Inorg. Chem. **2004**, *43*, 5253–5257

Inorganic Chemistry
Article

Preparation of CH_3TiF and $(CH_3)_2TiF_2$ from the Reaction of CH_3F with Laser-Ablated Ti Atoms

Han-Gook Cho and Lester Andrews*

Department of Chemistry, University of Virginia, P.O. Box 400319,
Charlottesville, Virginia 22904-4319

Received May 19, 2004

Laser-ablated Ti atoms react with CH_3F upon condensation with excess argon to form primarily CH_3TiF and $(CH_3)_2TiF_2$. Irradiation in the UV region promotes α-hydrogen rearrangement of CH_3TiF to $CH_2{=}TiHF$ and increases the yield of $(CH_3)_2TiF_2$. Annealing to allow diffusion and reaction of more CH_3F markedly increases the yield of $(CH_3)_2TiF_2$. This shows that the $CH_3TiF + CH_3F$ reaction is spontaneous and that triplet state CH_3TiF is an extremely reactive molecule. B3LYP calculations are extremely effective in predicting vibrational frequencies and isotopic shifts for CH_3TiF and $(CH_3)_2TiF_2$ and thus in confirming their identification from matrix infrared spectroscopy.

Introduction

Little is known about the structure of methyltitanium compounds although they are important in catalysis. Titaniumtetramethyl, $Ti(CH_3)_4$, is an elusive compound, but it has been crystallized as a diethyl ether adduct and the X-ray crystal structure reveals a 2.09 Å Ti−C bond length.[1] This result is in good agreement with the results of density functional calculations for $Ti(CH_3)_4$.[1] The CH_3TiCl_3 derivative has attracted attention because the structure of the methyl group might be affected by a Ti⋯H−C agostic interaction.[2] The $(CH_3)_2TiCl_2$ species has been investigated for the same reason[2] and for the relationship between π bonding, electronegativity, and bond angles in high valent transition metal complexes.[3] Infrared spectra have been measured for $(CH_3)_2TiCl_2$ in the gas phase and in solid argon, and its structure has been determined in the gas phase by electron diffraction.[2,4] In addition, extensive computations have been done for $(CH_3)_2TiCl_2$ and compared to electron diffraction results to consider possible explanations of the unusual skeletal bond angles.[2−7] Finally, this compound is an active catalyst for metathesis polymerization reactions.[8] There is, however, no information on the analogous methyl titanium fluorine compound $(CH_3)_2TiF_2$ in the literature nor for the simple CH_3TiF molecule. The similar Grignard molecule CH_3MgF is formed in reactions of laser-ablated Mg with CH_3F in excess argon.[9] To prepare methyl titanium derivatives, we have investigated the reaction of laser-ablated Ti atoms with CH_3F in argon condensing at 7 K, and we have found evidence for CH_3TiF and an interesting reversible photochemical rearrangement to the methylidene $CH_2{=}TiHF$.[10] The methylidine is formed by α-H migration in CH_3TiF on 240−380 nm irradiation, and this process reverses on visible light ($\lambda > 530$ nm) illumination. The computed structure for $CH_2{=}TiHF$ reveals an agostic hydrogen interaction.[10] Additional absorptions in these experiments are due to $(CH_3)_2TiF_2$, which is produced by further reaction of CH_3TiF with CH_3F, as will be reported here.

Experimental and Computational Methods

Laser-ablated titanium atoms (Johnson-Matthey) were reacted with CH_3F (Matheson), CD_3F (synthesized from CD_3Br and HgF_2), and $^{13}CH_3F$ (MSD Isotopes, 99%) in excess argon during condensation at 7 K using a closed-cycle refrigerator (Air Products HC-2). The methods have been described in detail elsewhere.[11] Concentrations of gas mixtures ranged between 0.2 and 0.5% in argon. After reaction, infrared spectra were recorded at 0.5 cm^{-1} resolution using a Nicolet 550 spectrometer with an HgCdTe detector. Samples were later irradiated by a combination of optical filters and a mercury

---

* Author to whom correspondence should be addressed. E-mail: lsa@virginia.edu.

(1) Kleinhenz, S.; Seppelt, K. *Chem. Eur. J.* **1999**, *5*, 3573.
(2) McGrady, G. S.; Downs, A. J.; Bednall, N. C.; McKean, D. C.; Thiel, W.; Jonas, V.; Frenking, G.; Scherer, W. *J. Phys. Chem. A* **1997**, *101*, 1951, and references therein.
(3) Kaupp, M. *Chem. Eur. J.* **1999**, *5*, 3631.
(4) McGrady, G. S.; Downs, A. J.; McKean, D. C.; Haaland, A.; Scherer, W.; Verne, H. P.; Volden, H. V. *Inorg. Chem.* **1996**, *35*, 4713.
(5) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Comput. Chem.* **1992**, *13*, 919.
(6) Berger, S.; Bock, W.; Frenking, G.; Jonas, V.; Müller, F. *J. Am. Chem. Soc.* **1995**, *117*, 3820.
(7) Jonas, V.; Böhme, C.; Frenking, G. *Inorg. Chem.* **1996**, *35*, 2097.
(8) Lui, J.; Zhang, D.; Huang, J.; Qian, Y.; Chan, A. S. C. *J. Polym. Sci. A* **2000**, *38*, 1639.
(9) Bare, W. D.; Andrews, L. *J. Am. Chem. Soc.* **1998**, *120*, 7293.
(10) Cho, H.-G.; Andrews, L. *J. Phys. Chem. A* **2004**, *108* (30), 6294−6301 (Ti+CH_3F).
(11) (a) Burkholder, T. R.; Andrews, L. *J. Chem. Phys.* **1991**, *95*, 8697. (b) Andrews, L.; Citra, A. *Chem. Rev.* **2002**, *102*, 885.

10.1021/ic049342m CCC: $27.50

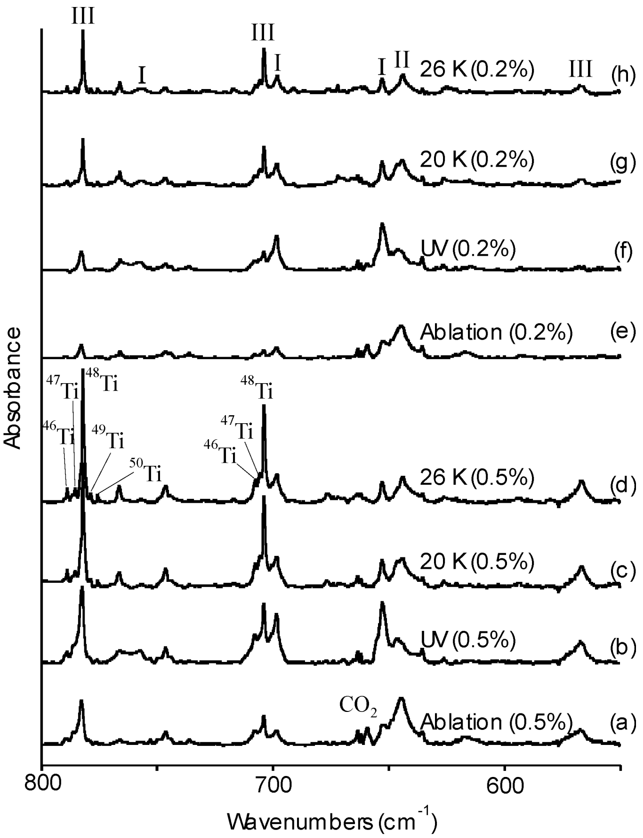

Figure 1. IR spectra in the 800−550 cm^{-1} region for laser-ablated Ti atoms co-deposited with Ar/CH$_3$F at 7 K: (a) Ti + 0.5% CH$_3$F in Ar co-deposited for 1 h, (b) after 240−380 nm irradiation for 30 min, (c) after annealing to 20 K, and (d) after annealing to 26 K; and (e) Ti + 0.2% CH$_3$F in Ar co-deposited for 1 h, (f) after 240−380 nm irradiation for 30 min, (g) after annealing to 20 K, and (h) after annealing to 26 K. The labels I, II, and III identify the product absorption group (see text).

arc lamp (175 W, quartz envelope) or annealed, and more spectra were recorded. Complementary density functional theory (DFT) calculations were done using the Gaussian 98 package,[12] with the B3LYP density functional, 6-311+G(2d,p) basis sets for C, H, F, and SDD pseudopotential and basis set for Ti (18 electron core) to provide vibrational frequencies for the anticipated reaction products. Geometries were fully relaxed during optimization, and the optimized geometry was confirmed via vibrational analysis. Calculation with the keyword STABLE ensured that the converged electronic state is the stable ground state. All calculations employed quadratic convergence (QC). The vibrational frequencies were calculated analytically.

Table 1. Frequencies (cm^{-1}) of Observed Product Absorptions

group	CH$_3$F	^{13}CH$_3$F	CD$_3$F	mode
I	1602.8	1602.8	1158.6	Ti−H str[b]
	757.8	748.8	644.9	Ti−C str[b]
	698.6	692.0	702.6	Ti−F str[b]
	652.8	646.6	522.1	CH$_2$ wag[b]
II	1105.7	1096.9	871.1	CH$_2$ def
	646.3	643.3	642.3	Ti−F str
	504.3	494.7	450.9	Ti−CH$_3$ str
III	1385.2	1381.9	1010.9	CH$_3$, antisym scis
	782.3[a]	782.0	776.4	Ti−F$_2$, antisym str
	703.8[a]	703.6	masked	Ti−F$_2$, sym str
	566.9	557.5	513.9	Ti−C$_2$, antisym str

[a] Ti isotopic satellites at 789.1, 785.6, 779.0, and 775.9 cm^{-1} for the upper band and at 707.6 and 705.6 cm^{-1} for the lower band. [b] Reference 10.

Results and Discussion

Figure 1 shows IR spectra in the 800−550 cm^{-1} region for laser-ablated Ti atoms co-deposited with Ar/CH$_3$F at 7 K and their variation upon irradiation, annealing, and concentration of CH$_3$F. Important new absorptions are observed at 782.3, 703.8 cm^{-1} (labeled III), 698.6, 652.8 cm^{-1} (labeled I), and 646.3 cm^{-1} (labeled II). Note that the III absorptions are stronger relative to the I and II absorptions with higher CH$_3$F concentration. Note also that UV (240−380 nm) radiation increases the I and III bands at the expense of II, and that annealing markedly increases the III bands. Additional absorptions that track with those above are listed in Table 1.

Analogous reactions with ^{13}CH$_3$F gave small shifts in the product absorptions as listed in Table 1. However, larger shifts were found in most cases for CD$_3$F substitution. Figure 2 shows spectra for the Ti reaction with CD$_3$F in excess argon. The major bands are shifted to 774.4 cm^{-1} (labeled III), 702.6, 644.9 cm^{-1} (labeled I), and 642.3 cm^{-1} (labeled II). Again, UV irradiation increases I and III absorptions and decreases those of II, while annealing increases III absorptions. The Group I and Group II frequencies are assigned to CH$_2$=TiHF and CH$_3$−TiF in another paper where their reversible photochemical α-hydrogen transfer is discussed in detail.[10] Here we summarize the evidence for the identification of CH$_3$−TiF, which is the precursor for (CH$_3$)$_2$TiF$_2$. The strongest Group II absorption at 646.3 cm^{-1} with CH$_3$F shifts to 643.3 cm^{-1} with ^{13}CH$_3$F and to 642.3 cm^{-1} with CD$_3$F. The small ^{13}C and D shifts indicate that other atoms are more heavily involved in this normal mode, which is a predominately Ti−F stretching mode. Our B3LYP calculations for triplet ground-state CH$_3$−TiF predict this mode at 678.1 cm^{-1}. The band at 504.3 cm^{-1} shifts to 494.7 cm^{-1} with ^{13}CH$_3$F and to 450.9 cm^{-1} with CD$_3$F, which suggests a Ti−CH$_3$ stretching mode. This vibration is computed at 539.6 cm^{-1}. The weaker absorption at 1105.7 cm^{-1} shifts 8.8 cm^{-1} with ^{13}C and 234.6 cm^{-1} with D, as is appropriate for a C−H deformation mode predicted at 1150.7 cm^{-1}. These three modes are computed 4.9, 7.0, and 4.1% too high, respectively, which may be compared to other results for the B3LYP density functional.[13] The 1105.7 cm^{-1} absorption for CH$_3$TiF may be compared with a similar mode observed at 1127.2 cm^{-1} for CH$_3$MgF.[9]

The structure of the triplet (^{3}A) ground state ($< s^2 > =$ 2.000) for CH$_3$TiF is given in Figure 3. From natural bond orbital (NBO) analysis,[12] the natural electron configuration

---

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11.4; Gaussian, Inc.: Pittsburgh, PA, 1998.

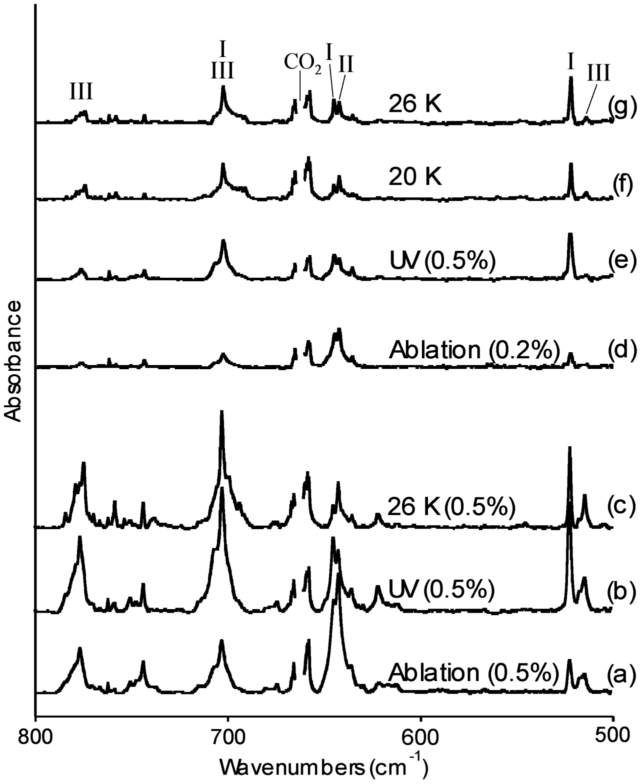

Figure 2. IR spectra in the 800−500 cm^{-1} region for laser-ablated Ti atoms co-deposited with Ar/CD_3F at 7 K: (a) Ti + 0.5% CD_3F in Ar co-deposited for 1 h, (b) after 240−380 nm irradiation for 30 min, and (c) after annealing to 26 K; and (d) Ti + 0.2% CD_3F in Ar co-deposited for 1 h, (e) after 240−380 nm irradiation for 30 min, (f) after annealing to 20 K, and (g) after annealing to 26 K.

for Ti in triplet CH_3TiF is [core] 4s (0.60) 3d (2.14). The d-orbital natural population is *xy* (0.27), *xz* (0.11), *yz* (0.98), $x^2 - y^2$ (0.42), and z^2 (0.37) where the C−Ti−F skeleton defines the *xy* plane. The 128.4° C−Ti−F bond angle is clearly determined by nonbonded repulsions involving the two unpaired 3d electrons with considerable out-of-plane (*yz*) contribution. Similar computations have found the analogous CH_3MgF molecule to be linear with equal C−H bond lengths that are the average of our CH_3TiF values.[9]

The Group III absorptions are assigned to $(CH_3)_2TiF_2$, the first methyltitanium fluoride compound to be characterized. The spectra show that $(CH_3)_2TiF_2$ absorptions increase at the expense of CH_3−TiF bands on UV photolysis, and that both increase on annealing to allow diffusion and further reaction of trapped reagent molecules. The two strongest absorptions at 782.3 and 703.8 cm^{-1} exhibit natural abundance titanium isotopic band splittings, which show that one Ti atom is involved, and the frequency separations characterize these as antisymmetric and symmetric Ti−F_2 stretching modes. The stronger 782.3 cm^{-1} ^{48}Ti band exhibits 789.1, 785.6, 779.0, and 775.9 cm^{-1} satellites for ^{46}Ti, ^{47}Ti, ^{49}Ti, and ^{50}Ti. These separations (3.1, 3.3, 3.3, and 3.5 cm^{-1}) are about the same as those reported for the antisymmetric TiF_3 stretching mode at 792.8 cm^{-1} and slightly larger than those observed for the antisymmetric TiO_2 stretching mode.[14,15] The weaker 703.8 cm^{-1} band exhibits 705.6 and 707.6 cm^{-1} satellites (1.8 and 2.0 cm^{-1} spacings) for these ^{48}Ti, ^{47}Ti, ^{46}Ti absorptions. These smaller Ti isotopic shifts are due to the greater F contribution to the symmetric TiF_2 stretching mode as has also been reported for the symmetric TiO_2 stretching mode.[15] The small observed ^{13}C and D shifts are in agreement with these mode characterizations.

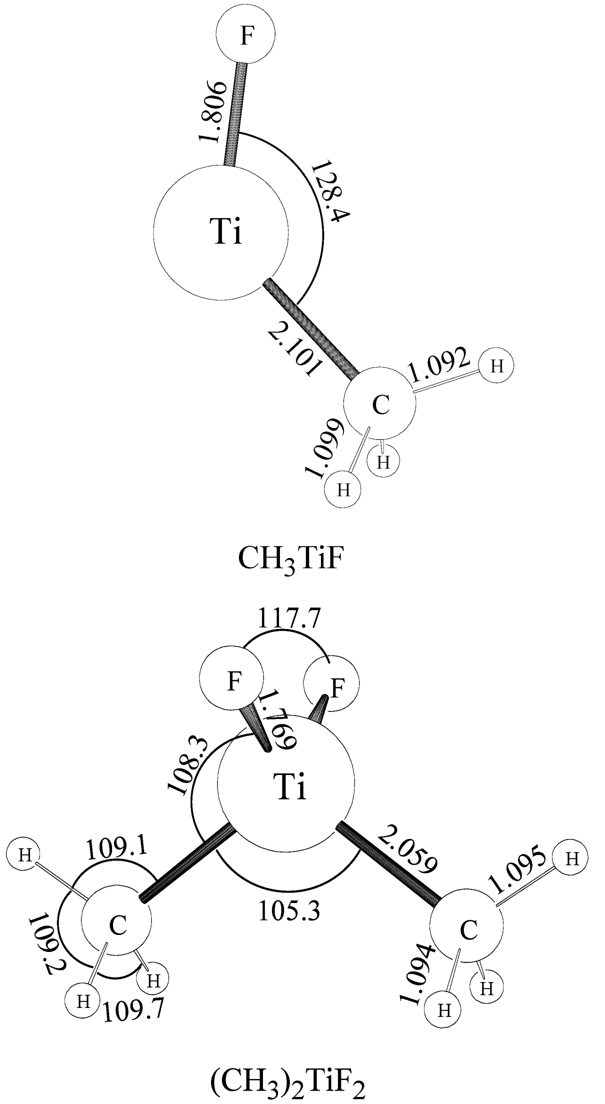

Figure 3. Structural diagrams for CH_3TiF and $(CH_3)_2TiF_2$. Bond distances (Å) and angles (deg) calculated at the B3LYP/6-311+G(2d,p)/SDD level of theory.

Our B3LYP calculation for singlet ground state $(CH_3)_2TiF_2$ predicts these modes at 797.3 and 719.3 cm^{-1} with 235 and 165 km/mol intensities. The frequencies are computed 1.9 and 2.2% too high and the relative intensities are qualitatively correct. Small (0.7, 0.4 cm^{-1}) ^{13}C shifts are predicted and observed (0.3, 0.2 cm^{-1}). A 7.9 cm^{-1} CD_3 shift is predicted and observed for the strongest mode, but the weaker $(CD_3)_2Ti$−F_2 mode is masked by the strong 702.6 cm^{-1} Group I band. The next strongest absorption at 566.9 cm^{-1} is just above the strong, antisymmetric Ti−C_2 mode observed at 557.5 cm^{-1} for $(CH_3)_2TiCl_2$.[2] Our B3LYP calculation

---

(13) Bytheway, I.; Wong, M. W. *Chem. Phys. Lett.* **1998**, *282*, 219.

(14) Hastie, J. W.; Hauge, R. H.; Margrave, J. L. *J. Chem. Phys.* **1969**, *51*, 2648.

(15) Chertihin, G. V.; Andrews, L. *J. Phys. Chem.* **1995**, *99*, 6356 (TiO_2).

Table 2. Calculated Fundamental Frequencies of CH_3TiF in the Ground Electronic State (^3A)[a]

	$CH_3{-}Ti{-}F$		$CD_3{-}Ti{-}F$		$^{13}CH_3{-}Ti{-}F$	
description	calcd[c]	int	calcd[c]	int	calcd[c]	int
ν_1 A′ CH_3 str.	3089.1	4	2281.0	1	3078.9	4
ν_2 A′ CH_3 str.	3027.2	6	2235.9	1	3016.9	6
ν_3 A′ CH_3 str.	2967.9	6	2129.6	1	2964.4	7
ν_4 A′ CH_3 scis.	1428.2	4	1035.8	4	1425.0	4
ν_5 A′ CH_3 scis.	1420.1	1	1030.4	1	1417.0	1
ν_6 A′ CH_3 deform	1150.7	10	904.7	25	1141.2	9
ν_7 A′ Ti−F str.	678.1	183	676.4	174	678.0	183
ν_8 A′ Ti−CH_3 str.	539.6	49	477.0	43	530.0	47
ν_9 A″ TiCH bend	414.7	19	329.0	11	409.7	20
ν_{10} A″ CH_3 rock	408.4	22	304.6	15	406.4	21
ν_{11} A″ CH_2 rock	134.2	5	125.1	5	133.2	5
ν_{12} A″ CTiF bend	98.8	1	74.7	2	98.7	0

[a] Frequencies and intensities are in cm^{-1} and km/mol.

Table 3. Calculated Vibrational Characteristics of $(CH_3)_2TiF_2$ Isotopomers[a]

	$(CH_3)_2TiF_2$		$(CD_3)_2TiF_2$		$(^{13}CH_3)_2TiF_2$	
description	freq.	int.	freq.	int.	freq.	int.
ν_1 A_1 CH_3 str. (a)	3088.4	5	2283.9	1	3077.5	6
ν_2 A_1 CH_3 str. (s)	3003.9	0	2150.6	0	3001.3	0
ν_3 A_1 CH_3 scis.	1421.5	6	1032.1	4	1418.3	6
ν_4 A_1 CH_3 deform.	1176.3	9	927.1	21	1166.8	8
ν_5 A_1 TiF_2 str. (s)	719.3	165	714.4	147	718.9	164
ν_6 A_1 TiC_2 str. (s)	556.3	13	501.2	14	545.3	14
ν_7 A_1 CH_3 rock	509.7	0	397.2	1	503.4	0
ν_8 A_1 TiF_2 bend	183.2	10	181.4	10	182.7	10
ν_9 A_1 TiC_2 IP bend	155.6	0	135.0	0	152.2	1
ν_{10} A_2 CH_3 str.	3094.7	0	2290.6	0	3083.6	0
ν_{11} A_2 CH_3 scis.	1416.0	0	1027.6	0	1412.9	0
ν_{12} A_2 CH_3 rock	550.2	0	423.0	0	546.1	0
ν_{13} A_2 TiF_2 twist	158.3	0	144.1	0	156.3	0
ν_{14} A_2 CH_3 distort	75.8	0	54.0	0	75.8	0
ν_{15} B_1 CH_3 str.	3097.7	11	2292.5	3	3086.7	11
ν_{16} B_1 CH_3 scis.	1422.6	14	1031.7	9	1419.6	13
ν_{17} B_1 TiF_2 str. (a)	797.3	235	789.4	228	796.6	235
ν_{18} B_1 CH_3 rock	550.6	0	431.2	1	547.1	0
ν_{19} B_1 TiF_2 rock	172.3	0	156.1	0	170.6	0
ν_{20} B_1 CH_3 distort	102.0	0	72.8	0	102.0	0
ν_{21} B_2 CH_3 str. (a)	3088.6	2	2285.0	1	3077.6	3
ν_{22} B_2 CH_3 str. (s)	3002.4	0	2149.3	1	2999.8	0
ν_{23} B_2 CH_3 scis.	1413.6	7	1026.3	4	1410.4	7
ν_{24} B_2 CH_3 deform.	1164.4	4	923.8	21	1154.1	3
ν_{25} B_2 TiC_2 str. (a)	582.7	112	527.2	93	573.3	108
ν_{26} B_2 CH_3 rock	488.2	3	372.2	0	483.8	4
ν_{27} B_2 TiF_2 OOP bend	174.2	7	165.6	7	172.8	7

[a] Frequencies and intensities are in cm^{-1} and km/mol.

predicts this mode at 582.7 cm^{-1} (2.9% too high) with ^{13}C shift of 9.5 cm^{-1} (observed shift 9.4 cm^{-1}) and a CD_3 shift of 55.6 cm^{-1} (observed shift 53.0 cm^{-1}), which is superb agreement. A weak 1385.2 cm^{-1} absorption also tracks with the stronger $(CH_3)_2TiF_2$ bands. The 1385.2 cm^{-1} band shifts 3.3 cm^{-1} with $^{13}CH_3F$ and 374 cm^{-1} with CD_3F. Our B3LYP calculation predicts this antisymmetric $C{-}H_3$ bending mode at 1422.6 cm^{-1} with 3.1 cm^{-1} ^{13}C and 396 cm^{-1} CD_3 shifts, and again the agreement is excellent. The analogous mode for $(CH_3)_2TiCl_2$ was observed at 1375.5 cm^{-1}.[2]

Calculated frequencies are listed in Tables 2 and 3 for CH_3TiF and $(CH_3)_2TiF_2$, and Figure 3 compares their calculated structures. Note that the Ti−C and Ti−F bond lengths are shorter in the Ti(IV) than in the Ti(II) compound as expected. The $(CH_3)_2TiF_2$ molecule has effectively C_{2v} symmetry. Our computed Ti−C and Ti−F bond lengths (2.059 and 1.769 Å, respectively) may be compared to 2.060 and 1.746 Å values computed by Kleinhenz and Seppelt and by Gillespie et al. for $Ti(CH_3)_4$ and TiF_4, respectively, at the DFT level with similar basis sets.[1,16] It is also interesting to compare the calculated and experimental structures of $(CH_3)_2TiCl_2$. Kaupp reported Ti−C (2.047 Å), Ti−Cl (2.196 Å), C−Ti−C (104.5°), and Cl−Ti−Cl (118.2°).[3] Although different density functional (BP86) and basis sets were employed, the common structural elements for $(CH_3)_2TiCl_2$ and $(CH_3)_2TiF_2$ agree within computational error. Both calculations agree very well with the experimental values Ti−C (2.058 Å), C−Ti−C (102.8°), Ti−Cl (2.185 Å), and Cl−Ti−Cl (117.3°).[4] This similarity suggests that differences in titanium−halogen π bonding have little effect on the $Ti(CH_3)_2$ subunit structure. Stretching frequencies are compared for Ti−F bonds in simple titanium fluoride compounds in Table 4. The single Ti−F stretching mode for CH_3TiF is slightly below the fundamental for gaseous TiF.[17] The higher antisymmetric $Ti{-}F_2$ stretching mode for $(CH_3)_2TiF_2$ falls between this mode for TiF_2 and for TiF_3 and TiF_4.[14,18] This stretching frequency increases with Ti oxidation state as the Ti−F bond length decreases (Figure 3).

Table 4. Stretching Frequencies (cm^{-1}) for Ti−F Bonds in Simple Compounds Isolated in Solid Argon

molecule	ν(Ti−F)	ref.
CH_3TiF	646	this work
TiF (gas)	651	ref 17
TiF_2	741	ref 14
$(CH_3)TiF_2$	782, 704	this work
TiF_3	793	ref 14
TiF_4 (gas)	800	ref 18

The present results indicate that CH_3TiF is readily generated in the reaction of Ti atoms and methyl fluoride, and we expect that the reaction is promoted by excited Ti atoms produced in metastable states by laser ablation. Furthermore, the extra electron density around fluorine appears to foster insertion by Ti as similar reactions with CH_4 gave weaker product spectra.

$$Ti\ (^3F_2) + CH_3F \rightarrow CH_3TiF\ (^3A) \qquad (1)$$

Although reaction 1 is promoted by excitation of Ti (laser-ablation and UV irradiation), the growth of CH_3TiF on annealing could arise from a spontaneous reaction 1. Recall that the Ti + O_2 → OTiO insertion reaction also proceeds on annealing in solid argon.[15] It is clear from the spectra presented in Figure 1 that CH_3TiF spontaneously adds another CH_3F molecule to form $(CH_3)_2TiF_2$ on annealing in solid argon, reaction 2.

$$CH_3TiF + CH_3F \rightarrow (CH_3)_2TiF_2 \qquad (2)$$

It therefore appears that triplet CH_3TiF is an extremely reactive Grignard-type molecule. In addition, a similar

---

(16) Gillespie, R. J.; Noury, S.; Pilmé, J.; Silvi, B. *Inorg. Chem.* **2004**, *43*, 3248. The 260.5 pm Ti−C distance in Table 1 probably contains a transposition error based on the 206.0 pm value in ref 1.

(17) Ram, R. S.; Peers, J. R. D.; Teng, Y.; Adam, A. G.; Muntianu, A.; Bernath, P. F.; Davis, S. P. *J. Mol. Spectrosc.* **1997**, *184*, 186.

(18) Beattie, I. R.; Jones, P. J. *J. Chem. Phys.* **1989**, *90*, 5209.

investigation in progress with Ti and CH_3Cl gives a larger yield of the analogous CH_3TiCl and $(CH_3)_2TiCl_2$ compounds, and the latter absorptions are in excellent agreement with spectra of the authentic material.[2] The singlet methylidene $CH_2{=}TiHF$ molecule apparently does not react further with CH_3F. In similar studies with Zr, the methylidene $CH_2{=}ZrHF$ is the major initial product, and no evidence for $(CH_3)_2ZrF_2$ is found although this should be a stable molecule.[19] In investigations with Hf, the methylidene $CH_2{=}HfHF$ is the only product formed, and $(CH_3)_2HfF_2$ is not observed.[20]

Conclusions

Laser-ablated Ti atoms react with CH_3F upon condensation with excess argon to form primarily CH_3TiF and $(CH_3)_2TiF_2$. Irradiation in the UV region promotes α-hydrogen rearrangement of CH_3TiF to $CH_2{=}TiHF$ and increases the yield of $(CH_3)_2TiF_2$.[10] Annealing to allow diffusion and reaction of more CH_3F markedly increases the yield of $(CH_3)_2TiF_2$. This shows that the $CH_3TiF + CH_3F$ reaction is spontaneous and that triplet state CH_3TiF is an extremely reactive molecule. B3LYP calculations are extremely effective in predicting vibrational frequencies and isotopic shifts for CH_3TiF and $(CH_3)_2TiF_2$ and thus in confirming their identification from matrix infrared spectroscopy. The structure predicted for $(CH_3)_2TiF_2$ is essentially the same as that computed for $(CH_3)_2TiCl_2$.[2,3] The strong $C{-}H_3$ bending and antisymmetric $Ti{-}C_2$ stretching modes are 1385 and 567 cm^{-1}, and 1376 and 558 cm^{-1}, respectively, for these two dimethyl titanium dihalides. Any difference in ligand-to-metal π bonding in these compounds has no significant effect on the dimethyl titanium subunits.

Acknowledgment. We gratefully acknowledge financial support for this work from NSF Grant CHE 00-78836 and sabbatical leave support (H.-G.C.) from the Korea Research Foundation (KRF-2003-013-C00044).

IC049342M

---

(19) Cho, H.-G.; Andrews, L. *J. Am. Chem. Soc.* **2004**, in press ($Zr+CH_3F$).

(20) Cho, H.-G.; Andrews, L. *Organometallics* **2004**, in press ($Hf+CH_3F$).