Formation of a Novel η3

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be attributed to $p_{CN}$ of coordinatively bonded acetonitrile on very strong Lewis sites.

In conclusion, the acetonitrile adsorption on the two catalysts suggests the following surface properties: (i) both medium-strong and very strong Lewis sites are present on the (VO)$_2$P$_2$O$_7$-surface and (ii) a much higher concentration of very strong Lewis sites is present in the catalyst prepared in an organic medium ([b]) as compared to the catalyst prepared in an aqueous medium ([a]).

The catalytic properties of these two catalysts in n-butane and but-1-ene selective oxidation to maleic anhydride are reported in Table I. Catalyst (b) is much more active in n-butane-selective oxidation than catalyst (a), whereas no significant differences are found in but-1-ene oxidation.

It has been shown that the first step in the conversion of n-butane on solid super acid is the extraction of an $H^+$ from the butane by very strong Lewis sites. Similarly it is possible to hypothesize that the very strong Lewis sites evidenced on catalyst (b) and to a lesser extent on catalyst (a) are the sites responsible for the first step in alkane activation. The presence on the vanadium–phosphorus oxides of an oxidizing function ($V=O$ double bond) together with the strong Lewis sites modifies the successive steps of the reaction and leads to selective products (maleic anhydride) instead of the isomerization or cracking products which occur on solid super acid.

The presence of medium-strong Lewis sites is related to the structure itself of the (VO)$_2$P$_2$O$_7$ and it is not usual on vanadium oxides. Our FT-IR studies of the adsorption of bases indicate that such sites are not present on VO$_2$PO$_4$ even after reducing treatments. On the predominantly exposed (020) plane of (VO)$_2$P$_2$O$_7$ coupled vanadyl ions in trans positions leave coordinatively unsaturated IV(V) ions that, due to the higher electronegativity of the neighboring phosphorus atoms, give rise to a medium-strong Lewis site. Accordingly, the quantitative determination by temperature-programmed desorption of the presence of medium-strong Lewis sites indicates that their concentration is fairly independent of the preparation method and depends only on the surface area, just as in the case for the oxidation of but-1-ene. The presence of very strong Lewis sites, on the contrary, would be due to defective crystal states, their concentration depending on the preparation method, as shown in Figure 1.

During the VOHPO$_4$-H$_2$O precursor preparation in an organic medium, alcohol remains trapped between the layers. During successive calcination to form (VO)$_2$P$_2$O$_7$, the presence of the alcohol provokes local deformation of the crystalline structure as shown by X-ray diffraction analysis, thus inducing local straining of the V–(O–P) bonds. As a result, the coordination requirements of the vanadium are not completely satisfied, with the consequent enhancement of the Lewis acid strength and creation of new very active sites able to activate the paraffins.

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Registry No. (VO)$_2$P$_2$O$_7$, 58334-75-6; n-butane, 106-97-8; but-1-ene, 106-98-9; acetonitrile, 75-05-8.

Formulation of a Novel $n^+\eta^1$-1,2,3-Trimethyl-4,5-dimethylenecyclopentenyl Ligand by Hydrogen Abstraction from a Permethylcyclopentadienyl Group in Permethyltitanocene Carbyl and Related Systems

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We wish to report a new type of transformation of a permethylcyclopentadienyl group (Cp*) by stepwise hydrogen abstraction into an $n^+\eta^1$-1,2,3- trimethyl-4,5-dimethylenecyclopentenyl ligand.

The reaction was observed during a study of the thermolysis of paramagnetic titanium(III) compounds Cp*Ti(R). A stepwise reaction was observed, with the stoichiometry given in eq 1.

$$\text{Cp^*TiR} \rightarrow \text{Cp^*Ti(C}_5\text{Me}_4\text{CH}_2\text{Ti)}$$

The reaction was also observed for a reaction of titanium (III) with a Cp* ligand in a solvent such as benzene, IR, and $^1$H NMR.


(2) (a) The stochiometry was confirmed by isolation of the titanium compounds and Toepfer pump determination of the gaseous products. (b) Thermolysis of 1 was carried out with 10.0 g (30 mmol) of Cp*TiMe$_3$ in 25 mL of toluene at 110 °C. In 12 h the color of the solution had changed from green to purple. The solvent was stripped and the product crystallized from ether. Yield 7.5 g (93.3 mmol, 75%) of II.


(8) Identical with the compound in ref 5, on basis of elemental analyses (C, H, Ti), mass spectrum, molecular weight (cycoscopically determined in benzene), IR, and $^1$H NMR.

Table I. Specific Rate per Meter Squared of Surface Area of Maleic Anhydride Formation from n-Butane, Specific Rate of n-Butane Depletion, and Specific Rate of But-1-ene Depletion on the Catalysts (a) and (b)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>temp. K</th>
<th>n-butane oxidn</th>
<th>but-1-ene oxidn</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 560</td>
<td>0.29 X 10^-9</td>
<td>0.88 X 10^-4</td>
<td></td>
</tr>
<tr>
<td>(a) 620</td>
<td>1.02 X 10^-9</td>
<td>0.93 X 10^-4</td>
<td></td>
</tr>
<tr>
<td>(a) 660</td>
<td>1.58 X 10^-9</td>
<td>1.95 X 10^-4</td>
<td></td>
</tr>
<tr>
<td>(b) 570</td>
<td>2.58 X 10^-9</td>
<td>3.79 X 10^-4</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Modes of bonding in Cp*(C5Me3(CH2)2)Ti.

Figure 2. Molecular structure of Cp*Ti(C5Me3(CH2)2)CH2CO(Me)(Ph).

structurally characterized monomeric titanium fulvene complex. Relevant for the structure of III is the fact that the two methylene functions are indeed on neighboring ring C-atoms, thus confirming the 1,2,3-trimethyl-4,5-dimethylenecyclopentenyl ligand structure proposed for III. The bonding of the fulvene methylene group is very interesting. The short C≡CH bond (1.437 (5) Å), the angle HCC(16) (116 (3)°), and the rather small deviation of the CH2 hydrogen atoms from a planar array with C(15) and C(16) (the angle between C(15)-C(16) and the plane HC(16)H is 27.8 (2)°) indicate that in first approximation we are dealing with an sp hybridized methylene carbon atom. The coupling constants (\(J_{CH} = 3.6\) Hz and \(J_{HH} = 150\) Hz) are in agreement with this view. However, the deviation of the C≡CH fragment from the ring plane (36.3°) indicates an n\(^{2}\)-bonding of this olefinic function to the metal. Comparison with a real titanium olefin complex Cp*Ti(CH2)4 reveals indeed a strong similarity. The C–C–C angle (37.8 (1)° in IV and 38.9 (1)° in Cp*TiC5H4) is virtually the same in both compounds. The Ti–C distances, however, (Ti–C(15) = 2.317 (3), Ti–C(16) = 2.281 (3) Å against 2.160 (4) Å in Cp*2TiC5H4) differ considerably.

In conclusion we may state that both molecular structure and NMR data for IV favor bonding structure B for III, containing a so far unknown bifunctional, e.g., an n\(^{2}\)-allyl, n\(^{2}\)-diene organic ligand.

Compound III is not accessible through II only. Thermal decomposition of Cp*2TiMe3 is known to undergo hydrogen abstraction from a Cp* ligand giving Cp*(C5Me3CH2)TiMe. We observed that heating of the latter compound in mesitylene at 160 °C also produces III (obtained yield 22%) (eq 2).

\[
\text{Cp}^*\text{TiMe}_3 \xrightarrow{\text{MeH}} \text{Cp}^*(\text{C}_5\text{Me}_3\text{CH}_2)\text{TiMe} \xrightarrow{\text{MeH}} \text{Cp}^*(\text{C}_5\text{Me}_3\text{CH}_2)\text{Ti} (2) \III
\]

This stepwise hydrogen abstraction from Cp* ligands is not limited to titanium. The group 4 homologue Cp*2ZrMe3,\(^{13}\) gives the same reaction. Cp*(C5Me3CH2)Zr could be isolated in 4% yield as a red crystalline material after heating Cp*ZrMe3 at 160 °C in mesitylene.\(^{14}\)

We are at the moment investigating the reactivity of the new n\(^{2}\)-allyl, 1,2,3-trimethyl-4,5-dimethylenecyclopentenyl ligand and the scope of the stepwise hydrogen abstraction from Cp* ligands in metal carbays.

Note Added in Proof: Recently, observations similar to ours have been reported for the tungsten system Cp*2WH3, which under irradiation produces tungsten analogues of II and III.\(^{15}\)

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Supplementary Material Available: Details of the synthesis of and analytical data for I, thermal decomposition of II, thermolysis of Cp*2MMMe3 (M = Ti, Zr), and synthesis of IV and tables of fractional atomic coordinates, thermal parameters, bond distances, and structure of IV (10 pages). Ordering information is given on any current masthead page.