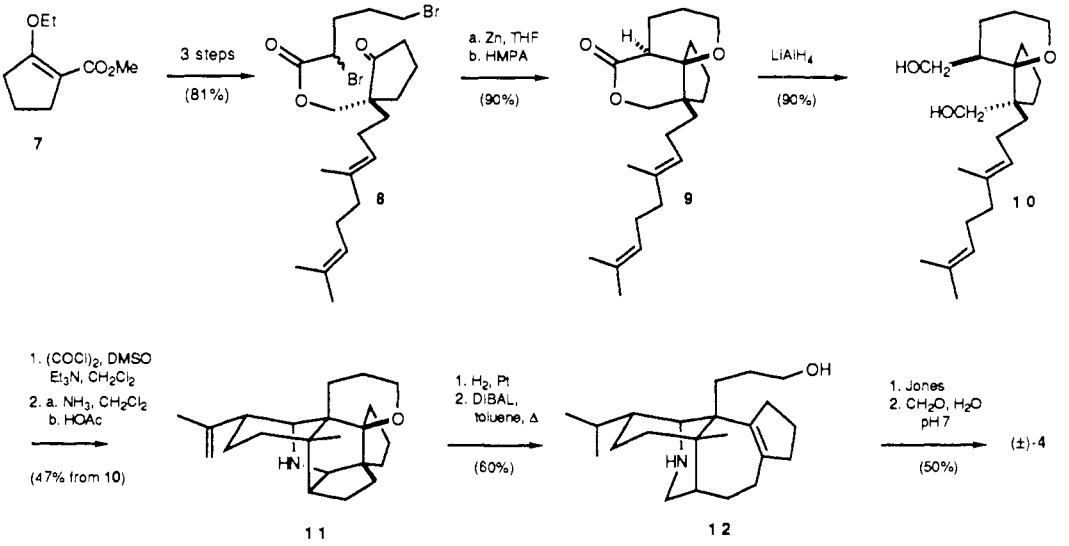
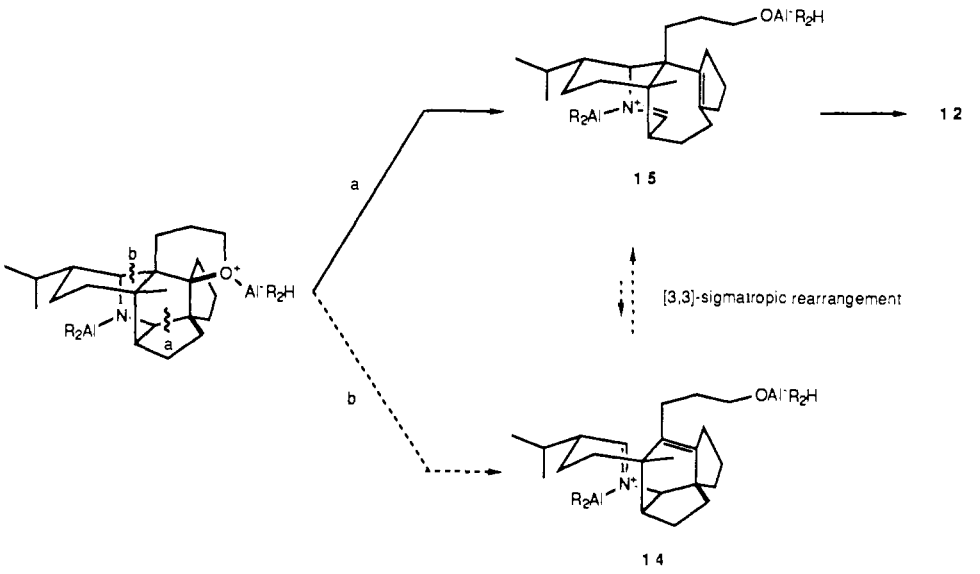
Scheme I



Scheme II



other hand, the observed product might result from fragmentation to **14** followed by Cope rearrangement to **15**.

The total synthesis of (±)-daphnilactone A reported here is brief (11 steps from methyl 2-ethoxycyclopentenecarboxylate, 9% overall yield) and represents the first total synthesis of this structurally unique *Daphniphyllum* alkaloid. More importantly, the synthesis provides easy access to unsaturated amino ester **6**, analogues of which are attractive candidates for conversion into more complex *Daphniphyllum* alkaloids, such as yuzurimine (**3**). Further progress in this direction will be reported in due course.

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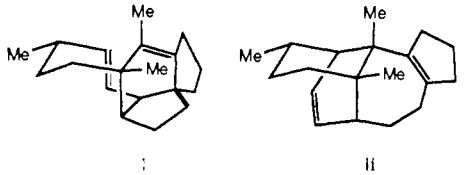
Supplementary Material Available: Physical properties, ^1H NMR spectral data, ^{13}C NMR spectral data, and analytical data for compounds **4**, **6**, and **9**–**12** and copies of the ^1H NMR spectra of synthetic and natural daphnilactone A (4 pages). Ordering information is given on any current masthead page.

(7) Calculations were performed with the Allinger MM2 force field using Still's MACROMODEL program on hydrocarbon analogues of **14** and **15**, further simplified by replacement of the isopropyl and hydroxypropyl side chains by methyl groups (i and ii). Hydrocarbon i is more strained than hydrocarbon ii by more than 20 kcal/mol.



i ii

Reversible Alkoxide β-Hydrogen Elimination in a Homoleptic Rhenium Alkoxide Complex. Synthesis of $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$

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Alkoxide β-hydrogen elimination and the reverse reaction, insertion of a ketone into a metal hydride bond, are known pro-

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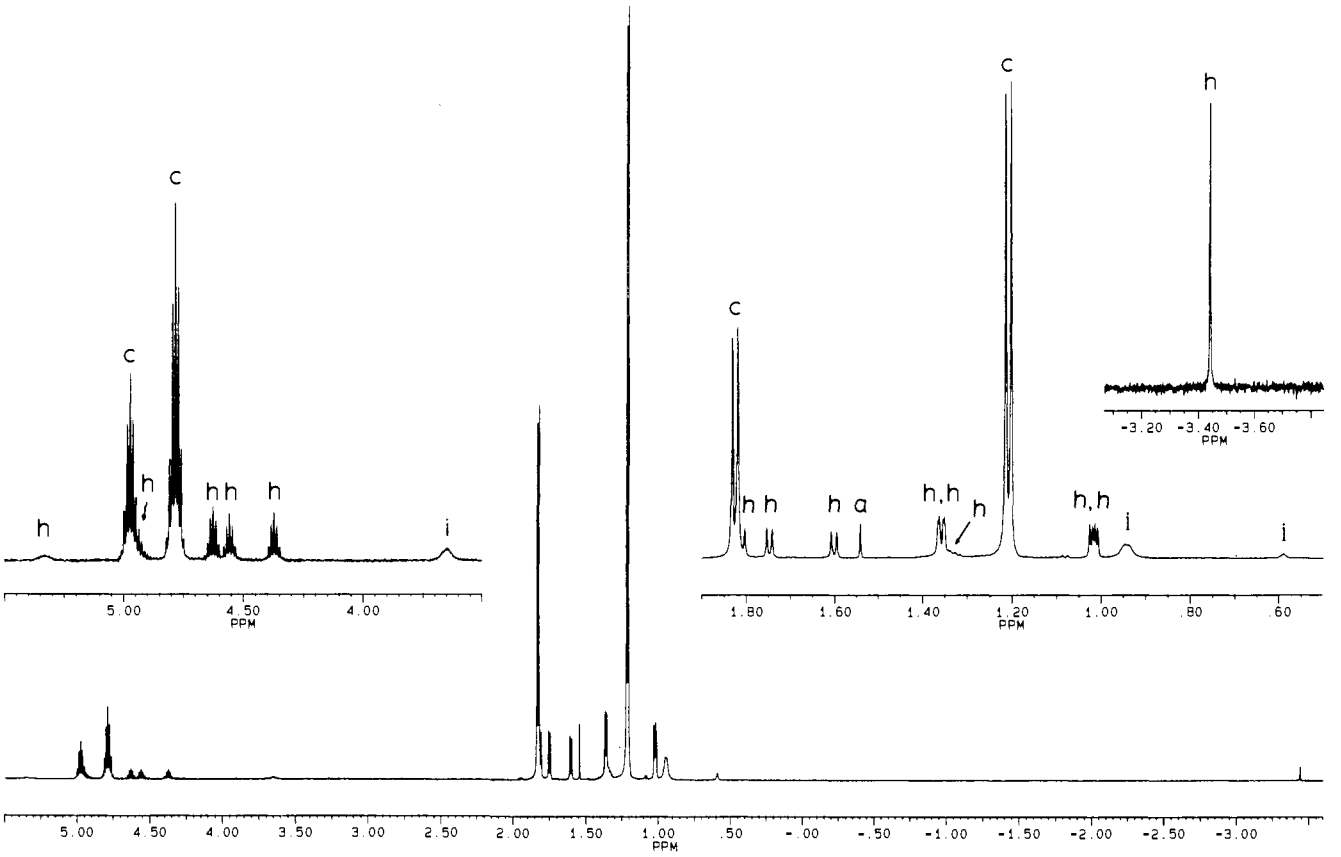


Figure 1. Proton NMR recorded for a benzene-d_6 solution of crystalline **2** (23 °C, 500 MHz). Labeling scheme: $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$, c; $Re_3(\mu\text{-O-}i\text{-Pr})_3H(O\text{-}i\text{-Pr})_5$, h; acetone, a; isopropyl alcohol, i.

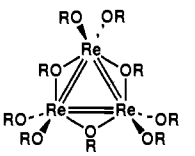
cesses, and there is evidence for reversible alkoxide β-hydrogen elimination (eq 1) in certain systems.[1] We report here the *direct* observation of reversible isopropoxide β-hydrogen activation in *triangulo*-$[Re(O\text{-}i\text{-Pr})_3]_3$. This cluster is the first example of a homoleptic rhenium alkoxide complex.

$$\text{M-O-C(H)R'R''} \rightleftarrows \text{M-H} + \text{O=CR'R''} \qquad (1)$$

In an attempt to synthesize $Re_3(O\text{-}i\text{-Pr})_6Cl_3$, an analogue of $Re_3(O\text{-}t\text{-Bu})_6Cl_3$,[2,3] we reacted $Re_3(\mu\text{-Cl})_3Cl_6(THF)_3$ (**1**)[4] with 6 equiv of NaO-*i*-Pr at room temperature in THF. Workup of the reaction, which included the separation of unreacted **1**, and crystallization from cold *i*-PrOH (−50 °C) produced green hexagonal needles of $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6{\cdot}^1/_3i\text{-PrOH}$ (**2**). In subsequent synthetic work, reaction of **1** with 9 equiv of NaO-*i*-Pr in THF gave **2** in 31% yield (eq 2).[5]

$$Re_3(\mu\text{-Cl})_3Cl_6(THF)_3 + 9NaO\text{-}i\text{-Pr} \xrightarrow[23\ ^\circ C]{THF} Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6 + 9NaCl \qquad (2)$$

An X-ray crystallographic analysis shows that crystals of **2** are severely disordered,[6] but at the current refinement level it is clear that the cluster units have the triangular structure shown below. The Supplementary Material section contains details of the X-ray structure solution.



R = *i*-Pr

2

Proton NMR spectra recorded for **2** indicate that it is in equilibrium with a metal hydride cluster formulated as *triangulo*-$Re_3(\mu\text{-O-}i\text{-Pr})_3H(O\text{-}i\text{-Pr})_5$ (**3**) and acetone. In Figure 1 is shown the ^1H NMR spectrum recorded for a benzene-d_6 solution of **2** at 23 °C. The resonances labeled c, two septets (3:6 integral ratio) and two doublets (18:36), are assigned to cluster **2**. The singlet resonance at δ 1.54, labeled a, arises from free acetone and the singlet at δ −3.43 from the metal hydride ligand of **3**. In addition to the hydride singlet, other resonances assignable to **3** (labeled h) include four septets (1:2:2:2) and seven doublets of equal intensity, all sharp, and a broad septet and doublet. Resonances arising from isopropyl alcohol, which are also broad, are labeled i.

The spectrum shown in Figure 1 is consistent with the simultaneous occurrence of equilibria 3 and 4. In the forward

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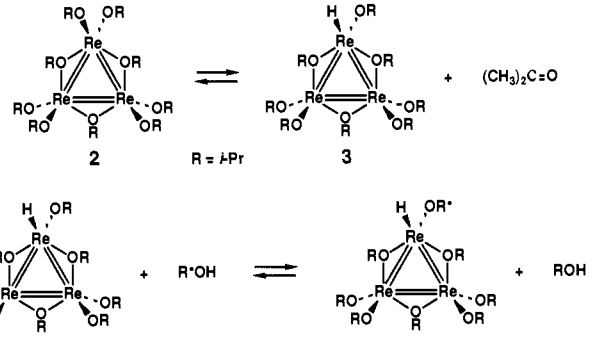
(5) Workup of the reactions includes removal of THF in vacuo, extraction of the residue with pentane, and removal of the pentane in vacuo. The reduced pressure distillation of THF and pentane must also remove acetone, thereby shifting eq 3 to **3**. The isolation of **2** by crystallization from isopropyl alcohol is therefore dependent on the presence of an acetone impurity in the isopropyl alcohol solvent. Consistent with this, stripped reaction mixtures are composed of **3** and only a small amount of **2** (by ^1H NMR). Also, the addition of a few drops of acetone to the isopropyl alcohol crystallization solution increases the yield of **2** to 31% from 18%.

(6) Crystal data for **2** at −80 (1) °C: $C_{28}H_{65.7}O_{9.3}Re_3$, hexagonal, space group $P6_3/m$, a = 20.335 (3) Å, c = 16.509 (4) Å, Z = 6, D_c = 1.87 g cm^{-3}. Current residuals: $R(F)$ = 0.0656, $R_w(F)$ = 0.0617. Anal. Calcd: C, 30.30; H, 5.97. Found: C, 30.05; H, 5.67.



direction, equilibrium 3 represents β-hydrogen activation at a terminal isopropoxide ligand of **2** and accounts for the presence of **3** and acetone in solution. Equilibrium 4 is an exchange process between the unique terminal isopropoxide ligand of **3** and free isopropyl alcohol; thus, 4 accounts for the observed broadening in the resonances of one isopropoxide ligand of **3** and isopropyl alcohol.

Further evidence for the assigned structure of **3** and equilibria 3 and 4 comes from the following NMR experiments: (i) Proton NMR resonances arising from **3** grow in intensity relative to those from **2** at temperatures above room temperature, whereas at lower temperatures the concentration of **3** decreases relative to **2**. The spectral changes are fully reversible, consistent with eq 3. (ii) Addition of acetone to a benzene-d_6 solution of **2** results in the complete disappearance of resonances arising from **3**. This is consistent with a shift of eq 3 to the left. (iii) Addition of an excess of pyridine-d_5 (≈100 equiv) to a benzene-d_6 solution of **2** gives, by ^{1}H NMR, a mixture of free acetone, free isopropyl alcohol, and a pyridine adduct of **3** (**3-py**). On the basis of the NMR spectrum, **3-py**, like **3**, has virtual mirror symmetry. Assignable to **3-py** are a hydride resonance at δ −1.97, five sharp OC(*H*)Me$_2$ septets in the ratio of 2:2:2:1:1, and eight sharp methyl doublets of equal intensity. The free isopropyl alcohol resonances are also sharp. These observations are consistent with 3 and 4 in that pyridine is expected to coordinate to the sterically accessible ReH(OR) site, thereby blocking the position and shutting down acetone reinsertion (shifting 3 to the right) and isopropyl alcohol–isopropoxide exchange. (iv) Addition of an excess of isopropyl alcohol-d_8 (≈100 equiv) to a benzene-d_6 solution of **2** results (<30 min) in the complete disappearance of proton resonances arising from the terminal alkoxide positions of **2** and **3** as well as the hydride resonance of **3**. This indicates that isopropyl alcohol–isopropoxide exchange involves only terminal alkoxides and that bridge-terminal alkoxide exchange in **2** and **3** is slow compared to 3 and 4. Moreover, because resonances from only one alkoxide are broad under conditions of fast exchange (e.g., at 23 °C, Figure 1), the rapidly exchanging isopropoxide must be the one indicated in eq 4. Presumably, rapid isopropyl alcohol–isopropoxide exchange occurs only for this alkoxide because there is less steric crowding at this site.[7] (v) Addition of an excess of acetone-d_6 (≈100 equiv) to a benzene-d_6 solution of **2** gives, after 1 h, a ^{1}H NMR spectrum that is consistent with $Re_3(\mu\text{-}OC(H)(CH_3)_2)_3(OC(H)(CD_3)_2)_6$ and $(CH_3)_2C{=}O$ in solution.[8] Two conclusions can be drawn from this result: The source of the hydride ligand in **3** cannot be a bridging alkoxide ligand, and, because deuterium is not incorporated into the methine position of the terminal isopropoxides of **2**, the hydride ligand in **3** must originate from the β-hydrogens of the terminal alkoxides of **2**.

In summary, we have synthesized the first homoleptic rhenium alkoxide complex and have established that it undergoes reversible alkoxide β-hydrogen elimination. Further mechanistic and synthetic studies, including the isolation of **3** and **3-py**, are in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

(7) A referee suggested that the ReH(OR) metal center is also more Lewis acidic than the Re(OR)$_2$ centers because it has one less π-donor ligand. Greater Lewis acidity would also account for the enhanced exchange rate.

(8) Spectra recorded over 48 h indicate that more extensive deuterium scrambling occurs at longer reaction times.

Supplementary Material Available: Tables of crystal data, atomic coordinates, and thermal parameters and a ball-and-stick plot of **2** (7 pages); table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Two-Dimensional Solid-State NMR of a Captive Intermediate: Structure of the Radical Centers in 3,4-Dimethylenethiophene

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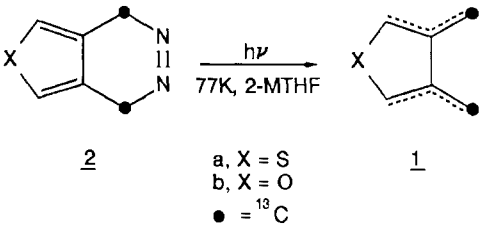
Matrix isolation studies are important for furthering our understanding of reaction mechanisms and provide an experimental means of checking theoretical predictions of novel molecular geometries. However, no direct methods have yet been developed for experimentally determining the structures of matrix-isolated species. In this paper we report on a two-dimensional (2D) solid-state NMR technique which provides a convenient method for determining the structures of matrix-isolated molecules and for spectroscopically assigning their ^{13}C CPMAS spectra. This technique has been used in the first direct structure determination of a captive intermediate, 3,4-dimethylenethiophene, **1a**. Both the H–C–H angle and C–H distances have been determined for the radical centers in **1a**, and the results confirm the assignment[1] of the singlet biradical structure to this intermediate.



Previous studies[2] have demonstrated the feasibility of using dipolar coupled powder NMR spectra for measuring bond lengths in small molecules trapped in rare gas matrices. The principal difficulty in using this method to study more complex captive intermediates is spectral overlap of the dipolar coupled powder patterns.[2c] The combination[3,4] of CPMAS methods with 2D separated local field (MASSLF) spectroscopy[5] circumvents this difficulty by separating the proton dipolar coupled spectra for each carbon on the basis of their isotropic chemical shifts. For each line in the ^{13}C CPMAS spectrum a dipolar coupled sideband pattern is generated by taking a slice in the 2D MASSLF spectrum along the first frequency dimension. The envelope of these

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