The framework of italicene (**4a**) was constructed by the sequence shown in Scheme III. Olefin **17**, derived from cyclohexanone (**16**), was transformed into **18** via addition of carbene.[13] The unsaturated ester **19** was prepared as a 1:7 mixture of two diastereoisomers, separable by HPLC. Treatment of both stereoisomers of **19**, separately with TBDMSOTf in the presence of Et_3N in CH_2Cl_2 at 20 °C for 5 min gave rise to the tandem reaction and produced the tetracyclic compound **20** in 97% yield as a single product. The stereochemistry of **20** was determined by observations of NOE between CH_2 at C(2) and H at C(11), and $Bu^t\mathit{Me}_2SiO$ at C(1) and H at C(2) of alcohol **21**, formed by reduction of **20**.

Thus, an efficient route to a variety of polycyclic compounds having a cyclobutane has been developed by the intramolecular Michael-aldol reaction conducted with TBDMSOTf in the presence of Et_3N.

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Supplementary Material Available: Spectral data including IR, ^1H (500 MHz) and ^{13}C (125 MHz) NMR, and MS data of compounds **7**, **15**, **20**, and **21** (2 pages). Ordering information is given on any current masthead page.

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Reactions of Allyl Chloride on Ag(110) To Form η^3-C_3H_5 and 1,5-Hexadiene

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Because activation energies for Langmuir-Hinshelwood reactions in heterogeneous systems are often larger than for desorption of reactants and products, alternative approaches are required for investigating the mechanisms of these reactions in an ultrahigh-vacuum environment. One possibility is to use reactions of model compounds to form adsorbed intermediates of interest, after which their reactivity can be investigated to elucidate the energetics and mechanisms of elementary steps that would be otherwise undetectable. Here, we address via allyl chloride (C_3H_5Cl) chemisorption on Ag(110) the formation and stability of π-allyl, η^3-C_3H_5, and its subsequent reactivity to form 1,5-hexadiene.

The role of η^3-C_3H_5 in propylene combustion on silver is controversial: Madix and co-workers propose it as the reactive intermediate formed in the rate-limiting step,[1,2] whereas Carter and Goddard argue that alternative reaction pathways are energetically more favorable than combustion via η^3-C_3H_5.[3] Propylene and oxygen coadsorption experiments fail to resolve this controversy, since the initial Langmuir-Hinshelwood step limits the overall combustion rate,[1] precluding the isolation of stable intermediates.

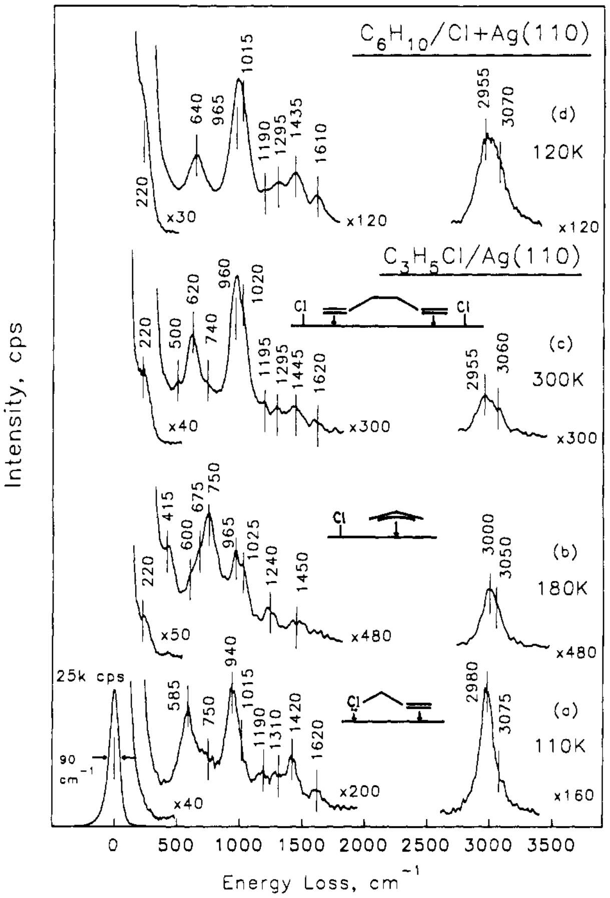

Figure 1. High-resolution electron energy loss vibrational spectra collected after (a) a submonolayer exposure (5×10^{-7} Torr s) of the clean Ag(110) surface at 110 K to allyl chloride; (b) an exposure sufficient to saturate the monolayer ($>2 \times 10^{-6}$ Torr s), followed by momentary annealing at 180 K; and (c) heating of sample b to 300 K. Schematic diagrams of the chemisorbed species identified in each circumstance accompany the spectra. Spectrum d was recorded after exposure of the chlorinated surface at 120 K to 2×10^{-6} Torr s of 1,5-hexadiene.

More substantial evidence verifies the critical role of η^3-C_3H_5 in the partial oxidation of propylene to acrolein over oxide catalysts,[4] and η^3-C_3H_5 has been shown to dimerize to 1,5-hexadiene on bismuth oxide[5] and a homogeneous palladium compound.[6] Although η^3-C_3H_5 has not been isolated previously in studies of this type, the structural homologue π-2-methylallyl, η^3-$CH_3C(CH_2)_2$, has recently been identified as a product of isobutylene oxidation on Ag(110).[7]

A submonolayer exposure (5×10^{-7} Torr s) of the Ag(110) surface to allyl chloride at 110 K yields the high-resolution electron energy loss (HREEL[8]) vibrational spectrum of Figure 1a. All features agree well with the major infrared bands of either gas-phase or matrix-isolated allyl chloride,[9] indicating that initial adsorption is molecular and is mediated by weak donor interactions at the C=C bond and possibly a Cl lone electron pair, as depicted schematically with spectrum a. Aliphatic and/or olefinic CH_2 stretching modes are evident at 3075 and 2980 cm^{-1}; the skeletal modes ν(C=C) and ν(C—Cl) appear near 1620 and 750 cm^{-1},

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respectively; $\delta(CH_2)$ is observed at 1420 cm^{-1}; $\delta(CH)$ and CH wags are evident at 1310, 1015, and 585 cm^{-1}; and the remaining modes at 1190 and 940 cm^{-1} are attributable to CH_2 twists or wags.[10]

For exposures sufficient to saturate the monolayer at 110 K ($>2 \times 10^{-6}$ Torr s), followed by momentary annealing at 180 K to desorb any condensed allyl chloride, the HREEL spectrum of Figure 1b results. A very strong band at 220 cm^{-1} attributable to ν(Ag–Cl) appears, indicating clearly that atomically adsorbed chlorine is present and that dissociation of the allyl chloride has occurred. Consistent with this conclusion, the remaining features can be reconciled convincingly with the presence of π-allyl, η^3-C_3H_5, as shown schematically with spectrum b. Note particularly by comparison to spectrum a that a discernible feature for $\nu(C{=}C)$ near 1620 cm^{-1} is absent, and that the bands from about 500 to 1500 cm^{-1} are significantly altered. These changes are expected for a species containing C–C bonds of both sp^2 and sp^3 hybridization transforming to one in which all C–C bonds are equivalent, as would be the case for η^3-C_3H_5. All features in spectrum b compare well with the IR spectrum of the inorganic compound $(\eta^3\text{-}C_3H_5)Fe(CO)_2NO$[11] and can be assigned as follows: $\nu_{as}(CH_2) \approx 3050$ cm^{-1}; $\nu_s(CH_2) \approx 3000$ cm^{-1}; ν_{as}(C–C–C) and $\delta(CH_2) \approx 1450$ cm^{-1} (not resolved); $\pi(CH)$ and $\delta(CH) \approx 1240$ cm^{-1} (not resolved); $\rho(CH_2) \approx 1025$ cm^{-1}; ν_s(C–C–C) ≈ 965 cm^{-1}; $\rho(CH_2) \approx 750$ and 675 cm^{-1}; and δ(C–C–C) ≈ 600 cm^{-1}. We assign the feature at 415 cm^{-1} to $\nu[Ag\text{–}(\eta^3\text{–}C_3H_5)]$, the frustrated translation of π-allyl perpendicular to the surface; its frequency falls within the range observed for $\nu[M\text{–}(\eta^3\text{-}C_3H_5)]$ in various inorganic compounds.[11,12]

When the surface is heated further, significant changes in the vibrational spectrum of the adsorbed layer begin near 280 K and are complete by 300 K, resulting in the HREEL spectrum of Figure 1c. Most notably the feature at 415 cm^{-1} due to $\nu[Ag\text{—}(\eta^3\text{-}C_3H_5)]$ disappears, a $\nu(C{=}C)$ mode appears at 1620 cm^{-1}, and the band in the CH stretching region broadens, indicating the return of a mixture of olefinic and aliphatic CH vibrations. We identify this species as 1,5-hexadiene, formed by the dimerization of η^3-C_3H_5's and bound to the surface through π-donor interactions at both C=C bonds, as depicted with spectrum c. This conclusion is substantiated by temperature-programmed desorption measurements, which show the signature cracking fragments of 1,5-hexadiene (m/e = 41, 54, 67 amu) desorbing near 310 K, suggesting that the heat of adsorption of 1,5-hexadiene on the chlorinated Ag(110) surface is approximately 20 kcal/mol.[13] This reaction consumes η^3-C_3H_5 completely, leaving only adsorbed chlorine. Further confirmation is provided by spectrum d, which was measured after exposure of the chlorinated but otherwise clean surface to 2×10^{-6} Torr s of 1,5-hexadiene at 120 K. Spectra c and d agree almost perfectly, the only distinctions being the higher absolute intensity in spectrum d, due to higher coverage, and the absence of the weak features near 500 and 740 cm^{-1}, which are probably present but not resolved.

In summary, we have successfully isolated and identified the reactive intermediate η^3-C_3H_5 on Ag(110) by adsorption and thermally activated dissociation of allyl chloride. This synthesis approach is the starting point for mechanistic investigations of its interaction with adsorbed OH and atomic oxygen, to be reported later.[10] Furthermore, we have observed the dimerization of η^3-C_3H_5's on Ag(110) to yield 1,5-hexadiene, which is the only reaction we are aware of that couples hydrocarbon fragments on silver in vacuum by C–C bond formation.

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Single-Step Preparation of Rigid-Rod, Cationic, Bimetallic, σ-Diyne Complexes: $L_5M^+C{\equiv}C(C_6H_4)C{\equiv}CM^+L_5{\cdot}2TfO^-$, M = Ir, Rh†

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There is considerable current interest in bimetallic complexes, either bridged or connected by an organic group, due to their possibly unique role in catalytic processes.[1] Particularly interesting are the rigid, acetylide-connected complexes[2-5] **1–3**, due not only to potential catalytic activity but also to their role in new, nonlinear optical materials.[6,7]

$$\underset{\mathbf{1}}{L_nMC{\equiv}CML_n} \qquad \underset{\mathbf{2}}{L_nMC{\equiv}CC{\equiv}CML_n}$$

$$\underset{\mathbf{3}}{L_nMC{\equiv}C(C_6H_4)C{\equiv}CML_n}$$

To date these complexes have been prepared via traditional acetylide, $RC{\equiv}C^-$, chemistry.[2-5] In this communication, we wish to report a single-step, high-yield preparation of **2** and **3** involving alkynyl(phenyl)iodonium species[8] as precursors. Recently, we established that alkynyl(phenyl)iodonium triflates **4** serve as synthons for electrophilic acetylene, "$RC{\equiv}C^{+}$", and allow the high-yield formation of σ-acetylide complexes via "alkynylation" and umpolung of the normal acetylene reactivity.[9]

$$\underset{\mathbf{4}}{RC{\equiv}CI^+Ph{\cdot}{}^-OSO_2CF_3}$$

Interaction of Vaska's complex **7** or its rhodium analog **8** with the bis[(phenyl)iodonium] diyne triflates[10] **5** and **6**, respectively, in CH_3CN at room temperature affords the corresponding cationic, bimetallic, diyne complexes **9** and **10**, respectively (Scheme I). Likewise, reaction of iodonium triflate[11] **11** with **7** affords complex **12**. Complexes **9** and **10** are isolated as stable microcrystalline, yellow solids[12] by precipitation with ether and standard workup; their physical and spectral properties are summarized in Table I. Likewise, **12** is a semistable, pale brown, microcrystalline solid that decomposes upon standing at room temperature, or over

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† Dedicated to Professor Robert W. Parry on the occasion of his 75th birthday.

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