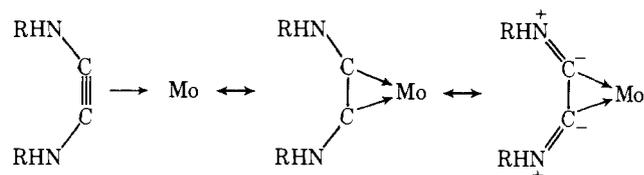


**Figure 1.** Molecular geometry of the cations in (left)  $[(t\text{-C}_4\text{H}_9\text{NC})_6\text{Mo}]^+$ ,<sup>4</sup> the starting material, and (right)  $[(t\text{-C}_4\text{H}_9\text{NC})_4(t\text{-BuNC})_2\text{Mo}]^+$ , the product, as determined by x-ray diffraction. Interatomic distances (in Å) shown have estimated standard deviations of 0.03 Å or less.

with ether. The N—H deformation similarly shifted to a lower frequency upon deuteration. The 100-MHz proton NMR spectrum of the compound in  $\text{CDCl}_3$  showed methyl resonances of the *tert*-butyl groups at  $\delta$  1.48 and 1.66 ppm of relative intensities 2:1. A small peak at 9.68 ppm with an integrated intensity about one-thirtieth that of the combined *tert*-butyl resonances provided further confirmation of the empirical formula. This resonance did not appear when the complex was dissolved in acetone- $d_6$  containing a few drops of  $\text{D}_2\text{O}$ . Pulsed Fourier-transform  $^{13}\text{C}$  NMR spectra also revealed two *tert*-butyl environments, with methyl carbon resonances at 29.96 and 30.28 ppm and tertiary carbon shifts of 56.89 and 54.75 ppm, relative intensities 2:1, respectively. The resonances of the carbon atoms of the *tert*-butyl isocyanide ligands bonded to molybdenum appeared at 157.1 ppm, and the chemical shift of the corresponding carbon atoms of the  $(\text{LH})_2$  ligand was 192.9 ppm.

An x-ray crystallographic study was required to establish the true nature of the product. Using 4038 observed reflections collected with Mo  $K\alpha$  radiation ( $2\theta \leq 55^\circ$ ), the structure was solved by heavy atom methods and refined to a current value of 0.059 for  $R_1$ , the conventional agreement factor.<sup>11</sup> As shown in Figure 1, the molecular geometry is very similar to that of the starting  $[(\text{RNC})_6\text{Mo}]^+$  cation with one major difference. In the product there is a bond between the two carbon atoms on the edge opposite the capped face. The resulting C—C ( $1.38 \pm 0.02$  Å) and C—N ( $1.33 \pm 0.02$  Å) distances in the coupled ligand require multiple bond character, and the mean C—N—C angle of  $128^\circ$  is consistent with the presence of N—H bonds. There has not yet been any attempt to locate hydrogen atoms in the difference Fourier maps.

The structural and spectroscopic results indicate that the product of the reductive coupling reaction may be considered as a bis(alkylamino)acetylene derivative with substantial bond delocalization,  $\text{RHN}\equiv\text{C}\cdots\text{C}\cdots\text{NHR}$ .<sup>12</sup> Although the free ligand does not appear to be a known compound,<sup>14</sup> its stability is enhanced by coordination to the molybdenum atom. Regarding the ligand as an acetylene molecule would result in a 16-electron molybdenum(II) cation for which there is some precedence.<sup>15</sup> Alternatively, the complex achieves a closed shell configuration if the ligand is viewed as a dicarbene. These two extremes and one of several possible charged resonance forms are depicted below. We may view the present reaction formally



as the addition of one electron and one proton to each of two

isocyanide ligands which then couple to one another on the unique edge. Such a process would be similar to carbene formation by addition of  $\text{H}-\text{X}$  across the  $\text{C}\equiv\text{N}$  triple bond of a coordinated isocyanide ligand.<sup>16</sup> Here the group X is an adjacent carbon atom in the coordination sphere.

Although we emphasize that the mechanism in which two isocyanide ligands are reductively coupled is presently unknown, the reaction may be an example of a higher coordination effect. The close nonbonded contact between the ligands in  $[(\text{RNC})_6\text{Mo}]^+$  might enhance the propensity for carbon-carbon bond formation. Molecular orbital calculations<sup>17</sup> of  $d^4$  capped trigonal prismatic compounds such as  $[(\text{RNC})_6\text{Mo}]^+$  show a small positive overlap population between the two ligands on the unique edge of the coordination polyhedron. Further work is in progress to test this and other mechanistic possibilities.

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- (11) Crystallographic data:  $\text{C}_{30}\text{H}_{56}\text{N}_6\text{Mo}$ ;  $M = 850.6$ , orthorhombic;  $a = 21.995$  (3),  $b = 19.849$  (3),  $c = 18.536$  (3) Å;  $V = 8092$  Å<sup>3</sup>;  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.396$ ,  $\rho_{\text{obsd}} = 1.395$  (2) g/cm<sup>3</sup>; space group  $Pbca$ ;  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , for  $F_o^2 \geq 3\sigma(F_o^2)$ .
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#### The Structure of Juncusol. A Novel Cytotoxic Dihydrophenanthrene from the Estuarine Marsh Plant *Juncus roemerianus*<sup>1</sup>

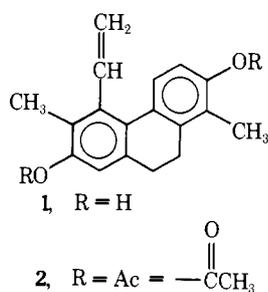
Sir:

The Mississippi salt marsh is an irregularly flooded estuary dominated by the needlerush *Juncus roemerianus* (Juncaeeae). Studies by de la Cruz<sup>2</sup> on the ecology of Mississippi salt marsh on the primary production and decomposition of marsh plants have served to focus attention on their value to estuarine animals including those of commercial importance. We therefore have initiated a continuing chemoecological study

of the Mississippi salt marsh with examination of the essential oils<sup>3</sup> of *J. roemerianus* and related species. We have also evaluated extracts of *J. roemerianus* with resulting confirmed level activity against the National Cancer Institute's murine P-388 lymphocytic leukemia (PS system).

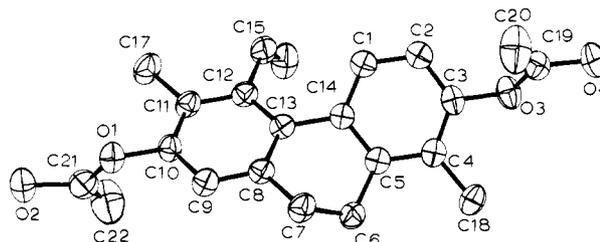
We now wish to report the isolation and structure determination of the compound juncusol (**1**) from *J. roemerianus*. Juncusol (**1**) has demonstrated confirmed cytotoxic activity ( $ED_{50}$  0.3  $\mu\text{g}/\text{ml}$ ) against the NCI 90 KB (human epidermoid carcinoma of the nasopharynx) test system. The unique arrangement of the carbon atoms in juncusol (**1**) provides a target for biogenetic speculation. The 9,10-dihydrophenanthrene skeleton lends credence to the possibility that juncusol (**1**) is a phytoalexin.<sup>4</sup>

The finely ground plant tops (above ground) of *J. roemerianus* were extracted with ethanol. The residue from the alcoholic fraction was partitioned between 1 N sulfuric acid and chloroform. The concentrated chloroform extract was triturated with chloroform–benzene (1:1). Chromatography of the soluble portion on silica gel followed by crystallization from benzene yielded (0.01% dry weight) juncusol,  $\text{C}_{18}\text{H}_{18}\text{O}_2$  ( $M^+$  266), mp 176 °C. The IR spectrum of juncusol (**1**) in Nujol showed bands at 3350 (OH), 1603 (aromatic), and 930  $\text{cm}^{-1}$  (monosubstituted double bond). The 100-MHz  $^1\text{H}$  nuclear magnetic resonance spectrum was obtained in chloroform-*d* with a few drops of deuterated acetone and  $\text{Me}_4\text{Si}$  as an internal standard. The spectrum showed the following absorptions: sharp singlets at  $\delta$  2.25 (3 H, Ar- $\text{CH}_3$ ), 2.3 (3 H, Ar- $\text{CH}_3$ ), and 2.7 (4 H), ABX types of signals for vinyl protons consisting of a set of two doublets centered around  $\delta$  5.2 (1 H,  $J_{\text{AX}} = 17$  Hz,  $J_{\text{AB}} = 2$  Hz) and 5.4 (1 H,  $J_{\text{BX}} = 11$  Hz,  $J_{\text{AB}} = 2$  Hz), and a quartet centered around  $\delta$  6.8 (1 H,  $J_{\text{AX}} = 17$  Hz), two ortho aromatic proton doublets at  $\delta$  7.6 (1 H,  $J = 7$  Hz) and 6.9 (1 H,  $J = 7$  Hz) and a broad signal around 6.95 (2 H, 2-OH). The integration accounted for another proton in the aromatic region.



That the oxygen atoms were present as hydroxyl groups was confirmed by the formation of the diacetate **2**,  $\text{C}_{22}\text{H}_{22}\text{O}_4$  ( $m/e$  350), mp 110 °C. The structure of the diacetate **2** was determined by a single-crystal x-ray diffraction experiment. Juncusol diacetate (**2**) was crystallized from chloroform as colorless plates which belong to the monoclinic system. Single crystals of the substance were sealed in thin-walled capillaries prior to x-ray examination. The unit cell parameters are  $a = 8.144$  (6) Å,  $b = 11.439$  (6) Å,  $c = 19.712$  (8) Å, and  $\beta = 94.12$  (5)°; the space group  $P_{21/c}$  was uniquely defined by systematic absences  $P_{\text{calcd}} = 1.27$   $\text{g cm}^{-3}$  for four molecules in the unit cell). A total of 1229 independent observed reflections [ $I \geq 3\sigma(I)$ ] were collected out to  $2\theta \approx 50^\circ$  using graphite-crystal monochromated Mo  $K\alpha$  radiation (0.710 69 Å) on an Enraf-Nonius CAD-4-diffractometer.

The diffracted intensities were collected by the  $\omega$ - $2\theta$  scan technique with a takeoff angle of 3.0°. The scan rate was variable and was determined by a fast 20°  $\text{min}^{-1}$  prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 0.2°  $\text{min}^{-1}$ . Moving-crystal moving-counter backgrounds were collected for 25% of the total



**Figure 1.** Molecular structure of juncusol with the atoms displayed as a 30% probability ellipsoids for thermal motion. Hydrogen atoms are not shown.

scan width at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B \tan \theta$$

where  $A = 1.00^\circ$  and  $B = 0.25^\circ$ . Aperture settings were determined in a like manner with  $A = 4.0$  mm and  $B = 0.87$  mm. Other diffractometer and the method of estimation of the standard deviations have been described previously.<sup>5</sup> As a check on the stability of the instrument and the crystal, two reflections were measured after every 30 reflections; the standards fluctuated within a range of  $\pm 2\%$ .

One independent quadrant of data was measured out to  $2\theta = 50^\circ$ ; a slow scan was performed on a total of 1229 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 20 was obtained in the prescan. Based on these considerations, the data set of 1229 reflections (used in the subsequent structure determination and refinement) was considered observed and consisted in the main of those for which  $I > 3\sigma(I)$ . The intensities were corrected for Lorentz and polarization effects, but not for absorption ( $\mu = 0.93$ ).

The structure was solved by direct methods using the program MULTAN<sup>6</sup> and refined by full-matrix least-squares techniques<sup>7</sup> to give discrepancy indexes of  $R_1 = 0.044$  and  $R_2 = 0.051$  where  $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ ;  $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ . Carbon and oxygen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located on a difference Fourier map. Bond lengths and angles agree well (esd's of 0.007 Å and 0.5°, respectively) with generally accepted values.<sup>8</sup> Figure 1 is a computer generated drawing of the final x-ray model. See the paragraph at the end of the paper regarding supplementary material.

While a number of 9,10-dihydrophenanthrenes have been reported<sup>4,9</sup> the occurrence of an alkenyl substituent and two alkyl groups, as in juncusol (**1**), is without precedent. Furthermore there has been no report of 9,10-dihydrophenanthrenes from marine sources. Three 9,10-dihydrophenanthrenes which are phytoalexins have been isolated<sup>4</sup> from European orchids. The possibility exists that juncusol (**1**) is also a phytoalexin since it shares in common the 9,10-dihydrophenanthrene ring system and occurs in a plant which grows in an area with high fungal activity.

The detailed structural features as well as the interesting chemical transformations of juncusol will be discussed in a complete presentation. Evaluation of juncusol and related substances from *Juncus roemerianus* is in progress.

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**Supplementary Material Available:** The fractional coordinates (Table I), important bond distances and angles (Table II), and a complete listing of structure factor amplitudes (15 pages). Ordering information is available on any current masthead page.

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### Synthesis of "Skewered Complexes": Reaction of Rhenium Carbonyl Porphyrin Complexes with Antimony Pentachloride

Sir:

The syntheses and x-ray diffraction analyses of novel metalloporphyrin complexes in which the metal ions sit out of the plane of the porphyrin molecule have been previously reported by our laboratories.<sup>1-4</sup> Particular attention has been paid to metalloporphyrins of the type  $[(CO)_3M]_2TPP$  ( $M = Re, Tc$ ;  $TPP = meso$ -tetraphenylporphyrin). The metal ions lie on either side of the macrocycle. In previous work the rhenium and technetium ions have been formally in the +1 oxidation state. It would be unlikely that a metal-metal bond would exist in this case and the observed M-M distances of  $3.1 \text{ \AA}$ <sup>4</sup> indicate that any interaction, if present, must be weak. We are at present investigating the reaction of these complexes with a variety of oxidizing agents in an attempt to further elucidate their chemical properties and to obtain new porphyrin complexes containing higher formal oxidation states of the metal ions. In such complexes a metal-metal bond could exist and would be evidenced by a shorter M-M distance than in the starting complexes. If a metal-metal bond were formed, it would necessarily pass through the center of the porphyrin core, resulting in a material that can be described as a "skewered complex".

In this paper, we wish to report the synthesis and characterization of a series of mono- and biscationic rhenium por-

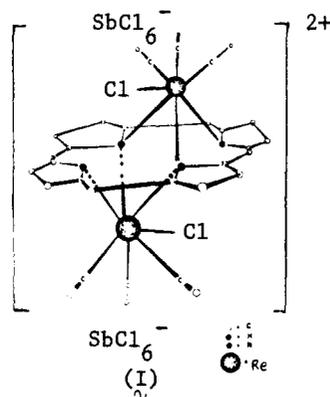


Figure 1. Proposed structure.

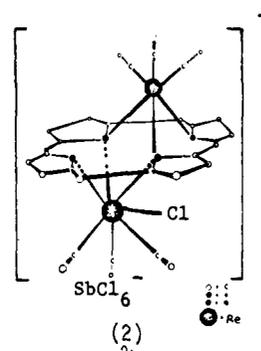
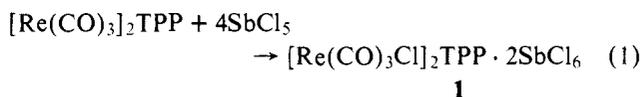


Figure 2.

phyrin species. In all of these antimony hexachloride serves as the anion. An x-ray determination of the structure of these complexes provides definite evidence for a "skewered complex", that is a metalloporphyrin in which a metal-metal bond exists through the "hole" of the macrocycle. A solution of antimony pentachloride (0.05 mmol) in dichloromethane (0.5 ml) was added dropwise to a solution of bis(tricarbonylrhenium)- $\mu$ -tetraphenylporphyrin (0.0125 mmol) in the same solvent (15 ml) kept below  $-70^\circ C$ . When the reaction mixture was allowed to stand overnight kept below  $-60^\circ C$ , a large quantity of a black substance crystallized out. This solid was separated by decantation at  $-50^\circ C$ , and then washed three times with 2-3 ml of dichloromethane and finally with a 1:1 mixture of dichloromethane-*n*-hexane. Very fine hexagonal crystals, identified as the salt **1**, were obtained in almost quantitative yield (eq 1).



A proposed structure of the salt **1** is suggested by visible and infrared spectra and by elemental analysis. Compound **1** has visible absorption maxima in dichloromethane at 405 (Soret band), 493, 532, and 590 nm, and four intense infrared absorption bands at 1990, 2010, 2040, and 2070  $cm^{-1}$  due to metal carbonyl stretching vibrations, in the solid state. The elemental analysis<sup>5</sup> of **1** gave results which exactly fit the suggested structure.

This reaction indicates a similarity between the reactions of bis(tricarbonyl)- $\mu$ -tetraphenyl compounds and on the analogous cyclopentadienyl metal carbonyl complexes (i.e.,  $CpM(CO)_3$ ,  $M = W^6$  and  $Re^7$ ) with antimony pentachloride. Although a search for further examples of reactions of this general type is difficult because of the limited number of out-of-plane metal carbonyl porphyrins, an analogous monocationic salt (**2**)<sup>8</sup> is obtained from the reaction of 1:2 mole ratio of the bisrhenium porphyrin complex and antimony pentachloride (eq 2 and Figure 2).