	141.0	4		70.0	102.8	3

^aFrequencies and intensities are in cm^{-1} and km/mol . ^bObserved in an argon matrix. ^cFrequencies computed with BPW91/6-311++G(3df,3pd). The SDD core potential and basis set are used for Os. ^dFrequencies and intensities computed with B3LYP/6-311++G(3df, 3pd)/SDD. $\text{HC}\equiv\text{OsHF}_2$ has a C_s structure with two equal Os-F bonds. The symmetry notations are based on the C_s structure. ^eCovered by precursor bands.

Table S1 continued: Observed and Calculated Fundamental Frequencies of CH₂=OsF₂ Isotopomers in the ³B₁ Ground State^a

Approximate Description	CH ₂ =OsF ₂ (T)		CD ₂ =OsF ₂ (T)			
	BPW91 ^b	B3LYP ^c	Int ^c	BPW91 ^b	B3LYP ^c	Int ^c
A ₁ CH ₂ str.	2995.7	3069.2	2	2165.7	2219.2	1
A ₁ CH ₂ scis.	1322.1	1369.2	0	1042.5	1070.8	0
A ₁ C-Os str.	818.3	802.4	0	722.4	714.2	0
A ₁ OsF ₂ str.	632.8	644.0	14	632.6	643.8	15
A ₁ OsF ₂ scis.	167.2	170.1	8	167.0	169.8	8
A ₂ CH ₂ twist	179.0	251.8	0	127.4	179.2	0
B ₁ CH ₂ wag	891.8	927.1	47	700.0	726.9	26
B ₁ OsF ₂ wag	169.2	175.7	2	167.6	174.3	2
B ₂ CH ₂ str.	3105.1	3182.4	0	2311.3	2369.2	0
B ₂ CH ₂ rock	680.4	700.9	39	509.1	524.3	0
B ₂ OsF ₂ str.	623.8	634.1	166	631.0	642.6	202
B ₂ OsF ₂ rock	127.2	139.9	0	117.9	129.1	0

^aFrequencies and intensities are in cm⁻¹ and km/mol. ^bFrequencies computed with BPW91/6-311++G(3df,3pd). The SDD core potential and basis set are used for Os. ^cFrequencies and intensities computed with B3LYP/6-311++G(3df, 3pd). CH₂=OsF₂(³B₁) has a planar C_{2v} structure. The symmetry notations are based on the C_{2v} structure.

Table S2: Observed and Calculated Fundamental Frequencies of HC≡OsHFCI Isotopomers in the Singlet Ground State^a

Approximate Description	HC≡OsHFCI			DC≡OsDFCI			H ¹³ C≡OsHFCI				
	^b obs	^c BPW91	^d B3LYP	^b obs	^c BPW91	^d B3LYP	^b obs	^c BPW91	^d B3LYP		
C-H str.	3107.3	3210.9	3270.1	2351.6	2392.7	2437.0	41	3095.9	3198.7	3257.7	63
OsH str.		2317.1	2348.2	0	1643.7	1665.7	0		2317.1	2348.2	0
C≡Os str.		1097.2	1121.9	5	1044.1	1067.6	3		1060.7	1084.7	5
COsH bend		921.8	955.8	3	719.6	747.5	2		914.7	948.1	3
HCOs bend	665.0	679.8	697.6	45	490.4	502.0	22		678.6	696.6	45
Os-F str.	612.1	598.2	610.7	50	594.3	605.3	130	611.8	598.0	610.2	58
HCOs bend	568.7	560.9	588.6	165	427.8	449.8	44	565.0	558.2	585.9	157
Os-Cl bend		375.4	376.0	38	371.8	372.7	47		375.3	375.9	39
OsH bend		314.3	305.4	11	235.8	227.2	3		314.1	305.1	11
OsCFCl as def.		173.9	177.4	1	164.4	167.4	1		169.3	174.8	1
OsCFCl s def.		159.6	172.3	0	147.1	160.1	1		158.3	168.7	0
OsFCl bend		124.9	126.7	1	124.2	126.3	1		124.8	126.7	1

^aFrequencies and intensities are in cm⁻¹ and km/mol. ^bObserved in an argon matrix. ^cFrequencies computed with BPW91/6-311++G(3df,3pd). The SDD core potential and basis set are used for Os. ^dFrequencies and intensities computed with B3LYP/6-311++G(3df, 3pd)/SDD. HC≡OsHFCI has a C₁ structure.

Table S3: Observed and Calculated Fundamental Frequencies of $\text{HC}\equiv\text{OsHCl}_2$ Isotopomers in the Ground $^1\text{A}'$ State^a

Approximate Description	$\text{HC}\equiv\text{OsHCl}_2$			$\text{DC}\equiv\text{OsDCl}_2$			$\text{H}^{13}\text{C}\equiv\text{OsHCl}_2$		
	^b obs	^c BPW91	^d B3LYP	^b obs	^c BPW91	^d B3LYP	^b obs	^c BPW91	^d B3LYP
A' C-H str.	3101.3	3206.5	3266.9	2335.3	2389.4	2434.4	3090.1	3194.4	3254.5
A' OsH str.		2316.0	2341.5	0	1642.9	1661.0	0	2316.0	2341.5
A' C≡Os str.		1093.1	1118.6	3	1040.3	1064.5	2	1056.8	1081.5
A' COsH bend		916.8	949.7	3	714.7	741.5	2	909.7	942.2
A' HCOs bend	657.7	676.0	693.5	40	486.0	497.5	19	655.8	692.5
A' OsCl ₂ str.		365.9	366.0	11	365.7	365.8	11	365.9	365.9
A' OsCl ₂ wag		153.2	155.4	1	145.0	147.2	0	151.4	153.6
A' OsCl ₂ bend		102.8	103.1	0	102.7	103.0	0	102.8	103.1
A'' HCOs bend	580.7, 577.7	581.1	614.3	81	445.1	470.7	39	577.5, 574.5	610.5
A'' OsCl ₂ str.		378.6	381.2	72	372.7	372.5	102	378.5	381.1
A'' OsHCl ₂ def.		291.7	319.3	38	211.4	233.7	9	291.7	319.2
A'' OsCCl ₂ def.		173.8	175.5	1	162.1	163.2	1	169.1	170.7

^aFrequencies and intensities are in cm^{-1} and km/mol . ^bObserved in an argon matrix. ^cFrequencies computed with BPW91/6-311++G(3df,3pd). The SDD core potential and basis set are used for Os. ^dFrequencies and intensities computed with B3LYP/6-311++G(3df,3pd)/SDD. $\text{HC}\equiv\text{OsHCl}_2$ has a C_s structure with two equal Os-Cl bonds. The symmetry notations are based on the C_s structure.

Table S3 continued: Observed and Calculated Fundamental Frequencies of CH₂=OsCl₂ Isotopomers in the Ground ³B₁ State^a

Approximate Description	CH ₂ =OsCl ₂ (T)			CD ₂ =OsCl ₂ (T)			¹³ CH ₂ =OsCl ₂ (T)		
	BPW91 ^b	B3LYP ^c	Int ^e	BPW91 ^b	B3LYP ^c	Int ^e	BPW91 ^b	B3LYP ^c	Int ^e
A ₁ CH ₂ str.	2999.3	3072.2	2	2168.3	2221.5	1	2994.7	3067.4	2
A ₁ CH ₂ scis.	1324.4	1373.7	0	1041.8	1073.0	0	1316.1	1365.2	0
A ₁ C-Os str.	817.9	807.8	0	723.2	719.3	0	793.8	784.0	0
A ₁ OsCl ₂ str.	374.7	371.5	5	374.7	371.5	5	374.7	371.5	5
A ₁ OsCl ₂ scis.	102.9	103.3	2	102.8	103.2	2	102.8	103.3	2
A ₂ CH ₂ twist	152.3	167.8	0	108.0	119.0	0	152.3	167.8	0
B ₁ CH ₂ wag	871.9	908.0	35	684.1	712.1	19	864.2	900.0	35
B ₁ OsCl ₂ wag	107.3	108.8	0	105.1	106.5	0	106.7	108.2	0
B ₂ CH ₂ str.	3104.5	3180.2	0	2310.3	2366.6	0	3091.8	3167.1	0
B ₂ CH ₂ rock	680.3	698.1	2	514.6	528.2	6	676.8	694.5	3
B ₂ OsCl ₂ str.	382.2	379.6	103	379.0	376.6	100	382.2	379.6	103
B ₂ OsCl ₂ rock	152.5	156.7	1	139.5	143.3	1	148.8	152.9	1

^aFrequencies and intensities are in cm⁻¹ and km/mol. ^bFrequencies computed with BPW91/6-311++G(3df,3pd). The SDD core potential and basis set are used for Os. ^cFrequencies and intensities computed with B3LYP/6-311++G(3df, 3pd). CH₂=OsCl₂(³B₁) has a planar C_{2v} structure. The symmetry notations are based on the C_s structure.

Table S4: Observed and Calculated Fundamental Frequencies of HC≡OsCl₃ Isotopomers in the Ground ³A' State^a

Approximate Description	HC≡OsCl ₃ (T)			DC≡OsCl ₃ (T)			H ¹³ C≡OsCl ₃					
	^b obs	^c BPW91	^d B3LYP	^b obs	^c BPW91	^d B3LYP	^b obs	^c BPW91	^d B3LYP			
A' C-H str.	3091.5	3187.0	3261.8	80	2326.8	2371.8	2429.7	46	3080.7	3175.2	3249.5	79
A' C≡Os str.		1059.2	1112.3	1		1009.2	1059.3	1		1024.0	1075.3	1
A' HCOs bend	595.6	603.6	623.9	59		467.8	490.3	30	591.3	599.4	619.0	59
A' OsCl ₃ as str.		359.9	381.3	66		359.6	380.9	62		359.9	381.2	66
A' OsCl ₃ s str.		333.3	367.8	11		332.9	365.8	13		333.3	367.7	11
A' COsCl bend		178.6	235.7	12		166.6	216.7	10		174.6	230.1	10
A' OsCl ₂ scis.		121.7	160.8	0		121.4	160.5	0		121.5	160.6	0
A' OsCl ₃ def.		53.0	108.8	1		53.0	108.6	1		52.9	2.1	0
A'' HCOs bend ^e covered		641.1	741.8	70	^e covered	509.1	576.7	36	^e covered	635.3	736.1	70
A'' OsCl ₃ as str.		366.6	358.9	26		366.2	357.9	27		366.6	358.9	26
A'' COsCl bend		220.9	141.9	0		199.6	133.3	0		215.5	138.9	0
A'' OsCl ₃ def.		107.3	1.3	0		107.2	3.2	0		107.2	108.6	1

^aFrequencies and intensities are in cm⁻¹ and km/mol. ^bObserved in an argon matrix. ^cFrequencies computed with BPW91/6-311++G(3df,3pd). The SDD core potential and basis set are used for Os. ^dFrequencies and intensities computed with B3LYP/6-311++G(3df, 3pd)/SDD. HC≡OsCl₃ has a C_s structure with two equal Os-Cl bonds. The symmetry notations are based on the C_s structure. ^eCovered by precursor band.

Table S5: Observed and Calculated Fundamental Frequencies of ClC≡OsF₃ and FC≡OsF₂Cl Isotopomers in the Ground Triplet States^a

Approximate Description	ClC≡OsF ₃ (² A'')			FC≡OsF ₂ Cl(² A'')			Cl ¹³ C≡OsF ₃ (² A'')			F ¹³ C≡OsF ₂ Cl(² A'')						
	^b obs	^c BPW91	^d B3LYP	^d int	^b obs	^c BPW91	^d B3LYP	^d int	^b obs	^c BPW91	^d B3LYP	^d int				
A' C-X str.	covered	1296.2	1311.3	210	1580.9	1562.7	1605.4	545	1224.2	1249.3	1263.9	195	1532.7	1514.1	1556.0	515
A' CX ₃ str.		616.0	633.2	83.4		608.8	622.9	7		616.0	633.2	84		602.6	616.7	8
A' OsX ₃ str.	^e covered	571.4	586.9	76	585.7	578.2	594.9	92	^e covered	571.1	586.6	77	^e covered	577.8	594.3	89
A' C-Os str.		451.4	458.3	16		389.3	404.5	4		447.3	453.6	15		380.0	393.5	5
A' XCOs bend		313.2	322.6	6		368.5	370.6	35		304.9	314.0	6		366.8	370.1	34
A' OsX ₃ deform		211.1	225.7	2		222.0	228.1	4		212.3	225.6	2		222.0	228.0	4
A' OsX ₂ wag		147.5	159.7	5		175.5	178.5	1		147.4	159.6	5		175.4	178.4	1
A' OsX ₃ Rock		84.2	88.7	4		82.4	82.3	2		84.2	88.6	4		82.4	82.3	2
A'' OsX ₃ str.		616.3	628.3	176	615.6	607.6	625.9	132		616.3	628.3	176	615.4	607.6	625.9	133
A'' XCOs bend		421.9	443.6	2		485.0	515.4	2		407.3	428.7	1		468.3	497.6	2
A'' OsX ₃ scis.		212.4	227.9	3		115.2	118.1	4		211.1	227.9	3		115.2	118.1	4
A'' OsX ₃ rock		89.5	94.5	0		96.0	95.6	1		89.4	94.4	0		96.0	95.6	1

^aFrequencies and intensities are in cm⁻¹ and km/mol. ^bObserved in an argon matrix. ^cFrequencies computed with BPW91/6-311++G(3df,3pd). The SDD core potential and basis set are used for Os. ^dFrequencies and intensities computed with B3LYP/6-311++G(3df, 3pd)/SDD. Both ClC≡OsF₃ and FC≡OsF₂Cl have C_s structures. The symmetry notations are based on the C_s structure. ^eCovered by precursor band.

Table S6: Observed and Calculated Fundamental Frequencies of $\text{FC}\equiv\text{OsFCl}_2$, $\text{ClC}\equiv\text{OsF}_2\text{Cl}$, $\text{FC}\equiv\text{OsCl}_3$, and $\text{ClC}\equiv\text{OsFCl}_2$ ^a

Approximate Description	$\text{FC}\equiv\text{OsFCl}_2(^3\text{A}'')$			$\text{ClC}\equiv\text{OsF}_2\text{Cl}(^3\text{A}')$			$\text{FC}\equiv\text{OsCl}_3(^1\text{A}')$			$\text{ClC}\equiv\text{OsFCl}_2(^3\text{A})$						
	^b obs	⁴ BPW91	⁴ B3LYP	^b obs	⁴ BPW91	⁴ B3LYP	^b obs	⁴ BPW91	⁴ B3LYP	^b obs	⁴ BPW91	⁴ B3LYP				
A' C-X str.	1571.6	1560.8	1603.2	569	1271.3	1280.6	1302.3	240	1551.2	1605.0	1658.0	544	1283.0	1281.7	1306.3	252
A' C-Os str.	607.0	622.2	5	5	303.4	309.3	35	35	612.0	633.2	14	14	445.0	452.7	21	
A' Os-X str.	597.9	581.9	600.6	98	348.2	351.3	27	27	378.8	378.7	74	74	344.8	347.9	29	
A' OsCX bend	383.5	399.9	3	3	447.9	455.9	20	20	386.7	396.3	2	2	297.1	303.2	33	
A' OsX ₂ str.	353.7	356.5	7	7	606.5	602.4	618.3	42	331.5	342.2	18	18	372.1	372.4	33	
A' OsX ₃ deform	142.4	141.7	1	1	206.9	217.9	1	1	172.1	171.7	0	0	179.3	180.6	1	
A' COsX str.	97.4	96.8	4	4	154.5	161.6	3	3	114.6	115.6	0	0	112.5	112.9	1	
A' OsX ₃ rock	81.9	81.4	1	1	63.5	63.3	2	2	97.5	97.0	1	1	63.2	63.4	1	
A'' OsCF bend	483.6	513.0	1	1	400.3	419.9	0	0	392.0	412.3	0	0	386.3	404.5	0	
A'' OsX ₂ str.	367.3	368.6	88	88	621.3	610.3	623.5	158	331.3	339.3	28	28	608.2	595.2	115	
A'' OsX scis	196.5	198.4	2	2	163.9	171.8	0	0	75.9	77.6	0	0	142.0	141.9	0	
A'' OsX ₃ rock	89.5	87.8	0	0	88.9	95.5	0	0	47.5	35.7	0	0	76.3	74.4	0	

^aFrequencies and intensities are in cm^{-1} and km/mol . ^bObserved in an argon matrix. ^cFrequencies computed with BPW91/6-311++G(3df,3pd). The SDD core potential and basis set are used for Os. ^dHarmonic Frequencies and intensities computed with B3LYP/6-311++G(3df,3pd)/SDD. $\text{FC}\equiv\text{OsFCl}_2$, $\text{ClC}\equiv\text{OsF}_2\text{Cl}$, and $\text{FC}\equiv\text{OsCl}_3$ have a C_s structure, whereas $\text{ClC}\equiv\text{OsFCl}_2$ a C_1 structure. The symmetry notations are based on the C_s structure.

Table S7: Observed and Calculated Fundamental Frequencies of ClC≡OsCl₃ Isotopomers in the ¹A' and ³A'' States^a

Approximate Description	ClC≡OsCl ₃ (¹ A')			Cl ¹³ C≡OsCl ₃ (¹ A')			ClC≡OsCl ₃ (³ A'')			Cl ¹³ C≡OsCl ₃ (³ A'')						
	^b obs	^c BPW91	^d B3LYP	^b obs	^c BPW91	^d B3LYP	^b obs	^c BPW91	^d B3LYP	^b obs	^c BPW91	^d B3LYP	^e Int			
A' X-C-Os as str.	1346.3	1343.2	1371.3	218	1298.4	1294.4	1321.4	203	1295.6	1287.3	1311.7	256	1249.4	1240.6	1264.2	239
A' X-C-Os s str.		440.3	451.3	15		438.9	449.8	14		438.4	445.8	19		435.2	442.8	18
A' OsX ₃ as str.		381.3	380.3	74		380.7	379.5	78		362.1	363.6	14		361.7	363.1	13
A' OsX ₃ s str.		370.5	375.2	7		369.5	373.6	4		339.0	340.8	28		338.0	339.3	32
A' X-C-Os bend		301.2	313.6	14		292.2	305.0	13		288.3	295.2	27		280.9	288.1	23
A' OsX ₂ scis.		166.4	165.4	0		166.3	165.3	0		125.9	125.6	0		125.9	125.5	0
A' OsX ₃ def.		108.7	108.5	0		108.6	108.4	0		82.4	82.5	0		82.4	82.5	0
A' OsX ₃ rock		73.0	73.9	1		73.0	73.9	1		62.0	62.0	1		62.0	62.0	1
A'' OsX ₂ as str.		363.0	369.7	6		361.2	366.7	9		365.6	366.0	76		358.6	365.1	68
A'' X-C-Os bend		299.9	314.8	25		290.5	305.9	22		376.2	395.0	4		369.7	381.6	11
A'' OsX ₃ def.		73.8	74.7	0		73.8	74.7	0		130.2	129.8	0		130.2	129.8	0
A'' OsX ₂ twist		39.0	26.5	0		39.0	26.5	0		69.7	68.9	0		69.7	68.9	0

^aFrequencies and intensities are in cm⁻¹ and km/mol. ^bObserved in an argon matrix. ^cFrequencies computed with BPW91/6-311++G(3df,3pd). The SDD core potential and basis set are used for Os. ^dFrequencies and intensities computed with B3LYP/6-311++G(3df,3pd)/SDD. ClC≡OsCl₃ has a C_s structure in the ground triplet and singlet states. The symmetry notations are based on the C_s structure.