Structure, and Reactivity of Cyclopentadienyl-bis(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,1 very few complexes have actually been isolated, especially for the 3d-metals. For Ti the only compound known is Cp2Ti(ethylene)(PMe3), with some aspects of its reactivity. For V only two compounds are fully characterized: Cp2V(EtO2CCH=CHC02Et)3 and V(CO)5[PPh2(2-alkenylnaphylyl)]2, the latter stabilized by the chelate effect. Here we wish to report a simple olefin complex of V(I), CpV(ethylene)(PMe3), with some aspects of its reactivity.

When CpVCl(PMe3), (produced by reduction of CpVCl(PMe3) (CpVCl(PMe3)2 reacts with diphenyldisulfide to give the insoluble dimeric V(II)-species,14 all CpV(1)-species known so far form a-backdonation into the ethylene a*-orbital in the latter compound. This can be seen from both the ethylene C-C distances (despite formally being a d4-species) may be caused by competition from the two phosphine ligands.

The ethylene complex exhibits a wide range of reactivity. With (hard or soft) Lewis bases displacement of the ethylene ligand can occur. E.g., 2 reacts with CO, diphenylacetylene, or 2,2'-bipyridine to form CpV(CO)(PMe3).15 CpV(P2-PhC=C(Ph)(PMe3)2, and the paramagnetic CpV(bpy)PMe3, respectively.

Figure 1. Molecular structure of CpV(ethylene)(PMe3).2 (1). Selected structural parameters are as follows: V(1)-P(1) = 2.427 (2) Å, V(1)-P(2) = 2.427 (2), V(1)-C(12) = 2.535 (3), V(1)-C(13) = 2.173 (3), C(12)-C(13) = 1.365 (5), 2,2'-bipyridine to form CpV(C0)2(PMe3)2,13 CpV(q*-PhC=CHC02Et)2, and the paramagnetic CpV(bpy)PMe3, respectively. Thus through 2 various CpV(I)-species that do not contain CO ligands can be synthesized under mild conditions (0 °C). Apart from CpV(arene) species,1 all CpV(I)-compounds known so far contain at least one carbonyl ligand. The ethylene ligand is retained in reaction with CO, where the 2-oxavanadacyclo-3-pentanone CpV(ethylene)(PMe3) (ethylene) exhibits a wide range of reactivity. For example, 38 mol/mol V of 1-hexene is transformed into C12H24 (three isomers, GCMS m/z = 168) in 48 h (1-hexene, room temperature).

10) 2 crystallizes in the orthorhombic space group P2ba, a = 12.351 (3), b = 15.526 (4), c = 16.948 (3) Å (140 K), Z = 8. Reflections (2474) with 1.2 ≤ ≤ 26.0° were considered observed. All hydrogen atoms were located from the Fourier difference map and refined isotropically. R = 0.0035, R = 0.0041 (w = 1/F2) for 254 refined parameters.


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Stereochemistry of the Biosynthesis of \( \text{sn}-2,3-\text{O-Diphanytanyl} \) Glycerol, Membrane Lipid of Archaeabacteria \textit{Halobacterium halobium}

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

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

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

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