

Gold Makes the Termolecular Assembly Possible: Surface-Catalyzed Conversion of an Aldehyde to Its Cyclic Trimer

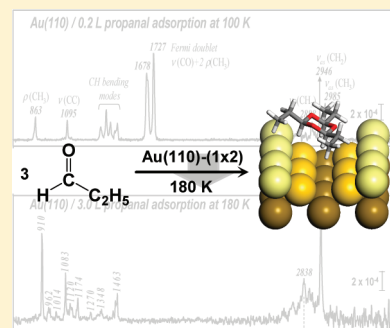
Shin-Mou Wu and Chao-Ming Chiang*

Department of Chemistry, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424

S Supporting Information

ABSTRACT: Propanal ($\text{C}_2\text{H}_5\text{CHO}$) trimerizes to 2,4,6-triethyl-1,3,5-trioxane ring on the (110) face of gold in vacuo. The three-component coupling is not only selective about which crystal plane to react upon but also metal-dependent. Low-coordinated sites, surface-specific morphology, and electronic properties of gold act in concert to construct the cyclic C—O—C linkages. Interplay between metal coordination and molecule—surface and molecule—molecule interactions help gather the reaction components and preorganize them on the surface, promoting an otherwise termolecular reaction to a unimolecular (intracomplex) one and making the cyclization possible.

SECTION: Surfaces, Interfaces, Catalysis



Gold's reputation as an inactive catalyst has been changed since the discoveries made by pioneers, including Bond,¹ Hutchings,² and Haruta.^{3,4} Today, exploring gold's potential to catalyze a range of heterogeneous and homogeneous reactions has become a hot topic.⁵ Meanwhile, huge efforts have been stimulated to identify the intrinsic metal effects responsible for the efficacy of gold. The chemical and physical properties of gold are strongly influenced by relativistic effects. For example, electronically, Au is the metal with the highest Pauling electronegativity,⁶ and cationic Au species are viewed as superior Lewis acids.⁷ Structurally, Au is the only coinage metal whose low-index surfaces reconstruct at room temperature.⁸ Establishing the correlation between these peculiarities and catalysis by gold would be essential.

To resolve the roles of gold and the oxide support in heterogeneous catalysis, Au single-crystal surfaces (flat and vicinal) often serve as model systems.^{9–12} However, most molecules are known to adsorb weakly on clean well-defined gold surfaces in vacuo. It is only very recently that covalent bond-making reactions have been reported.^{13–15} Here, we show, with a combination of surface science techniques and density functional theory calculations, that cyclic 2,4,6-triethyl-1,3,5-trioxane can be formed after the propanal ($\text{C}_2\text{H}_5\text{CHO}$) adsorption at 180 K on a missing-row reconstructed (110) face of gold. This rare termolecular cyclization process was found to be highly selective about the identity of the metal and the crystal plane used. The cyclotrimerization reaction did not transpire on a variety of fcc metals, including Cu(110), Ag(110), Pt(110), and close-packed Au(111). We argue that low-coordinated sites, surface-specific morphology, and electronic properties of gold need to act in concert to drive the formation of cyclic C—O—C linkages on Au(110).

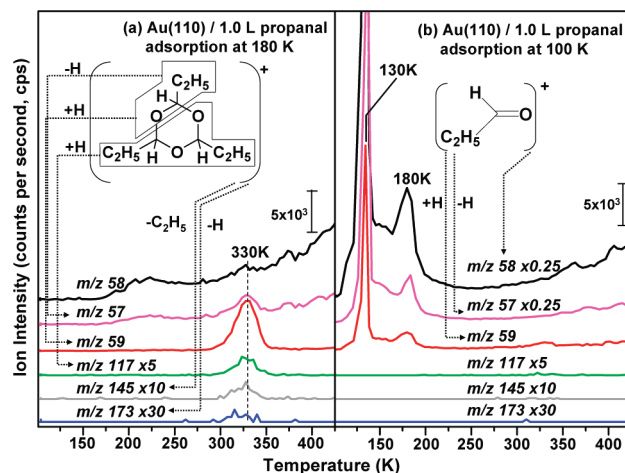


Figure 1. Multiple-ion thermal desorption spectra after exposing Au(110) to 1.0 L of $\text{C}_2\text{H}_5\text{CHO}$ at (a) 180 and (b) 100 K. The desorbing species are deduced from the possible ion fragmentation pathways shown in the schematic diagrams.

Figure 1 shows the thermal desorption (TD) spectra of m/z (mass-to-charge ratio) 58, 57, 59, 117, 145, and 173 selected on the basis of the characteristic fragment ions of 2,4,6-triethyl-1,3,5-trioxane. The schematic diagrams delineate the reasoned electron impact cracking patterns. In Figure 1a, formation of the heterocyclic trimer is evidenced by the set of parallel desorption

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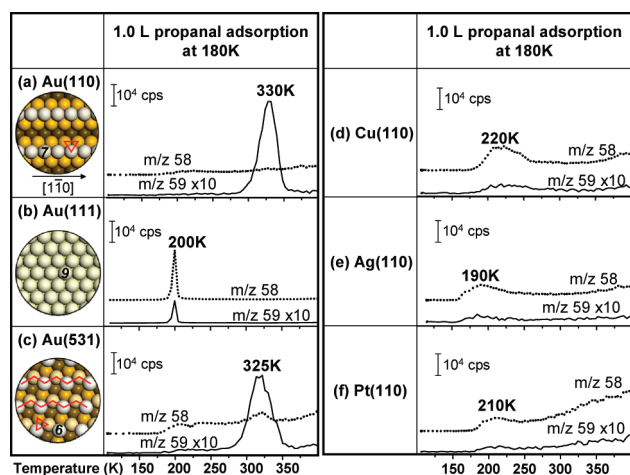
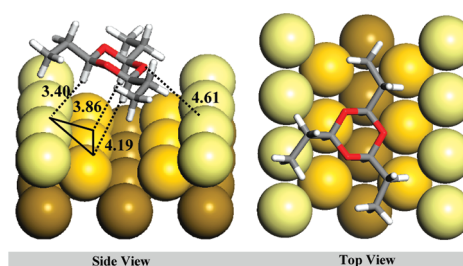


Figure 2. (Left panel) TD spectra measured after adsorbing 1.0 L of $\text{C}_2\text{H}_5\text{CHO}$ on (a) Au(110), (b) Au(111), and (c) Au(531) at 180 K. (Right panel) TD spectra with the same $\text{C}_2\text{H}_5\text{CHO}$ exposure yet on different metals, including (d) Cu(110), (e) Ag(110), and (f) Pt(110).

features bearing a common peak temperature at 330 K after the adsorption of 1.0 L of propanal on Au(110) at 180 K. Noteworthy is the predominance of the m/z 59 signals in association with a relatively featureless m/z 58 TD trace. In stark contrast, adsorption of propanal at 100 K only results in molecular desorption at 130 (multilayer) and 180 K (monolayer)¹⁶ in Figure 1b, where the parent $\text{C}_2\text{H}_5\text{CHO}^+$ (m/z 58) instead arises as the most abundant ion concomitant with minor m/z 57 ($M-1$ hydride transfer ion) and 59 ($M+1$ proton transfer ion) fragments. This observation serves as a control to demonstrate that the $(\text{C}_2\text{H}_5\text{CHO})_3$ was generated by the reaction on the surface and was not a consequence of the sample impurity admitted to the chamber. The 180 K requirement for the cyclotrimerization is thought to bestow a certain degree of lateral and conformational mobility, not available at 100 K (adsorbates are randomly distributed), upon adsorbed molecules to orient themselves for the intermolecular assembly. After the desorption of trioxane, X-ray photoemission spectra (XPS) showed no carbon and oxygen residues (see Supporting Information).

The cyclotrimerization of propanal is further proven to be metal-dependent. Again, on Au(110), the prominent TD peak of m/z 59 at 330 K against the flat m/z 58 baseline in Figure 2a is indicative of the evolution of trioxane. In Figure 2d and e, the same exposure of propanal at 180 K to other coinage metal Cu(110) and Ag(110) surfaces renders small m/z 58 TD features centered at 220 and 190 K, respectively, with insignificant m/z 59 contributions, suggesting reversible molecular desorption without reactions. On the more active 5d Pt(110) surface, which exhibits the well-known (1×2) reconstruction by losing the alternate atomic rows like the clean Au(110), the trimerization does not proceed either, verified by the absence of any substantial m/z 59 peak in Figure 2f. In fact, a stronger binding to the Pt surface causes decarbonylation to take place (data not shown). The Au(111) surface is also reconstructed, however, into a herringbone structure, and is capable of promoting several unusual coupling reactions.^{13–15} Yet, as shown in Figure 2b, propanal appears not to cyclize on this surface because the measured ion intensities around 200 K simply characterize monolayer molecular desorption. It is logical to ascribe this

Scheme 1. Optimized $(\text{C}_2\text{H}_5\text{CHO})_3\text{--Au}_{26}$ Complex Structure



difference in reactivity between Au(111) and Au(110) to the distinct features such as (1) the low-coordinated gold atoms (coordination number $N_c = 7$) on top of the (1×2) surface layer and (2) the unidirectional trenches existing on the Au(110) missing-row structure but lacking on Cu(110) and Ag(110) (see the inset of Figure 2a).

In the solution phase, aldehyde cyclization is known to be catalyzed by acids,^{17,18} and on the surface, oligomerization to cyclic trimers is assumed to be favorable only for aldehyde weakly adsorbed in the $\eta^1(\text{O})$ state, as opposed to $\eta^2(\text{C}, \text{O})$.¹⁹ Accordingly, we propose that the uppermost Au atoms on (110) must possess the adequate activity to anchor aldehyde molecules monodentately via the carbonyl oxygen lone pair even at 180 K. The surface Au atoms further behave as effective Lewis acidic initiators to transfer charge to the monomer and reduce the $\text{C}=\text{O}$ double bond character, namely, $\text{C}^{\delta+}=\text{O}^{\delta-}\cdots\text{Au}$. The open trenches on Au(110) allow such a geometric fit that three monomers can poise their polar carbonyl bonds in correct head-to-tail orientations to form a termolecular complex, and the ring conformation is in proper registry with the underlying metal framework. To validate the above view, density functional theory (DFT) calculations were performed. Scheme 1 represents the theoretically predicted and energetically most stable structure of the adsorbed 2,4,6-triethyl-1,3,5-trioxane on a rigid three-layer Au_{26} cluster modeling the missing-row Au(110) surface.²⁰ Here, the puckered ring geometry exhibits that the single trioxane molecule binds to the Au substrate in a chair configuration (the closest Au–O distance = 4.61 Å) with three CH bonds directed toward the surface. The ring plane is tilted, and the triangular array of the axial CH bonds is projected onto the (111)-type microfacets on the side of the trench. The closest Au–H distance is 3.4 Å, where the calculated charges by natural population analysis (NPA) reveal that $\text{C}^{\delta+}=\text{H}^{\delta-}\cdots\text{Au}^{\delta-}$ type interaction ($\delta = +0.38, +0.19$, and -0.048 for C, H, and Au) might be substantial. Gold's high electronegativity (2.54, higher than 2.20 for H, comparable with 2.55 for C, and the highest of all metals) and the relatively high desorption temperature (>300 K) for the 2,4,6-triethyl-1,3,5-trioxane rationalize the presence of such attraction. Considering their lower electronegativity (1.95, 1.93, and 2.28 for Cu, Ag, and Pt), the lack of the ring formation activity on Cu, Ag, and Pt surfaces then becomes interpretable. These additional hydrogen-bond-like forces help gather the reaction components and preorganize them at specific surface sites while the intracomplex reaction takes place. An overall template effect has promoted an otherwise termolecular reaction (intermolecular) to a unimolecular (intramolecular) one and made the cyclization possible.

The optimized structural parameters were utilized to compute the vibrational frequencies, which are corrected by a scaling

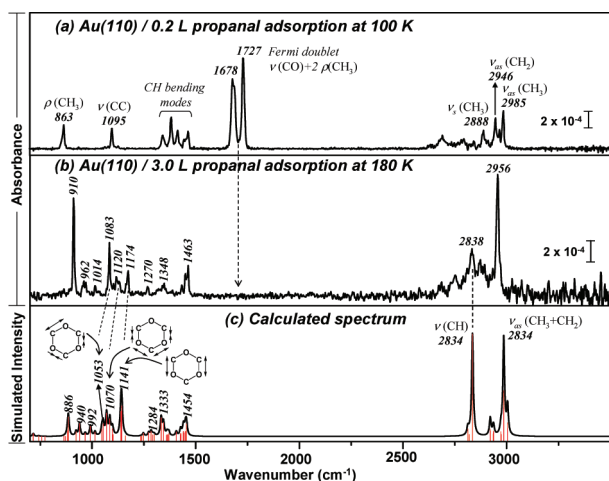
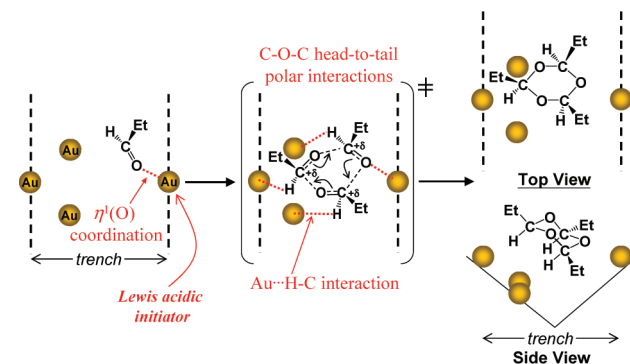


Figure 3. (a) Experimental RAIR spectrum collected after exposing Au(110) to 0.2 L of $\text{C}_2\text{H}_5\text{CHO}$ at 100 K, resulting in a submonolayer coverage of physisorbed molecules. (b) Separate RAIR spectrum measured after a 3.0 L $\text{C}_2\text{H}_5\text{CHO}$ exposure at 180 K, which led to cyclization. (c) Theoretically predicted IR spectrum for $(\text{C}_2\text{H}_5\text{CHO})_3$, the heterocyclic trimer, bound to a Au_{26} cluster model, shown in Scheme 1. A 4 cm^{-1} bandwidth is added to each peak in order to match the experimental resolution.

factor of 0.9603 (B3LYP)²¹ and plotted by adding Lorentzian line shapes with a bandwidth of 4 cm^{-1} . The resulting simulated IR spectrum, Figure 3c, is compared with the experimental reflection–absorption infrared (RAIR) spectra from $\text{C}_2\text{H}_5\text{CHO}$ both physisorbed and chemisorbed on Au(110)-(1 × 2) at 100 and 180 K, respectively. The physisorbed spectrum, Figure 3a, was found to agree well with the data of propanal in the solid phase reported by Sbrana et al.²² The doublet bands at 1678 and 1727 cm^{-1} are attributable to Fermi resonance between the normal carbonyl stretch mode $\nu(\text{C}=\text{O})$ and the overtone of the methyl rocking mode $2\rho(\text{CH}_3)$. Figure 3b, taken after propanal adsorption at 180 K, clearly differs from Figure 3a, indicating that surface reaction has occurred. By contrasting Figure 3b and c, reasonable conformity between the calculated and the experimental results is achieved (the discrepancy may be due to the fact that calculations were done on a cluster with limited numbers of gold atoms). Therefore, the new bands at 1083, 1120, and 1174 cm^{-1} , shown in Figure 3b, can be assigned to characteristic vibrations of the cyclic ether C–O–C linkage on the basis of the animated vibrations obtained from the calculated structure. Together with the disappearance of the $\nu(\text{C}=\text{O})$ mode, the ring synthesis in a single operational step is strongly suggested. It should be noted that to reach a preferable match between the predicted and the measured axial C–H stretching frequencies ($\nu(\text{CH}) = 2834$ versus 2838 cm^{-1}), the trioxane ring must point its axial CH bonds at the surface (see Supporting Information for spectra from other geometries), consolidating the proposed molecular–surface C–H...Au type interactions. Upon further annealing, the spectral features did not alter much until the IR absorption signals finally became difficult to distinguish from noise at 300 K, which coincides with the liberation temperature of 2,4,6-triethyl-1,3,5-trioxane. Desorption of the cyclic trimer product appears to be the rate-limiting process.

We extended the analogies over to the Au(531) surface (inset of Figure 2c), anticipating that its step edges separated by narrow (111) terraces can act like templates, similar to the role played by

Scheme 2. Proposed Reaction Mechanism



the trenches on Au(110), while the kinked sites with N_c as low as 6 can be in charge of tethering the monomers and catalytically initiating the cyclization. As illustrated in Figure 2c, the same propanal dosage at 180 K indeed affords 2,4,6-triethyl-1,3,5-trioxane with a yield and the TD maximum all comparable to those resulting from Au(110). We also tested the accessibility of the most well-known metal-catalyzed three-component reaction,²³ namely, cyclootrimerization of alkynes. Acetylene and propyne were surveyed on Au(110), but benzenes were not found.

Through the literature on the subject, the only precedent for conversion of aldehyde to its cyclic trimer ($3\text{RCHO} \rightarrow (\text{RCHO})_3$) was observed from acetaldehyde adsorbed on a $p(2 \times 2)$ sulfur-covered Ni(100) by Madix et al.²⁴ Here, we found no evidence for cyclootrimerization of acetaldehyde on clean Au(110)-(1 × 2). Instead, CH_3CHO reversibly desorbs at $\sim 160\text{ K}$. Because CH_3 has less electron-donating power than C_2H_5 , this dependence on the alkyl group attached to the carbonyl moiety reflects a cationic polymerization mechanism involving intermediate carbocations ($\text{RHC}=\text{O} + \text{Au} \rightarrow \text{RHC}^+-\text{O}-\text{Au}$) in the initiation step. It should be mentioned that King et al. reported that acetaldehyde was subject to nucleophilic attack only by precovered surface atomic oxygen on Ag(111); thereby, polymerization, in lieu of cyclootrimerization, was initiated at 140 K to construct helical polyacetaldehyde chains.^{25,26}

Gold single-crystal surfaces are not entirely inactive, but rather selective. If key conditions are stringently met, a termolecular reaction that is otherwise hard to achieve can be activated. A summary of our proposed mechanism for the cyclization is provided in Scheme 2. The coordination to the low-coordinated gold atoms (Lewis acid site) installs a tether and opens the carbon–oxygen double bond of the aldehyde, creating a situation to join the three polar carbonyl groups in a head-to-tail fashion inside of the confined space unique to the reconstructed or stepped/kinked gold surfaces. The underlying C–H...Au interactions assist preassociation of the reacting partners to form an adsorbate/surface complex. Therefore, the intermolecular reaction becomes an intramolecular one, eliminating the change of entropy term in the activation process. Observation of this gold surface-catalyzed reaction not only expands the repertoire of bond synthesis chemistry on extended gold structures but also demonstrates that understanding the local atomic structure and the chemical nature of active species from a fundamental aspect is essential for elucidating the catalytic phenomena and designing more active and selective gold catalysts in a rational manner.

■ ASSOCIATED CONTENT

S Supporting Information. Surface C1s and O1s XP spectra, calculated structures, charges, vibrational frequencies, and energies. Comparison between the experimental and the calculated spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: (+886) 7-525-3939. E-mail: cmc@mail.nsysu.edu.tw.

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■ REFERENCES

- (1) Bond, G. C.; Sermon, P. A.; Webb, G.; Buchanan, D. A.; Wells, P. B. Hydrogenation over Supported Gold Catalysts. *J. Chem. Soc., Chem. Commun.* **1973**, 444–445.
- (2) Hutchings, G. J. Vapor Phase Hydrochlorination of Acetylene: Correlation of Catalytic Activity of Supported Metal Chloride Catalysts. *J. Catal.* **1985**, 96, 292–295.
- (3) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature far below 0 Degree C. *Chem. Lett.* **1987**, 16, 405–408.
- (4) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. Gold Catalysts Prepared by Coprecipitation for Low-Temperature Oxidation of Hydrogen and of Carbon Monoxide. *J. Catal.* **1989**, 115, 301–309.
- (5) Hashimi, A. S. K.; Hutchings, G. J. Gold Catalysis. *Angew. Chem., Int. Ed.* **2006**, 45, 7896–7936.
- (6) Meyer, R.; Lemire, C.; Shaikhutdinov, Sh. K.; Freund, H.-J. Surface Chemistry of Catalysis by Gold. *Gold Bull.* **2004**, 37, 72–124.
- (7) Gorin, D. J.; Toste, F. D. Relativistic Effects in Homogeneous Gold Catalysis. *Nature* **2007**, 446, 395–403.
- (8) Bond, G. C. Relativistic Effects in Coordination, Chemisorption, and Catalysis. *J. Mol. Catal. A: Chem.* **2000**, 156, 1–20.
- (9) Jiang, T.; Mowbray, D. J.; Dobrin, S.; Falsig, H.; Hvolbæk, B.; Bligaard, T.; Nørskov, J. K. Trends in CO Oxidation Rates for Metal Particles and Close-Packed, Stepped, and Kinked Surfaces. *J. Phys. Chem. C* **2009**, 113, 10548–10553.
- (10) Xu, B.; Liu, X.; Haubrich, J.; Friend, C. M. Vapor-Phase Gold-Surface-Mediated Coupling of Aldehydes with Methanol. *Nat. Chem.* **2010**, 2, 61–65.
- (11) Gong, J.; Mullins, C. B. Surface Science Investigations of Oxidative Chemistry on Gold. *Acc. Chem. Res.* **2009**, 42, 1063–1073.
- (12) Davis, K. A.; Goodman, D. W. Propene Adsorption on Clean and Oxygen-Covered Au(111) and Au(100) Surfaces. *J. Phys. Chem. B* **2000**, 104, 8557–8562.
- (13) Kanuru, V. K.; Kyriakou, G.; Beaumont, S. K.; Papageorgiou, A. C.; Watson, D. J.; Lambert, R. M. Sonogashira Coupling on an Extended Gold Surface in Vacuo: Reaction of Phenylacetylene with Iodobenzene on Au(111). *J. Am. Chem. Soc.* **2010**, 132, 8081–8086.
- (14) Jensen, S.; Früchtl, H.; Baddeley, C. J. Coupling of Triamine with Diisocyanates on Au(111) Leads to the Formation of Polyurea Networks. *J. Am. Chem. Soc.* **2009**, 131, 16706–16713.
- (15) Weigelt, S.; Schnadt, J.; Tuxen, A. K.; Masini, F.; Bombis, C.; Busse, C.; Isvoranu, C.; Ataman, E.; Lægsgaard, E.; Besenbacher, F.; Linderoth, T. R. Formation of Trioctylamine from Octylamine on Au(111). *J. Am. Chem. Soc.* **2008**, 130, 5388–5389.
- (16) Shekhar, R.; Barteau, M.; Plank, M. A.; Vohs, R. V. J. M. Adsorption and Reaction of Aldehydes on Pd Surfaces. *J. Phys. Chem. B* **1997**, 101, 7939–7951.
- (17) Bevington, J. C. The Polymerization of Aldehydes. *Q. Rev. Chem. Soc.* **1952**, 6, 141–156.
- (18) Sato, S.; Sakurai, C.; Furuta, H.; Sodesawa, T.; Nozaki, F. A Heteropoly Acid Catalyst and Its Convenient, Recyclable Application to Liquid-Phase Cyclotrimerization of Propionaldehyde. *J. Chem. Soc., Chem. Commun.* **1991**, 1327.
- (19) Davis, J. L.; Barteau, M. A. Polymerization and Decarbonylation Reactions of Aldehydes on the Pd(111) Surface. *J. Am. Chem. Soc.* **1989**, 111, 1782–1792.
- (20) Computations were executed by using the B3LYP functional and a split basis set method with 6-31G*(d,p) for main group elements and the Los Alamos 19 electron shape consistent relativistic effective core potential (LANL2DZ) for gold atoms. Choosing a cluster size containing 26 gold atoms was a compromise between accuracy and cost in modeling such an adsorbate/surface complex.
- (21) NIST Computational Chemistry Comparison and Benchmark Database <http://srdata.nist.gov/cccbdb/vsf.asp> (accessed August 12, 2011).
- (22) Sbrana, G.; Schettino, V. Vibrational Spectra and Isomerism in Propyl- and Butylaldehydes. *J. Mol. Spectrosc.* **1970**, 33, 100–108.
- (23) Galan, B. R.; Rovis, T. Beyond Reppe: Building Substituted Arenes by [2 + 2+2] Cycloaddition of Alkynes. *Angew. Chem., Int. Ed.* **2009**, 48, 2830–2834.
- (24) Madix, R. J.; Yamada, T.; Johnson, S. W. The Modification of Surface Reactivity by Sulfur; Effects on Dehydrogenation of Ethanolamine, Ethylene Glycol, and Acetaldehyde on Ni(100). *Appl. Surf. Sci.* **1984**, 19, 43–58.
- (25) Sim, W. S.; Gardner, P.; King, D. A. Surface-Bound Helical Polyacetaldehyde Chains and Bidentate Acetate Intermediates on Ag{111}. *J. Am. Chem. Soc.* **1996**, 118, 9953–9959.
- (26) Webb, M. J.; Driver, S. M.; King, D. A. Acetaldehyde Chemistry on Ag{111}-(4 × 4)-Ag_{1.83}O between 77 and 200 K Studied by STM. *J. Phys. Chem. B* **2004**, 108, 1955–1961.