

Formation of η^3 -Allyl and Its Cryogenic Coupling Reaction with Allyl Bromide on Cu(100)

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Over the past three decades, a variety of transition metal-catalyzed coupling reactions between organometallic nucleophiles and organic halide electrophiles have become important processes for the formation of carbon–carbon bond in both heterogeneous catalysis and organometallic chemistry.^{1,2} η^3 -Allyl groups (C_3H_5) complexes, for example, are versatile intermediates in cross-coupling reactions (Scheme 1).² While general features of the mechanism for coupling reactions have been proposed, details of the individual steps are less well understood.² We report for the first time the facile formation of 1,5-hexadiene at cryogenic temperatures (110 K) while dosing allyl bromide on Cu(100) covered with η^3 -allyl and bromide atoms. This cryogenic coupling reaction in ultrahigh vacuum (UHV) conditions is akin to metal-catalyzed coupling reactions in solutions and on heterogeneous catalysts. Furthermore, it contrasts with typical carbon–carbon coupling reactions of adsorbed alkyl and vinyl groups on Cu and other transition metals under ultrahigh vacuum (UHV) conditions.^{3,4} We also report the first high-resolution reflection absorption infrared spectrum (RAIRS) of the chemisorbed η^3 -allyl group. Such spectra have the potential to address ambiguities in the mechanistic interpretations of the formation of C_3 species, for example, propylene.^{5,6}

Our experiments were performed in a two-level UHV chamber with a base pressure of 2×10^{-10} Torr.⁷ The preparation and cleaning of the Cu(100) followed published processes.⁸ Allyl bromide (3-bromopropene, Aldrich, 98+%; stabilized with Cu) and 1,5-hexadiene (Aldrich, 99%) were purified by several freeze–pump–thaw cycles prior to each experiment. The exposures are given in units of langmuir, L, with $1 \text{ L} = 1 \times 10^{-6}$ Torr·sec.

Figure 1 shows 39 amu TPD spectra as a function allyl bromide exposure at 110 K. There are four peaks assigned to allyl radical (355 and 450 K), allyl bromide (130 K), and 1,5-hexadiene (150 K). The assignment to allyl is consistent with the results for allyl chloride on Cu(100),⁸ and the two peaks suggest that allyl groups exist in two distinct local environments. For exposures ≥ 0.6 L, the area of both high-temperature peaks decrease and new peaks at 130 and 150 K emerge. The peak at 130 K is due to allyl bromide desorption.⁹ The 150 K peak reaches saturation at 1.4 L allyl bromide and is assigned to 1,5-hexadiene based on the mass spectrometer cracking pattern. The correlation of the reduction

Scheme 1

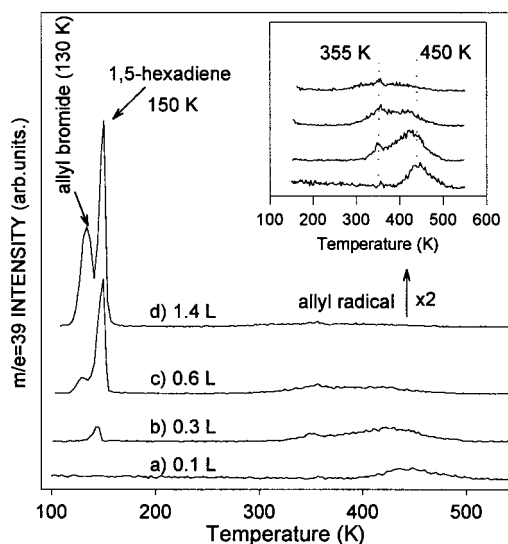
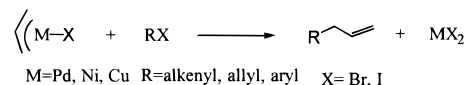


Figure 1. Temperature programmed desorption spectra of allyl radicals (350–450 K), allyl bromide (130 K), and 1,5-hexadiene (150 K) after indicated exposures of allyl bromide on Cu(100) at 110 K. The heating rate was 2.5 K/s and the $m/e = 39$ signal was used to monitor the desorption products. The inset shows the desorption of allyl radicals at 355 and 450 K.

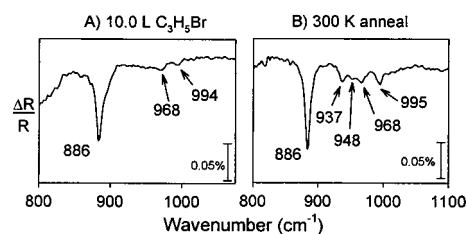


Figure 2. (A) RAIR spectrum of the formation of η^3 -allyl groups from 10.0 L of allyl bromide on Cu(100) dosed at 225 K and the corresponding spectrum (B) after annealing to 300 K. Both spectra were taken at 225 K with 4 cm^{-1} resolution.

of allyl radical desorption and the formation of 1,5-hexadiene is discussed below.

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Scheme 2

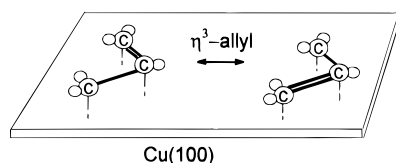


Table 1. Comparison of the Vibrational Frequencies (cm^{-1}) of an Allyl Radical in an Argon Matrix, $(\pi\text{-allyl})\text{Fe}(\text{CO})_2\text{NO}$ Complex, and Allyl Groups Adsorbed on Metal Crystals

band ^a	allyl radical in Ar matrix ^a	$(\pi\text{-allyl})\text{-Fe}(\text{CO})_2\text{NO}^b$	Ag(110) ^c	Pt(111) ^d	Cu(100) ^e
$\rho_\omega(\text{CH}_2)$	802	926		890/940	886
$\rho_\omega(\text{CH})$	984	1018	1025	1050	995
$\nu(\text{CCC})_{\text{sym}}$	1242	966	~965	985	968

^a Reference 14. ^b Reference. 10. ^c Reference 18. ^d Reference 9. ^e This work.

at 937 and 948 cm^{-1} were below the detection limit of the MCT detector. This observation is consistent with the TPD data in Figure 1 which shows that the desorption of some allyl groups occurs near 355 K.

An analysis of the 886, 968, and 995 cm^{-1} bands in Figure 2 indicates that the local symmetry of allyl groups on Cu(100) is C_s and the adsorption structure is analogous to typical $\eta^3\text{-allylmetal}$ complexes. Scheme 2 shows two resonance forms of the proposed adsorption structure of $\eta^3\text{-allyl}$ group on Cu(100). In C_s symmetry, the 18 vibrational modes of an allyl group are distributed as $10A'$ and $8A''$, where A' represents the totally symmetric modes and A'' represents the nontotally symmetric modes. On the basis of the surface selection rule,¹³ all of the A' modes are infrared active, and the A'' modes are infrared inactive. Table 1 lists mode descriptions of the three observed A' vibrational bands and makes comparisons with analogous species.^{9,10,14,15,17} The intensities of the remaining seven A' modes lie below the detection limits of the MCT detector (peak-to-peak noise <0.004%). The mode description employed here follows that used for allyl groups trapped in an argon matrix.¹⁴ Furthermore, the proposed orientation of the allyl group is consistent with a near edge X-ray absorption fine structure (NEXAFS) measurement.⁸

From the evidence presented in Figures 1 and 2 we conclude that dosing allyl bromide at 225 K forms only $\eta^3\text{-allyl}$. This dissociative adsorption via the carbon–bromine bond rupture is a process analogous to oxidative-addition of an organic halide to a metal complex in organometallic chemistry.³ However, dosing at or below 135 K leads to significant changes in the RAIR spectra attributed to facile reactions involving C–C bond formation. This is indicated in Figure 3A. Compared to a dose at 225 K, a 1.4 L dose of allyl bromide at 110 K yields $10 \times$ lower $\eta^3\text{-allyl}$ intensity and new features. These new features are intensified by annealing to 130 K (B) and are identified unambiguously as 1,5-hexadiene by a comparison (C) with directly dosed 1,5-hexadiene on bromine-covered Cu(100) at 110 K. The band positions and relative intensities in (B) and (C) are identical within experimental error. The presence of some unreacted allyl bromide in Figure 3A is evident since, for example, the CH_2 wag mode at 1212 cm^{-1} of the CH_2Br moiety of allyl bromide is clearly observed.¹⁶ A detailed assignment of the infrared spectrum of 1,5-hexadiene

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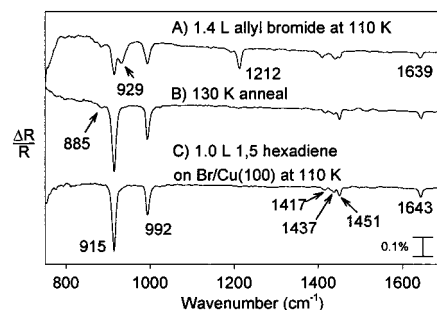
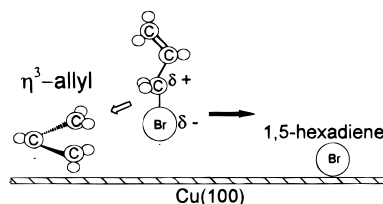


Figure 3. RAIR spectra showing direct evidence of the formation of 1,5-hexadiene from allyl bromide on Cu(100) at 110 K. (A) 1.4 L of allyl bromide at 110 K, (B) after a 130 K anneal of (A) to desorb unreacted allyl bromide. (C) 1 L of 1,4-hexadiene on a Br-covered Cu(100) surface at 110 K. Each spectrum was taken at 4 cm^{-1} resolution.

Scheme 3



on clean and Br-covered Cu(100), including the CH stretching region, will be presented elsewhere.⁷ Briefly, parts B and C of Figure 3 show relatively strong and sharp bands at 915, 992, and 1643 cm^{-1} , which are assigned to CH_2 wagging, CH_2 twisting, and C=C stretching modes, respectively, of 1,5-hexadiene.¹⁷

At cryogenic temperatures, the formation of 1,5-hexadiene has not been previously reported on Cu(100) or on other single-crystal metal surfaces. Although the dissociative adsorption of allyl bromide occurs throughout the 110–300 K temperature range, the reaction path changes with substrate temperature. During dosing above 225 K no 1,5-hexadiene forms, whereas below 135 K its formation occurs readily. In contrast on Ag(110), $\eta^3\text{-allyl}$ groups (from allyl chloride) dimerize to form 1,5-hexadiene near 310 K,¹⁸ a process presumably limited, in agreement with calculations,¹⁹ by the surface diffusion of allyl groups bound to Ag. In contrast, between 225 and 300 K, allyl groups on Cu(100), Figure 2, become more highly ordered but do not dimerize since no 1,5-hexadiene appears in TPD.

Since there is no evidence for the dimerization of $\eta^3\text{-allyl}$ via a diffusion mechanism, we propose that 1,5-hexadiene forms in a reaction between chemisorbed allyl groups and molecular allyl bromide in a precursor-assisted process (Scheme 3). In this precursor state, allyl bromide molecules on top of the $\eta^3\text{-allyl}$ groups monolayer reorient in a geometrical configuration that is more favorable for the reaction to proceed. We propose that this process does not occur above 225 K because the residence time of molecular allyl bromide becomes too short. It either desorbs intact or dissociates at Cu sites rather than reacting with chemisorbed allyl groups. Since spectra B and C of Figure 3 are identical, we suggest that the reaction to form 1,5-hexadiene leaves the product adsorbed on bromine atoms rather than directly bonded to the Cu(100) surface. This is consistent with the proposal of Scheme 3. This study points to a mechanistic link between low-energy coupling reactions occurring in UHV conditions and under conditions of heterogeneous/homogeneous catalysis.

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