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Hydrogenation of Unsaturated Dicarboxylic Acids by Dicarbonylbis(η^5-cyclopentadienyl)titanium(II) and Molecular Structure of (μ-Acetylenedicarboxylato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]

David R. Corbin,*[†‡] J. L. Atwood,[§] and Galen D. Stucky[‡]

The acidic hydroxyl groups of unsaturated maleic, fumaric, itaconic, glutaconic, 3-methylenecyclopropane-*trans*-1,2-dicarboxylic, and acetylenedicarboxylic acids are found to be an effective source of hydrogen in the hydrogenation of these same acids to the corresponding saturated species upon reaction with (η^5-C$_5$H$_5$)$_2$Ti(CO)$_2$ (I). Hydrogenation is not observed for the monocarboxylic acid acrylic acid or for acids with steric hindrance such as 5-*cis*-norbornene-*endo*-2,3-dicarboxylic acid and 4-cyclohexene-*cis*-1,2-dicarboxylic acid. The presence of an alcoholic -OH group in oxalacetic acid results in CO$_2$ elimination along with hydrogenation of the olefinic bond to form (μ-succinato)bis[bis(η^5-cyclopentadienyl)titanium(III)]. (μ-Acetylenedicarboxylato)bis-[bis(η^5-methylcyclopentadienyl)titanium(III)], [(η^5-CH$_3$C$_5$H$_4$)$_2$TiCCO$_2$]$_2$ (II), was synthesized from the dipotassium salt of acetylenedicarboxylic acid and [(η^5-CH$_3$C$_5$H$_4$)$_2$TiCl]$_2$ to study the coordination of an unsaturated acid to Ti(III). II crystallizes in the monoclinic crystal system, space group $C2/c$, with unit cell parameters $a = 24.620$ (8) Å, $b = 32.997$ (9) Å $c = 8.901$ (5) Å, and $\beta = 94.84°$ with $Z = 12$. The coordination of the titanium atom is similar to that observed for (μ-1-3-η:2-4-η-*trans*,-*trans*-1,4-diphenylbutadiene)bis[bis(η^5-methylcyclopentadienyl)titanium], which is obtained by the reaction of I with 1,4-diphenylbutadiyne. Two titanium atoms coordinate to the 2- and 3-carbon atoms, respectively, and to a carboxylate oxygen atom to form five-membered chelate rings. A reaction model for oxidative addition of the carboxylic acid -OH group to the titanium atom with concurrent coordination of the unsaturated group is suggested by the structural results.

Introduction

Dicarbonylbis(η^5-cyclopentadienyl)titanium(II) (I) is a useful reagent in a number of reactions[1-5] including the homogeneous hydrogenation of acetylene.[6] In our investigation of exchange and electron transfer in various bis(η^5-cyclopentadienyl)titanium complexes,[7-10] I has also been found to be a useful reagent for the preparation of (η^5-C$_5$H$_5$)$_2$Ti^{III} complexes. The latter are synthesized with ligands having acidic protons such as various substituted pyrimidines, related heterocyclic molecules,[11] and carboxylic acids.[12-14] A reasonable pathway in these reactions is oxidative addition of an -XH bond to Ti(II) with subsequent elimination of H$_2$ in a bimolecular or radical solvent abstraction process to give the Ti(III) derivative. For example, reaction of the dicarboxylic acid succinic acid with I gives the dimeric product (μ-succinato)bis[bis(η^5-cyclopentadienyl)titanium(III)].[12] Coutts and Wailes have reported the preparation of the analogous complexes of unsaturated dicarboxylic acids by reacting bis[bis(η^5-cyclopentadienyl)titanium(III) chloride] with the appropriate sodium salt.[15] In this paper we report the interesting and unexpected result that reaction of I with certain unsaturated carboxylic acids gives the saturated, not the unsaturated, products. Namely, we report the reduction of maleic, fumaric, and acetylenedicarboxylic acids to the saturated complex (μ-succinato)-bis[bis(η^5-cyclopentadienyl)titanium(III)] by reaction with I, as well as the reduction of 3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid to the saturated (μ-3-methylcyclopropane-*trans*-1,2-dicarboxylato)bis[bis(η^5-cyclopentadienyl)titanium(III)], itaconic acid to (μ-methylsuccinato)bis[bis(η^5-cyclopentadienyl)-titanium(III)], and glutaconic acid to (μ-glutarato)bis[bis(η^5-cyclopentadienyl)titanium(III)]. The systems included for investigations in this study are important in defining the role of dicarboxylic vs. monocarboxylic acid groups, steric and chain length effects, and the presence of basic -OH groups adjacent to the carboxylic acid fragment.

Experimental Section

A. Compound Preparation. Maleic and fumaric acids were purchased from Matheson Coleman and Bell; acetylenedicarboxylic acid, 3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid, itaconic acid, glutaconic acid, 5-*cis*-norbornene-*endo*-2,3-dicarboxylic acid (mp 170 °C),

acrylic acid, oxalacetic acid, acetylenedicarboxylic acid, and the mono-potassium salt of acetylenedicarboxylic acid were purchased from Aldrich. All were used as received with the exception of the acrylic acid, which was distilled under nitrogen. The dipotassium salt of acetylene-dicarboxylic acid was prepared by literature methods.[16] The deuterated acids were also prepared by literature methods[17] using D$_2$O purchased from Sigma Chemical. Bis(η^5-cyclopentadienyl)titanium dichloride was purchased from Pressure Chemical Co. Samples of dicarbonylbis(η^5-cyclopentadienyl)titanium(II), (η^5-C$_5$H$_5$)$_2$Ti(CO)$_2$, were prepared by literature methods[18] with a slight modification. The aluminum sheets were activated by stirring overnight with a solution of I$_2$ prior to use. [(η^5-CH$_3$C$_5$H$_4$)$_2$TiCl]$_2$ was prepared by procedures described by Sekutowski and Stucky[19] and Manzer.[20] Solvents were distilled from sodium and benzophenone under a nitrogen atmosphere. Most synthetic work was performed in a Vacuum Atmospheres inert-atmosphere glovebox with a helium atmosphere. Mass spectral data were obtained on a MAT-Varian CH-5 spectrometer. Proton NMR data were obtained on

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Table I. Crystal Data

compd	$\text{Ti}_2\text{O}_4\text{C}_{28}\text{H}_{28}$
mol wt	524.36
space group	$C2/c$
cell constants	
a, Å	24.6201 (8)
b, Å	32.997 (9)
c, Å	8.901 (5)
β, deg	94.84 (5)
cell vol, Å^3	7205.3
molecules/unit cell	12
ρ(calcd), g cm^{-3}	1.45
μ(calcd), cm^{-1}	7.26
radiation	Mo Kα
max cryst dimens, mm	$0.30 \times 0.20 \times 0.15$
scan width, deg	$0.8 + 0.2 \tan \theta$
std reflcns	800; 0,$\overline{14}$,0; 002
decay of stds	<3%
no. of reflcns measd	2850
2θ range, deg	2–36
no. of obsd reflcns	1784
no. of params varied	280
GOF	9.48
R	0.077
R_w	0.084

acetone-d_6 solutions treated with HCl(g) by using a Nicolet 360.

1. General Preparation of the Binuclear Titanium(III) Metallocenes. Dicarbonylbis(η^5-cyclopentadienyl)titanium(II) (2.0 mmol) was added to a solution of the ligand (1.0 mmol) in approximately 75 mL of THF under an inert atmosphere. After the mixture was stirred for about 12 h, the solvent was removed under reduced pressure. The product was washed with refluxing hexanes and extracted with refluxing toluene. The filtrate was heated to reflux and allowed to cool slowly. After several days, crystals formed in some cases but mostly blue-green powders were recovered. The mass spectral results are illustrated in Figures 1–9 of the supplementary material.

2. Preparation of (μ-Acetylenedicarboxylato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]. Bis(η^5-methylcyclopentadienyl)titanium(III) chloride (2.4 g, 5.0 mmol) was dissolved in approximately 25 mL of deoxygenated water under an inert atmosphere. This solution was filtered into a flask containing the dipotassium salt of acetylenedicarboxylic acid (3.8 g, 2.0 mmol). After being stirred at ambient temperature for 2 h, the solution was filtered and the dark product was collected on the frit. This material was recrystallized from toluene, in which it is very slightly soluble. Mass spectrum: calcd, m/e 524; found, m/e 524.

3. Characterization of Reaction Products of (η^5-C$_5$H$_5$)$_2$Ti(CO)$_2$ and Carboxylic Acids. The complexes resulting from reaction of I and the carboxylic acids were characterized by electron-impact mass spectrometry. The experimental and calculated intensities for the isotopic multiplet parent ion peak of the resulting titanium(III) metallocenes are given in Figures 1–9 of the supplementary material. ^{1}H NMR spectra of the HCl-oxidized titanium(III) metallocenes were also obtained to establish the nature of the hydrogenated species.

B. X-ray Data Collection, Solution, and Structure Refinement. Single crystals of (μ-acetylenedicarboxylato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)] were sealed in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of [(sin θ)/λ]^2 values for 15 reflections ($2\theta > 20°$) accurately centered on the diffractometer are presented in Table I. Data were collected on an Enraf-Nonius CAD-4 diffractometer in the usual manner.[21] Measurements were made to $2\theta = 36°$, giving a total of 2850 reflections of which 1784 were considered observed [$I > 3\sigma(I)$]. The intensities were corrected for Lorentz and polarization effects but not for absorption. Full-matrix least-squares refinement was carried out by using the Sheldrick SHELX program. The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Deduction of the metal atom position from a Patterson map and the subsequent calculation of a difference Fourier map allowed the location of all non-hydrogen atoms. The hydrogen atoms of the methylcyclopentadienyl rings were placed at calculated positions 1.00 Å from the bonded carbon atoms, and their positions were not varied. Conversion of all other positions to anisotropic thermal parameters and further refinement led to reliability indices of $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.077$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.084$. The final values of the positional parameters, selected

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Table II. Final Positional and Thermal Parameters for [(η^5-CH$_3$C$_5$H$_4$)$_2$TiCCO$_2$]$_2$

atom	x/a	y/b	z/c	U(eq)^a
Ti(1)	0.1512 (1)	0.57178 (9)	0.6566 (3)	0.041
Ti(2)	0.1637 (1)	0.68565 (9)	0.2848 (3)	0.048
Ti(3)	0.4229 (1)	0.61008 (9)	0.0451 (3)	0.042
O(1)	0.1496 (4)	0.5557 (3)	0.443 (1)	0.049
O(2)	0.1508 (5)	0.5748 (4)	0.200 (1)	0.065
O(3)	0.1727 (4)	0.6995 (3)	0.500 (1)	0.053
O(4)	0.1636 (5)	0.06805 (4)	0.739 (2)	0.075
O(5)	0.4030 (4)	0.6138 (3)	0.253 (1)	0.046
O(6)	0.4300 (4)	0.6116 (4)	0.502 (2)	0.068
C(1)	0.1536 (6)	0.5833 (6)	0.335 (2)	0.043
C(2)	0.1603 (6)	0.6257 (6)	0.392 (2)	0.041
C(3)	0.1613 (6)	0.6292 (5)	0.545 (2)	0.043
C(4)	0.1660 (6)	0.6718 (6)	0.605 (2)	0.049
C(5)	0.5011 (6)	0.6135 (4)	0.175 (2)	0.041
C(6)	0.4407 (8)	0.6130 (5)	0.368 (2)	0.042
Me(1)	0.2782 (7)	0.5663 (6)	0.505 (2)	0.071
Me(2)	0.0277 (8)	0.5609 (6)	0.436 (2)	0.083
Me(3)	0.2963 (8)	0.6796 (6)	0.475 (2)	0.080
Me(4)	0.0661 (9)	0.7456 (7)	0.438 (3)	0.109
Me(5)	0.4172 (8)	0.7061 (6)	0.211 (2)	0.079
Me(6)	0.345 (1)	0.5345 (7)	0.186 (3)	0.117
Cp(01)	0.2478 (7)	0.5619 (5)	0.653 (2)	0.055
Cp(02)	0.2394 (6)	0.5929 (5)	0.759 (2)	0.047
Cp(03)	0.2115 (7)	0.5736 (5)	0.879 (2)	0.054
Cp(04)	0.2053 (7)	0.5326 (5)	0.839 (2)	0.065
Cp(05)	0.2254 (7)	0.5250 (5)	0.697 (2)	0.060
Cp(06)	0.0535 (6)	0.5673 (5)	0.596 (2)	0.046
Cp(07)	0.0705 (7)	0.5359 (6)	0.701 (2)	0.071
Cp(08)	0.0896 (6)	0.5561 (6)	0.840 (2)	0.075
Cp(09)	0.0876 (8)	0.5965 (6)	0.819 (2)	0.074
Cp(10)	0.0648 (7)	0.6052 (5)	0.666 (2)	0.066
Cp(11)	0.2639 (7)	0.6859 (5)	0.324 (2)	0.055
Cp(12)	0.2468 (7)	0.7240 (6)	0.257 (2)	0.069
Cp(13)	0.2198 (7)	0.7161 (6)	0.111 (2)	0.067
Cp(14)	0.2188 (7)	0.6735 (5)	0.086 (2)	0.058
Cp(15)	0.2458 (7)	0.6545 (5)	0.218 (2)	0.053
Cp(16)	0.0766 (7)	0.7179 (5)	0.304 (2)	0.064
Cp(17)	0.0979 (8)	0.7310 (6)	0.164 (2)	0.079
Cp(18)	0.0987 (8)	0.6951 (6)	0.071 (2)	0.077
Cp(19)	0.0805 (7)	0.6618 (6)	0.152 (2)	0.070
Cp(20)	0.0668 (7)	0.6758 (5)	0.297 (2)	0.059
Cp(21)	0.4116 (7)	0.6626 (5)	0.063 (2)	0.051
Cp(22)	0.3646 (7)	0.6666 (5)	-0.014 (2)	0.061
Cp(23)	0.3759 (7)	0.6490 (5)	-0.154 (2)	0.062
Cp(24)	0.4337 (7)	0.6535 (5)	-0.162 (2)	0.054
Cp(25)	0.4563 (6)	0.6737 (5)	-0.029 (2)	0.048
Cp(26)	0.3852 (7)	0.5430 (5)	0.062 (2)	0.056
Cp(27)	0.4414 (7)	0.5387 (5)	0.086 (2)	0.064
Cp(28)	0.4633 (8)	0.5500 (5)	-0.045 (2)	0.070
Cp(29)	0.4222 (8)	0.5620 (6)	-0.154 (2)	0.079
Cp(30)	0.3712 (8)	0.5582 (5)	-0.084 (2)	0.070

^{a} U(eq) $= \frac{1}{3}\sum_i\sum_j B_{ij} a_i^* a_j^* a_i a_j$.

Table III. Selected Interatomic Distances (Å) for [(η^5-CH$_3$C$_5$H$_4$)$_2$TiCCO$_2$]$_2$

Ti(1)–C(3)	2.16 (2)	Ti(1)–C(Cp1) (av)	2.39 (1)
Ti(1)–O(1)	1.97 (1)	Ti(1)–C(Cp2) (av)	2.39 (2)
Ti(2)–C(2)	2.20 (2)	Ti(1)–Cnt(Cp1)	2.054
Ti(2)–O(3)	1.97 (1)	Ti(1)–Cnt(Cp2)	2.062
Ti(3)–C(5)	2.16 (2)	Ti(2)–C(Cp3) (av)	2.40 (4)
Ti(3)–O(5)	1.96 (1)	Ti(2)–C(Cp4) (av)	2.407 (9)
C(1)–C(2)	1.49 (2)	Ti(2)–Cnt(Cp3)	2.103
C(1)–O(2)	1.23 (2)	Ti(2)–Cnt(Cp4)	2.072
C(1)–O(1)	1.33 (2)	Ti(3)–C(Cp5) (av)	2.39 (2)
C(2)–C(3)	1.36 (2)	Ti(3)–C(Cp6) (av)	2.39 (2)
C(3)–C(4)	1.50 (2)	Ti(3)–Cnt(Cp5)	2.055
C(4)–O(3)	1.33 (2)	Ti(3)–Cnt(Cp6)	2.072
C(4)–O(4)	1.23 (2)		
C(5)–C(5)	1.35 (3)		
C(6)–O(5)	1.32 (2)		
C(6)–O(6)	1.24 (2)		

interatomic distances, and selected bond angles are given in Tables II–IV. Anisotropic thermal parameters, interatomic distances, interatomic bond
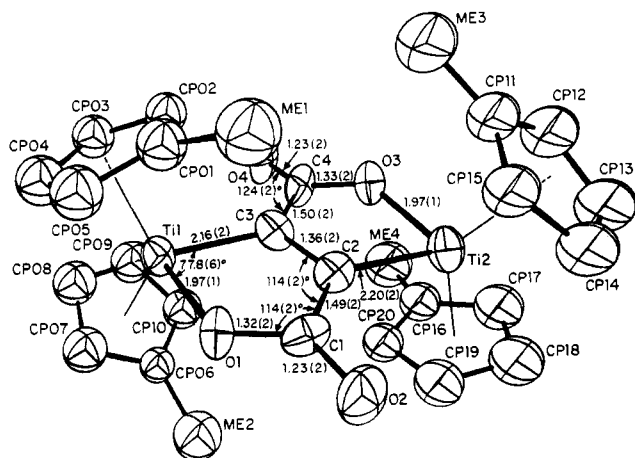
Figure 1. Molecular structure of $[(\eta^5\text{-}CH_3C_5H_4)_2TiCCO_2]_2$ in general position.

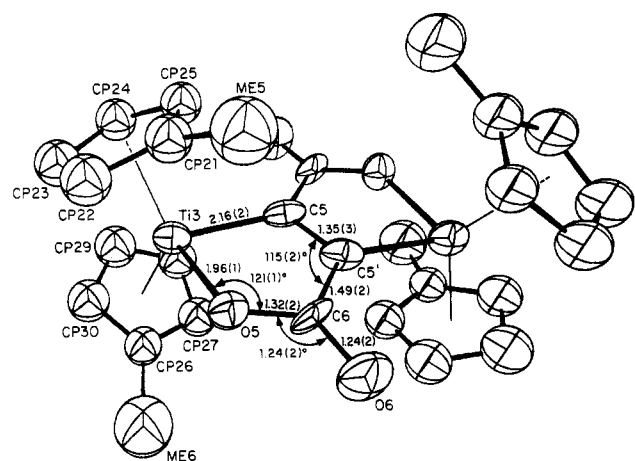**Figure 2.** Molecular structure of $[(\eta^5\text{-}CH_3C_5H_4)_2TiCCO_2]_2$ in the two-fold axis.

angles, and structure factor tables are available in the supplementary material.

C. Structure. (μ-Acetylenedicarboxylato)bis[bis(η^5-methylcyclo-pentadienyl)titanium(III)] crystallizes in the monoclinic crystal system, space group $C2/c$, with two independent molecular units with $C1$ and $C2$ symmetries, respectively (Figures 1 and 2). Selected interatomic bond distances and bond angles for non-hydrogen atoms are given in Tables III and IV. The titanium–cyclopentadiene ring carbon distances [2.35 (2)–2.46 (2) Å], cyclopentadiene carbon–carbon distances [1.35 (2)–1.46 (2) Å], and the dihedral angle (133.3°) between the cyclopentadiene rings on one titanium atom are in accord with earlier structures.[7-14] The configuration of the $C_4O_4{}^{2-}$ group approaches that of fumaric acid.[22] The $C(2)-C(3)'$ and $C(5)-C(5')$ bond lengths of 1.36 (2) and 1.35 (2) Å, respectively, are similar to those expected for an olefinic bond. The titanium–carbon bond lengths of 2.16 (2), 2.20 (2), and 2.16 (2) Å for $Ti(1)-C(3)$, $Ti(2)-C(2)$, and $Ti(3)-C(5)$, respectively, are in the range of those reported in the literature as are the titanium–oxygen distances of 1.96 (1), 1.97 (1), and 1.97 (1) Å for $Ti(1)-O(1)$, $Ti(2)-O(3)$, and $Ti(3)-O(5)$.

Discussion

Recent studies[11-14] have shown that the stoichiometric reaction of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ (I) with a ligand containing "active" protons results in the formation of the titanium(III) metallocene complex with that ligand. This has been shown to be true for the various substituted pyrimidines and related heterocycles,[11] aliphatic dicarboxylic acids,[12,13] and aromatic dicarboxylic acids.[14] It was similarly thought that reaction of I with the unsaturated carboxylic acids (Figure 3) might give the unsaturated $(\eta^5\text{-}C_5H_5)_2Ti^{III}$ complexes of these acids. Although $(\eta^5\text{-}C_5H_5)_2Ti^{III}$ complexes of these acids have been prepared by reaction of $[(\eta^5\text{-}C_5H_5)TiCl]_2$

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Table IV. Selected Bond Angles (deg) for Non-Hydrogen Atoms in $[(\eta^5\text{-}CH_3C_5H_4)_2TiCCO_2]_2$

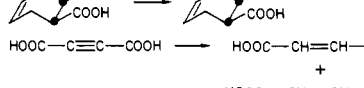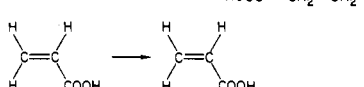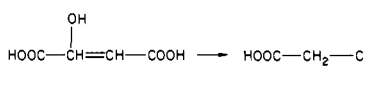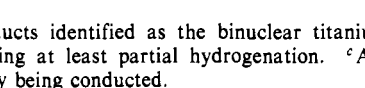|	
C(3)–Ti(1)–O(1)	77.8 (6)
C(3)–Ti(1)–Cnt(Cp1)	106.83
O(1)–Ti(1)–Cnt(Cp2)	109.90
C(2)–Ti(2)–O(3)	77.8 (6)
C(2)–Ti(2)–Cnt(Cp3)	105.68
Cnt(Cp3)–Ti(2)–Cnt(Cp4)	140.68
C(5)–Ti(3)–O(5)	77.0 (5)
C(5)–Ti(3)–Cnt(Cp5)	107.91
O(5)–Ti(3)–Cnt(Cp6)	109.42
C(2)–C(1)–O(1)	114 (2)
C(2)–C(1)–O(2)	123 (2)
Ti(2)–C(2)–C(3)	111 (1)
Ti(1)–C(3)–C(2)	113 (1)
C(2)–C(3)–C(4)	115 (2)
O(3)–C(4)–O(4)	123 (2)
O(5)–C(6)–O(6)	124 (2)
Ti(2)–O(3)–C(4)	121 (1)
O(1)–Ti(1)–Cnt(Cp1)	109.75
Cnt(Cp1)–Ti(1)–Cnt(Cp2)	132.66
O(3)–Ti(1)–Cnt(Cp2)	105.93
O(3)–Ti(2)–Cnt(Cp3)	100.23
C(2)–Ti(2)–Cnt(Cp4)	104.24
O(5)–Ti(3)–Cnt(Cp5)	108.87
Cnt(Cp5)–Ti(3)–Cnt(Cp6)	133.97
C(5)–Ti(3)–Cnt(Cp6)	104.74
O(1)–C(1)–O(2)	123 (2)
Ti(2)–C(2)–C(1)	134 (1)
C(1)–C(2)–C(3)	114 (2)
Ti(1)–C(3)–C(4)	132 (1)
C(3)–C(4)–O(3)	114 (2)
C(3)–C(4)–O(4)	124 (2)
Ti(1)–O(1)–C(1)	121 (1)
Ti(3)–O(5)–C(6)	121 (1)
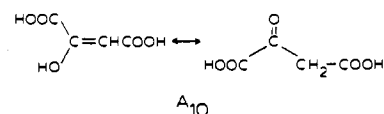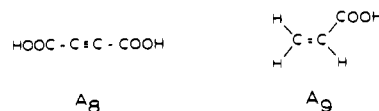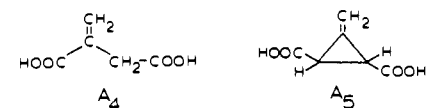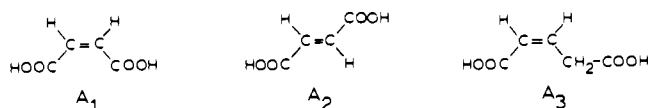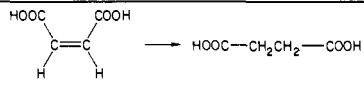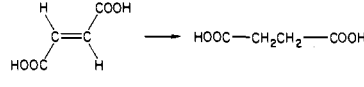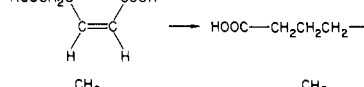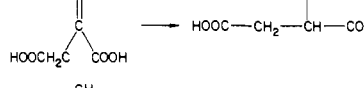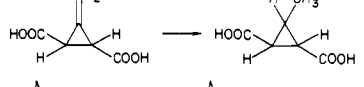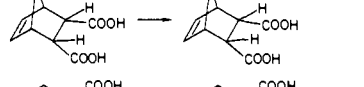
Figure 3. Unsaturated carboxylic acids examined.

and the sodium salt of the acid,[15] results have shown that this is not the case on reaction of I with the unsaturated acids. Instead, in most cases, both electron mass spectrometry and NMR confirmed that the diacids in Figure 3 were hydrogenated between 40 and 100% upon complex formation.

Table V. Reduction of Unsaturated Diacids upon Reaction with $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(CO)}_2$

acid	reaction[a]	% hydrogen-ation
A₁	HOOC—CH₂CH₂—COOH	81
A₂	HOOC—CH₂CH₂—COOH	80
A₃	HOOC—CH₂CH₂CH₂—COOH	40
A₄	HOOC—CH₂—CH—COOH (CH₃)	100
A₅		100
A₆		0
A₇		0
A₈[b]	HOOC—C≡C—COOH → HOOC—CH=CH—COOH	33
	+ HOOC—CH₂—CH₂—COOH	67
A₉		0
A₁₀	HOOC—CH=CH—COOH (OH) → HOOC—CH₂—CH₂—COOH	c

[a] Products identified as the binuclear titanium(III) metallocenes. [b] Assuming at least partial hydrogenation. [c] Additional studies are presently being conducted.

Blaszczak and McMurray have reported that titanium(III) chloride in a 20% aqueous solution is capable of effecting reduction of enedicarbonyl compounds to their saturated analogues.[23] The authors found that this technique is about 45% effective in converting maleic acid to the saturated succinic acid. Similar reduction of enedicarbonyl compounds using chromous ion[24] and zinc/acetic acid reagents[25] has been reported.

Coutts and Wailes have reported the preparation and mass spectral characterization of a number of carboxylato derivatives of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}^{\text{III}}$ from aqueous solutions of $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}]_2$ and the sodium salt of the acid, including the dimeric complexes (μ-maleato)bis[bis(η^5-cyclopentadienyl)titanium(III)] and (μ-fumarato)bis[bis(η^5-cyclopentadienyl)titanium(III)].[15] Reaction of I with maleic acid (A₁) gives primarily the saturated complex, (μ-succinato)bis[bis(η^5-cyclopentadienyl)titanium(III)]. Percentage yields were not obtained on the air-sensitive reaction products. Percent hydrogenation of the reaction product mixture from the mass spectral peak intensities can be calculated if similar volatilities and comparable ionization energies for saturated and unsaturated species are assumed. The percent hydrogenation obtained will also be dependent upon the reaction temperature and time. Table V summarizes the results obtained. Maleic acid (A₁) and the trans analogue, fumaric acid (A₂), which also gives (μ-succinato)bis[bis(η^5-cyclopentadienyl)titanium(III)], showed
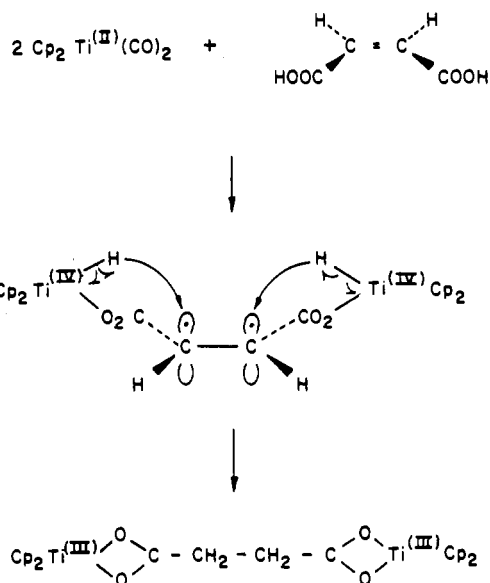
Figure 4. Proposed mechanism for hydrogenation of maleic acid (A₁) upon complexation by reaction with $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(CO)}_2$.

approximately 80% hydrogenation.

Glutaconic acid (A₃), which only exists in the cis configuration,[26] was examined because of the additional methylene unit separating the carboxyl group from the carbon–carbon double bond. The effect of this is seen in the mass spectrum (Figure 3, supplementary material), which shows the product to contain 40% of the saturated complex, (μ-glutarato)bis[bis(η^5-cyclopentadienyl)titanium(III)].

Itaconic acid (A₄) and 3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid (A₅) were found to be completely hydrogenated. The mass spectra of both products (Figures 4 and 5, supplementary material) gave very good fits to the calculated spectra for the saturated complexes (μ-2-methylsuccinato)bis[bis(η^5-cyclopentadienyl)titanium(III)] and (μ-3-methylcyclopropane-*trans*-1,2-dicarboxylato)bis[bis(η^5-cyclopentadienyl)titanium(III)].

4-Cyclohexene-*cis*-1,2-dicarboxylic acid (A₇) and 5-*cis*-norbornene-*endo*-2,3-dicarboxylic acid (A₆) were the only dicarboxylic acids that were not hydrogenated upon complexation. The product of the reaction with A₆ was the unsaturated (5-*cis*-norbornene-*endo*-2,3-dicarboxylato)bis[bis(η^5-cyclopentadienyl)titanium(III)] (Figure 6, supplementary material), and similarly for A₇, the product was (4-cyclohexene-*cis*-1,2-dicarboxylato)bis[bis(η^5-cyclopentadienyl)titanium(III)].

To test the source of the hydrogen atoms in the hydrogenation, a deuteration study was performed on the maleic acid (A₁) reaction. Deuterated maleic acid was reacted with I. The resulting mass spectrum of the product material showed that the parent molecular ion is 2 mass units higher than the undeuterated ion. The carboxylic acid groups are therefore the primary source of the hydrogen atoms in the hydrogenation.

Some interesting results were obtained for acetylenedicarboxylic acid (A₈). The mass spectrum (Figure 8, supplementary material), shows that the product contains 67% of the fully saturated (μ-succinato)bis[bis(η^5-cyclopentadienyl)titanium(III)] complex. Approximately 33% of the product was only partially hydrogenated with the possible isomeric products being (μ-fumarato)bis[bis-(η^5-cyclopentadienyl)titanium(III)] and (μ-maleato)bis[bis(η^5-cyclopentadienyl)titanium(III). At present, the source of all the hydrogen atoms in the hydrogenation of acetylenedicarboxylic acid has not been confirmed. It does appear that the most probable sources of the hydrogen atoms are uncomplexed ligand and THF solvent. This solvent was recently found to be a hydrogen atom source in an electron-transfer system involving I.[27] Interestingly, other preparations of this material showed complete hydrogenation in the NMR spectra.

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(27) Corbin, D. R.; Willis, W. S.; Duesler, E. N.; Stucky, G. D. *J. Am. Chem. Soc.* **1980**, *102*, 5969.

The monocarboxylic acid, acrylic acid (A_9), was reacted with I to test for the possible involvement of a radical mechanism. A radical mechanism could result in dimeric products. No such peaks were observed in the mass spectrum of the product material. The experimental and calculated peak intensities for the parent molecular ion (Figure 9, supplementary material) show that there is no apparent hydrogenation of the carbon–carbon double bond.

Floriani and co-workers[5] have proposed a titanium hydride species as an intermediate in the reaction of excess acetic acid with I to give bis(acetato)bis(η^5-cyclopentadienyl)titanium(IV). This intermediate is unstable in the presence of acetic acid. Such a hydride intermediate can be proposed in a mechanism for the hydrogenation of the various unsaturated dicarboxylic acids reported in this work. In acids A_1–A_5, both lobes of the π orbital of the carbon–carbon double bond are readily accessible by a hydride intermediate. For acid A_3, there are greater steric problems, leading to a decreased percentage of the hydrogenated product. 5-cis-Norbornene-endo-2,3-dicarboxylic acid (A_6) was not hydrogenated. Steric hindrance prevents access of the hydrogen atom of the hydride intermediate to the site of unsaturation. Also, there is no access to both lobes of the π-bond. Apparently in this case, the hydride intermediates react with one another to give the binuclear complex and hydrogen, which is observed in the gas above the reaction mixtures of these and similar systems.

Figure 4 shows a mechanism for the reactions with maleic acid (A_1). The formal oxidation state of the titanium atoms goes from (II) in the starting material to (IV) in the intermediate to (III) in the final titanium(III) product. Arrows are drawn on the intermediate species to indicate hydrogen atom transfer. In this connection, it is of interest to consider the structure of the intermediate formed upon –OH oxidative addition in somewhat more detail.

(μ-Acetylenedicarboxylato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)] (II) was synthesized from the dipotassium salt of acetylenedicarboxylic acid and [(η^5-$CH_3C_5H_4$)$_2$TiCl]$_i$ to study the coordination of an unsaturated acid to Ti(III). This complex has the structure shown in Figures 1 and 2. The coordination of the titanium atom to the olefinic portion of the dicarboxylic acid is similar to that observed for (μ-1-3-η:2-4-η-trans,trans-1,4-diphenylbutadiene)bis[bis(η^5-methylcyclopentadienyl)titanium].[28] It is reasonable to expect that the reaction of I with unsaturated carboxylic acids would give an intermediate with a similar structure
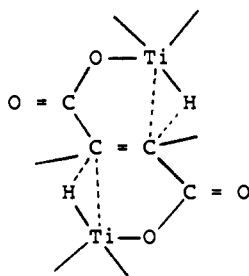

in which the vacant d orbitals of the titanium atom accept electron density from the unsaturated olefinic bond. The geometry is appropriate for hydrogen atom transfer to the β olefinic carbon atom.[29]

If for steric reasons this geometry is not possible, as for A_6 and A_7, hydrogenation does not take place and hydrogen is eliminated instead, either by solvent hydrogenation or via an intermolecular interaction between two Ti–H groups. It is also noteworthy that the monocarboxylic acid, A_9, does not hydrogenate or dimerize but also gives H_2 as the product. Apparently, both of the hydrogen atoms needed for olefinic hydrogenation must be accessible to the olefinic group.

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(29) An alternative view would be a "reductive protonation" mechanism as is observed in the reduction of low-valent dinitrogen complexes of titanium with acids to give ammonia and hydrazine. In the case discussed here, the charge is transferred to the electron-poor unsaturated acid followed by protonation.

The last diacid examined was oxalacetic acid (A_{10}). It was thought that this system would behave similarly to acids A_1–A_5 and especially to the analogous glutaconic acid. The mass spectrum of the product shows the parent molecular ion to be 14 mass units less than expected (472 vs. 486). Gas chromatographic studies of the gas above the reaction mixture show CO_2 to be a major product. A reasonable explanation is loss of oxygen as CO_2 and hydrogenation to give (μ-succinato)bis[bis(η^5-cyclopentadienyl)titanium(III)] (M_r = 472).

CO_2 elimination from HOOC—C(OH)=CH—COOH could be rationalized by an intermediate analogous to (η^5-C_5H_5)$_2$Zr-$(CO)(H)_2$,[30] in which one CO molecule remains coordinated to the titanium atom after oxidative addition. Attack at the carbon atom of the CO group by the basic –OH group, CO_2 elimination, and hydrogen atom transfer to the olefin would then give the intermediate expected for A_1 or A_2 and the observed hydrogenated product. The actual intermediate in this case may also be an oxycarbene as proposed by Bercaw for organozirconium CO hydrogenation by organozirconium intermediates.[30]
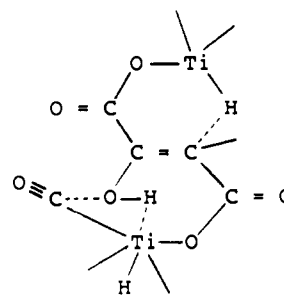
In summary, –OH hydrogenation of olefins by (η^5-C_5H_2)$_2$Ti-$(CO)_2$ is particularly effective within the steric and geometrical constraints described above. Deuterium-exchange experiments confirm that the primary hydrogen source is the hydrogen atom of the carboxylic acid –OH group. The presence of an alcoholic –OH group on the olefin results in CO_2 elimination along with hydrogenation of the olefinic bond. The importance of hydrogenation by –OH groups to heterogeneous catalysis is becoming increasingly apparent. Brenner[31] given convincing evidence that CO hydrogenation involving the carbon monoxide associated with supported metal carbonyls does not proceed through the intermediate formation of H_2 or give CO_2 as a final product. The most probable route is through successive oxidations of a transition-metal center via interaction with surface hydroxyl groups alone.[32] These results together with the single-crystal structural results for (μ-acetylenedicarboxylato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)] (II) reported here suggest that this type of multifunctional site may be part of an important hydrogenation route in supported metal oxide hydrogenation reactions. We suggest that the homogeneous chemistry described in this paper provides a simple molecular model for hydrogenation using acidic protons and for hydroxyl oxidative addition.

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(31) Brenner, A.; Hucul, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 2484.
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