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## **Infrared Spectra of $\text{XC}\equiv\text{IrX}_3$ and $\text{CX}_2=\text{IrX}_2$ Prepared by Reactions of Laser-Ablated Iridium Atoms with Halomethanes**

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### **Abstract**

Small iridium high oxidation-state complexes with carbon-iridium multiple bonds are identified in the product matrix infrared spectra from reactions of laser-ablated Ir atoms with tetra-, tri- and dihalomethanes. In contrast to the previously studied Rh case, Ir carbyne complexes ( $\text{XC}\equiv\text{IrX}_3$ ) are generated in reactions of tetrahalomethanes, and their short Ir-C bondlengths of 1.725-1.736 Å are appropriate for the carbon-metal triple bonds. DFT calculations also show that the Ir carbynes with an Ir-F bond have unusual square planar structures, similar to the recently discovered Ru planar complexes. Diminishing preference for the carbyne complexes leads to methylidene product absorptions in the tri- and dihalomethane spectra, marking a limit for generation of small metal carbynes. The insertion complexes, on the other hand, are not observed in this study, suggesting that X migration from C to Ir following initial C-X insertion is swift.

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Table S1: Observed and Calculated Fundamental Frequencies of  $\text{FC}\equiv\text{IrCl}_3$  and  $\text{FC}\equiv\text{IrFCl}_2$  in the Ground  ${}^2\text{A}_2$  and  ${}^2\text{A}'$  States<sup>a</sup>

Approximate Description	$\text{FC}\equiv\text{IrCl}_3$					Approximate Description	$\text{FC}\equiv\text{IrFCl}_2$				
	Obs <sup>b</sup>	B3LYP <sup>c</sup>	Int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>		Obs <sup>b</sup>	B3LYP <sup>c</sup>	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>
A' F-C-Ir as. str.	1545.4	1573.8	658	1524.3	567	$\text{A}_1$ F-C-Ir as. str.	1643.6, <b>1635.4</b>	1662.9	641	1613.8	541
A' F-C-Ir s. str.	629.4	630.3	14	616.4	22	$\text{A}_1$ F-C-Ir ip. bend		613.3	6	585.9	9
A' F-C-Ir ip. bend		410.8	1	394.8	1	$\text{B}_2$ C-Ir-F as. str.	619.4	610.8	60	596.3	69
A'' F-C-Ir oop. bend		406.4	10	381.7	10	$\text{A}_1$ C-Ir-F s. str.		602.3	26	586.2	4
A' IrCl <sub>3</sub> s. str.		353.1	6	349.5	5	$\text{B}_1$ F-C-Ir oop. bend		570.8	6	552.4	6
A'' IrCl <sub>2</sub> as. str.		344.1	95	339.2	88	$\text{B}_2$ IrCl <sub>2</sub> as. str.		370.9	80	362.8	57
A' Ir-Cl str.		316.8	23	313.1	20	$\text{A}_1$ IrCl <sub>2</sub> s. str.		355.2	0	348.1	1
A' IrCl <sub>2</sub> wag		139.5	0	137.1	0	$\text{B}_2$ Ir-F ip. bend		239.9	1	237.1	1
A' IrCl <sub>3</sub> s. deform		102.8	1	100.9	1	$\text{A}_1$ IrCl <sub>2</sub> ip. bend		154.7	0	153.8	0
A'' IrCl <sub>3</sub> as. deform		97.8	5	89.0	4	$\text{B}_1$ IrFCl <sub>2</sub> deform		94.4	2	95.9	1
A' InCl <sub>3</sub> rock		56.1	1	56.8	1	$\text{B}_2$ IrFCl <sub>2</sub> rock		56.2	0	56.6	0
A'' InCl <sub>3</sub> rock		40.0	9	97.8	27	$\text{B}_1$ IrCl <sub>2</sub> oop. bend		39.7	0	41.0	0

<sup>a</sup> Frequencies and intensities are in  $\text{cm}^{-1}$  and km/mol. <sup>b</sup> Observed in an argon matrix, and the stronger one in an absorption pair is bold.

<sup>c</sup> Computed with B3LYP/6-311++G(3df,3pd). <sup>d</sup> Computed with BPW91/6-311++G(3df,3pd).  $\text{FC}\equiv\text{IrCl}_3(\text{D})$  and  $\text{FC}\equiv\text{IrFCl}_2(\text{D})$  have  $\text{C}_s$  and square planar  $\text{C}_{2v}$  structures, and the symmetry notations are based on the structures.

Table S2: Observed and Calculated Fundamental Frequencies of  $\text{CCl}\equiv\text{IrFCl}_2$  and  $\text{CCl}\equiv\text{IrF}_2\text{Cl}$  in the Ground  ${}^2\text{A}_2$  and  ${}^2\text{A}''$  States<sup>a</sup>

Approximate Description	$\text{CCl}\equiv\text{IrFCl}_2$				Approximate Description	$\text{CCl}\equiv\text{IrF}_2\text{Cl}$					
	Obs <sup>b</sup>	B3LYP <sup>c</sup>	Int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	B3LYP <sup>c</sup>	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	
A <sub>1</sub> Cl-C-Ir as. str.	1318.9, <b>1316.7</b> , 1314.5	1332.5	381	1312.8	298	A' Cl-C-Ir as. str.	1318.0	1331.1	365	1311.2	280
A <sub>1</sub> Ir-F str.	608.4, <b>607.3</b>	595.8	110	581.7	94	A' IrF <sub>2</sub> s. str.	629.2	623.6	145	606.2	117
B <sub>2</sub> Cl-C-Ir ip bend		525.6	0	505.1	0	A' IrF <sub>2</sub> as. str.	covered	592.3	94	574.9	77
B <sub>1</sub> Cl-C-Ir oop bend		474.2	0	461.6	0	A' Cl-C-Ir ip bend		533.9	1	513.1	1
A <sub>1</sub> Cl-C-Ir s. str.		431.7	4	422.5	5	A'' Cl-C-Ir oop bend		476.0	0	464.2	0
B <sub>2</sub> IrCl <sub>2</sub> as. str.		367.9	83	360.7	60	A' Cl-C-Ir s. str.		430.9	5	421.2	6
A <sub>1</sub> IrCl <sub>2</sub> s. str.		353.0	0	346.8	1	A' Ir-Cl str.		377.6	26	370.5	18
B <sub>2</sub> Ir-F ip bend		237.8	1	235.9	1	A' IrF <sub>2</sub> scis.		266.6	1	263.2	2
A <sub>1</sub> IrCl <sub>2</sub> ip bend		152.8	0	152.2	0	A' FlrCl bend		191.8	0	191.5	0
B <sub>1</sub> IrFCl <sub>2</sub> deform		85.9	2	88.2	1	A'' IrCClF <sub>2</sub> deform		109.5	4	111.5	2
B <sub>2</sub> IrFCl <sub>2</sub> rock		44.5	0	44.4	0	A' IrF <sub>2</sub> Cl rock		50.5	0	54.4	0
B <sub>1</sub> IrCl <sub>2</sub> oop bend		31.9	0	34.2	0	A'' IrF <sub>2</sub> twist		39.4	0	42.9	0

<sup>a</sup> Frequencies and intensities are in  $\text{cm}^{-1}$  and km/mol. <sup>b</sup> Observed in an argon matrix, and the strongest one in an absorption set is bold.

<sup>c</sup> Computed with B3LYP/6-311++G(3df,3pd). <sup>d</sup> Computed with BPW91/6-311++G(3df,3pd).  $\text{ClC}\equiv\text{IrFCl}_2(\text{D})$  and  $\text{ClC}\equiv\text{IrF}_2\text{Cl}(\text{D})$  have square planar  $\text{C}_{2v}$  and  $\text{C}_s$  structures, and the symmetry notations are based on the structures.

Table S3: Observed and Calculated Fundamental Frequencies of CHCl=IrCl<sub>2</sub> Isotopomers in the Ground <sup>2</sup>A'' State<sup>a</sup>

Approximate Description	CHCl=IrCl <sub>2</sub>						CDCl=IrCl <sub>2</sub>						<sup>13</sup> CHCl=IrCl <sub>2</sub>			
	Obs <sup>b</sup>	B3LYP <sup>d</sup>	Int <sup>d</sup>	BPW91	Int	Obs <sup>b</sup>	B3LYP <sup>d</sup>	Int <sup>d</sup>	BPW91	Int	Obs <sup>b</sup>	B3LYP <sup>d</sup>	Int <sup>d</sup>	BPW91	Int	
A' C-H str.	3107.8	4		3038.6	4		2286.8	2	2235.6	2		3098.4	5		3029.4	4
A' HCl bend	1185.7, 1182.2, <b>1174.8</b>	1220.1	74	1166.0	70	1000.1	1013.0	232	977.3	219	1177.7, 1173.9, <b>1166.2</b>	1212.6	60	1158.9	56	
A' Ir-C-Cl as. str.	914.9, 909.9	918.0	212	899.8	191	775.6	795.7	63	768.5	47	888.3, 884.0	890.2	208	872.3	188	
A' C-H oop bend	730.3	757.2	19	717.9	20	604.3, <b>601.0</b>	641.8	27	624.5	38	covered <sup>e</sup>	747.0	19	708.3	21	
A' Ir-C-Cl s. str.	covered <sup>e</sup>	667.8	39	651.8	51		626.5	8	593.5	10	covered <sup>e</sup>	650.1	36	634.6	48	
A' IrCl <sub>2</sub> as. str.		384.7	89	388.1	70		384.7	89	380.1	67		384.7	89	388.1	70	
A' IrCl <sub>2</sub> s. str.		367.2	11	370.8	9		367.2	11	361.0	8		367.2	11	370.8	9	
A' IrCCl bend		230.7	0	224.8	0		229.5	0	219.6	0		229.2	0	223.4	0	
A'' HCClIr deform		200.3	4	208.8	4		175.1	3	181.6	3		196.0	4	204.3	4	
A'' IrCl <sub>2</sub> scis.		114.0	0	115.1	0		113.9	0	112.4	0		113.9	0	115.0	0	
A'' IrCl <sub>2</sub> wag		78.4	1	80.3	0		78.3	1	78.7	0		78.4	1	80.3	0	
A'' CHCl twist		38.7	0	45.1	0		38.1	0	43.5	0		38.7	0	45.1	0	

<sup>a</sup> Frequencies and intensities are in cm<sup>-1</sup> and km/mol. <sup>b</sup> Observed in an argon matrix, and the strongest one in an absorption set is bold. <sup>c</sup> Computed with B3LYP/6-311++G(3df,3pd). <sup>d</sup> Computed with BPW91/6-311++G(3df,3pd). CHCl=IrCl<sub>2</sub>(T) has a C<sub>s</sub> structure with two equal Ir-Cl bonds. The symmetry notations are based on the C<sub>s</sub> structure. <sup>e</sup> Covered by precursor band.

Table S4: Observed and Calculated Fundamental Frequencies of  $\text{CH}_2=\text{IrCl}_2$  Isotopomers in the Ground  ${}^2\text{A}_2$  State<sup>a</sup>

Approximate Description	$\text{CH}_2=\text{IrCl}_2$				$\text{CD}_2=\text{IrCl}_2$				${}^{13}\text{CH}_2=\text{IrCl}_2$							
	Obs <sup>b</sup>	B3LYP <sup>d</sup>	Int <sup>d</sup>	BPW91	int	Obs <sup>b</sup>	B3LYP <sup>d</sup>	Int <sup>d</sup>	BPW91	int	Obs <sup>b</sup>	B3LYP <sup>d</sup>	Int <sup>d</sup>	BPW91	int	
B <sub>1</sub> as. CH <sub>2</sub> str.	3150.1	0	3069.4	2		2346.7	0	2287.0	1		3136.9	0	3056.6	2		
A <sub>1</sub> s. CH <sub>2</sub> str.	3036.5	3	2955.8	6		2194.1	3	2134.1	5		3032.0	3	2951.6	5		
A <sub>1</sub> CH <sub>2</sub> scis.	1350.8	1406.4	8	1352.7	10	1067.6	1107.5	8	1069.3	8	1342.5	1397.1	7	1343.8	10	
B <sub>2</sub> CH <sub>2</sub> scis.	890.4	949.6	25	901.2	26	covered <sup>e</sup>	751.8	12	713.6	13	882.4	940.6	25	892.7	26	
A <sub>1</sub> C-Ir str.	847.8	4	839.9	2		749.1	1	739.9	0		823.0	4	815.4	2		
B <sub>1</sub> CH <sub>2</sub> rock	807.6	4	785.2	4		607.2	2	590.0	2		803.2	5	780.9	4		
B <sub>2</sub> as. IrCl <sub>2</sub> str.	386.8	93	391.6	75		386.8	93	391.6	75		386.8	93	391.6	75		
A <sub>1</sub> s. IrCl <sub>2</sub> str.	371.2	7	376.2	5		371.1	7	376.2	5		371.2	7	376.2	5		
A <sub>2</sub> CH <sub>2</sub> twist	256.0	0	294.0	0		181.6	0	208.5	0		256.0	0	294.0	0		
B <sub>2</sub> IrCl <sub>2</sub> rock	203.0	3	206.0	2		184.7	2	187.4	2		198.1	3	201.1	2		
A <sub>1</sub> IrCl <sub>2</sub> scis.	119.5	0	121.0	0		119.4	0	120.9	0		119.4	0	120.9	0		
B <sub>1</sub> IrCl <sub>2</sub> wag	92.7	0	95.5	0		90.2	0	92.9	0		92.1	0	94.9	0		

<sup>a</sup> Frequencies and intensities are in  $\text{cm}^{-1}$  and km/mol. <sup>b</sup> Observed in an argon matrix. <sup>c</sup> Computed with B3LYP/6-311++G(3df,3pd). <sup>d</sup> Computed with BPW91/6-311++G(3df,3pd).  $\text{CH}_2=\text{IrCl}_2$  has a  $\text{C}_{2v}$  structure with two equal Ir-Cl bonds, and the symmetry notations are based on the structure. <sup>e</sup> Covered by precursor band.

Table S5: Observed and Calculated Fundamental Frequencies of  $\text{CH}_2=\text{IrFCl}$  Isotopomers in the ground  ${}^2\text{A}''$  State<sup>a</sup>

Approximate Description	$\text{CH}_2=\text{IrFCI}$					$\text{CD}_2=\text{IrFCI}$				
	Obs <sup>b</sup>	B3LYP <sup>d</sup>	Int <sup>d</sup>	BPW91	int	Obs <sup>b</sup>	B3LYP <sup>d</sup>	Int <sup>d</sup>	BPW91	int
A'' as. $\text{CH}_2$ str.	3155.5	0		3078.3	2		2350.8	0	2293.8	1
A' s. $\text{CH}_2$ str.	3041.5	3		2964.4	5		2197.7	3	2140.5	4
A' $\text{CH}_2$ scis.	1406.4	7		1353.7	10		1107.0	7	1069.8	8
A' $\text{CH}_2$ wag	918.5	952.0	32	905.7	32	covered <sup>e</sup>	757.1	13	717.2	18
A' C-Ir str.	848.7	3		842.2	2		748.0	5	743.2	0
A'' $\text{CH}_2$ rock	817.6	6		795.8	5		615.2	2	598.8	2
A' Ir-F str.	620.8, <b>615.7</b>	620.7	121	615.0	103	620.6, <b>615.4</b>	620.6	121	614.9	101
A' Ir-Cl str.	386.8	38		392.5	30		386.8	38	392.5	30
A'' $\text{CH}_2$ twist	300.2	0		324.7	0		215.0	0	231.9	0
A' ClIrF bend	217.8	3		221.6	2		200.7	2	204.7	2
A' FIrCl bend	157.9	0		161.7	0		156.3	0	159.8	0
A'' IrFCI wag	120.7	1		121.1	0		117.4	1	117.7	0

<sup>a</sup> Frequencies and intensities are in  $\text{cm}^{-1}$  and km/mol. <sup>b</sup> Observed in an argon matrix, and the stronger one in an absorption pair is bold.

<sup>c</sup> Computed with B3LYP/6-311++G(3df,3pd). <sup>d</sup> Computed with BPW91/6-311++G(3df,3pd). <sup>e</sup>  $\text{CH}_2=\text{IrFCl}(T)$  has a  $C_s$  structure, and the symmetry notations are based on the structure. <sup>e</sup> Covered by precursor band.

Table S6: Observed and Calculated Fundamental Frequencies of  $\text{CH}_2=\text{IrF}_2$  Isotopomers in the  ${}^2\text{A}_2$  ground State<sup>a</sup>

Approximate Description	$\text{CH}_2=\text{IrF}_2$					$\text{CD}_2=\text{IrF}_2$				
	Obs <sup>b</sup>	B3LYP <sup>d</sup>	Int <sup>d</sup>	BPW91	int	Obs <sup>b</sup>	B3LYP <sup>d</sup>	Int <sup>d</sup>	BPW91	int
$\text{B}_1 \text{CH}_2$ as. str.	3161.9	0	3084.6	1		2355.7	0	2298.7	1	
$\text{A}_1 \text{CH}_2$ s. str.	3046.8	2	2969.7	5		2201.6	2	2144.4	4	
$\text{A}_1 \text{CH}_2$ scis.	1405.0	6	1353.0	8		1104.9	6	1068.9	7	
$\text{B}_2 \text{CH}_2$ wag	covered <sup>e</sup>	948.9	35	902.6	35	covered <sup>e</sup>	755.1	19	718.6	20
$\text{A}_1 \text{C-Ir}$ str.	847.6	2	843.9	1		750.0	0	743.8	0	
$\text{B}_1 \text{CH}_2$ rock	826.2	8	805.5	7		622.2	4	606.6	3	
$\text{B}_2 \text{IrF}_2$ as. str.	643.7, <b>642.3</b>	649.0	169	641.7	143	643.6, <b>642.6</b>	648.9	168	641.6	141
$\text{A}_1 \text{IrF}_2$ s. str.	602.3	629.8	35	621.9	28	602.3	629.7	35	621.8	28
$\text{A}_2 \text{CH}_2$ twist	304.1	0	337.1	0		216.4	0	239.9	0	
$\text{B}_2 \text{IrF}_2$ rock	235.4	3	238.7	3		216.5	2	219.4	2	
$\text{A}_1 \text{IrF}_2$ scis.	202.9	2	202.1	1		202.8	2	202.0	1	
$\text{B}_1 \text{IrF}_2$ wag	162.3	2	160.1	1		160.0	2	157.6	1	

<sup>a</sup> Frequencies and intensities are in  $\text{cm}^{-1}$  and km/mol. <sup>b</sup> Observed in an argon matrix, and the stronger one in a absorption pair is bold. <sup>c</sup> Computed with B3LYP/6-311++G(3df,3pd). <sup>d</sup> Computed with BPW91/6-311++G(3df,3pd). <sup>e</sup> Covered by precursor band.  
 $\text{CH}_2=\text{IrF}_2$  has a  $\text{C}_{2v}$  structure with two equal Ir-F bonds, and the symmetry notations are based on the structure.