An Ethylene Complex of Vanadium: Synthesis, Structure, and Reactivity of Cyclopentadienylbis(trimethylphosphine)(ethylene)vanadium(I)

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Although olefin complexes of the early transition metals are frequently named as intermediates in catalytic reactions such as olefin polymerization and hydrogenation, very few complexes have actually been isolated, especially for the 3d-metals. For Ti the sole representative of this class of compounds is (7-C5Me5)2Ti(ethylene), which actually has been isolated, especially for the 3d-metals. For Ti the only two compounds are Cp2V(EtO2CCCH=CH2CO2Et)3 and V(CO),(PPh2(2-alkenylphenyl)3, the latter stabilized by the chelate effect. Here we wish to report a simple olefin complex of V(I), CpV(v2-ethylene)(PMe3)2, with some of its reactivity.

When Cp2VCl(PMe3)6 is reacted with 1 mol of 1,4-bis-(bromomagnesiobutane)ethane in THF at 0 °C, the ethylene complex Cp2V(PMe3)2 can be isolated in 38% yield, instead of a possibly anticipated vanadio-cyclopentane product. The blue Cp2VCl(PMe3)6 was observed as an intermediate in the reaction. 2 can also be obtained, in 49% overall yield, from the reaction of Cp2VCl(PMe3)2 (produced by reduction of 1 with 1 mol of Na/Hg) with 0.5 mol of the diGrignard. Thus it seems likely that 2 is not formed by elimination of ethylene from a vanadio-cyclopentane intermediate but by rearrangement of a 1,4-dibromobutane complex.

Selected spectral and analytical data for 2: 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Mass spectrum (THF)</td>
<td>372.3 Da</td>
</tr>
<tr>
<td>IR (KBr)</td>
<td>2152, 1565, 1595 cm^-1</td>
</tr>
<tr>
<td>1H NMR (CDCl3)</td>
<td>δ (ppm): 1.2 (s), 3.8 (t), 4.2 (q)</td>
</tr>
<tr>
<td>13C NMR (CDCl3)</td>
<td>δ (ppm): 21.5, 30.7, 39.6</td>
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</tbody>
</table>

Figure 1. Molecular structure of Cp2V(v2-ethylene)(PMe3)2.

Unprecedented for 1,4-dimethylenecyclobutane, however, the production of ethylene from reduction of 1,4-dibromobutane by a nickel tetraazaannulene complex was reported. One of the mechanisms suggested there (a concerted electron transfer)


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Olefin dimerization has been observed for the \((\text{C}_5\text{Me}_5)\text{Ta(olefin)}\) system\(^{(3)}\) but not for the Ti complex \((\text{C}_5\text{Me}_5)\text{Ti(ethylene)}\).\(^{(2)}\) Full reactivity of 2 will be reported elsewhere.

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**Supplementary Material Available:** Experimental details and spectral data for all compounds, crystal data, and lists of positional and thermal parameters (11 pages); listing of observed and calculated structure factors for 2 (13 pages). Ordering information is given on any current masthead page.

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**Stereochemistry of the Biosynthesis of sn-2,3-O-Diphytanyl Glycerol, Membrane Lipid of Archaeabacteria *Halobacterium halobium***

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One of the most striking and characteristic differences of archaebacteria from other evolutionary diverged eu-bacteria and eukaryotes is the stereostructure of a unit lipid of the cell membrane, sn-2,3-O-dialkylated glycerol, having, when present, a polar head group on the sn-C-1 position.\(^{(1,2)}\) Eubacteria and eukaryotic cells mostly contain antipodal sn-1,2-O-diacyl glycerol as a major lipid. Biochemical pathway concerning to this intriguing stereochemical divergence has yet to be uncovered. This paper deals with the cryptic stereochemistry of glycerol incorporation into the archaebacterial lipid studied by tracing stereospecifically deuteriated glycerol and demonstrates for the first time that stereochemical inversion takes place at the C-2 position of glycerol.

Biosynthetic studies on the lipid and related metabolite have been reported recently by using two classes of archaebacterial strains, i.e., halophilic *Halobacterium cutirubrum*\(^{(3)}\) and extreme acidothermophile *Sulfolobus sp.* ( *Calderiella acidophilia*).\(^{(4)}\) The latter actually contains an interesting 72-membered ring structure of biphytanyl diacylglycerol tetraether as a principal membrane lipid which can also be classified in the sn-2,3-O-dialkylated glycerol family.\(^{(5)}\) In either case, glycerol was reported to be incorporated efficiently into the membrane lipid,\(^{(1,2)}\) and all the hydrogens of glycerol except hydroxyl groups were reported to be retained in the biosynthesis of the lipid in *Sulfolobus*\(^{(3,5)}\). If, as emphasized previously,\(^{(2,4)}\) formation of the ether linkages might take place between glycerol or its derivative and prenyl phosphatidate, stereochemical inversion would not occur at the C-2 position of glycerol. Alternatively, antipodal stereochemistry might arise from stereocidentally opposite phosphorylation or other activation of glycerol to the case of eubacteria or eukaryotes.

Separate feeding of chemically synthesized \((RS)-[1,1-^2H_2]\text{-glycerol}, (R)-[1,1-^2H_2]\text{-glycerol}, and (S)-[1,1-^2H_2]\text{-glycerol to the}}