Chiral Actinide Complexes

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Chirality, Agostic Interactions, and Pyramidality in Actinide Methylidene Complexes**

Jun Li, Han-Shi Hu, Jonathan T. Lyon, and Lester Andrews**

Chirality is important in organic and biological chemistry owing to chiroptical properties of chiral compounds and their applications in asymmetric organic synthesis, biological processes, enantioselective catalytic reactions, and pharmaceutical industries.[1,2] Chiral complexes are also of interest in inorganic chemistry, because the steric configuration of a chiral molecule is vital to its function.[3] While chiral transition-metal and lanthanide compounds are well-known,[4] chiral actinide complexes are rare. Herein, we report the experimental preparation, theoretical investigation, and spectroscopic characterization of a series of chiral actinide complexes. Reactions of laser-ablated thorium and uranium atoms with chlorofluoromethane (CH_2FCl) have formed new actinide methylidene complexes [H_2C=AnFCl], where An = Th and U. Through relativistic density functional theory (DFT) and ab initio studies at the CCSD(T) level, we find that these two actinide molecules have strong agostic interactions[5,6] and display pyramidalization. These effects lead to chiral actinide complexes with C=An bonds. Extensive theoretical calculations on a series of thirty [H_2C=AnXY] (An = Th, U; X, Y = F, Cl, Br, I, and H) molecules reveal that they all show the agostic H_2C interactions and strong pyramidality at the actinide center, thus rendering all of these actinide methylidene complexes chiral.

In searching for actinide complexes with C=An double bonds, we performed a variety of matrix-isolation experiments to investigate the reactions of laser-ablated thorium and uranium atoms with CH_2FCl. Through isotopic substitutions and DFT calculations of the energetics, vibrational frequencies, and infrared intensities of the resulting compounds, we have identified and characterized two simple actinide methylidene complexes, [CH_2=ThFCl] and [CH_2=UFCl] (see the Experimental Section). The infrared spectra of the product species isolated in argon matrix samples are shown in Figure 1. Theoretical and experimental studies suggest that these C=An complexes are likely formed by α-Cl transfer in the initially formed, energized [CH_2Cl–AnF] insertion product, and that the final methylidene complex is relaxed by the cold matrix [Eq. (1), * denotes excited species].

$$An^* + CH_2FCl \rightarrow [CH_2Cl{-}AnF]^* \rightarrow [CH_2{=}AnFCl] \quad (An = Th, U) \tag{1}$$

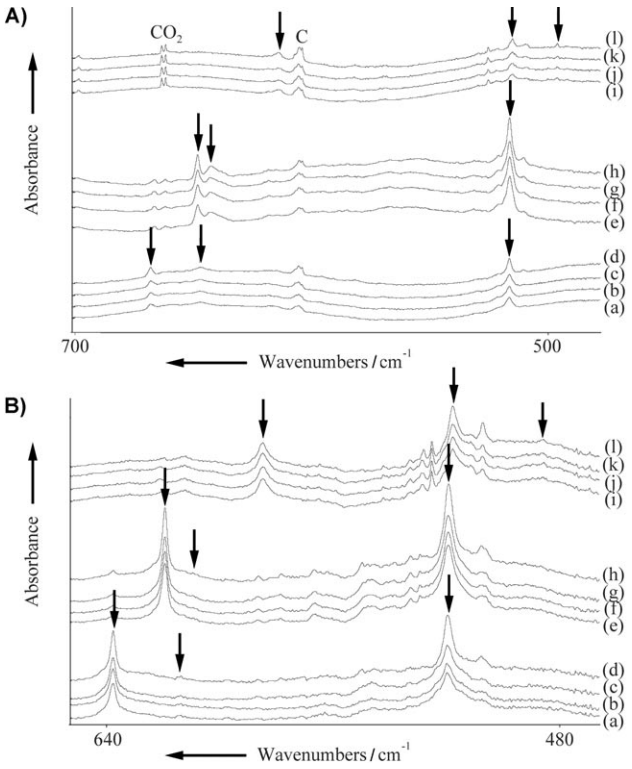

Figure 1. Matrix infrared spectra of [$H_2CAnFCl$] (An = Th (A) and U (B)) complexes formed by laser-ablated actinide atoms reacting with 0.6–1% CH_2FCl in argon at 8 K. a) CH_2FCl and An codeposited in argon for 1 h, b) after irradiation above 290 nm, c) after irradiation above 220 nm, and d) after annealing to 30 K. e) $^{13}CH_2FCl$ and An codeposited in argon for 1 hr, f) after irradiation above 290 nm, g) after irradiation above 220 nm, and h) after annealing to 30 K. i) CD_2FCl and An codeposited in argon for 1 h, j) after irradiation above 290 nm, k) after irradiation above 220 nm, and l) after annealing to 30 K. C indicates a band common to thorium experiments. The arrows indicate bands arising from [$H_2CAnFCl$] species.

[*] Prof. Dr. J. Li, H.-S. Hu
Department of Chemistry and Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education
Tsinghua University
Beijing 100084, China
Fax: (+86) 10-6277-1149
E-mail: junli@tsinghua.edu.cn
Dr. J. T. Lyon, Prof. Dr. L. Andrews
Department of Chemistry
University of Virginia
Charlottesville, Virginia 22904-4319 (USA)
Fax: (+1) 434-924-3710
E-mail: lsa@virginia.edu

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These [CH_2=AnFCl] complexes are heavy-element analogues of 1-chloro-1-fluoroethylene (H_2C=CFCl), which is known to have a planar structure.[7] It is not inherently clear whether the actinide methylidene molecules would adopt such an ethylene-like structure or whether the methylene group would behave as a classic carbene ligand. To understand the geometry and electronic structures of the actinide complexes, we have investigated the potential-energy surfaces, energetics, and isotopic effects of various possible structures of [H_2CAnFCl] using DFT at the level of the PW91 generalized gradient approach[8] and scalar–relativistic zero-order regular approximation.[9] The calculated gas-phase harmonic frequencies and infrared experimental values observed in the argon matrix are listed in Table 1. The

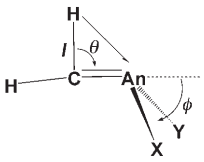
Table 1: Observed and calculated vibrational frequencies of [H_2CAnFCl] in the ground electronic states.[a,b]

Mode	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
	[H_2C=ThFCl]		[$H_2{}^{13}$C=ThFCl]		[D_2C=ThFCl]	
C=Th str	668.0	671(97)	648.3	651(90)	614.2	612(80)
CH_2 wag	647.1	638(152)	642.9	633(147)	496.2	496(106)
Th–F str	516.2	532(150)	516.1	532(151)	516.0	530(150)
	[H_2C=UFCl]		[$H_2{}^{13}$C=UFCl]		[D_2C=UFCl]	
C=U str	637.8	654(92)	619.7	635(88)	585.2	597(77)
CH_2 wag	614.6	619(97)	609.5	614(93)	485.5	482(71)
U–F str	519.7	560(144)	519.7	560(144)	517.9	559(138)

[a] The experimental frequencies (in cm^{-1}) are observed in argon matrix, and the calculated PW91/TZ2P frequencies and infrared intensities (in parenthesis) are listed in cm^{-1} and km mol^{-1}. [b] The abbreviations str and wag denote the stretching and wagging vibrational modes, respectively.

excellent correlation of the theoretical and experimental vibrational frequencies, infrared intensities, and isotopic frequency shifts confirms unequivocally the assignment of the reaction products as [H_2C=AnFCl].[10] These assignments are supported by similar detailed evidence presented for the [H_2C=AnHX] systems.[11,12]

Our DFT and CCSD(T) calculations show that the geometries of the [H_2C=AnFCl] molecules are neither symmetric at H_2C as in ethylene nor planar as in H_2C=CFCl (Scheme 1). Instead, the [H_2C=AnFCl] complexes exhibit a large agostic effect in the H_2C group (i.e. forming an agostic bond between H and An), as measured by the calculated H-C-An angles and C–H bond lengths, and strong pyramidalization at {AnFCl}, as measured by the ⊂C–AnXY bond–plane angles (defined as zero for planar structures). We use H_{ag} to denote the agostic hydrogen atom. The presence of agostic interactions in these molecules is corroborated by the calculated C–H stretching frequencies and by the predicted ^{1}H NMR spectroscopic properties. The symmetric and asymmetric C–H stretching frequencies only differ by 91 and 104 cm^{-1} in non-agostic [H_2CUFCl] and H_2CCFCl, whereas in the molecules with agostic interactions, the difference increases to 272 and 369 cm^{-1} for [H_2CAnFCl] (An = Th, U), consistent with elongation and weakening of the C–H bond involved in the agostic interaction. In the ^{1}H NMR spectrum of [H_2CThFCl], the resonance for H_{ag} is shifted to higher field by −1.7 ppm, while that of the non-agostic proton is shifted to lower field by +0.9 ppm relative to the symmetric carbene H atoms in H_2CCFCl. Moreover, the nuclear spin–spin coupling constant $J_{C,H}$ in [H_2CThFCl] is calculated to be 102 Hz for the C–H_{ag} bond involved in the agostic interaction, which is 46 Hz lower than the value for the non-agostic C–H bond.



Scheme 1. Illustration of the agostic interaction measured by the C–H distance and H-C-An angle (l, θ) and the pyramidalization measured by the ⊂C–AnXY bond–plane angle (ϕ).

The pyramidality of these actinide molecules is in contrast with the planar ethylene derivatives but is similar to the *trans*-bent structures of heavier Group 14 compounds with slipped double bonds.[13] The structures of the chlorofluoro-substituted molecules are akin to those of [CH_2=AnH_2] and [CH_2=AnHX] (An = Th, U) formed in reactions of Th and U atoms with methane and halomethanes[11,12] and to analogous transition-metal methylidene complexes.[14] Inasmuch as the actinide 5f and 6d orbitals do not usually form strongly directional hybrid orbitals, it is not surprising that these molecules do not favor planar structures following the valence shell electron pair repulsion (VSEPR) rule.[15]

Table 2 lists the parameters for agostic interaction and pyramidalization calculated using the ZORA PW91 approach for the [CH_2=AnXY] molecules with all possible combinations of X, Y = F, Cl, Br, I, and H. Our calculations show that all of the Th complexes are closed-shell, while the U complexes are open-shell with $5f^2$ configurations, consistent with the An^{IV} oxidation states. The optimized non-agostic C–H bond lengths (ca. 1.09 Å) are smaller than for the C–H_{ag} bonds, which are elongated and weakened when the

Table 2: Agostic interactions and pyramidalization in [H_2CAnXY] (An = Th, U; X, Y = F, Cl, Br, I, H).[a,b]

XY	[H_2CThXY] C=Th [Å]	l [Å]	θ [°]	ϕ [°]	[H_2CUXY] C=U [Å]	l [Å]	θ [°]	ϕ [°]
FF	2.1522	1.1150	102.1	56.7	2.0662	1.1349	88.9	63.3
FCl	2.1319	1.1225	94.8	54.7	2.0584	1.1328	89.2	65.3
FBr	2.1282	1.1233	94.2	52.8	2.0578	1.1326	89.2	63.2
FI	2.1233	1.1250	92.8	52.4	2.0572	1.1333	88.5	61.0
FH	2.1243	1.1272	91.1	62.8	2.0630	1.1445	83.3	66.6
ClCl	2.1192	1.1239	93.4	53.6	2.0489	1.1346	88.5	65.0
ClBr	2.1160	1.1247	92.9	51.7	2.0471	1.1345	88.4	63.5
ClI	2.1111	1.1265	91.6	51.0	2.0445	1.1352	87.9	63.1
ClH	2.1103	1.1302	89.5	62.3	2.0369	1.1457	83.5	70.5
BrBr	2.1134	1.1256	92.4	49.0	2.0470	1.1350	88.0	60.4
BrI	2.1091	1.1272	91.3	48.6	2.0438	1.1363	87.3	60.0
BrH	2.1077	1.1313	89.1	60.2	2.0354	1.1460	83.5	68.7
II	2.1053	1.1274	90.9	48.3	2.0410	1.1373	86.9	59.6
IH	2.1028	1.1322	88.6	60.6	2.0308	1.1468	83.4	69.8
HH	2.1075	1.1306	89.5	69.3	2.0266	1.1457	83.8	76.8

[a] All the geometric parameters were optimized using the scalar relativistic ZORA PW91 approach (see text). [b] Parameters l, θ, and ϕ represent the C–H_{ag} bond length, H-C-An angle, and ⊂C–AnXY bond–plane angle, respectively (see Scheme 1).

strength of the agostic interaction increases. From Th to U complexes the strength of the agostic interaction increases, because the C=An bond is shorter for U than for Th. This trend has been analyzed and documented for a series of $[CH_2{=}MH_2]$ complexes using CASSCF/CASPT2 and B3LYP calculations.[12c] The optimized geometry parameters listed in Table 2 also indicate that across the series of X, Y = F, Cl, Br, and I, the C=An bond lengths decrease and the strength of the agostic interaction increases. This trend agrees well with the radial expansion of An 6d and 5f orbitals and the consequent enhancement of the strength of C=An bonds upon substitution by less electronegative substituents at the actinide center. On the other hand, the pyramidality of these $[H_2C{=}AnXY]$ complexes is smaller for Th than for U and is smaller for halogens than for hydrogen. The pyramidality decreases when the electronegativity of the substituents on the An center decreases. It is therefore possible to tune the C=An bond lengths and bond strengths, agostic interactions, and pyramidalization of these complexes through bonding of diverse ligands to the actinide and carbene carbon centers.

As expected for molecules with C_1 symmetry, the geometry optimizations of the $[CH_2{=}AnFCl]$ molecules reveal two optical isomers, as shown in Figure 2 A, B for An = U. The calculated geometry parameters, energies, and vibrational

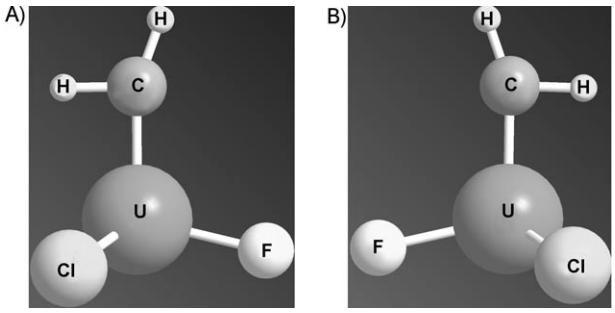


Figure 2. The two enantiomers of $[H_2CUFCl]$.

frequencies of these two isomers are necessarily identical; they are enantiomers that can not be superimposed through rotation. Recall that the ubiquitous chirality at carbon atoms in organic chemistry occurs when a C center is attached to four different substituents, as in CXYZW. The chirality of the $[CH_2{=}AnFCl]$ molecules, on the other hand, is caused by the pyramidalization and the agostic interaction. The $[CH_2{=}AnFCl]$ species represent rare examples of chiral molecules in f-element complexes, and they are expected to exhibit chiroptical properties. The predicted circular dichroism (CD) spectrum of $[CH_2{=}ThFCl]$ molecule is shown in Figure S1 in the Supporting Information.

In these actinide complexes, the strong pyramidalization of the coordination shell of the actinide metal center leads to nonplanar structures with large ⊂C–AnXY bond–plane angles. As a result, not only $[CH_2{=}AnXY]$ ($X \neq Y$) but also $[H_2C{=}AnX_2]$ possess chirality. Indeed, our calculations show that all of the molecules listed in Table 2 are chiral, which is mainly a consequence of the strong pyramidalization that spoils the planar symmetry. The agostic interaction that revokes the axial equality of the two H atoms also helps to induce chirality in $[H_2C{=}AnX_2]$. Therefore, these actinide molecules and the previously identified transition-metal $[H_2C{=}MXY]$ (M = Zr, Hf; X, Y = H, F, Cl, Br) complexes are chiral.[14] They are in contrast with the analogous $H_2C{=}CF_2$ and $[H_2C{=}MCl_2]$ (M = Ti, Zr, Hf) compounds, which have been reported to be planar or achiral.[16]

The energy effects of the agostic interaction, pyramidalization, and enantiomerization of $[CH_2{=}UFCl]$ calculated on the basis of optimized PW91 geometries are shown in Figure 3. Configuration **b** is the ethylene-like planar structure,

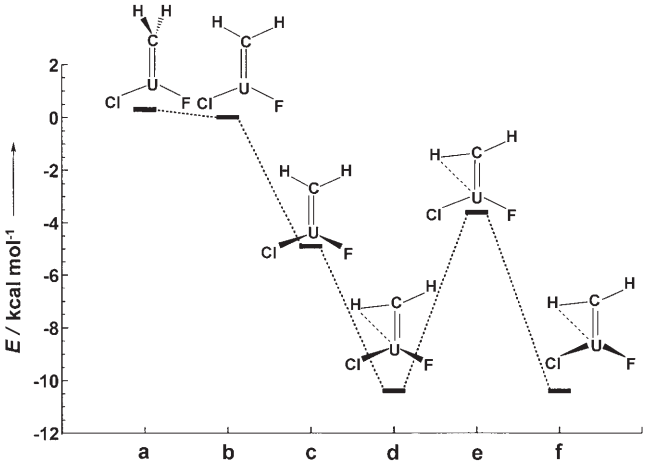


Figure 3. The relative PW91 energies of $[H_2CUFCl]$ in different configurations: **a** C_s symmetry with H_2C perpendicular to {UFCl}; **b** C_s symmetry with H_2C coplanar with {UFCl}; **c** C_1 symmetry with pyramidalization at {UFCl}; **d** C_1 symmetry with agostic interaction at H_2C and pyramidalization at {UFCl}; **e** C_s symmetry with agostic interaction at H_2C; **f** enantiomer of **d**. Note the configurations **d** and **f** differ by the directions of the F and Cl ligands.

and configuration **a** is formed from **b** by a 90° rotation of CH_2 around the C=U axis. When pyramidalization is allowed at {UFCl} (configuration **c**), the molecule is stabilized by 4.9 kcal mol^{-1}, and when agostic interaction through the H_2C group is allowed (configuration **d**), forming the chiral molecule $[CH_2{=}UFCl]$, the compound is stabilized by another 5.5 kcal mol^{-1}. Therefore, the global minimum structure (**d**) is 10.4 kcal mol^{-1} more stable than the ethylene-like planar structure (**b**), with the agostic interaction and pyramidalization accounting for roughly half of the energetic effects. When the chiral molecule (**d**) is transformed into its enantiomer (configuration **f**), the system has to go through a transition state (configuration **e**). The barrier calculated for interconversion of the enantiomers in $[H_2CUFCl]$ is 6.7 kcal mol^{-1}. Inasmuch as chiral lanthanide compounds are thermally labile, they usually fluctuate with very small energy cost.[4] The actinide chiral compounds under consideration are more rigid than their lanthanide counterparts. Because the energy difference between enantiomers of a chiral molecule whose chirality stems from weak interactions is negligible,[17] the two enantiomers of $[H_2C{=}AnXY]$ are calculated to have identical thermodynamic energies. Therefore, the experimentally observed species should be a racemic mixture of them. The

moderate enantiomerization barrier implies that it would be possible to separate these chiral isomers if they were synthesized in bulk.

Natural bond orbital (NBO) analyses[18] (see Table S1 in the Supporting Information) indicate that the agostic interaction arises from the donor–acceptor interactions between C=An and C–H_{ag}, as discussed in previous theoretical studies.[5,6] The natural hybrid orbitals of carbon are approximately sp^1 for bonding to the non-agostic hydrogen atoms and approximately sp^3 (or nearly pure p) for the agostic hydrogen atoms, consistent with the calculated bond lengths, C–H stretching vibrational frequencies, and $J_{C,H}$ spin–spin coupling constants. Therefore, pyramidalization and agostic interactions play significant roles in forming the chiral actinide complexes. Similar stabilizations have been noted for $[CH_2{=}ZrH_2]$.[14]

The NBO analyses further reveal that the actinide methylidene complexes have significant bonding interactions between the An 6d and 5f orbitals and the C 2s and 2p orbitals. The C–An σ bond and π bond are $(df–sp^2)\sigma$ and $(df–p)\pi$, respectively, confirming the nature of the C=An bonds.[19] The 6d character is much higher in the Th species than in the U species, which agrees well with the calculated diabatic C=An bond energies of 120 kcal mol^{-1} (Th) and 106 kcal mol^{-1} (U) for $[H_2C{=}AnFCl]$. The C=An bond strength can be tuned by attaching different substituents to the actinide atom; the calculated bond energies support this argument. The fragment molecular orbital analysis shows that the An 5f and 6d bands are significantly broadened through the agostic interaction with hydrogen atoms and through the pyramidalization at An. The low-lying 6d and 5f orbitals form the foundation of the energetic preference for structures stabilized by agostic interactions in these actinide methylidene complexes.

In summary, we have prepared two $[CH_2{=}AnFCl]$ actinide complexes through reactions of laser-ablated actinide atoms with H_2CFCl. Theoretical investigations indicate that the $[CH_2{=}AnFCl]$ molecule has two enantiomers arising from pyramidalization effects and agostic interactions. These molecules and the previously identified actinide methylidene complexes[11,12] thus constitute a series of chiral molecules in actinide chemistry. In particular, coordination of the An and C centers by bulky ligands will likely increase the thermodynamic and kinetic stabilities of such species and influence the chirality of actinide methylidene complexes. Such chiral actinide complexes might be useful for the synthesis of organometallic compounds and as enantioselective and enantiospecific catalysts. The discovery of these simple chiral actinide complexes and the investigations of their structures, bonding, and electronic structures have provided insight for rational design of stable chiral actinide complexes.

Experimental Section

Laser-ablated Th and U atoms were reacted with the CH_2FCl precursor (Du Pont) and isotopic modifications[20] in excess argon (0.5 to 1% concentrations) during condensation onto an 8-K cesium iodide window as described previously.[11,12,14] Infrared spectra were recorded on a Nicolet 550 spectrometer after sample deposition, after annealing, and after irradiation using a 175-W mercury arc street lamp. Reaction of U atoms with CH_2FCl produced three new absorptions (marked with arrows in Figure 1) at 637.8, 614.6, and 519.7 cm^{-1}. The intensity of these absorptions increased by 10% upon 220-nm irradiation. The ^{13}C-substituted product showed absorptions at 619.5, 609.5, and 519.5 cm^{-1}, and the reaction with CD_2FCl yielded bands at 585.2, 517.9, and 485.5 cm^{-1}. Similar reactions of Th atoms with CH_2FCl produced three new absorptions at 668.9, 647.1, and 516.2 cm^{-1}. The intensity of these absorptions also increased slightly upon 220-nm irradiation. The ^{13}C-substituted product provided absorptions at 648.3, 642.9, and 516.1 cm^{-1}, and the corresponding reaction with CD_2FCl yielded bands at 614.2, 496.2, and 516.0 cm^{-1}. These absorptions and the isotopic frequency shifts characterize the vibrational modes as C=An stretching, CH_2 wagging, and An–F stretching, as noted in Table 1, and thus identify these newly formed molecules as $[CH_2{=}UFCl]$ and $[CH_2{=}ThFCl]$.[10]

The geometries, vibrational frequencies, and electronic structures of the Th and U products were calculated using quasi-relativistic DFT with the generalized gradient approach of PW91,[8] which has been shown to have good performance for actinide complexes.[21] In the PW91 calculations, the zero-order-regular approximation (ZORA) was used to account for the scalar relativistic effects.[9] We used uncontracted Slater basis sets of triple-zeta quality plus two polarization functions (TZ2P).[22] The frozen-core approximation was applied to the $[1s^2]$ cores of C and F, $[1s^2–2p^6]$ of Cl, $[1s^2–3d^{10}]$ of Br, $[1s^2–4d^{10}]$ of I, and $[1s^2–5d^{10}]$ of U.[23] The geometry optimizations and vibrational frequency calculations were performed with inclusion of the scalar relativistic effects. To investigate the agostic effects and pyramidalization of these actinide complexes, we also explored the potential-energy surfaces at various geometries. All of these calculations were performed using the Amsterdam Density Functional (ADF 2006.01) program.[24] The SDD pseudopotentials and basis sets[25] were also employed in the calculations using coupled cluster with single, double, and perturbative triple excitations [CCSD(T)]. Natural bond orbital analysis were performed using the Gaussian 03 program with SDD pseudopotentials and 6-311++G(2d,p) basis sets for the light atoms.[18,26]

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[10] The Th–Cl and U–Cl stretching frequencies (intensities), calculated at 316(60) and 303(56) cm^{-1}($km\,mol^{-1}$), respectively, are below our instrumental limit. Our observation of the [CH_2=AnXY] methylidene complexes is corroborated by their observation in similar experiments with CH_2F_2 and CH_2Cl_2. For the [CH_2=AnF_2] species, we observe two An–F stretching modes in addition to the C=An and CH_2 modes, which clearly demonstrates the presence of two An–F bonds in these species. Furthermore, the species [CHFCl–AnH], [CH_2Cl–AnF], [CH_2Cl–AnCl], and [HC≡AnHFCl] are excluded, because they are calculated to be more than 36 $kcal\,mol^{-1}$ higher in energy than the methylidene compounds, and their calculated frequencies do not match our observed bands.

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