(Figure 1).[11,12] The structure, which differs from that of $\{[HB(pz)_3]Cu\}_2$ and $\{[HB(3,5\text{-}Me_2pz)_3]Cu\}_2$[13] because of the noncoordinated pyrazolyl rings, is retained in solution (MW measurements[14] and ^1H NMR at −50 °C, with intramolecular exchange of bound and unbound pyrazolyl groups evident from NMR peak broadening and coalescence at higher temperatures).

Complex **1** afforded monomeric, pseudotetrahedral $[HB(t\text{-}Bupz)_3]CuX$ species in the presence of added ligands [X = CH_3CN (**2**), CO (**3**), or NO (**4**)].[11] Notably, treatment of a colorless solution of compound **1** or **2** in aromatic solvent at room temperature with NO (1 atm) yielded a deep red solution that deposited $[HB(t\text{-}Bupz)_3]Cu(NO)\cdot nS$ (**4**·*n*S; S = toluene, *n* = 1; S = mesitylene, *n* = 0.5) as red prisms upon cooling to −20 °C.[11] Identification of **4** as the first example of a molecule containing a terminal nitrosyl ligand bonded to copper is based on observation of a strong absorption in its FTIR spectrum at 1712 cm^{-1} [$\nu(^{15}NO)$ = 1679 cm^{-1}], hyperfine coupling of the unpaired electron to Cu and NO in the X- and S-band EPR spectra of ^{14}NO and ^{15}NO adducts,[15] and a low-temperature (−101 °C) X-ray crystal structure determination (Figure 2).[16] Like most other transition metal nitrosyls,[17] the Cu1–N1 distance in **4** is short [1.759 (6) Å], indicating the presence of some degree of multiple bonding. Small but significant bending of the unique, electron-rich $\{CuNO\}^{11}$ unit [Cu1–N1–O1 angle = 163.4 (6)°] suggests some occupation of antibonding π-type orbitals, however.[17a,c] The overall geometry about copper is approximately tetrahedral [dihedral angles = 90 (1)°], although intraligand angles between the pyrazole nitrogens (N_{pz}) are less than 109.5° (average N_{pz}–Cu–N_{pz} = 93.0°), N1–Cu1–N_{pz} angles are greater than that value (average = 123.1°), and N1 resides 0.083 Å from the normal of the plane defined by the N_{pz} atoms.

Solutions of **4** are stable for weeks when stored at −20 °C, but the UV–vis absorption features [λ_{max} (ϵ): 356 (1870), 490 (940) nm] at room temperature bleached upon brief application of vacuum or purging with argon, signaling ejection of NO (identified by GC). Readdition of NO (1 atm) restored the original spectrum, implicating reversible binding of NO to either **1** or **2**. In contrast, displacement of NO from **4** by CO (1 atm) quantitatively (UV–vis), rapidly, and irreversibly afforded **3**. Complex **4** also immediately reacted with O_2 at room temperature to yield $[HB(t\text{-}Bupz)_3]Cu(NO_3)$.[10,18]

Complex **4** provides the first unequivocal chemical precedent for NO coordination to isolated copper sites in proteins. Because of its pseudotetrahedral geometry and biomimetic triad of heterocyclic N donor ligands, the compound is a particularly suitable model for the *A. cycloclastes* NiR active site. Although it differs from the proposed enzymatic nitrite dehydration product with respect to oxidation level [$\{CuNO\}^{11}$ for **4** vs $\{CuNO\}^{10}$ proposed for NiR],[3] a species resembling **4** both in terms of structure and lability of coordinated NO may be envisioned to arise either upon one-electron reduction of the purported NiR nitrosonium intermediate by the nearby type 1 copper center[6] or upon binding of NO(g) to a previously reduced active site.[19] Such a species may play a significant role in denitrification pathways,[3,19] as well as in nitrogen oxide reactions with other copper proteins.[4] Future studies of the chemistry of **4** and other related molecules[20] will assess these possibilities.

Acknowledgment. We thank Professor Doyle Britton for his work on the X-ray structure of **4**, Professors Kenneth D. Karlin, Elinor T. Adman, and Bruce A. Averill for supplying preprints of refs 7, 6, and 3c, respectively, Professor John Lipscomb for providing access to his EPR facility, and the University of Minnesota for financial support.

Supplementary Material Available: Analytical and spectroscopic data for **1–4**, procedures used for analysis of the X-ray crystallographic data for $\mathbf{4}\cdot 0.5C_9H_{12}$, and tables of bond lengths and angles as well as atomic positional and thermal parameters for $\mathbf{1}\cdot C_4H_{10}O$ and $\mathbf{4}\cdot 0.5C_9H_{12}$ (30 pages). Ordering information is given on any current masthead page.

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(11) Analytical and spectroscopic data for compounds **1–4** are reported in the supplementary material.

(12) Crystal data for $\mathbf{1}\cdot C_4H_{10}O$, size 0.55 × 0.35 × 0.10, M_r = 963.91, space group $P2_1/n$ (No. 14), at −101 °C: a = 19.001 (8) Å, b = 13.629 (8) Å, c = 21.490 (7) Å, β = 113.01 (3)°, V = 5122 (8) Å^3, Z = 4, σ_{calcd} = 1.250 g cm^{-3}. For a total of 8123 unique, observed reflections with $I > 2\sigma(I)$ and 541 variable parameters, the discrepancy indices are R = 0.082 and R_w = 0.075. Full tables of bond lengths, bond angles, and atomic positional and thermal parameters for $\mathbf{1}\cdot C_4H_{10}O$ are available in the supplementary material.

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(14) MW found (calcd) = 940 (890) g mol^{-1} (Signer method: Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; pp 80–98).

(15) Estimated values from simulations of X- and S-band data are $A(Cu_\perp)$ = 65 G, $A(Cu_\parallel)$ = 117 G, $A(^{14}NO)$ = 34 G, and $A(^{15}NO)$ = 43 G (Antholine, W. E.; Ruggiero, C. E.; Carrier, S. M.; Tolman, W. B. Unpublished results). A full description of the EPR properties of **4** will be presented elsewhere.

(16) (a) Crystal data for $\mathbf{4}\cdot 0.5C_9H_{12}$ ($C_{25.5}H_{40}BCuN_7O$), size 0.60 × 0.50 × 0.40 mm, M_r = 535.00, space group $P2_1/n$ (No. 14), at −101 °C: a = 10.28 (1) Å, b = 17.40 (2), Å, c = 16.12 (1) Å, β = 90.0 (1)°, V = 2882 (8) Å^3, Z = 4, ρ_{calcd} = 1.233 g cm^{-3}. Although the cell dimensions suggested an orthorhombic unit cell, the Laue symmetry, $2/m$, indicated a monoclinic cell. For 3399 unique, observed reflections with $I > 2\sigma(I)$ and 287 variables, least-squares refinement converged with unsatisfactory values for the discrepancy indices R and R_w of 0.128 and 0.155, respectively, due to twinning that was estimated[13b] to be 10–15% from the pattern of observed intensities of pairs of reflections *hkl* and *h,k−l*. In the absence of any untwinned crystals, refinements continued with the program CRYSTALS (Chemical Crystallography Laboratory, Oxford University, Oxford, England) using calculated structure factors that included contributions from the twin elements (see supplementary material for full description of procedure used). Least-squares refinements then converged smoothly to values for R and R_w of 0.052 and 0.065 for 2866 reflections having $I > 3\sigma(I)$ and 293 variable parameters. (b) Britton, D. *Acta Crystallogr., Sect. A* **1972**, *28*, 296–297.

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Novel Construction of Polycyclic Systems Fused to Cyclobutane by Tandem Intramolecular Michael–Aldol Reaction

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A number of polycyclic compounds possessing a cyclobutane, such as endiandric acids A (**1a**),[1] B (**1b**),[1] and C (**2**),[1] trihydroxydecipiadiene (**3**),[2] italicene (**4a**),[3] and isoitalicene (**4b**),[3] have been found in nature (Chart I). Although several methods are available for the synthesis of cyclobutane derivatives having a high degree of ring strain, [2 + 2] photocycloaddition is the most common synthetic method for assembling the cyclobutane skeleton.[4] Here we disclose a novel construction of polycyclic ring

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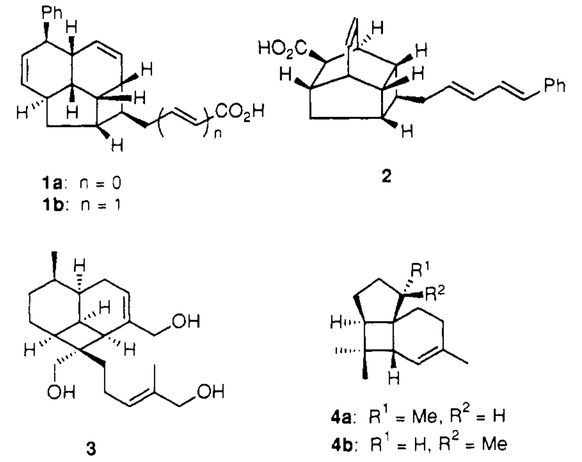
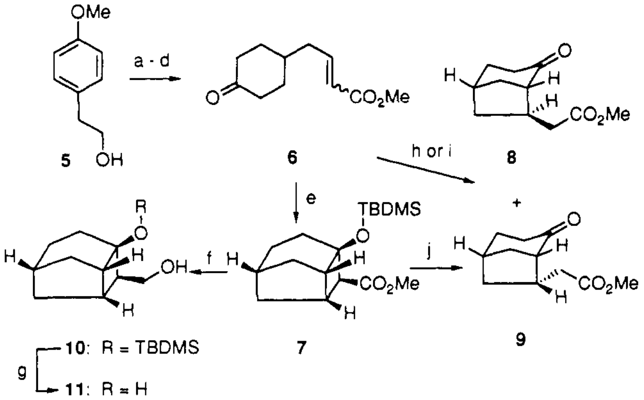
Chart I



Scheme I. Synthesis of Tricyclo$[4.2.1.0^{3,8}]$nonane[a]



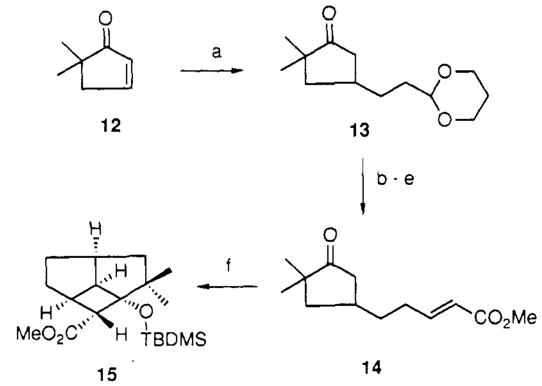
[a] (a) Li, liquid NH_3, Bu^tOH, then $(CO_2H)_2$, 53%; (b) H_2, 10% Pd–C, 64%; (c) PCC; (d) $Ph_3P{=}CHCO_2Me$, 64% for two steps; (e) TBDMSOTf, Et_3N, 48%; (f) DIBALH, 83%; (g) $Bu^n{}_4NF$, 94%; (h) LHMDS, 39%; (i) $ZnCl_2$, TMSCl, Et_3N, 160 °C, then dilute $HClO_4$, 19%; (j) dilute AcOH, 51%.

systems fused to a cyclobutane by tandem intramolecular Michael–aldol reaction of α,β-unsaturated esters carrying a ketone function at an appropriate position. The methodology provides new approaches to various cyclobutane derivatives including the above natural products.

The tandem reaction giving cyclobutane **7**, a partial framework of **2**, was investigated first. The starting material **6** of the key reaction was prepared from phenethyl alcohol **5** in four steps as shown in Scheme I. The (*E*)- and (*Z*)-isomers of **6**, formed in a 15:1 ratio, were readily separated by chromatography. The desired cyclization was achieved by treatment with TBDMSOTf in the presence of Et_3N.[5,6] Thus, reaction of the (*E*)-isomer of **6** using 4 equiv of TBDMSOTf and 7 equiv of Et_3N in CH_2Cl_2 at 20 °C for 1 h produced **7** in 48% yield. The same compound **7** was obtained in a similar yield from the (*Z*)-isomer of **6** by the same treatment. This result indicates a stepwise process through a common intermediate.

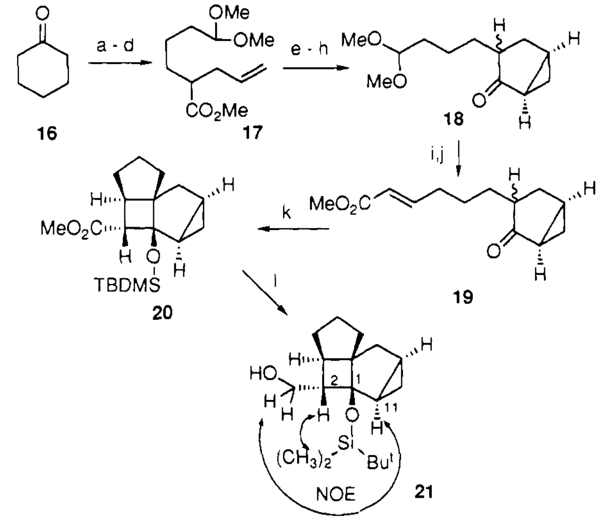
Reaction of **6** with LHMDS[7] in THF at −78 to 0 °C gave a 3:1 mixture of the intramolecular Michael adducts **8** and **9**, which were obtained in a 10:1 ratio by heating **6** with $ZnCl_2$, TMSCl, and Et_3N[8] in toluene in a sealed tube at 160 °C for 17 h, followed by treatment with acid. Reaction of **7** with dilute acetic acid at 60 °C caused deprotection of the TBDMS group accompanied by a retro aldol reaction affording **9** as a single stereoisomer. The TBDMS group was removed, leaving the cyclobutane ring intact by reduction with DIBALH followed by treatment of **10** with tetrabutylammonium fluoride. Thus, **7** was transformed into diol **11** in 78% overall yield.

Scheme II. Synthesis of Tricyclo$[5.1.1.0^{4,8}]$nonane[a]



[a] (a) 2-(2,6-Dioxanyl)ethylmagnesium bromide, $CuBr{\cdot}Me_2S$, TMSCl, HMPA, 68%; (b) $NaBH_4$; (c) dilute $HClO_4$; (d) $Ph_3P{=}CHCO_2Me$, 80% for three steps; (e) Dess–Martin periodinane,[11] 90%; (f) TBDMSOTf, Et_3N, 20%.

Scheme III. Synthesis of Tetracyclo$[5.4.0.0^{3,7}.0^{9,11}]$undecane[a]



[a] (a) Pyrrolidine, PTSA, then $CH_2{=}CHCH_2Br$, 55%; (b) LDA; MoOPH,[12] 56%; (c) $Pb(OAc)_4$, MeOH; (d) MeOH, NH_4Cl, 70% for two steps; (e) KOH; (f) $(COCl)_2$, pyridine; (g) CH_2N_2, 52% for three steps; (h) Cu, 83%; (i) dilute AcOH; (j) $Ph_3P{=}CHCO_2Me$, 74% for two steps; (k) TBDMSOTf, Et_3N, 97%; (l) DIBALH, 99%.

The tricyclo$[5.1.1.0^{4,8}]$nonane derivative **15** was assembled as summarized in Scheme II. Conjugate addition[9] to enone **12**[10] provided ketone **13**, which was converted into ester **14** in four steps. Heating **14** with TBDMSOTf in the presence of Et_3N in CH_2Cl_2 under reflux for 1 h furnished, in 20% yield, the tricyclic compound **15** having a similar framework to **1**, **2**, or **3**.

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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*Me*$_2$SiO 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.

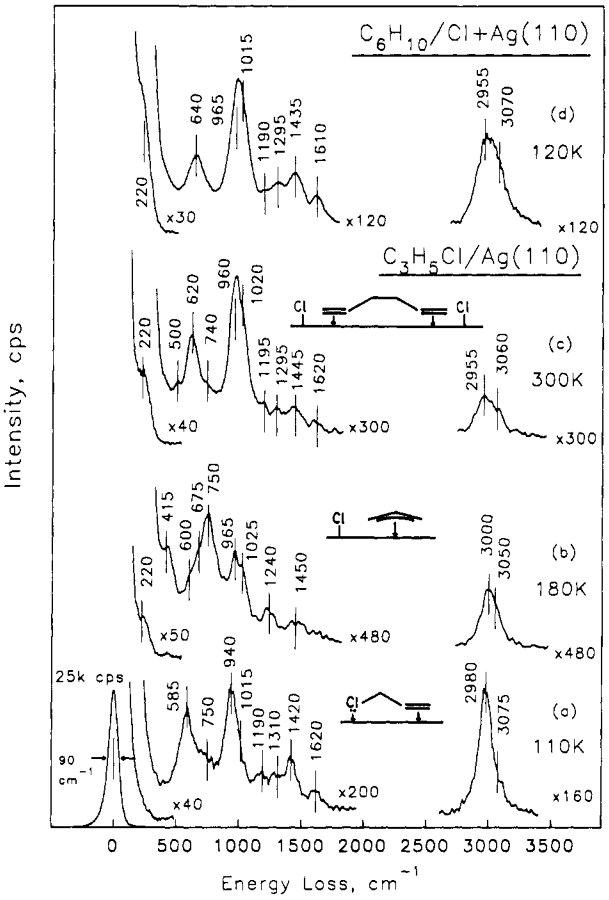

Figure 1. High-resolution electron energy loss vibrational spectra collected after (a) a submonolayer exposure (5×10^{-7} Torr s) of the clean Ag(110) surface at 110 K to allyl chloride; (b) an exposure sufficient to saturate the monolayer ($>2 \times 10^{-6}$ Torr s), followed by momentary annealing 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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