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Electron Deficient Carbon–Titanium Triple Bonds: Formation of Triplet $XC{\div}TiX_3$ Methylidyne Complexes

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Laser-ablated titanium atoms react with CX_4 (X = F and Cl) to produce triplet state $XC{\div}TiX_3$ complexes trapped in an argon matrix. Products are identified by their infrared spectra and comparison to theoretically predicted vibrations. Density functional theory calculations converge to C_{3v} symmetry structures for these lowest-energy products. The two unpaired electrons in the carbon 2p orbitals are shared with empty titanium d orbitals leading to degenerate singly occupied π molecular orbitals and an electron-deficient triple bond between the carbon and titanium centers, on the basis of DFT bonding analysis and spin density calculations. The carbon–titanium distances are near typical C=Ti double bond lengths, and the C–X bonds in the resulting products are shorter than in the CX_4 precursors. It appears that X lone-pair conjugation contributes to the C–X bond strength and somewhat to the C–Ti bond, and Cl does better in this regard than F.

Introduction

The activation of C−F bonds is of considerable interest for possible remediation of freon compounds (chlorofloro-carbons), which are hazardous to the earths ozone layer.[1] However, C−F bonds are the strongest single bond involving carbon,[2] and activation of such bonds is not always a simple task. Most C−F-activated complexes have been formed with transition metal centers and C−F oxidative addition reactions.[3−6] Of particular interest, the role transition metals play in catalysts is due, in part, to the high density of low-lying electronic states of the metal, and organotitanium chemistry remains an active field of research.[7−9] We have recently formed carbon−titanium double-bonded methylidene complexes $CH_2{=}TiX_2$ (X = H and F) by reacting titanium atoms with CH_4, CH_3F, and CH_2F_2.[10−12] Here, we extend this work to CF_4 and discover a new class of electron-deficient $FC{\div}TiF_3$ titanium methylidyne complexes, which require breaking three strong C−F bonds to form three stronger Ti−F bonds. This is in contrast to the analogous Group 6 $HC{\equiv}MH_3$ (M = Mo and W) complexes where sufficient valence electrons are available to satisfy a complete carbon-metal triple bond.[13,14]

We also report the reaction of Ti and CCl_4, which gives rise to the analogous $ClC{\div}TiCl_3$ complex. This reaction is of special interest as a source of possible intermediates in the chlorination of titanium carbide to form nanostructural carbon materials.[15−17]

Titanium−carbon triple-bonded complexes are rare. Titanium−carbon intermediate species are physically stable and

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(1) Molina, M. J.; Rowland, F. S. *Nature (London)* **1974**, *249*, 810.
(2) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.
(3) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373.
(4) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber.* **1997**, *130*, 145.
(5) Edelbach, B. L.; Rahman, A. K. F.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 3170.
(6) Reinhold, M.; McGrady, J. E.; Perutz, R. N. *J. Am. Chem. Soc.* **2004**, *126*, 5268.
(7) Bini, F.; Rosier, C.; Saint-Arroman, R. P.; Neumann, E.; Dadlemont, C.; de Mallmann, A.; Lefebvre, F.; Niccolai, G. P.; Basset, J.-M.; Crocker, M.; Buijink, J.-K. *Organometallics* **2006**, *25*, 3743.
(8) Zhang, Y.; Mu, Y. *Organometallics* **2006**, *25*, 631.
(9) Anthis, J. W.; Filippov, I.; Wigley, D. E. *Inorg. Chem.* **2004**, *43*, 716.
(10) Andrews, L.; Cho, H.-G.; Wang, X. *Inorg. Chem.* **2005**, *44*, 4834 (Ti + CH_4).
(11) Cho, H.-G.; Andrews, L. *J. Phys. Chem. A* **2004**, *108*, 6294 (Ti + CH_3F).
(12) Lyon, J. T.; Andrews, L. *Organometallics* **2006**, *25*, 1341 (Ti + CH_2F_2).
(13) Cho, H.-G.; Andrews, L. *J. Am. Chem. Soc.*. **2005**, *127*, 8226 (Mo + CH_4).
(14) Cho, H.-G.; Andrews, L.; Marsden, C. *Inorg. Chem.* **2005**, *44*, 7634 (W + CH_4).
(15) Leis, J.; Perkson, A.; Arulepp, M.; Nigu, P.; Svensson, G. *Carbon* **2002**, *40*, 1559.
(16) Zetterström, P.; Urbonaite, S.; Lindberg, F.; Delaplane, R. G.; Leis, J.; Svensson, G. *J. Phys.: Condens. Matter* **2005**, *17*, 3509.
(17) Permann, L.; Lätt, M.; Leis, J.; Arulepp, M. *Electrochim. Acta* **2006**, *51*, 1274.

10.1021/ic0610379 CCC: $33.50

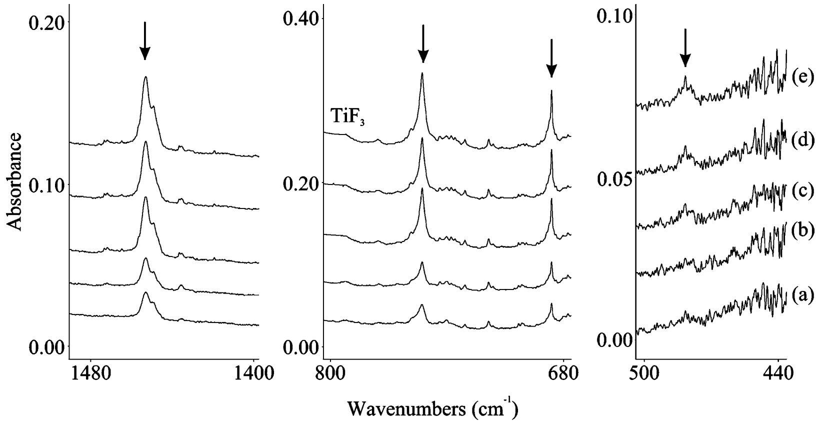

Figure 1. Infrared spectra in the 1480−1400, 780−680, and 500−440 cm^{-1} regions taken after (a) laser-ablated titanium atoms were reacted with 1% CF$_4$/Ar during condensation at 8 K for 1 h, and the resulting matrix was subjected to (b) irradiation with light λ > 290 nm, (c) irradiation with λ > 220 nm, (d) annealing to 30 K, and (e) irradiation with λ > 220 nm.

well documented by calculations.[18−21] Likewise, gaseous Ti≡CH has been investigated in neutral and ionic forms both theoretically and experimentally.[22−26] Most recently, a terminal titanium alkylidyne intermediate has been proposed for C−H activation reactions.[27] We now present the first experimental observation of a titanium alkylidyne complex with an electron-deficient or partially occupied triple bond ($\sigma^2\pi\pi$) from the reactions of Ti and CX$_4$ molecules.

Experimental and Theoretical Methods

Our experimental apparatus has been described in detail elsewhere.[10,11,28] In brief, laser-ablated (Nd:YAG laser; 1064 nm) titanium atoms were reacted with CF$_4$, CCl$_4$, or ^{13}CCl$_4$ at a 0.1−1.0% concentration in argon during condensation at 8 K. Low laser energy was employed to minimize any contribution from Ti cluster species. In previous work, a major product exhibited resolved natural Ti isotopic splittings for a vibration involving one Ti atom.[11] Infrared spectra of the products were collected on a Nicolet Magna 550 spectrometer with a mercury cadmium telluride type B detector cooled to 77 K. Reaction products were subjected to irradiation from a mercury arc lamp with the globe removed (λ > 220 nm) using select filters and to sample annealings. Additional IR spectra were recorded after each procedure.

All theoretical computations were performed using the Gaussian 98 package with the B3LYP hybrid density functional.[29,30] The 6-311+G(3df) basis was used to represent the electronic density of the carbon, halogen, and titanium atoms.[31] Frequencies were computed analytically, and all energy values reported include zero-point vibrational corrections. The calculation of vibrational frequencies is not an exact science, and density functional theory (DFT) provides a very good approximation for observed frequencies. Calculated frequencies are usually a few percent higher than the observed values,[32,33] but that is not always the case. Relevant comparisons can be made to CH$_2$═TiF$_2$, where two strong Ti−F stretching modes were calculated 23.6 and 24.5 cm^{-1} (3.2 and 3.5%) too high,[12] and to TiCl$_4$, where the strong 502.6 cm^{-1} antisymmetric Ti−Cl fundamental is calculated 0.8% lower at 499.8 cm^{-1} by using the above methods.

Results and Discussion

Laser-ablated titanium atoms react with CF$_4$ to produce one weak 481.7 cm^{-1} band and three strong absorptions at 686.1, 752.8, and 1453.1 cm^{-1}. All four absorptions showed slight increases upon irradiation by mercury arc light passing through a Pyrex filter (λ > 290 nm), substantial growth on full arc photolysis (λ > 220 nm), no change on annealing to 30 K, and slight growth on a subsequent full arc irradiation (Figure 1). These four absorptions exhibit constant relative intensities in experiments with different reagent concentrations, and they can be assigned to a common reaction product. The two lower strong peaks are above and below the 740 cm^{-1} antisymmetric Ti−F stretching frequency of TiF$_2$,[34] whereas the upper product band is 179 cm^{-1} higher

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(18) Gutsev, G. L.; Andrews, L.; Bauschlicher, C. W. *Theor. Chem. Acc.* **2003**, *109*, 298.

(19) Pyykkö, P.; Riedel, S.; Patzschke, M. *Chem.—Eur. J.* **2005**, *11*, 3511.

(20) Clemmer, D. E.; Elkind, J. L.; Aristov, N.; Armentrout, P. B. *J. Chem. Phys.* **1991**, *95*, 3387.

(21) Kerkines, I. S. K.; Mavridis, A. *J. Phys. Chem. A* **2000**, *104*, 11777.

(22) Mavridis, A.; Alvarado-Swaisgood, A. E.; Harrison, J. F. *J. Phys. Chem.* **1986**, *90*, 2584.

(23) Kalemos, A.; Dunning, T. H.; Harrison, J. F.; Mavridis, A. *J. Chem. Phys.* **2003**, *119*, 3745.

(24) Zhang, R. Q.; Lu, W. C.; Cheung, H. F.; Lee S. T. *J. Phys. Chem. B* **2002**, *106*, 625.

(25) Barnes, M.; Merer, A. J.; Metha, G. F. *J. Mol. Spectrosc.* **1997**, *181*, 168.

(26) Vidal, I.; Melchor, S.; Dobado, J. A. *J. Phys. Chem. A* **2005**, *109*, 7500.

(27) Bailey, B. C.; Fan, H.; Baum, E. W.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 16016.

(28) (a) Andrews, L. *Chem. Soc. Rev.* **2004**, *33*, 123. (b) Andrews, L.; Cho, H.-G. *Organometallics* **2006**, *25*, 4040 (review article).

(29) 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.

(30) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, Y.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(31) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(32) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(33) Andersson, M. P.; Uvdal, P. *J. Phys. Chem. A* **2005**, *109*, 2937.

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

Table 1. Observed and Calculated Fundamental Frequencies of $FC\div TiF_3$[a]

approximate mode[b]	$FC\div TiF_3$ obsd[c]	$FC\div TiF_3$ calcd (int)
C−F wag (e)		80.6 (0)
FTiF bend (e)		179.3 (6)
TiF_3 umbrella (a_1)		185.9 (9)
FCTi bend (e)		217.4 (17)
F−C−Ti stretch (a_1)	481.7	475.7 (48)
Ti−F stretch (a_1)	686.1	691.0 (197)
Ti−F stretch (e)	752.8	751.8 (443)
C−F stretch (a_1)	1453.1	1479.8 (283)

[a] B3LYP//6-311+G(3df) level of theory. All frequencies are unscaled and given in cm^{-1}, the computed infrared intensities are in km mol^{-1}. [b] Mode symmetries for the C_{3v} molecule. [c] Argon matrix.

than the 1274 cm^{-1} antisymmetric C−F stretching mode of the CF_4 precursor. We also detect a very weak 792.5 cm^{-1} absorption for TiF_3.[34]

The first reaction products in the CH_3F and CH_2F_2 activation by Ti are the triplet state CH_3−TiF and CH_2F−TiF insertion products, but the latter is bridge-bonded CH_2(μ-F)TiF.[11,12] Accordingly, we attempted to calculate CF_2(μ-F)TiF, but this calculation converged to the lowest-energy triplet-state product $FC\div TiF_3$, which is the subject of this report. Next we computed the expected singlet $CF_2{=}TiF_2$ alkylidene complex, analogous to products formed when titanium was reacted with CH_4, CH_3F, and CH_2F_2.[10−12] Although the computed Ti−F stretching frequencies of this complex (683.6 and 759.3 cm^{-1}) match the observed absorption peaks fairly well, two strong C−F stretching modes are predicted at 1096.8 and 1241.8 cm^{-1}. The former symmetric C−F stretch would appear in a clean region of the spectrum, but it was not observed, and the latter antisymmertic C−F stretch would be covered by the strong CF_4 absorption. Then we computed the bridged singlet-state complex FC(μ-F)TiF_2, but this calculation converged to a FC−TiF_3 complex. This calculation was repeated starting with the FC−TiF_3 input geometry, and this singlet state structure is 1 kcal/mol lower in energy than the methylidene complex. However, the predicted frequencies do not represent the observed spectrum (the strong C−F stretching frequency was computed at 1271.8 cm^{-1}). Last, we converged this species with triplet spin multiplicity to a stable $^3A_1$ state with C_{3v} symmetry. This very stable complex is 17 kcal/mol lower in energy than the singlet-state analogue and 145 kcal/mol lower in energy than the sum of the titanium and CF_4 reactants. This gain in stability is the result of replacing three strong C−F bonds by three stronger Ti−F bonds. In summary, the triplet $FC\div TiF_3$ complex is the lowest-energy structure we can find with this stoichiometry.

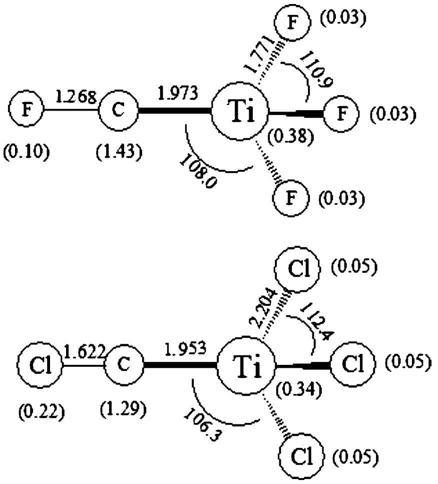

Figure 2. Optimized geometries of the $FC\div TiF_3$ and $ClC\div TiCl_3$ complexes computed at the B3LYP//6-311+G(3df) level of theory. Bond lengths are given in angstroms, and angles are in degrees. Structures are in C_{3v} symmetry. Mulliken atomic spin densities given parenthetically.

This complex has one C−F stretching frequency calculated very high at 1479.8 cm^{-1}, which is within the range of agreement expected from DFT for the strong 1453.1 cm^{-1} observed band (Table 1). This unique diagnostic frequency is 208.0 cm^{-1} higher than that predicted for the singlet-state analogue. The triplet species is the only structure we found with such a very high calculated C−F stretching vibration. The next two strong computed absorptions for the triplet $FC\div TiF_3$ complex (Ti−F symmetric and antisymmetric stretching modes) were predicted at 691.0 and 751.8 cm^{-1}, accurately representing the observed values within the expected limits of the B3LYP calculation.[32,33] The weak 481.7 cm^{-1} absorption almost matches that computed for the symmetric F−C−Ti stretching mode.

Geometrical parameters of the optimized structure are shown in Figure 2. The very short C−F bond length (1.268 Å) is 0.056 Å shorter than we calculated for CF_4, making this bond in the $FC\div TiF_3$ complex one of the strongest known C−F bonds in a neutral molecule.[2] Conjugation of the F lone-pair electrons to the carbon center appears to strengthen the C−F bond. It is interesting to note that the $^2\Pi$ CF radical has nearly the same bond length (1.271 Å), but it has a much lower fundamental frequency (1286 cm^{-1}).[35] The unusual C÷Ti bond (1.973 Å) is closer in length to the double bond of the computed $CF_2{=}TiF_2$ (1.961 Å) complex than to the single bond in the singlet FC−TiF_3 (2.154 Å) species indicating that each of the unpaired electrons in the triplet complex resides in a degenerate π molecular orbital made from carbon p and titanium d orbitals. Hence, the novel $FC\div TiF_3$ complex has one electron pair σ bond and two singly occupied π bonds, which result in an electron-deficient triple bond of approximate bond order two.

The singly occupied doubly degenerate C−Ti-bonding π molecular orbitals are shown in Figure 3. Notice from the plot that the orbital has more carbon than titanium character. The natural bond orbital (NBO) analysis[29,36] shows these orbitals to be 71.5% C (2p) and 28.5% Ti (3d) and each to contain 0.979 electron with α spin and 0 electron with β spin. The Mulliken atomic-spin densities (total 2.00) are also given in Figure 2: the substantial spin density on Ti at the expense of C confirms the π-bonding interaction. The natural electron configurations [F, $2s^{1.84}$, $2p^{5.42}$; C, $2s^{1.43}$, $2p^{2.33}$; Ti, $4s^{0.17}$ $3d^{2.12}$; F, $2s^{1.93}$, $2p^{5.59}$ for $FC\div TiF_3$, respectively] show

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(35) Kawaguchi, K.; Yamada, C.; Hamada, Y.; Hirota, E. *J. Mol. Spectrosc.* **1981**, *86*, 136.

(36) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

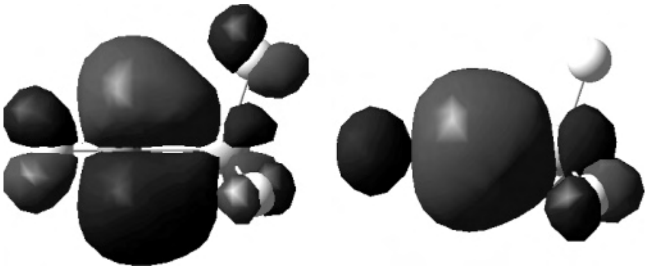

Figure 3. The doubly degenerate π molecular orbitals of FC÷TiF$_3$ which are each occupied by a single electron in the $^3A_1$ state with C_{3v} symmetry.

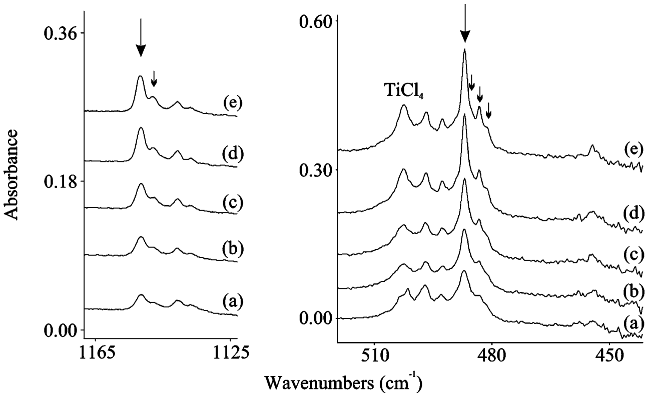

Figure 4. Infrared spectra in the 1170−1120 and 520−440 cm^{-1} regions taken after (a) laser-ablated titanium atoms were reacted with 0.25% CCl$_4$/Ar during condensation at 8 K for 1 h, and the resulting matrix was subjected to (b) irradiation with λ > 290 nm, (c) irradiation with 380 nm > λ > 240 nm, (d) irradiation with λ > 220 nm, and (e) annealing to 30 K.

considerable polarity, and the calculated dipole moment is 2.19 D. Finally, the expectation value, $\langle s^2 \rangle = 2.007$, is in excellent agreement with the 2.000 value expected for a pure triplet state with two unpaired electrons.[29]

We next reacted laser-ablated titanium atoms with carbon tetrachloride. In this experiment, major new product absorptions were observed at 487.0 and 1151.5 cm^{-1} with natural chlorine isotopic satellite features at 481.2, 483.2, 485.1 shoulder, and 1147.8 cm^{-1} (marked with small arrows). These product absorptions increased stepwise in intensity on UV irradiation cycles and remained unchanged after annealing to 30 K (Figure 4), and they maintained constant relative intensity when the CCl$_4$ concentration was reduced from 1.0 to 0.25 to 0.1% and when the Ti concentration was decreased by a factor of 2 at constant CCl$_4$ concentration in the argon matrix. The 1147.8 cm^{-1} satellite with 1/3 of the relative intensity comes from the ^{37}Cl component in natural abundance for a vibration involving one Cl atom. This absorption is 361 cm^{-1} above the 790 cm^{-1} antisymmetric C−Cl stretching mode of the CCl$_4$ precursor, which is unusually high for a C−Cl stretching mode. When ^{13}CCl$_4$ was used in further experiments, the upper band at 1151.5 cm^{-1} showed a large 37.4 cm^{-1} red shift (Figure 5). The observation of only two major bands at 1151.5 and 1114.1 cm^{-1} for the ^{12}CCl$_4$ and ^{13}CCl$_4$ products in this 90% carbon-13 enriched sample verifies that a single carbon atom is involved in this vibrational mode. The strongest absorption at 487.0 cm^{-1} shifted slightly to 486.9 cm^{-1} when ^{13}CCl$_4$ was reacted, indicating a Ti−Cl stretching mode with virtually no associated carbon character. The 487.0−485.1−483.2−481.2 cm^{-1} band profile is a match for the natural chlorine isotopic distribution expected for the doubly degenerate vibration of three equivalent chlorine atoms.[37,38] When the mode degeneracy, accidental degeneracy, and isotopic distribution are considered, an equally spaced 9/1/3/1 relative intensity band pattern is expected with the pure ^{35}Cl and pure ^{37}Cl absorptions as frequency limits. In addition, another reaction product absorption at 502.6 cm^{-1} agrees precisely with that reported for TiCl$_4$ in solid argon.[39] This observation indicates that single titanium atom−chlorine intermediate species are logical reaction products. Thus, we seek a new molecule with one C−Cl bond and a TiCl$_3$ functional group.

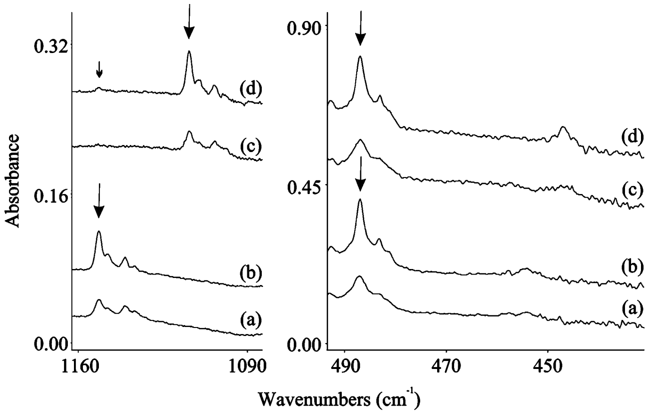

Figure 5. IR spectra in the 1160−1090 and 490−430 cm^{-1} regions of the spectra taken after (a) the laser-ablated titanium atoms were reacted with 0.25% CCl$_4$/Ar, (b) the matrix sample was photolyzed with λ > 220 nm, (c) the titanium atoms were reacted with 1% ^{13}CCl$_4$/Ar, and (d) the matrix sample was photolyzed with λ > 220 nm.

A weak absorption at 454.2 cm^{-1} appears to decrease in intensity relative to the 487.0 cm^{-1} band as precursor concentration is decreased from 1.0 to 0.25 to 0.1% in a series of experiments with constant laser energy. Furthermore, this band increased more on 290 nm than on 220 nm irradiation relative to the 487.0 cm^{-1} absorption. This 454.2 cm^{-1} band showed a small 7.1 cm^{-1} carbon-13 shift, which is about half of that calculated for a C−Cl stretching mode. Hence, this weak absorption is not a result of the major reaction product but is probably from a CCl$_4$ complex with the major product molecule being responsible for the 487.0 cm^{-1} band.

Following the pattern of previous Ti reactions with methane, methyl halides, and methylene fluoride,[10−12,40] we expect the first reaction product to be the triplet state CCl$_3$−TiCl insertion product. Our DFT calculation for this molecule and a bridge-bonded Cl$_2$C(μ-Cl)TiCl intermediate converged instead to the lowest-energy (most-stable) triplet-state ClC÷TiCl$_3$ product characterized here.

The CCl$_2$=TiCl$_2$ singlet methylidene complex converged to near C_{2v} symmetry, is 151 kcal/mol lower in energy than Ti + CCl$_4$, and has two C−Cl stretching absorptions calculated at 750.5 and 935.5 cm^{-1}, which are not observed

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(37) Andrews, L. *J. Chem. Phys.* **1968**, *48*, 972.
(38) Comeford, J. J.; Abramowitz, S.; Levin, I. W. *J. Chem. Phys.* **1965**, *43*, 4536.
(39) Königer, F.; Carter, R. O.; Müller, A. *Spectrochim. Acta* **1976**, *32A*, 891.
(40) Cho, H.-G.; Andrews, L. *Inorg. Chem.* **2005**, *44*, 979 (Ti + CH$_3$X).

Table 2. Observed and Calculated Fundamental Frequencies of $ClC\div TiCl_3$[a]

approximate mode[b]	$ClC\div TiCl_3$		$Cl^{13}C\div TiCl_3$	
	obsd[c]	calcd (int)	obsd[c]	calcd (int)
C−Cl wag (e)		56.9 (0)		56.8 (0)
ClTiCl bend (e)		114.0 (0)		113.8 (0)
$TiCl_3$ umbrella (a_1)		115.3 (1)		115.0 (1)
ClCTi bend (e)		230.6 (0)		223.0 (0)
Cl−C−Ti stretch (a_1)		344.1 (0)		343.7 (0)
Ti−Cl stretch (a_1)		434.4 (119)		434.4 (119)
Ti−Cl stretch (e)	487.0	480.4 (277)	486.9	480.3 (277)
C−Cl stretch (a_1)	1151.5	1139.8 (72)	1114.1	1102.0 (67)

[a] B3LYP//6-311+G(3df) level of theory. All frequencies are unscaled and given in cm^{-1}; computed infrared intensities are in km mol^{-1}. [b] Mode symmeties for C_{3v} molecule. [c] Argon matrix.

Table 3. Observed and Calculated Isotopic Shifts in the Diagnostic Fundamental Frequencies for $ClC\div TiCl_3$[a]

	obsd		calcd	obsd	calcd
mode	$^{35}Cl^{12}C\div Ti^{35}Cl_3$	$\Delta^{35-37}Cl$	$\Delta^{35-37}Cl$	$\Delta^{12,13}C$	$\Delta^{12,13}C$
C−Cl stretch (a_1)	1151.5	3.7	3.7	37.4	37.8
Ti−Cl stretch (e)	487.0	5.8	5.9	0.1	0.1

[a] B3LYP//6-311+G(3df) level of theory. All frequencies are given in cm^{-1}.

here. A bridge-bonded isomer $ClC(\mu\text{-}Cl)TiCl_2$ converged to the singlet $ClC-TiCl_3$ complex, which is 3 kcal/mol lower in energy than the methylidene species. However, the C−Cl stretching mode for this singlet $ClC-TiCl_3$ complex predicted at 1100.6 cm^{-1} is too low for the observed band. A triplet bridge-bonded $ClC(\mu\text{-}Cl)TiCl_2$ isomer is 1 kcal/mol higher in energy than the singlet $ClC-TiCl_3$ complex, and the diagnostic C−Cl stretching mode (1003.9 cm^{-1}) is lower still and not observed here. Next, the triplet $ClC\div TiCl_3$ complex was calculated to be 17 kcal/mol lower in energy than the singlet analogue, with the highest-computed C−Cl stretching mode of the four converged complexes (1139.8 cm^{-1}). Thus, the lowest-energy structure that we can find theoretically is the triplet-state $ClC\div TiCl_3$ complex. The good agreement between the computed and observed fundamentals (Table 2), including the unusually high C−Cl stretching mode, and the effect of isotopic substitution lead to the triplet $ClC\div TiCl_3$ product assignment. The observed and calculated carbon and chlorine isotopic shifts for the diagnostic 1151.5 and 487.0 cm^{-1} absorptions are summarized in Table 3. This agreement confirms our identification of $ClC\div TiCl_3$. The weaker symmetric $Ti-Cl_3$ stretching mode is probably below our 430 cm^{-1} instrumental limit.

In this regard, we have computed frequencies for the CH_3-TiCl_3 molecule for comparison with previously observed gas-phase values.[41] The very strong antisymmetric Ti−Cl stretching mode at 551 cm^{-1} is calculated at 566 cm^{-1} (138 km/mol intensity) and the medium intensity symmetric Ti−Cl stretching mode at 390 cm^{-1} is calculated at 393 cm^{-1} (15 km/mol). Thus, we can reasonably expect the weaker symmetric Ti−Cl stretching mode calculated at 434 cm^{-1} for $ClC\div TiCl_3$ to fall below 430 cm^{-1} in the argon matrix where we are not able to observe it. Finally, the 2.188 Å value we calculate for the Ti−Cl bond length in CH_3-TiCl_3 is nearly the same as the 2.198 Å distance computed for $ClC\div TiCl_3$.

The triplet $ClC\div TiCl_3$ product is probably formed via the reaction pathway outlined in eq 1, where T and S denote triplet and singlet electronic states. This mechanism is based on our previous work with halomethanes[11,12,40] and the present calculations of potential product structures, which lead to the lowest-energy final product. Matrix relaxation

$$\begin{aligned} Ti(T) + CCl_4\,(S) &\rightarrow [Cl_3C-TiCl]^*\,(T) \rightarrow \\ &[Cl_2C-TiCl_2]^*\,(T) \rightarrow Cl_2C{=}TiCl_2\,(S) \rightarrow \\ &ClC-TiCl_3^*\,(S) \rightarrow ClC\div TiCl_3\,(T) \end{aligned} \quad (1)$$

from the singlet to the triplet species is the final step in the reaction. The higher-energy singlet $ClC-TiCl_3$ complex has C_s symmetry, and the more stable triplet complex relaxes to C_{3v} symmetry. It is easy to see how the former energized bent complex could also eliminate C to produce $TiCl_4$ and serve as a precursor for the growth of nanostructural carbon. Thus, the singlet $ClC-TiCl_3$ complex is a possible intermediate in the chlorination of titanium carbide to form nanostructural carbon.[15−17]

Finally, the triplet $ClC\div TiCl_3$ complex is 171 kcal/mol lower in energy than the sum of the titanium atom and carbon tetrachloride precursors.

The computed structure of the triplet $ClC\div TiCl_3$ complex is shown alongside the fluorine analogue in Figure 2. Again, the C÷Ti bond length (1.953 Å) is close in length to the double bond in the computed methylidene complex (1.911 Å), indicating overlap of the two unpaired carbon p electrons with d orbitals on the titanium center. The net bonding effect of this electron-deficient triple bond ($\sigma^2\,\pi\,\pi$) and a classical double bond ($\sigma^2\ \pi^2$) is approximately the same. The computed C−Cl bond distance (1.622 Å) is 0.158 Å shorter than that calculated for the carbon tetrachloride precursor, which is a substantial contraction and suggests delocalization of Cl 3p electron density to the carbon center and partial C=Cl double bond character. In this regard, the NBO analysis shows that the C−Cl bond has more C (2p) and Cl (3p) character than a normal C−Cl single bond. Our C−Cl bond length is even shorter than that found for the CCl radical (1.645 Å), which has a much lower 866 cm^{-1} frequency.[42] The slightly shorter (0.020 Å) computed C÷Ti bond length in $ClC\div TiCl_3$, as compared to that of $FC\div TiF_3$, also suggests more conjugation of the chlorine 3p lone-pair electron density into the π molecular orbitals involving Ti 3d orbitals than in the case of fluorine 2p, which is revealed by the natural electron configurations.

The NBO analysis shows that the degenerate π orbitals for $ClC\div TiCl_3$ are 70.8% C (2p) and 29.2% Ti (3d) and contain 0.974 α-spin electron. Again, the atomic spin densities (Figure 2) verify the formation of C (2p)−Ti (3d) molecular orbitals, and the higher spin density on the single Cl than on F indicates more Cl conjugation as suggested from the unusually short C−Cl bond. The natural electron

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(41) McKean, D. C.; McQuillan, G. P.; Torto, I.; Bednell, N. C.; Downs, A. J.; Dickinson, J. M. *J. Mol. Struct.* **1991**, *247*, 73.

(42) Verma, R. D.; Mulliken, R. S. *J. Mol. Spectrosc.* **1961**, *6*, 419.

configurations [Cl, $3s^{1.81}$, $3p^{4.95}$; C, $2s^{1.44}$, $2p^{2.73}$; Ti, $4s^{0.32}$ $3d^{2.81}$; Cl, $3s^{1.91}$, $3p^{5.34}$] reveal bond polarity, and the calculated dipole moment is 3.14 D. In this case, the expectation value $\langle s^2 \rangle$ is 2.010, again describing a triplet-state complex.

Conclusions

The reaction products formed between laser-ablated titanium atoms and CX_4 (X = F and Cl) are studied in a solid argon matrix. The major products are the triplet XC÷TiX$_3$ methylidyne complexes which possess electron-deficient carbon−titanium triple bonds and halogen−carbon partial double bonds. These complexes differ from Group 6 HC≡MH$_3$ methylidynes where two more valence electrons are present.[13,14] The species are identified by their vibrational spectra, and comparison to theoretical predictions. The computed C÷Ti bond ($\sigma^2\pi\pi$) lengths (1.973 and 1.953 Å) are similar to those of a double bond, substantially shorter than a C−Ti single bond (2.107 Å computed for CH_3−TiH)[10] and longer than a complete C≡Ti triple bond (1.728 Å observed for Ti≡C−H).[25] In addition, the resulting C−X bonds are shorter than found in the CX_4 precursors. Theoretical bond orbital analysis shows that the degenerate π molecular orbitals have 71% C (2p) and 29% Ti (3d) character and each contains a single α-spin electron for this triplet electronic state molecule. Furthermore, substantial spin density on Ti at the expense of C substantiates the π-bonding interaction. Thus, we report here a new class of electron deficient C÷Ti methylidyne complexes.

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