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Crystallographic and Dynamic NMR Evidence for Organometallic Fragments Pivoting on a Molecular Oxide Surface

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Recently we found out that a vanadate-supported methallylrhodium complex $[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]^{2-}$ undergoes C−C coupling by the action of CO to yield a (dimethylhexadiene)rhodium complex $[\{(\eta^4\text{-}C_8H_{14})Rh\}_2(V_4O_{12})]^{2-}$, **1**.[2] Although X-ray structural analysis confirmed that all V atoms in **1** are equivalent, a solution prepared by dissolving analytically pure crystalline material gave two peaks in its ^{51}V NMR spectrum in a roughly 1:3 ratio at ambient temperature (Figure S1, Supporting Information). This puzzled us for some time until we realized that pivoting of the organometallic fragments on the vanadate surface could yield two different isomers of $[\{(\eta^4\text{-}C_8H_{14})Rh\}_2(V_4O_{12})]^{2-}$ (see the illustration given in the Table of Contents).

If the organometallic group on the vanadate surface had a local 2-fold symmetry, pivoting would cause no net structural change. In the current case, however, the $(\eta^4\text{-}C_8H_{14})Rh$ groups do not have such local symmetry, and their pivoting results in isomerization. The C−C single bonds that are orientated outward at the beginning point inward after pivoting. Assuming that the more thermodynamically stable form is isolated in the solid state, we tentatively assign the larger peak to the *exo* isomer of **1** and the smaller peak to the *endo* isomer.

A closely related compound $[\{(\eta^4\text{-}C_6H_{10})Rh\}_2(V_4O_{12})]^{2-}$, **2**, also gave two peaks in its ^{51}V NMR at lower temperatures, although it gave a single peak at room temperature (Figure S2, Supporting Information). The distinctive difference between the spectra of **1** and **2** was the pattern of the splitting. In the spectra of **1**, the intensity of the peak at the higher field (−496 ppm) was greater than that at the lower field (−473 ppm). On the other hand, in the spectra of **2**, it was the lower field peak (−474 ppm) that had the higher intensity. Is this indicating that the thermodynamically stable form is different for **1** and **2**? A single-crystal X-ray structural study of a $\{(C_6H_5)_3P\}_2N^+$ (=PPN) salt of **2** suggested that the answer is "yes".[3] The anion **2** assumed the *endo* form in the solid state (see Figure 1). The crystal consisted exclusively of the *endo* form, and no other isomer was found in the solid state. Although **2** has no rigorous crystallographic symmetry, it closely approximates its maximum possible symmetry of 2/*m* (C_{2h}), just like **1** and the other $[M_2(V_4O_{12})]^{2-}$ compounds structurally characterized so far.[4]

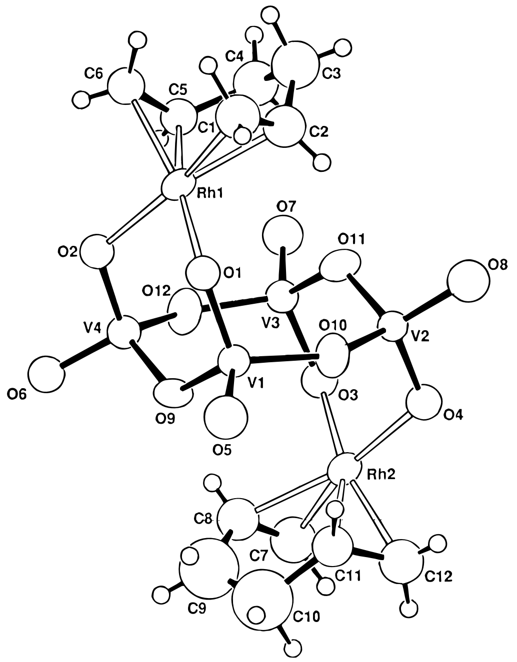

Figure 1. Structure of $[\{(\eta^4\text{-}C_6H_{10})Rh\}_2(V_4O_{12})]^{2-}$.

The isomerization of **2** in solution could also be followed by ^{1}H NMR (Figure 2). If **2** retains its solid state structure in solution, one would expect to observe five different ^{1}H peaks. However, it gave only four relatively broad peaks at room temperature. These peaks split at lower temperatures, and at −80 °C the spectrum basically consisted of two different sets of peaks; one set is the five peaks labeled A−E in Figure 2, and the other set is composed of the five smaller peaks labeled A*−E*. The intensity ratio of the large and small peaks was roughly 3:1, which coincides with the intensity ratio observed in ^{51}V NMR. Pairwise exchange between A and A* etc. was confirmed by spin saturation transfer experiments. Assuming once again that the thermodynamically favored form was isolated in the solid state, we tentatively assign the larger set of peaks to the *endo* isomer and the smaller ones to the *exo* isomer.

The NMR signals of hydrogens A, D, and E shifted upfield when the *endo* form isomerized to the *exo* isomer, while hydrogens B and C shifted downfield on isomerization. Those shifted downfield are the hydrogens that move closer to the vanadate ring concomitant with the pivoting of the organometallic fragment. Those that shifted upfield are the ones that move away from the ring. The vanadate ring seems to be working as a through-space electron abstractor. In fact the results of the X-ray structure determination of **2** indicate that there is some interaction between vanadate oxygens atoms and the methylene chains of the organometallic groups (O11−C4 3.52 Å).[5] This interaction may be what makes the *endo* isomer dominant in both the solid and solution phases. The organometallic fragment of **1** has bulky methyl groups. The steric repulsion between these methyl groups and the vanadate ring may be why the *exo* isomer is favored in this case.

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(3) Single crystals of $(PPN)_2[\{(\eta^4\text{-}C_6H_{10})Rh\}_2(V_4O_{12})]\cdot 2C_2H_4Cl_2$ (fw 2040.96) are, at 298 K, monoclinic, space group $P2_1/n$, with a = 18.075(2) Å, b = 17.965(2) Å, c = 28.117(2) Å, β = 102.20(1)°, V = 8924(2) Å^3, Z = 4, d_{calcd} = 1.519 g cm^{-3}, and d_{obsd} = 1.525 g cm^{-3}. R = 0.063 and R_w = 0.077 for 9947 independent absorption-corrected reflections having $2\theta_{\text{Mo K}\alpha} < 60°$ and $I > 3\sigma(I)$.

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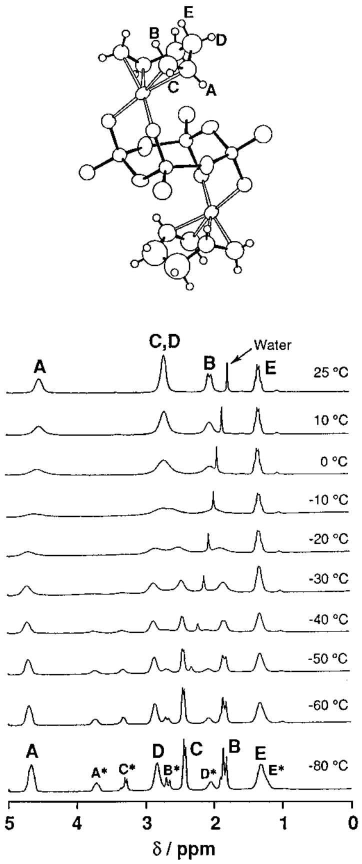

Figure 2. Top: Perspective drawing of $[\{(\eta^4\text{-}C_6H_{10})Rh\}_2(V_4O_{12})]^{2-}$ showing the labeling scheme of the hydrogen atoms. Bottom: Variable-temperature ^1H NMR of $(PPN)_2[\{(\eta^4\text{-}C_6H_{10})Rh\}_2(V_4O_{12})]$ in CD_2Cl_2.

Finally, we need to discuss whether the observed dynamic behavior can be explained by a mechanism other than pivoting. The possibility of intermolecular exchange (*i.e.*, where the $(\eta^4\text{-}C_6H_{10})Rh$ fragment dissociates from the vanadate ring) is excluded by the following observations: (1) The ^{51}V chemical shifts of both large and small peaks fall in the range characteristic of $[M_2(V_4O_{12})]^{2-}$ compounds ($M = (\eta^4\text{-}C_8H_{14})Rh$,[2a] $(\eta^4\text{-}C_8H_{12})Rh$,[4b] $(\eta^4\text{-}C_7H_8)Rh$,[6] $(\eta^4\text{-}C_8H_{12})Ir$,[4a] and $(\eta^2\text{-}C_8H_{14})_2Ir$[6]) and are distinctively different from those of the free tetrametavanadate (*ca.* −570 ppm)[6,7] and the $[M(V_4O_{12})]^{3-}$ compounds (−523 to −534 ppm).[4,6] (2) The ^1H NMR peaks of free $(\eta^4\text{-}C_6H_{10})Rh^+$ do not overlap with either set of peaks shown in Figure 2. (3) Only two peaks appeared in the ^{51}V NMR spectra. If the organometallic fragments dissociate from the vanadate ring and then rearrange themselves, three different isomers would be formed (*endo-endo*, *endo-exo*, and *exo-exo*), and we should have seen three ^{51}V peaks in a 1:2:1 ratio in this case. The same argument can be applied to the ^1H NMR spectra. (4) The NMR line shapes were independent of the concentrations of the solutions.

By elimination of the possibility of intermolecular exchange, we are left with a intramolecular mechanism. Pseudorotation-type ligand inversion involving solvent molecules[8] is one such mechanism. In fact, the rate of exchange was dependent on the solvent used. However, this mechanism fails to explain the observed ^{17}O NMR spectrum. Only three peaks (1061, 795, and 544 ppm) appeared in the spectrum of the 2% ^{17}O-enriched samples of **1**·TBA in CH_2Cl_2 at 23 °C. In the pseudorotation-type pathway no Rh−O bonds break and thus exchange between terminal oxygens and those bridging Rh and V atoms would not take place. Therefore the ^{17}O NMR spectrum would have shown four peaks if the pseudorotation-type mechanism were responsible for the isomerization.

All the observations mentioned above suggest an intramolecular mechanism that involves Rh−O bond breaking is responsible for the dynamic behavior of **1** and **2**. Pivoting is the simplest such mechanism. This simple mechanism explains the dynamic behavior of all the other $[M_n(V_4O_{12})]^{n-4}$ compounds synthesized so far.[4,6,9] Moreover, it also explains why the exchange rates of $[M(V_4O_{12})]^{3-}$ compounds are much greater than those of $[M_2(V_4O_{12})]^{2-}$ compounds.[4,6] In $[M_2(V_4O_{12})]^{2-}$, the organometallic fragments are attached to both sides of the V_4O_{12} moiety and thus they have to pivot in a concerted manner. This would make the activation energy higher and result in a low overall reaction rate. There is no such restriction for the $[M(V_4O_{12})]^{3-}$ complexes, and the organometallic fragment may pivot freely on the surface of V_4O_{12}. A quantitative study to determine the kinetics and activation enthalpy and entropy for pivoting is in progress.

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Supporting Information Available: Text giving preparation methods for **2** and a solution containing the free $(\eta^4\text{-}C_6H_{10})Rh^+$ cation and some details of the peak assignment of the ^1H NMR spectra of **2**, variable-temperature ^{51}V NMR spectra of **1**·TBA (Figure S1) and **2**·TBA (Figure S2), and tables of crystal data, atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, and interatomic distances and angles for **2**·PPN (15 pages). Ordering information is given on any current masthead page.

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(5) (a) It has been pointed out that C···O distances of 3.0−4.0 Å are characteristic of C−H···O hydrogen bonds.[7b] The free energy difference of the *endo* and *exo* isomers is estimated to be ~3 kJ mol^{-1} from their ratio (~3:1) in solution. This value compares well to the C−H···O bond energy of 4−8 kJ mol^{-1} reported in the literature.[5b] Similar relatively short C···O distances have also been found in $[(\eta^4\text{-}C_8H_{12})Ir(V_4O_{12})]^{3-}$ (3.55 Å),[4a] $[\{(\eta^4\text{-}C_8H_{12})Ir\}_2(V_4O_{12})]^{2-}$ (3.59 Å),[4a] and $[\{(\eta^4\text{-}C_8H_{12})Rh\}_2(V_4O_{12})]^{2-}$ (3.60 Å).[4b] (b) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290−296 and references cited therein.

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