

Facile Cyclization of Metallacyclobutane on Cu(110)

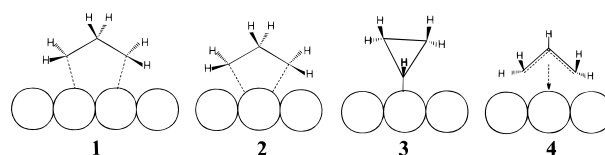
Richard Martel,[†] Alain Rochefort, and Peter H. McBreen*Département de Chimie, Université Laval
Quebec, Canada G1K 7P4

Received January 9, 1997

The chemistry of metallacyclobutanes¹ has been widely studied given the frequently proposed role of metallacycles as intermediates in metathesis,² skeletal isomerization,³ Zeigler–Natta polymerization,⁴ and cyclopropanation reactions.⁵ The presence of C₃ metallacycle reaction intermediates on supported metal catalyst surfaces has been inferred from studies of the hydrogenation of cyclopropane.⁶ There is, however, only one report of the spectroscopic identification of an adsorbed C₃ metallacycle species.⁸ The latter pentanuclear ring (structure **1** shown in Scheme 1) was prepared by the thermal decomposition of diiodopropane on Al(100) and was found to undergo thermal decomposition yielding propene at 500 K.

The present investigation describes the nonthermal preparation of metallacyclobutane (structure **2**) on Cu(110), its vibrational spectroscopic identification using high-resolution electron energy loss spectroscopy (HREELS), and its elimination from the surface as studied by thermal desorption spectroscopy (TPD). The central finding is that **2** undergoes facile cyclization at 205 K, leading to the reductive elimination of cyclopropane from the surface. The experiments were carried out under ultrahigh vacuum (UHV) conditions on a polished single-crystal surface bearing a sub-monolayer of weakly adsorbed cyclopropane. Cyclopropane-derived reactive surface species were prepared at 90 K through dissociative electron attachment (DEA)⁹ induced CH and competitive CC bond cleavage. The electron beam used to induce the dissociative resonance, at approximately 10 eV, was the beam intrinsic to the HREELS spectrometer. Hence, the same spectrometer was in turn used to record vibrational spectra of the electron beam produced adsorbed molecular fragments.¹⁰ Since the HREELS beam acts only on a 0.02 cm² area of the surface, electron bombardment of the entire surface using a simple filament biased at 10 eV was used to prepare samples for thermal desorption studies. Calibration HREELS measurements showed that both methods of electron irradiation yielded the same products, identified below as metallacyclobutane **2** and cyclopropyl **3** surface complexes. The presence of

Scheme 1



the electron beam generated surface species is clearly indicated by the appearance of a metal–carbon stretching vibration at approximately 419 cm⁻¹ and the emergence of a new and relatively intense $\nu(\text{CH})$ loss at 2806 cm⁻¹. Desorption of cyclopropane from Cu(110) was found to occur at 125 K; hence, the electron beam generated surface species could be isolated by heating the sample to 145 K to remove molecularly adsorbed c-C₃H₆. Further annealing of the sample gave rise to a reaction limited cyclopropane and propene desorption peaks at 205 and 290 K, respectively (Figure 1). The identification of cyclopropane as the sole desorption product at 205 K was verified by several calibration procedures involving the relative intensities of the $m/e = 41$ and 42 mass spectral peaks as measured on our system. The cracking patterns proper to each of the desorption peaks are included in histogram form in Figure 1. A comparison of the TPD data in Figure 1 with the HREELS spectra recorded at 90, 145, and 205 K (Figure 2) permits the identification and distinction of the surface intermediates which serve as the precursors to cyclopropane and propene formation. An unambiguous determination of the presence of adsorbed cyclopropyl may be made by comparing the spectra taken at 145 and 205 K to reference vibrational assignments (Table 1) for adsorbed cyclopropane,¹¹ bromocyclopropane,¹² and cyclopropyl groups.¹³ Both of the HREELS spectra display vibrational structure, in the 750–1250 cm⁻¹ region, characteristic of C₃ cycloalkane species.^{11–13} However, there is clearly a second species, on the surface at 145 K, since the latter spectrum (Figure 2C) contains an additional loss peak at the unusually low frequency of 2806 cm⁻¹. The 2806 cm⁻¹ loss is most readily assigned to a metallacyclobutane species. For example, W– and Mo–((bis-allyl)-(CH₂)₃) metallacyclobutane complexes display medium-strong IR bands at 2775 and 2786 cm⁻¹,¹⁵ and nickelacyclobutane displays a band at 2850 cm⁻¹.¹⁴ Furthermore, the removal of the loss at 2806 cm⁻¹ correlates with the reaction-limited desorption of cyclopropane at 205 K and is thus consistent with the reductive elimination of cyclopropane through the facile cyclization of **2**. Cyclopropyl can be ruled out as the precursor to cyclopropane formation since it is stable on Cu(110) to at least 260 K in the presence of surface hydrogen.¹⁶ The cyclopropyl species eventually decomposes to yield a propene desorption peak at 290 K as well as the deposition of a partially dehydrogenated fragment on the surface.

The observed propene to cyclopropane desorption ratio was estimated to be approximately 4:1, and this accounts for the fact that loss features due to cyclopropyl dominate the low-temperature HREELS spectra. Cyclopropane desorption has also been reported in the context of thermal decomposition studies of dihalopropanes on Ag(111)¹⁷ and Ni(100).¹⁸

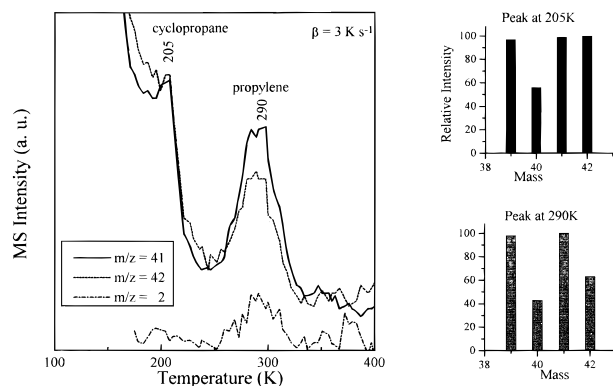
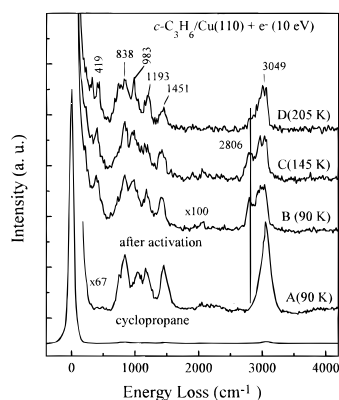
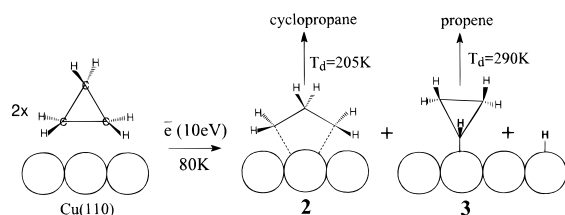
(11) Martel, R.; McBreen, P. H. *J. Phys. Chem. B* 1997, 101, 4966.(12) Wurrey, C. J.; Berry, R. J.; Yeh, Y. Y.; Little, T. S.; Kalasinsky, V. F. *J. Raman Spectrosc.* 1983, 14, 87.(13) (a) Spiekerman, M.; Schrader, B.; De Meijere, A.; Lüttke, W. *J. Mol. Struct.* 1981, 77, 1. (b) Little, T. S.; Vaughn, C. A.; Zhu, X.; Dakkouri, M.; Durig, J. R. *J. Raman Spectrosc.* 1994, 25, 735.(14) Kafafi, Z. H.; Hauge, R. H.; Fredin, L.; Billups, W. E.; Margrave, J. L. *J. Chem. Soc., Chem. Commun.* 1983, 1230.(15) (a) Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; MacKenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* 1977, 1131. (b) Adam, G. J. A.; Davies, S. G.; Ford, K. A.; Ephritikhine, M.; Todd, P. F.; Green, M. L. H. *J. Mol. Catal.* 1980, 8, 15.

(16) Martel, R.; Rochefort, A.; McBreen, P. H. Submitted for publication.

(17) Zhou, X.-L.; White, J. M. *J. Phys. Chem.* 1991, 95, 5575.(18) Tjandra, S.; Zaera, F. *J. Phys. Chem.* 1997, 101, 1006.[†] Present address: T. J. Watson Research Center, IBM, Yorktown Heights, NY.(1) (a) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* 1994, 94, 2241. (b) Grubbs, R. H. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1982; Vol. 8. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (d) Al-Essa, R. J.; Puddephatt, R. J.; Thompson, P. J.; Tipper, C. H. F. *J. Am. Chem. Soc.* 1980, 102, 7546. (e) Siegbahn, P. E. M.; Blomberg, M. R. A. *J. Am. Chem. Soc.* 1992, 114, 10548.(2) (a) Grubbs, R. H. *Prog. Inorg. Chem.* 1978, 24, 1. (b) Hamilton, R.; Mitchell, T. R. B.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* 1981, 456. (c) Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* 1982, 104, 448.(3) O'Cinnéide, A.; Gault, F. G. *J. Catal.* 1975, 37, 311.(4) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* 1978, 604.(5) (a) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* 1980, 102, 5698. (b) Hegedus, L. S.; Darlington, W. H.; Russel, C. E. *J. Org. Chem.* 1980, 45, 5193. (c) Formica, M.; Musco, A.; Pontellini, R.; Linn, K.; Mealli, C. *J. Organomet. Chem.* 1993, 448, C6. (d) Ohe, K.; Matsuda, H.; Morimoto, T.; Ogoshi, S.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* 1994, 116, 4125.(6) (a) Addy, J.; Bond, G. C. *Trans. Faraday Soc.* 1957, 53, 368. (b) Brown, R.; Kemball, C. *J. Chem. Soc., Faraday Trans.* 1990, 86, 3815.(7) Engstrom, J. R.; Goodman, D. W.; Weinberg, W. H. *J. Phys. Chem.* 1990, 94, 396.(8) (a) Bent, B. E.; Nuzzo, R. G.; Zegarski, G. R.; Dubois, L. H. *J. Am. Chem. Soc.* 1991, 113, 1143. (b) Bent, B. E. *Chem. Rev.* 1996, 96, 1361.(9) Rowntree, P.; Parenteau, L.; Sanche, L. *J. Phys. Chem.* 1991, 95, 4902.(10) Martel, R.; Rochefort, A.; McBreen, P. H. *J. Am. Chem. Soc.* 1994, 116, 5965.

Table 1. Vibrational Peak Assignments for Cyclopropane and Cyclopropyl Groups on Cu(110)

vibrational mode, approx. description ¹¹	HREELS data (freq. cm ⁻¹)			literature vibrational spectroscopy data (freq. cm ⁻¹)	
	c-C ₃ H ₆ /Cu(110)	adsorbed dissociation fragments	loss removed at 205 K	bromocyclopropane ¹²	cyclopropyl groups ¹³
CH ₂ stretch	3076	3048 2806		3008–3102	3002–3090
CH ₂ deformation	1470	1435		1417–1444	1416–1471
ring breathing	1179	1177	2806	1196	1186–1205
asym. ring deformation	1034	967		927	899–962
sym. ring deformation	872	838		852–864	784–887
CH ₂ twist	759				
metal–carbon stretch		419			

**Figure 1.** Thermal desorption spectra for 1 L of cyclopropane adsorbed on Cu(110) at 80 K after electron bombardment at 10 eV (electron dose; $1.1 \times 10^{17} \text{ e}^-/\text{cm}^2$).**Figure 2.** HREELS spectra for cyclopropane on Cu(110) recorded at 6.1 eV impact energy: (A) 1.6 L of cyclopropane on Cu(110) before activation; (B) spectrum obtained after irradiation with 10 eV electrons from the HREELS spectrometer at a resolution of 132 meV (electron dose; $1.7 \times 10^{17} \text{ e}^-/\text{cm}^2$); (C) and (D) same as B but annealed from 90 K to 145 and 205 K, respectively, for 2 min.**Scheme 2**

The organometallic^{1,2,5,19} and gas-phase chemistry²⁰ literature provides many examples showing that metallacyclobutane can undergo CC bond scission to form carbene–ethylene complexes, dehydrogenation to yield propene via a hydrido–metal–allyl intermediate, or cyclization to cyclopropane. This UHV study

(19) Tulip, H. T.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201.(20) (a) Jacobsen, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3900. (b) Haynes, C. L.; Armentrout, P. B. *Organometallics* **1994**, *13*, 3480.

provides evidence that only the latter, reductive elimination, reaction takes place on Cu(110) and that it occurs at low temperature (205 K). The cyclization reaction is thermoneutral, or exothermic, given that copper–alkyl bond strengths are approximately 33 kcal/mol,²¹ whereas the CC bond energy in cyclopropane is 65 kcal/mol. (Theoretical predictions for the bond dissociation energy of nickel and rhodium metallacyclobutanes, to yield metal plus cyclopropane, are in the range of 30–40 kcal/mol.²²) The formation of the relatively weak CC bond is partially offset by the fact that the CH bonds of cyclopropane are uniquely strong for an alkane.²³ In addition, the strain energies of the reactant and product are not expected to be very different since metallacyclobutanes display substantial strain energies.²⁴ The observation of the facile cyclization of **2** has to be taken into account in considering reaction mechanisms for the hydrogenation of cyclopropane on metal surfaces. The immediate implication is that cyclization may be competitive with β -hydride elimination and hydrogenation channels depending on the metal surface involved. Hydrogenation of cyclopropane to propane takes place on Pt/Al₂O₃ catalysts at temperatures as low as 235 K.^{6b} Metal–alkyl bonds may be slightly stronger on Pt than on Cu surfaces.^{8b,25} Hence, a stronger alkyl–metal bond for a surface platinacyclobutane complex, relative to that for the copper surface, might make hydrogenation competitive with ring closure on Pt surfaces. β -Hydride elimination can take place at low temperatures^{26,27} and could thus be considered as a competitive process with respect to facile cyclization, especially on transition metal surfaces. β -Hydride elimination would be expected to yield a surface π -allyl species (**4**), and this species has been proposed as a common intermediate in the Ir(111)-catalyzed reaction of H₂ and cyclopropane to form propane and propene.⁷ It is interesting to note that the present results show that **3** evolves on Cu(110) to yield a propene desorption product at 300 K. Presumably this reaction occurs following ring opening to form a π -allyl intermediate such as **4**. In conclusion, the integral approach of dissociative attachment and vibrational spectroscopy provides direct access to several possibly key facets of the surface reaction chemistry of the widely used cyclopropane hydrogenation catalytic probe reaction.

Acknowledgment. This work was funded by grants from FCAR and NSERC. R.M. gratefully acknowledges the receipt of an FCAR scholarship for graduate studies.

JA9700818

(21) Chiang, C. M.; Wentzlaff, T. H.; Bent, B. E. *J. Phys. Chem.* **1992**, *96*, 1836.(22) Kan, S. Z.; Byun, Y. G.; Freiser, B. S. *J. Am. Chem. Soc.* **1994**, *116*, 8815.(23) Hamilton, J. G.; Palke, W. E. *J. Am. Chem. Soc.* **1993**, *115*, 4159.(24) van Koppen, P. A. M.; Jacobson, D. B.; Illies, A.; Bowers, M. T.; Henratty, M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 1991.(25) Zaera, F. *J. Phys. Chem.* **1990**, *94*, 8350.(26) (a) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (b) Ephritikhine, M.; Green, M. L. H.; MacKenzie, R. E. *J. Chem. Soc., Chem. Commun.* **1976**, 619.(27) Teplyakov, A. V.; Bent, B. E. *J. Am. Chem. Soc.* **1995**, *117*, 10076.