

LETTERS

Direct Observation of CF₂ Insertion into the Carbon–Metal Bond on Cu(111)

Wen-Yi Chiu and Chao-Ming Chiang*

Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424

Received: December 16, 2002; In Final Form: April 21, 2003

Reflection–absorption infrared spectroscopy determined the coexistence of surface-bound trifluoromethyl (CF₃) and difluorocarbene (CF₂) moieties, resulting from C–I and subsequent C–F bond scission reactions below 160 K after the CF₃I adsorption on Cu(111). Upon further heating, concomitant with the depletion of Cu–CF₃ and Cu=CF₂, a new surface intermediate was identified unequivocally as the pentafluoroethyl (Cu–CF₂CF₃) groups. This observation provides evidence for the reaction of CF₂ migratory insertion into the carbon–copper bond. At about 300 K, together with the CF₂ coupling pathway, the Cu–CF₂CF₃ species undergo a β -fluoride elimination reaction to liberate tetrafluoroethylene (CF₂=CF₂) into the gas-phase as the final product.

The (trifluoromethyl)–copper complex has been pioneered by Burton and co-workers¹ as a versatile CF₂ transfer reagent which provides a novel pathway to the longer chain CF₃(CF₂)_n–CF₂–Cu ($n = 0–14$) or C₆F₅CF₂CF₂–Cu compounds. Selective C–F bond scission of the trifluoromethyl moieties, rendering a difluorocarbene copper complex intermediate, and sequential insertion of the CF₂ unit into the carbon–copper bond are invoked as two pivotal steps in the chain growth mechanism. Previously, we performed an ultrahigh vacuum (UHV) surface science study to demonstrate that chemisorbed CF₃ formed on Cu(111) led to the evolution of CF₂=CF₂ as the main gas-phase product upon heating the surface to 250 K in temperature programmed reaction/ desorption (TPR/D).² This observation inferred the existence of difluorocarbene bonded to the metal surface. Thus, the role of Burton’s organometallic reagent, serving as the source of CF₂ units, was adequately modeled. Nevertheless, definitive evidence for whether the CF₂ transfer process proceeds via the insertion reaction had remained elusive. Here, we report vibrational spectroscopic identification of stable surface intermediates, CF₂(ad) and CF₂CF₃(ad) on Cu(111). Particularly, the surface-bound pentafluoroethyl is a result of

direct interactions between CF₃(ad) and CF₂(ad), which presumably coexist as an equilibrium mixture after warming CF₃I adsorbed on Cu(111). The isolation of such a C₂ adspecies establishes that “carbene insertion” is responsible for the C–C bond formation in Burton’s reagent. Similar methylene insertion steps have also been previously reported on copper single-crystal surfaces by Bent and co-workers.^{3,4}

Reflection absorption infrared spectroscopy (RAIRS) experiments were conducted in a newly built UHV chamber with a base pressure below 8×10^{-11} Torr, interfaced with an FTIR spectrometer and a narrow band MCT detector.⁵ All spectra correspond to the average of 1500 scans at 4 cm^{−1} resolution and are ratioed against the background spectra from the clean metal surface. The (trifluoromethyl)–copper reagent was mimicked by the dissociative adsorption of CF₃I on Cu(111), the most efficient method to generate CF₃ moieties on metal surfaces,^{2,6–9} because of the facile cleavage of the C–I bond.¹⁰

Figure 1 shows the RAIR spectra obtained by exposing the Cu(111) at 110 K to 3×10^{-10} Torr of CF₃I for 690, 30, and 270 s, respectively. The spectrum 1a characterizes the condensed CF₃I multilayers, fingerprinted by two intense absorption peaks at 1194 and 1080/1073 (a split feature) cm^{−1} which are assigned to the asymmetric ν_a (CF) and symmetric ν_s (CF) stretch, respectively. The band at 743 cm^{−1} is assigned to the symmetric

* To whom correspondence should be addressed. Phone: 886-7-5253939. Fax: 886-7-5253908. E-mail: cmc@mail.nsysu.edu.tw.

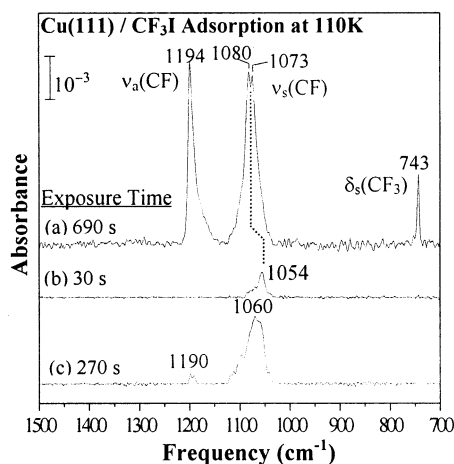


Figure 1. RAIRS for different surface coverage of CF_3I on $\text{Cu}(111)$ at 110 K. (a) multilayers (b) $\sim 1\%$ saturation (c) $\sim 60\%$ saturation. The saturation coverage is defined in ref 13.

CF_3 deformation (umbrella) $\delta_s(\text{CF}_3)$ mode. These frequencies agree well with the gas-phase values for CF_3I .¹¹ In contrast, Figure 1b (30 s) displays only a weaker and sharper band at 1054 cm^{-1} , similar to the relatively low frequency of the symmetric C–F stretch exhibited by the perfluoromethyl of transition metals, such as $\text{CF}_3\text{Mn}(\text{CO})_5$;¹² therefore, it is attributed to the CF_3 groups bonded directly to the surface. This assignment suggests that the C–I bond dissociates readily upon adsorption at this coverage ($\sim 1\%$ saturation coverage¹³).

The lack of $\nu_a(\text{CF})$ vibration, usually very strong in the gas-phase or condensed phase CF_3I , implicates that $\text{CF}_{3(\text{ad})}$ is oriented perpendicular to the surface on the basis of dipole selection rules. As $\text{Cu}(111)$ was dosed with CF_3I for 270 s ($\sim 60\%$ saturation coverage), spectrum 1c could be decomposed, at least, into two components. The main peak at 1060 cm^{-1} represents $\text{CF}_{3(\text{ad})}$, and the high-frequency shoulders together with the weak feature around 1190 cm^{-1} may indicate some intact $\text{CF}_3\text{I}_{(\text{ad})}$. Considering the detection limit of RAIRS, a substantial amount of chemisorbed trifluoromethyl moieties would be needed in search of reaction intermediates; therefore, we elected to use this coverage (Figures 1c or 2a) for further temperature-dependent RAIRS study.

A series of RAIR spectra obtained by warming 1c to various surface temperatures is illustrated in Figure 2. Annealing to 150 K results in a narrower peak at 1054 cm^{-1} and disappearance of the 1190 cm^{-1} band (see 2b), which coincides with the liberation of adsorbed CF_3I molecules (refer to the CF_3I^+ TPR/D feature shown on the right panel of Figure 2). Yet the remaining IR band still bears a shoulder, implicating the presence of other surface species in addition to $\text{CF}_{3(\text{ad})}$. In an earlier study,² we have proposed that activation of a single C–F bond, converting $\text{CF}_{3(\text{ad})}$ into $\text{CF}_{2(\text{ad})}$, takes place before 160 K. Jones et al.¹⁴ detected the evolution of gaseous CF_2 radicals following dissociative adsorption of CF_3I on $\text{Cu}(111)$. We wonder if this shoulder (2b), having been sharpened up with a peak maximum at 1105 cm^{-1} after heating to 200 K (see 2c), is characteristic of the intermediacy of the surface-bound CF_2 . Myli and Grassian^{7b} assigned an IR band at 1104 cm^{-1} to the symmetric C–F stretch mode for adsorbed CF_2 groups on $\text{Ni}(100)$. In a variety of organometallic model compounds containing the CF_2 ligand,¹⁵ their $\nu_s(\text{CF})$ frequencies also range from 1083 to 1170 cm^{-1} . Hence, it is logical to interpret the shoulder band as the surface-bound CF_2 species. Actually, Figure 2c might indicate an equilibrium state where $\text{CF}_{2(\text{ad})}$ (1105 cm^{-1}) and $\text{CF}_{3(\text{ad})}$ (1054 cm^{-1}) are both present on the surface. At 250 K, there has been

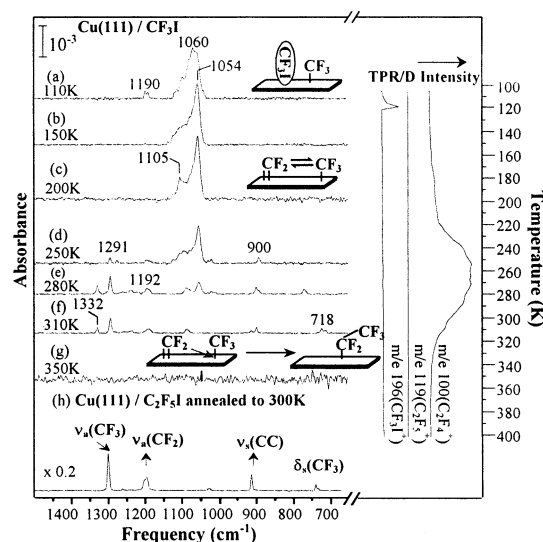


Figure 2. Left panel: RAIRS used to identify the key surface intermediates involved in the chemistry of CF_3I on $\text{Cu}(111)$. From top to bottom, these data correspond to (a–g) annealing sequence for $\sim 60\%$ saturation coverage of CF_3I after adsorption at 110 K. Spectra were taken after cooling the sample back to 110 K. (h) Obtained from adsorbed $\text{I}-\text{C}_2\text{F}_5$ as a reference to recognize the surface-bound C_2F_5 groups. Here the lack of 1332 cm^{-1} , $\nu_a(\text{CF}_3) A''$ mode could be due to the variation in symmetry at a different coverage. Right panel: TPR/D data used to highlight species liberating from the surface in association with the RAIRS annealing sequence.

an appreciable rate of desorption for C_2F_4 (see the TPR/D feature of $m/e\ 100$), attributable to coupling of two difluorocarbene units. In the corresponding IR spectrum 2d, major signals shrink due, in part, to the escape of product into the gas phase; however, new absorption bands emerge at 1291 , 1192 , and 900 cm^{-1} . These vibrational features become more prominent in Figure 2e, concomitant with the continuous loss of intensities for both $\text{CF}_{2(\text{ad})}$ and $\text{CF}_{3(\text{ad})}$ at 280 K. This trend proceeds up to 310 K where peaks at 1105 and 1054 cm^{-1} almost vanish and those remained are 1332 , 1291 , 1192 , 900 , and 718 cm^{-1} (see 2f). The insertion of CF_2 into the Cu–CF₃ bond and the formation of the Cu– CF_2CF_3 intermediate (the schematic below) can account for such spectral changes. This alternative reaction pathway, consuming $\text{CF}_{3(\text{ad})}$ and $\text{CF}_{2(\text{ad})}$ simultaneously, contributes to their peak attenuation. On the other hand, the identity for the “insertion intermediate” can be corroborated by measuring a RAIR spectrum of $\text{I}-\text{CF}_2\text{CF}_3$ adsorbed on $\text{Cu}(111)$ and annealed to 300 K (see 2h), which bears quite a resemblance to 2f. On the basis of IR analyses on the CF_2CF_3 free radical in the argon matrix as well as its iodo compound (spectrally indistinguishable),^{16,17} the reasonable assignments are 1332 cm^{-1} , asymmetric C–F stretch of CF_3 group with A'' symmetry (due to the geometry of the adspecies at low coverages); 1291 cm^{-1} , asymmetric C–F stretch of CF_3 group with A' symmetry; 1192 cm^{-1} , asymmetric C–F stretch of CF_2 group; 900 cm^{-1} , symmetric C–C stretch and 718 cm^{-1} , symmetric CF_3 deformation, respectively. Recently, the CuC_2F_5 compound has been synthesized by Naumann and co-workers.¹⁸ Although no specific assignments were given, their IR absorption bands were properly matched by those in the spectrum 2f, which should be fairly diagnostic of a surface-bound CF_2CF_3 intermediate. Because it lacks a feature of C_2F_5^+ ($m/e\ 119$) in TPR/D, the possibilities of C_2F_5 radical extrusion and C_2F_6 formation can all be ruled out. Finally, as shown in Figure 2g, annealing the surface to 350 K and above removes all of the fluorocarbon-induced IR signals. Synchrotron based X-ray photoelectron spectroscopy

has revealed the disappearance of carbon from the surface above 350 K. Thus, our interpretation is that the insertion intermediate, Cu-CF₂CF₃, undergoes a β -fluoride elimination step¹⁹ to evolve C₂F₄. Mechanistically, CF₂ coupling, CF₂ insertion, and β -elimination steps lead to one common product, yet they have somewhat different rates. Overall, the resultant TPR/D feature of C₂F₄ (*m/e* 100) appears quite broad (220–320 K). Because there is still a reasonable signal for Cu-CF₂CF₃ at 310 K despite the fact that C₂F₄ desorption is almost complete, the CF₂ insertion/ β -elimination reaction is slower in rate and less important than the CF₂ coupling channel.

The isolation and characterization of methylene groups have been shown on Fe(111),²⁰ Ru(0001),²¹ Pt(111),²² Rh(111),²³ Mo(110),²⁴ and Mo(100).²⁵ However, the conversion of methyl moieties to methylene groups was only clearly established on Pt(111) utilizing RAIRS by Zaera.^{26,27} Methylene insertion into coordinated alkyl groups has long been postulated as a chain-growth step in Fischer-Tropsch processes.²⁸ Although indirect evidence to infer this reaction, based mainly on the final gas-phase products, was presented on Cu,^{3,4,29} Ag,³⁰ and oxygen-modified Mo³¹ surfaces, it is difficult to isolate the transient intermediates due to CH₂ insertion. As opposed to their hydrocarbon counterparts, surface-bound perfluorocarbon species are very IR-sensitive and thermally stable. We are able not only to confirm that one bond is selectively cleaved to transform CF_{3(ad)} into CF_{2(ad)} reversibly on Cu(111) but also to identify unambiguously the Cu-CF₂CF₃ intermediacy, providing direct proof of the CF₂ insertion into the Cu-CF₃ bond. Strong parallels can thus be drawn between the fluorinated organo-metallic reagent and the adsorbate species created by adsorption of molecular precursors onto carefully prepared metallic surfaces under UHV conditions.

Acknowledgment. We thank the financial support from the National Science Council of the Republic of China under Contract No. 90-2113-M-110-012.

References and Notes

- (1) Wiemers, D. M.; Burton, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 832.
- (2) Yang, Z.-Y.; Wiemers, D. M.; Burton, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 4402.
- (3) Yang, Z.-Y.; Burton, D. J. *J. Fluorine Chem.* **2000**, *102*, 89.
- (4) Hou, Y.-C.; Chiang, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 8116.

- (5) Chiang, C.-M.; Wentzlaff, T. H.; Bent, B. E. *J. Phys. Chem.* **1992**, *96*, 1836.
- (6) Lin, J.-L.; Chiang, C.-M.; Jenks, C. J.; Yang, M. X.; Wentzlaff, T. H.; Bent, B. E. *J. Catal.* **1994**, *147*, 250.
- (7) Wu, Y.-J.; Wang, W.-H.; Chiang, C.-M. *Langmuir* **2002**, *18*, 1449.
- (8) Ag: (a) Castro, M. E.; Pressley, L. A.; Kiss, J.; Pylant, E. D.; Jo, S. K.; Zhou, X.-L.; White, J. M. *J. Phys. Chem.* **1993**, *97*, 8476. (b) Szabó, A.; Converse, S. E.; Whaley, S. R.; White, J. M. *Surf. Sci.* **1996**, *364*, 345. (c) Junker, K. H.; Sun, Z.-J.; Scoggins, T. B.; White, J. M. *J. Chem. Phys.* **1996**, *104*, 3788.
- (9) Ni: (a) Jones, R. G.; Singh, N. *Vacuum* **1988**, *38*, 213. (b) Myli, K. B.; Grassian, V. H. *J. Phys. Chem.* **1995**, *99*, 1498. (c) Myli, K. B.; Grassian, V. H. *J. Phys. Chem.* **1995**, *99*, 5581. (d) Jensen, M. B.; Thiel, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 438.
- (10) Pt: (a) Liu, Z.-M.; Zhou, X.-L.; Kiss, J.; White, J. M. *Surf. Sci.* **1993**, *286*, 233. (b) Armentrout, D. D.; Grassian, V. H. *Langmuir* **1994**, *10*, 2071.
- (11) Ru: (a) Dyer, J. S.; Thiel, P. A. *Surf. Sci.* **1990**, *238*, 169. (b) Jensen, M. B.; Myler, U.; Jenks, C. J.; Thiel, P. A.; Pylant, E. D.; White, J. M. *J. Phys. Chem.* **1995**, *99*, 8736. (c) Jensen, M. B.; Dyer, J. S.; Leung, W.-Y.; Thiel, P. A. *Langmuir* **1996**, *12*, 3472.
- (12) Zaera, F. *Acc. Chem. Res.* **1992**, *25*, 260.
- (13) McGee, P. R.; Cleveland, F. F.; Meister, A. G.; Decker, C. E. *J. Chem. Phys.* **1953**, *21*, 242.
- (14) Cotton, F. A.; Wing, R. M. *J. Organomet. Chem.* **1967**, *9*, 511.
- (15) The saturation coverage is defined as the integrated TPR/D peak area of C₂F₄ as a function of CF₃I exposure starts to reach a plateau.
- (16) Chan, A. S. Y.; Skegg, M. P.; Jones, R. G. *J. Vac. Sci. Technol. A* **2001**, *19*, 2007.
- (17) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293.
- (18) Jacox, M. E. *J. Phys. Chem.* **1984**, *88*, 445.
- (19) Compton, D. A. C.; Rayner, D. M. *J. Phys. Chem.* **1982**, *86*, 1628.
- (20) Naumann, D.; Roy, T.; Caenars, B.; Hütten, D.; Tebbe, K.-F.; Gilles, T. Z. *Anorg. Allg. Chem.* **2000**, *626*, 999.
- (21) This step was verified by using CF₃CH₂I as the precursor to generate CF₃CH_{2(ad)} on Cu(111), which indeed β -eliminates to yield CF₂=CH₂ at 250 K in TPR/D measurements.
- (22) McBreen, P. H.; Erley, W.; Ibach, H. *Surf. Sci.* **1984**, *148*, 292.
- (23) Henderson, M. A.; Radloff, P. L.; White, J. M.; Mims, C. A. *J. Phys. Chem.* **1988**, *92*, 4111.
- (24) Mitchell, G. E.; Radloff, P. L.; Greenlief, C. M.; Henderson, M. A.; White, J. M. *Surf. Sci.* **1987**, *183*, 403.
- (25) Klivényi, G.; Solymosi, F. *Surf. Sci.* **1995**, *342*, 168.
- (26) Weldon, M. K.; Friend, C. M. *Surf. Sci.* **1994**, *321*, L202.
- (27) Wu, G.; Bartlett, B. F.; Tysoe, W. T. *Surf. Sci.* **1997**, *373*, 129.
- (28) Zaera, F.; Hoffmann, H. *J. Phys. Chem.* **1991**, *95*, 6297.
- (29) Zaera, F. *Langmuir* **1991**, *7*, 1998.
- (30) Brady, R. C., III.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181.
- (31) Chuang, P.; Chan, Y. L.; Chien, S.-H.; Klauser, R.; Chuang, T. J. *Chem. Phys. Lett.* **2002**, *354*, 179.
- (32) Wu, H.-J.; Hsu, H.-K.; Chiang, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 4433.
- (33) Kim, S. H.; Stair, P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8535; *J. Phys. Chem. B* **2000**, *104*, 3035.