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Formation of $CH_2{=}TiF_2$ by C−F Activation and α-F Transfer

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Summary: Laser-ablated titanium atoms react with CH_2F_2 to form the methylidene complex $CH_2{=}TiF_2$, which is symmetrical and shows no agostic distortion, in contrast to the analogous methylidene complexes $CH_2{=}TiHF$ and $CH_2{=}TiH_2$.

Reactions with carbon−fluorine functional groups are a major challenge and opportunity for organometallic chemistry. Chlorofluorocarbons (or Freons) are detrimental to the ozone layer,[1] and perfluoroalkanes are effective greenhouse gases.[2] Although activation of C−F bonds is difficult, because they are the strongest single carbon bonds,[3] this reaction is necessary for the remediation of pollutant molecules. Hence, reactions of fluorocarbons to form disposable compounds is an important research goal. Most C−F bond activation methods involve transition metal centers and C−F oxidative addition reactions.[4−7]

Transition metal alkylidenes ($M{=}CR_1R_2$) are industrially important for their role in catalytic processes.[8−10] In particular, titanium alkylidene complexes have been proposed as intermediate species in a number of reactions.[9−12] However, stable group 4 alkylidenes are rare.[9] Recently we have investigated titanium atom reactions with methane and methyl halides.[13−15] In these studies, the major products, the methylidene complexes $CH_2{=}TiHR$ (R = H, F, Cl, Br), were formed by C−R bond activation followed by α-H transfer. These complexes exhibit strong agostic $H{-}C{=}Ti$ interactions, which distort the molecule. Agostic bonding helps to stabilize the complex, and recently this interaction was computed to have strengths comparable to hydrogen bonds.[16] We now react CH_2F_2 with titanium for comparison with three motivating questions in mind. First, which bond is activated: C−H or C−F? Second, does α-H or α-F transfer subsequently occur? Third, what is the role of agostic bonding in the methylidene complex so formed?

Laser-ablated Ti atoms were condensed with CH_2F_2 in excess argon, as described in detail elsewhere.[13−15,17] Theoretical computations were carried out with the *Gaussian 98* program to confirm vibrational assignments and product identification.[18] The B3LYP hybrid functional was employed,[19] and the 6-311++G(2d,p) basis set was used for all atoms.[20] All reported frequencies (not scaled) were computed analytically, and energy values include zero-point vibrational corrections.

When atomic titanium was reacted with CH_2F_2, four major product bands were observed at 612.9, 695.4, 705.8, and 740.3 cm^{-1}. All four absorptions increased together in intensity upon photolysis with a Pyrex filter ($\lambda > 290$ nm) and with full arc irradiation ($\lambda > 220$ nm) and remained nearly unchanged on annealing. Hence, all four new absorptions belong to a common product. The strongest absorption at 740.3 cm^{-1} shows only slight isotopic shifts (0.4 cm^{-1} ^{13}C and 1.6 cm^{-1} D), indicating that this mode corresponds to a Ti−F stretch. The satellite splittings observed on this peak arise from natural-abundance isotopic titanium and demonstrate that this product molecule contains only one titanium atom.[14,21] This absorption is observed at almost the same frequency as the antisymmetric Ti−F stretching mode of the TiF_2 molecule.[21] However, our product absorption shows ^{13}C and D isotopic shifts and must be assigned to a species also containing carbon and hydrogen. The second absorption at 705.8 cm^{-1} red-shifts 10.3 cm^{-1} upon carbon-13 isotopic substitution and 54.0 cm^{-1} with CD_2F_2 (Figure 1). Such a large ^{13}C shift identifies this peak as a mostly C=Ti stretching mode. The next absorption at 695.4 cm^{-1} shows the largest deuterium shift (138.6 cm^{-1}) and a small carbon-13 shift (6.0 cm^{-1}), which characterize a CH_2 wagging motion. Finally, the weaker fourth absorption at 612.9 cm^{-1} also reveals natural titanium isotopic splittings, has only a small carbon-13 shift, and can be assigned to a second Ti−F stretching mode. The deuterium counterpart of this absorption was not observed, indicating that the infrared intensity for this mode decreases substantially on D isotopic substitution. Hence, the observed infrared spectra arise from TiF_2, CH_2, and C=Ti subgroups in a new molecule.

The four observed vibrational modes (symmetric and antisymmetric Ti−F stretches, CH_2 wag, and C=Ti stretch) identify the $CH_2{=}TiF_2$ complex with certainty. The excellent correlation between these observed fundamentals and those computed for

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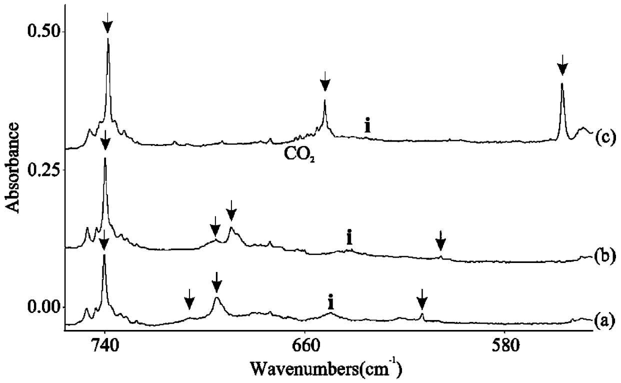

Figure 1. IR spectra in the 750−550 cm^{-1} region recorded after titanium atoms were reacted with (a) CH_2F_2, (b) $^{13}CH_2F_2$, and (c) CD_2F_2 using 1% reagent concentrations in argon at 8 K. All spectra recorded after full-arc irradiation. Arrows denote the $CH_2{=}TiF_2$ product absorptions, and **i** indicates the $CH_2F{-}TiF$ insertion product.

Table 1. Observed and Calculated Fundamental Frequencies of $CH_2{=}TiF_2$^{a}

approx mode	$CH_2{=}TiF_2$		$^{13}CH_2{=}TiF_2$		$CD_2{=}TiF_2$	
	obsd	calcd (int)	obsd	calcd (int.)	obsd	calcd (int)
HCTiF dist		79.1 (57)		78.8 (57)		76.5 (54)
CTiF bend		183.9 (4)		182.8 (1)		151.9 (0)
TiF_2 scis		184.7 (6)		184.0 (8)		183.1 (9)
CH_2 rock		365.8 (1)		360.8 (1)		315.1 (1)
CH_2 twist		517.4 (0)		517.4 (0)		368.9 (0)
Ti−F str	612.9	637.4 (62)	605.4	633.7 (52)		617.5 (18)
C═Ti str	705.8	743.0 (91)	695.5	730.3 (100)	651.8	686.0 (119)
CH_2 wag	695.4	748.5 (145)	689.4	741.1 (142)	556.8	592.3 (111)
Ti−F str	740.3	763.9 (269)	739.9	763.5 (268)	738.7	761.7 (265)
CH_2 scis		1325.8 (18)		1316.4 (17)		1040.5 (32)
CH str		3052.5 (0)		3046.9 (0)		2214.1 (1)
CH str		3143.4 (3)		3131.3 (4)		2332.6 (1)

[a] B3LYP calculations using the 6-311++G(2d,p) basis sets for all atoms. All frequencies are in cm^{-1}, and computed infrared intensities are in km/mol.

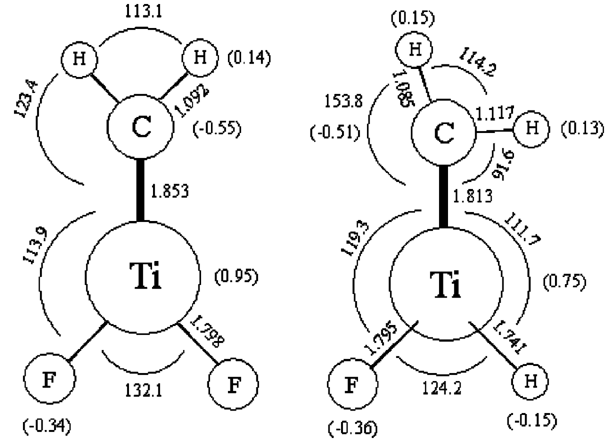

Figure 2. Structures of the $CH_2{=}TiF_2$ and $CH_2{=}TiHF$ complexes calculated at the B3LYP/6-311++G(2d,p) level of theory. All bond lengths are in angstroms, and bond angles are in degrees. Mulliken charges are given in parentheses.

the stable $CH_2{=}TiF_2$ complex is demonstrated in Table 1. Frequencies computed at the B3LYP level typically are slightly higher than observed values.[22]

It is of interest to discuss how this product forms. Initially, a titanium atom can insert into either a C−H or a C−F bond. Computations on the latter led to an optimized triplet $CH_2(\mu\text{-}F)TiF$ structure with a bridging fluorine atom, which is predicted to be 74 kcal/mol more stable than the energy sum of the two reactants and 60 kcal/mol more stable than another possible $CHF(\mu\text{-}F)TiH$ product complex. Primary insertion into either bond leaves the complex positioned in such a way that a single fluorine atom is initially bridging the C−Ti bond. The electron-deficient nature of the titanium metal center favors this configuration to achieve some overlap with fluorine lone electron pairs. Next we consider the lower energy structure, and either α-H or α-F transfer can occur. A possible triplet CHF−TiHF complex is 21 kcal/mol higher in energy, whereas the triplet $CH_2{-}TiF_2$ complex is 40 kcal/mol lower. From this triplet excited state, relaxation to the singlet $CH_2{=}TiF_2$ complex readily occurs. This final very stable methylidene product lies 139 kcal/mol lower in energy than the sum of the initial reactant energies.

The resulting singlet $CH_2{=}TiF_2$ complex is computed to have near-C_{2v} symmetry and to show no agostic distortion (Figure 2), in contrast to the case for $CH_2{=}TiH_2$ and $CH_2{=}TiHF$.[13,14] The C═Ti bond length, 1.853 Å, is longer than that of the analogous $CH_2{=}TiHF$ complex (1.813 Å), and the C−H bond length, 1.092 Å, is slightly *shorter* than the average (1.101 Å) of $CH_2{=}TiHF$.[14b] The titanium−fluorine distances were computed to be 1.798 Å, almost the same as in $CH_2{=}TiHF$ (1.795 Å) and slightly longer than earlier results for this complex.[23] Mulliken atomic charges for the carbon (−0.55), hydrogen (0.14), and fluorine (−0.34) atoms in this complex are nearly identical with those computed for the $CH_2{=}TiHF$ complex, but here the titanium atom has a considerably larger positive charge (0.95), owning to the additional electron density donated to the second fluorine atom, as compared to titanium (0.75) with one fluoride (−0.36) balanced by hydride (−0.15) in the monofluoride complex. Despite this larger positive charge on Ti, there is no agostic distortion in $CH_2{=}TiF_2$. The obvious difference from $CH_2{=}TiHF$ is the balance of lone-pair repulsions from two fluorine atoms to prevent agostic CH_2 distortion in $CH_2{=}TiF_2$.

To help explain the symmetrical structure of $CH_2{=}TiF_2$, two single-point energy calculations were done. First, the CH_2 subgroup was distorted and fixed at the angles and bond lengths first reported[14] for $CH_2{=}TiHF$ with the other parameters calculated for symmetrical $CH_2{=}TiF_2$ (all using SDD for Ti), and the energy increased 3.0 kcal/mol. Second, $CH_2{=}TiHF$ was recalculated fixed in the cis-agostic structure, and the energy increased 3.4 kcal/mol relative to the optimized trans-agostic structure,[14] although the agostic H to Ti distance was not changed. These results show that F-lone-pair repulsion for the agostic H *destabilizes* the cis-agostic $CH_2{=}TiHF$ structure and likewise prevents agostic distortion of $CH_2{=}TiF_2$.[24]

We also have evidence for the $CH_2(\mu\text{-}F)TiF$ primary insertion product in a weak absorption at 649.1 cm^{-1} (7.0 and 13.7 cm^{-1} ^{13}C and D shifts, respectively, marked **i** in Figure 1). Although there is only one vibration observed for this product, it is in good agreement with a strong, mostly C−F stretching mode predicted for the triplet insertion product with a single bridging fluorine atom (654.0 cm^{-1}; 11.7 and 11.3 cm^{-1} ^{13}C and D isotopic shifts, respectively), which lies 65 kcal/mol higher in energy than the $CH_2{=}TiF_2$ complex.

We have shown that excited titanium atoms react with methylene fluoride to form the $CH_2{=}TiF_2$ complex as the major

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product, which has near-C_{2v} symmetry. DFT frequency calculations and isotopic substitution of the CH_2F_2 precursor confirm this assignment. This product is formed by C−F bond activation with titanium followed by α-F transfer. The computed symmetrical $CH_2{=}TiF_2$ structure shows no evidence of agostic interaction, as fluorine lone-pair repulsions effectively prevent CH_2 distortion in this methylidene complex, in contrast to the case for the analogous $CH_2{=}TiH_2$ and $CH_2{=}TiHF$ complexes.[13,14]

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