

ruthenium and the C-H bond of interest.

A final consideration is whether steric crowding may hinder the interchange of the pertinent endo hydrogen atoms at the ruthenium coordination site. The X-ray structure gives no evidence that this may be the case. The site exchange of the endo hydrogen atoms of C(44) and C(48) requires movement of these two carbon atoms that do not appear to be restricted in any way by close non-bonded contacts with atoms of the phosphorus donor ligands. The closest contact distances are 3.475 Å between C(44) and P(1) and 3.478 Å between C(48) and C(221) (all other nonbonded contacts are  $\geq 3.60$  Å). A translational motion of C(48) toward the ruthenium coordination site will increase this distance, so atom C(221) cannot be considered to hinder the fluxional process. In addition,

the groups attached to the phosphorus atoms appear to adopt positions that minimize compressions with the  $\eta^3$ -cyclooctenyl ligand; thus the Ru-P-C angles of the phenyl substituents lying close to the  $\eta^3$ -enyl group have normal angles [114.5 and 111.1° for Ru-P(1)-C(121) and Ru-P(2)-C(221), respectively] whereas Ru-P(1)-C(111) (123.5°) and Ru-P(2)-C(211) (122.0°) have large angles to minimize steric repulsions between the P(OMe)Ph<sub>2</sub> ligands.

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**Supplementary Material Available:** Tables of observed and calculated structure factors and anisotropic temperature factors (15 pages). Ordering information is given on any current masthead page.

## Simple Synthesis of Enolate Complexes of Titanocene and Zirconocene. Molecular Structure of Cp<sub>2</sub>Ti(OC<sub>2</sub>H<sub>3</sub>)<sub>2</sub>

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Lithium enolates, e.g., LiOC<sub>2</sub>H<sub>3</sub>, prepared by the reaction of BuLi with THF, or LiOCH=CMe<sub>2</sub>, prepared from MeLi and Me<sub>3</sub>SiOCH=CMe<sub>2</sub>, react readily with Cp<sub>2</sub>MXCl (X = Me, Cl; M = Ti, Zr) to give the corresponding enolates Cp<sub>2</sub>M(OCH=CR<sub>2</sub>)Me and Cp<sub>2</sub>M(OCH=CR<sub>2</sub>)<sub>2</sub> (R = H, Me). These complexes are thermally quite stable and show no tendency to eliminate aldehyde and form ketene complexes. The crystal structure of Cp<sub>2</sub>Ti(OC<sub>2</sub>H<sub>3</sub>)<sub>2</sub> has been determined: orthorhombic, *Pbcn*, *a* = 14.046 (4) Å, *b* = 6.099 (2) Å, *c* = 14.709 (5) Å, *V* = 1250.1 (6) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}}$  = 1.39 g/cm<sup>3</sup>. The molecule has crystallographically imposed C<sub>2</sub> symmetry. Important bond distances (Å) and angles (deg) are as follows: Ti-Cp(centroid) = 2.088 (4), Cp-Ti-Cp = 131.2 (1), Ti-O = 1.903 (2), C-O = 1.329 (4), C=C = 1.306 (5), Ti-O-C = 145.5 (2), O-C-C = 128.4 (2).

### Introduction

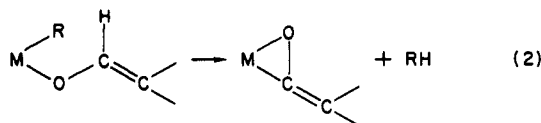
Enolate complexes of transition metals are a little studied class of compounds. The enolate ion is potentially ambidentate, capable of binding to metals through oxygen or carbon (eq 1). The mode of binding is expected to

$$M^+ + \{CH_2=CH-O^- \leftrightarrow ^-CH_2-CH=O\} \rightarrow$$

$$M-O-\underset{\text{A}}{CH=CH_2} \text{ or } M-\underset{\text{B}}{CH_2}-CH=O \quad (1)$$

depend on the oxophilicity of the metal with M-O bonding predominating for the early transition metals and M-C bonding possibly being favored by the softer, late transition metals.

Furthermore, hydrogen abstraction from an enolate ligand could lead to ketene complexes (eq 2). The ketene



ligand is a possible precursor to complexes with a bridging methylene functionality whose properties are of interest in connection with CO hydrogenation chemistry.<sup>1</sup> This

latter possibility is illustrated by the formation of Cp\*<sub>2</sub>Co<sub>2</sub>( $\mu$ -CH<sub>2</sub>)( $\mu$ -CO) from Cp\*Li, CoCl<sub>2</sub>, and LiOC<sub>2</sub>H<sub>3</sub> (Cp\* = C<sub>5</sub>Me<sub>5</sub>).<sup>2</sup>

Several enolate complexes have been prepared by indirect methods,<sup>3-8</sup> some of which are illustrated in eq 3-8.

Since enolate salts are readily prepared according to eq 9<sup>2,9</sup> and 10,<sup>10,11</sup> we undertook to investigate the reactions of simple enolate ions with metal halides. We here report our results with the metallocene halides Cp<sub>2</sub>MXCl (M =

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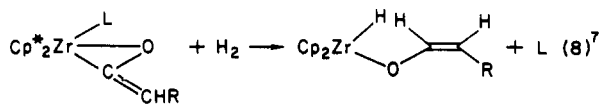
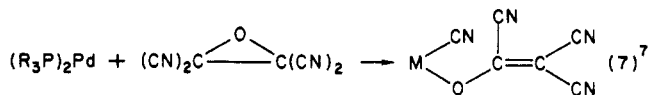
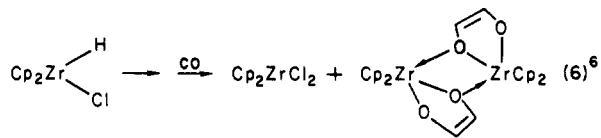
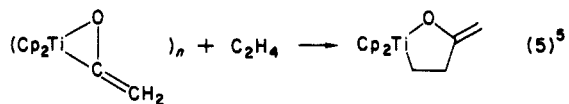
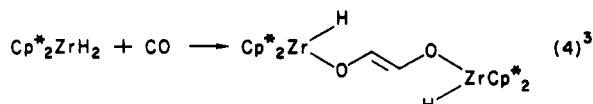
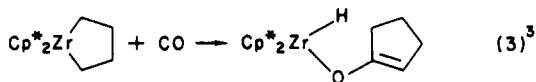
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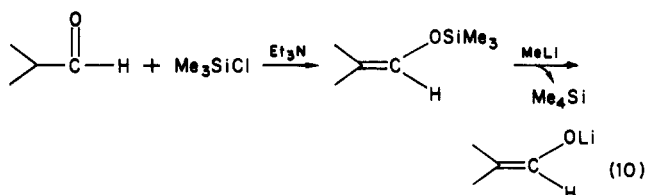
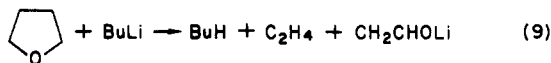
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Ti, Zr; X = Me, Cl). The first structure of a simple enolate  $\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_3)_2$  is also reported.



### Experimental Section

All air sensitive materials were handled by standard Schlenk-ware techniques or in an inert-atmosphere box equipped with a recirculating purification train. Solvents were distilled directly from their respective drying agents under  $\text{N}_2$  (solvent/drying agent):  $\text{CH}_2\text{Cl}_2/\text{P}_4\text{O}_{10}$ , THF/K-benzophenone,  $\text{Et}_2\text{O}/\text{Na}$ -benzophenone, toluene/Na-benzophenone, hexane/ $\text{CaH}_2$ . The enolate ions were prepared as shown in eq 9 and 10.<sup>2,9-11</sup> Titanocene and zirconocene dichlorides were obtained from commercial sources and used as received.  $\text{Cp}_2\text{ZrMeCl}$  was prepared from  $[\text{Cp}_2\text{ZrCl}]_2\text{O}$  and  $\text{Me}_3\text{Al}^{12}$  and  $\text{Cp}_2\text{TiMeCl}$  from  $\text{Cp}_2\text{TiCl}_2$  and  $\text{Me}_3\text{Al}^{13}$ .

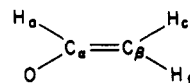
IR spectra were recorded on a Perkin-Elmer 1330 instrument.  $^1\text{H}$  NMR spectra were recorded on Bruker WM-360 or Varian T-60A instruments.  $^{13}\text{C}$  NMR spectra were obtained on the Bruker WM-360 at 90.56 MHz. Mass spectra were obtained with the direct inlet system of a Finnegan 4021 medium-resolution quadrupole spectrometer (ionization energy = 70 eV). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

**$\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_3)_2$ .** To a suspension of  $\text{Cp}_2\text{TiCl}_2$  (2.48 g, 10 mmol) in THF at  $-78^\circ\text{C}$  was added a THF solution containing 23 mmol of  $\text{LiOC}_2\text{H}_3$  over a period of 30 min. The solution was allowed to warm to room temperature over a period of ca. 3 h during which time the  $\text{Cp}_2\text{TiCl}_2$  dissolved and the color of the mixture lightened to red-orange. The THF was then removed under vacuum, and the orange-red solid was dissolved in 15 mL of  $\text{CH}_2\text{Cl}_2$ . This solution was filtered to remove the LiCl and unreacted  $\text{LiOC}_2\text{H}_3$ .

Table I. Summary of Crystal Data Conditions and Results

compd	$\text{C}_{14}\text{H}_{16}\text{O}_2\text{Ti}$
space group	<i>Pbcn</i>
<i>a</i> , Å	14.046 (4)
<i>b</i> , Å	6.099 (2)
<i>c</i> , Å	14.709 (5)
<i>V</i> , Å <sup>3</sup>	1260.1 (6)
mol wt	262.2
<i>Z</i>	4
<i>d</i> (calcd), g/mL	1.39
cryst dimens, mm	0.30 × 0.22 × 0.28
abs coeff, L/cm	6.6
scan range, deg	Mo $\text{K}\alpha$ - 0.8 to Mo $\text{K}\alpha$ + 0.9
bkgd time ratio	0.8
$2\theta$ , deg	50
data collected	1434
data > $3\sigma(I)$	744
final $R_1$	0.038
final $R_2$	0.036

The  $\text{CH}_2\text{Cl}_2$  was removed from the filtrate under vacuum and the solid taken up in a minimum amount of ether. Hexane was added to incipient precipitation, and the solution was then cooled slowly to  $-30^\circ\text{C}$  to yield orange needles. A second recrystallization from ether/hexane gave 2.1 g (80%) of pure product:  $^1\text{H}$  NMR (360 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  5.91 (10 H, Cp), 7.15 (2 H,  $\text{H}_a$ , dd,  $J_{\text{H}_a\text{H}_c} = 13.6$ ,  $J_{\text{H}_a\text{H}_b} = 5.6$  Hz), 4.11 (2 H,  $\text{H}_b$ , d,  $J = 13.6$  Hz), 3.99 (2 H,  $\text{H}_c$ , d,  $J = 5.6$  Hz);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , gated {H})  $\delta$  116.05 (Cp,  $J = 100$  Hz),



161.9 ( $\text{C}_\alpha$ , d,  $J = 107$  Hz); 87.89 ( $\text{C}_\beta$ , td,  $J^1 = 73$  Hz,  $J^2 = 7.4$  Hz); mass spectrum,  $m/e$  264 ( $\text{P}^+$ ), 221 ( $\text{P}^+ - \text{OC}_2\text{H}_3$ ), 179 ( $\text{Cp}_2\text{TiH}^+$ ), 178 ( $\text{Cp}_2\text{Ti}^+$ ), 156 ( $\text{CpTiOC}_2\text{H}_3^+$ ), 129 ( $\text{CpTiO}^+$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Ti}$ : C, 63.64; H, 6.06; O, 12.12. Found: C, 63.58; H, 6.01; O, 12.07.

**$\text{Cp}_2\text{Ti}(\text{OCHCMe}_2)_2$ .** This preparation follows that for  $\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_3)_2$ . Thus, 1.25 g (5 mmol) of  $\text{Cp}_2\text{TiCl}_2$  was treated with a freshly prepared solution of 12 mmol of  $\text{LiOCHCMe}_2$  in THF at  $-78^\circ\text{C}$ . After the mixture was warmed to room temperature, the THF was removed under vacuum, the residue dissolved in hexane, and the mixture was then filtered. The hexane in the filtrate was pumped off under vacuum and the residue dissolved in a minimum amount of ether. Cooling the ether solution to  $-78^\circ\text{C}$  gave 1.3 g (80%) of red, microcrystalline solid:  $^1\text{H}$  NMR (60 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  6.0 (10 H), 7.0 (2 H, m,  $J < 2$  Hz,  $\text{OCHCMe}_2$ ), 1.8 (12 H, br s,  $\text{OCHCMe}_2$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  115.5 (Cp,  $J = 98$  Hz), 151.5 ( $\text{C}_\alpha$ , d,  $J = 105$  Hz), 19.3 (Me, q,  $J = 40$  Hz),  $\text{C}_\beta$  was not observed; mass spectrum,  $m/e$  320 ( $\text{P}^+$ ), 249 ( $\text{P}^+ - \text{OCHCMe}_2$ ), 179 ( $\text{Cp}_2\text{TiH}^+$ ), 178 ( $\text{Cp}_2\text{Ti}^+$ ), 129 ( $\text{CpTiO}^+$ ). Anal. Calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_2\text{Ti}$ : C, 67.54; H, 7.50; O, 10.00. Found: C, 66.86; H, 7.35; O, 10.75.

**$\text{Cp}_2\text{TiMe}(\text{OC}_2\text{H}_3)$ .** This compound was prepared in the same manner as the above complex from 2.25 g (11.1 mmol) of  $\text{Cp}_2\text{TiCl}_2$  and an equimolar amount of  $\text{LiOC}_2\text{H}_3$  in THF at  $-10^\circ\text{C}$ . The solution turns from red to yellow. The THF was removed under vacuum, and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered. Concentration of the filtrate and addition of hexane (3 mL) gave 1.8 g (70%) of yellow crystalline solid upon cooling to  $-10^\circ\text{C}$ : mp 25–28  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (60 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  5.76 (10 H, Cp), 0.80 (3 H, TiMe), 7.05 (1 H,  $\text{H}_a$ , dd,  $J_{\text{H}_a\text{H}_c} = 14$  Hz,  $J_{\text{H}_a\text{H}_b} = 6$  Hz), 4.06 (1 H,  $\text{H}_b$ , d,  $J = 14$  Hz), 3.93 (1 H,  $\text{H}_c$ , d,  $J = 6$  Hz); mass spectrum,  $m/e$  236 ( $\text{P}^+$ ), 221 ( $\text{P}^+ - \text{Me}$ ), 193 ( $\text{P}^+ - \text{OC}_2\text{H}_3$ ), 179 ( $\text{Cp}_2\text{TiH}^+$ ), 178 ( $\text{Cp}_2\text{Ti}^+$ ), 129 ( $\text{Cp}_2\text{TiO}^+$ ), 113 ( $\text{CpTi}^+$ ). Anal. Calcd for  $\text{C}_{13}\text{H}_{16}\text{OTi}$ : C, 66.10; H, 6.78; O, 6.78. Found: C, 65.76; H, 6.42; O, 6.91.

**$\text{Cp}_2\text{Zr}(\text{OCHCMe}_2)_2$ .** This compound was prepared from 2.91 g (10 mmol) of  $\text{Cp}_2\text{ZrCl}_2$  and a THF solution containing 20 mmol of  $\text{LiOCHCMe}_2$ . The workup procedure was identical with that for the Ti analogue. The product was obtained as a thick, yellow oil that would not crystallize from toluene, hexane, or ether: yield 62%;  $^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  6.1 (10 H, Cp), 6.6 (2 H, m,  $\text{H}_a$ ); 1.5 (12 H, unresolved doublet,  $=\text{CMe}_2$ ); mass spectrum,  $m/e$  362 ( $\text{P}^+$ ), 291 ( $\text{P}^+ - \text{OCHCMe}_2$ ), 290 ( $\text{Cp}_2\text{ZrOCCMe}_2^+$ ), 221 ( $\text{Cp}_2\text{ZrH}^+$ ), 220 ( $\text{Cp}_2\text{Zr}^+$ ), 171 ( $\text{Cp}_2\text{ZrO}^+$ ), 145 ( $\text{CpZrOC}_2\text{H}_3^+$ ), 71

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Table II. Fractional Atomic Coordinates

atom	x	y	z
Ti1	0.0	0.2307 (01)	0.2500
O2	0.0656 (02)	0.4415 (04)	0.1781 (02)
C3	0.1266 (03)	0.4719 (07)	0.1102 (03)
C4	0.1622 (03)	0.3260 (08)	0.0549 (03)
C5	-0.0427 (03)	-0.0204 (07)	0.1333 (03)
C6	-0.0973 (04)	-0.0748 (07)	0.2086 (03)
C7	-0.1586 (03)	0.1017 (08)	0.2250 (03)
C8	-0.1414 (03)	0.2583 (07)	0.1582 (03)
C9	-0.0718 (03)	0.1811 (07)	0.1021 (03)
H1	0.1491 (23)	0.6223 (42)	0.1060 (24)
H2	0.1495 (25)	0.1706 (40)	0.0547 (25)
H3	0.2083 (21)	0.3697 (54)	0.0107 (20)
H4	0.0131 (03)	-0.1196 (07)	0.1040 (03)
H5	-0.0933 (04)	-0.2249 (07)	0.2473 (03)
H6	-0.2100 (03)	0.1139 (08)	0.2794 (03)
H7	-0.1772 (03)	0.4143 (07)	0.1519 (03)
H8	-0.0439 (03)	0.2648 (07)	0.0431 (03)

Table IV. Bond Distances (Å)<sup>a</sup>

O2-Ti1	1.903 (02)	C4-C3	1.306 (05)
C5-Ti1	2.378 (04)	C6-C5	1.388 (06)
C6-Ti1	2.389 (04)	C9-C5	1.373 (05)
C7-Ti1	2.391 (04)	C7-C6	1.399 (05)
C8-Ti1	2.408 (04)	C8-C7	1.391 (05)
C9-Ti1	2.416 (04)	C9-C8	1.364 (05)
C3-O2	1.329 (04)	Cp-Ti	2.088 (04)

<sup>a</sup> Cp = ring centroid.

(OCHCMe<sub>2</sub><sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>24</sub>O<sub>2</sub>Zr: C, 59.34; H, 6.59; O, 8.79. Found: C, 58.82; H, 6.32; O, 9.20.

**Cp<sub>2</sub>ZrMe(OCHCMe<sub>2</sub>)**. This complex was prepared from 3.00 g (11 mmol) of Cp<sub>2</sub>ZrMeCl and a THF solution containing 20 mmol of LiOCHCMe<sub>2</sub> at -20 °C for 2 h. After the solution was warmed to room temperature, the THF was pumped off and the residue taken up in hexane and then filtered. Removal of the hexane under vacuum gave a thick, yellow oil that would not crystallize from toluene, hexane, or ether: yield 87%; <sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>) δ 6.00 (10 H, Cp), 6.30 (1 H, m, *J* < 2 Hz, H<sub>a</sub>), 1.56, 1.53 (unresolved doublet, 6 H, =CMe<sub>2</sub>), 0.15 (3 H, T:Me); mass spectrum, *m/e* 3.06 (P<sup>+</sup>), 291 (P<sup>+</sup> - Me), 235 (Cp<sub>2</sub>ZrMe<sup>+</sup>), 221 (Cp<sub>2</sub>ZrH<sup>+</sup>), 220 (Cp<sub>2</sub>Zr<sup>+</sup>), 171 (Cp<sub>2</sub>ZrO<sup>+</sup>), 155 (CpZr<sup>+</sup>), 71 (OCHCMe<sub>2</sub><sup>+</sup>). Anal. Calcd for C<sub>15</sub>H<sub>20</sub>OZr: C, 58.44; H, 6.49; O, 5.20. Found: C, 58.13; H, 6.11; O, 4.92.

**Crystal Structure of Cp<sub>2</sub>Ti(OCHCMe<sub>2</sub>)<sub>2</sub>**. Crystals suitable for diffractometry were grown by allowing a concentrated solution in toluene to stand at -10 °C for several days. A suitable crystal was mounted on a Syntex P2<sub>1</sub> diffractometer, and the lattice parameters were determined by a least-squares refinement of 16 reflection settings obtained from the automatic centering routine.

Intensity data were obtained by using Mo Kα radiation monochromatized from a graphite crystal whose diffraction vector was perpendicular to the diffraction vector of the sample. Three standard reflections were measured every 50 reflections. The data were reduced by procedures previously described.<sup>14</sup> An absorption correction was not necessary.

The structure was solved by using MULTAN.<sup>14</sup> In the subsequent refinement the function Σω(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup> was minimized where |F<sub>o</sub>| and |F<sub>c</sub>| are the observed and calculated structure factor amplitudes. The agreement indices R<sub>1</sub> = Σ||F<sub>o</sub>| - |F<sub>c</sub>||/Σ|F<sub>o</sub>| and R<sub>2</sub> = [Σω(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup>/Σω|F<sub>o</sub>|<sup>2</sup>]<sup>1/2</sup> were used to evaluate the results. The atomic scattering factors are from ref 15.

Least-squares refinement results using anisotropic thermal parameters for all non-hydrogen atoms are shown in Table I.

(14) Computations were carried out on an Amdahl 5860 computer. Computer programs used during the structural analysis were from the SHELX program package by George Sheldrick, Institute für Anorganische Chemie der Universität Göttingen, Federal Republic of Germany. Other programs used include ORTEP, a thermal ellipsoidal drawing program by C. K. Johnson, PLUTO78, a structure plotting program by Sam Motherwell, and the direct methods program MULTAN78 by Peter Main.

(15) "International Tables for X-Ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Table 2.2 and Table 2.3.1.

Table V. Bond Angles (deg)<sup>a</sup>

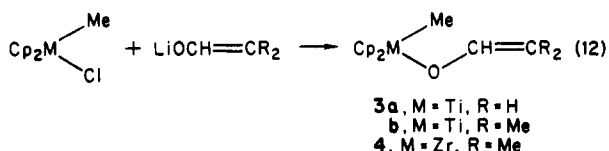
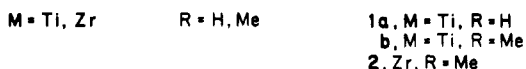
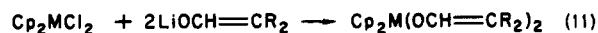
C5-Ti1-O2	99.0 (1)	C6-C5-Ti1	73.5 (2)
C6-Ti1-O2	131.5 (1)	C9-C5-Ti1	74.9 (2)
C6-Ti1-C5	33.8 (1)	C9-C5-C6	108.4 (4)
C7-Ti1-O2	126.0 (1)	C5-C6-Ti1	72.6 (2)
C7-Ti1-C5	56.1 (1)	C7-C6-Ti1	73.1 (2)
C7-Ti1-C6	34.0 (1)	C7-C6-C5	107.1 (4)
C8-Ti1-O2	92.3 (1)	C6-C7-Ti1	72.9 (2)
C8-Ti1-C5	55.4 (1)	C8-C7-Ti1	73.8 (2)
C8-Ti1-C6	55.9 (1)	C8-C7-C6	107.4 (4)
C8-Ti1-C7	33.7 (1)	C7-C8-Ti1	72.5 (2)
C9-Ti1-O2	77.7 (1)	C9-C8-Ti1	73.9 (2)
C9-Ti1-C5	33.3 (1)	C9-C8-C7	108.3 (4)
C9-Ti1-C6	55.6 (1)	C5-C9-Ti1	71.8 (2)
C9-Ti1-C7	55.4 (1)	C8-C9-Ti1	73.2 (2)
C9-Ti1-C8	32.8 (1)	C8-C9-C5	108.7 (4)
C3-O2-Ti1	145.5 (2)	O2-Ti-O2'	95.0 (1)
C4-C3-O2	128.4 (4)	Cp-Ti-Cp'	131.2 (1)

Positions of all cyclopentadienyl hydrogen atoms were calculated and added as fixed contributors. All other hydrogen atoms were refined with fixed temperature factors.

Final positional parameters with estimated standard deviations are shown in Table II. Anisotropic thermal parameters with their estimated standard deviations are listed in Table III. Table IV lists the crystallographically determined bond distances and angles.

## Results and Discussion

Group 4 enolate complexes are easily prepared in high yield by the simple metathetical reaction shown in eq 11 and 12. The titanium complexes 1 and 3 are red crys-



talline solids, readily soluble in most organic solvents. When pure, they are quite stable thermally (see below) and the solids may be handled in air for moderate periods. Attempts to prepare the Zr analogues of 1a and 3a gave yellow powders which once isolated would not redissolve in the solvents from which they were originally obtained. However, the methyl-substituted enolates 2 and 4 were readily obtained as yellow oils that are more susceptible to hydrolysis by atmospheric moisture than the solid Ti derivatives.

The NMR spectra of these complexes are all consistent with structures in which the oxygen binds to the metal center (structure A), and this mode of bonding is confirmed for 1a by a single-crystal structure determination (see below). The hydrogen attached to the α-carbon of the enolate resonates in the region δ 7.0–7.2 and shows the expected coupling to the hydrogens across the C=C double bond with *J*<sub>trans</sub> ≈ 14 Hz and *J*<sub>cis</sub> ≈ 6 Hz. In the complexes derived from the enolate of 2-methylpropionaldehyde (1b, 2, 3b, 4), four-bond coupling to the remote methyls is partially resolved (*J* < 2 Hz). The =CH<sub>2</sub> protons resonate in the δ 4.0 region with H<sub>c</sub> slightly upfield from H<sub>b</sub> (see Experimental Section).

In the <sup>13</sup>C NMR of 1a, C<sub>α</sub> resonates at δ 162 (*J* = 107 Hz) and C<sub>β</sub> at 87.9 (*J* = 73 Hz). The C-H coupling constants are appropriate for sp<sup>2</sup>-hybridized carbon, and the higher value for *J*<sub>C-H</sub> is consistent with localization of p character into the C-O bond and subsequently higher s character in the C<sub>α</sub>-H bond. C<sub>α</sub> in complex 1b resonates at δ 152 (*J* = 106 Hz).

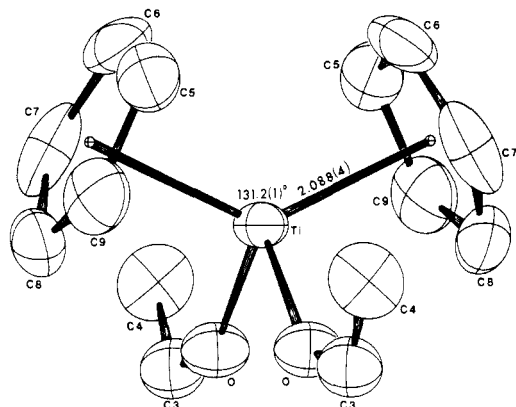
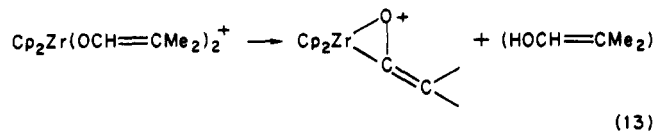


Figure 1. ORTEP plot of  $\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_3)_2$  (**1a**).

The IR spectra of the acetaldehyde enolates (**1a**, **3a**) show  $\nu_{\text{C}=\text{C}}$  absorptions at 1561 and 1568  $\text{cm}^{-1}$ , respectively. The methyl-substituted enolates display  $\nu_{\text{C}=\text{C}}$  stretches at somewhat higher frequencies ( $\sim 1625 \text{ cm}^{-1}$ ). In all the complexes,  $\nu_{\text{C}-\text{O}}$  occurs in the region 1170–1180  $\text{cm}^{-1}$ . The in-plane  $\text{CH}=\text{C}$  deformation occurs near 1290  $\text{cm}^{-1}$  in the complexes **1a** and **3a** but is found at 1245  $\text{cm}^{-1}$  in the methyl-substituted complexes. The in-plane  $=\text{CH}_2$  deformation occurs at 1362 and 1365  $\text{cm}^{-1}$  in **1a** and **3a**, respectively. This band is absent, of course, in the dimethyl-substituted enolate complexes. The Ti–O stretching frequency is tentatively assigned to a band at 450  $\text{cm}^{-1}$  in **3a** and to bands at 570 and 420  $\text{cm}^{-1}$  (asymmetrical and symmetrical stretches, respectively) in **1a**. Complex **1b** also exhibits a band at 570  $\text{cm}^{-1}$ , but the 420  $\text{cm}^{-1}$  region was obscured by absorption of the KBr disk. Ti–O stretching frequencies appear not to have been reported previously for  $\text{Cp}_2\text{Ti}(\text{OR})_2$  derivatives, but Zr–O stretching frequencies in  $\text{Cp}_2\text{Zr}(\text{OR})_2$  are reported to be in the range 570–420  $\text{cm}^{-1}$ .<sup>16</sup> The Ti–O–SiR<sub>3</sub> stretching mode lies in the 980–990  $\text{cm}^{-1}$  region.<sup>17,18</sup>

We were especially interested in determining whether or not the enolate complexes could be induced to undergo  $\beta$ -elimination according to eq 2 ( $\text{R} = \text{Me}$  or  $\text{OCHCR}'_2$ ). Except for an ill-defined polymerization of  $\text{Cp}_2\text{Zr}(\text{OC}_2\text{H}_3)_2$ , these enolate complexes appear to be thermally stable. Refluxing  $\text{Cp}_2\text{TiMe}(\text{OC}_2\text{H}_3)$  (**3a**) in benzene overnight gave only unreacted starting material. Furthermore, with the exception of  $\text{Cp}_2\text{Zr}(\text{OCHCMe}_2)_2$ , the mass spectra of the complexes studied here show no indication for the loss of MeH or aldehyde corresponding to the expected  $\beta$ -elimination of eq 2. The complex  $\text{Cp}_2\text{Zr}(\text{OCHCMe}_2)_2$  does show a weak peak at  $m/e$  290, presumably arising from the fragmentation shown in eq 13. However, the lack of ap-



preciable fragmentation via H abstraction in the mass spectrometer suggests that  $\beta$ -elimination according to eq 2 is not energetically feasible in these complexes. In fact, Moore et al.<sup>7</sup> have observed that Zr–ketene complexes add  $\text{H}_2$  to form the enolates (essentially the reverse of  $\beta$ -elimination, see eq 8).

**X-ray Crystal Structure.** Two views of the structure of  $\text{Cp}_2\text{iTi}(\text{OCH}=\text{CH}_2)_2$  are given in Figures 1 and 2. The

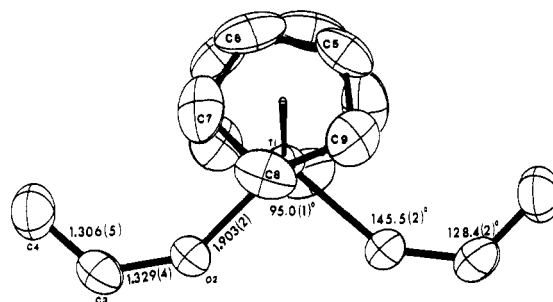
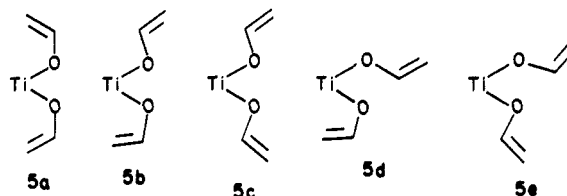


Figure 2. ORTEP view of **1a** showing the staggering of the Cp rings and the swept back position of the enolate groups.

molecule possesses imposed  $C_2$  symmetry in the solid state. The staggering of the Cp rings is similar to that found in  $\text{Cp}_2\text{TiCl}_2$  and is typical of the bent sandwich complexes without ring bridges.<sup>19</sup> All the structural parameters connected with the  $\text{Cp}_2\text{Ti}$  moiety are normal and will not be discussed further. The O–Ti–O angle of 95.0° is also within the usual range observed for  $\text{Cp}_2\text{TiX}_2$  structures.

The interesting part of this structure concerns the enolate ligands that are wrapped back toward the Ti atom. Steric considerations would suggest that the planar  $\text{OCH}=\text{CH}_2$  groups lie in the plane which bisects the Cp–Ti–Cp angle, but within this plane there are several conformations, e.g., **5a–e**, of the enolate groups that are



sterically acceptable. The observed conformation **5a** may result either from an electronic preference or from packing considerations in the solid. **5a** tends to make the molecule more spherical and would probably be favored from packing considerations. On the other hand, the electronic asymmetry in the p orbitals on oxygen, induced by in-plane asymmetry of the vinyl group, could lead to a maximization of p–d  $\pi$ -bonding in the observed conformer. The distance between the Ti and the C=C bond is too long for any direct interaction to be important.

The structural parameters are, in fact, consistent with some degree of multiple bonding between the oxygen atoms and the titanium. The Ti–O–C angle has opened up to 145.5 (2)° as compared to C–O–C angles that are normally in the neighborhood of 100–120°. The subject of oxygen to metal  $\pi$ -bonding has been discussed in detail by Huffman et al.,<sup>21</sup> who also find large Ti–O–C angles in cyclopentadienyltitanium alkoxides. For example,  $\text{Cp}_2\text{TiCl}(\text{OEt})$  and  $(\text{CpCl}_2\text{TiOCMe}_2)_2$  have Ti–O–C angles of 133.2 (2)° and 166.2 (2)°, respectively.<sup>21</sup> The very large increase in the angle observed in the latter compound may be due in part to steric congestion caused by the tertiary alkoxide, although this compound also has the shortest

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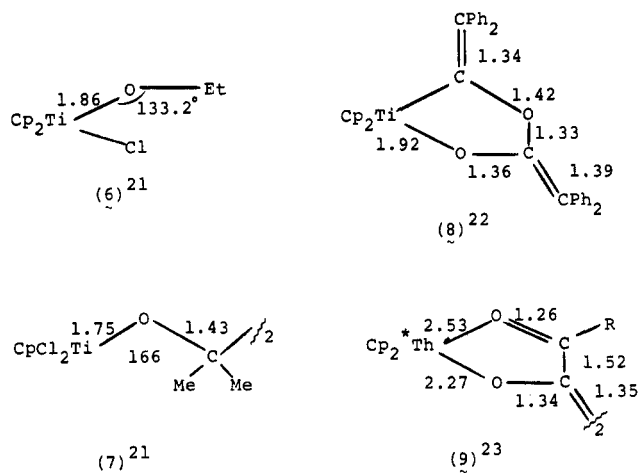
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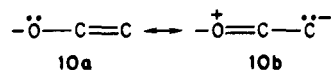
**Figure 3.** Comparison of structural parameters for structurally characterized enolate complexes. For 7 and 9, only one half of the centrosymmetric dimers are shown.

Ti-O bond and, hence, presumably the greatest Ti-O multiple-bond order.

Pertinent bond lengths of all the structurally characterized enolate structures of which we are aware are compared in Figure 3 (cf. Figure 2). The Ti-O bond length of 1.903 (2) Å in **1a** lies within the range, 1.75–1.92 Å, previously observed. As discussed in ref 21, the somewhat longer distance in **1a**, vis-à-vis,  $\text{Cp}_2\text{TiCl}(\text{OEt})$  (**6**) and  $(\text{CpCl}_2\text{TiOCMe}_2)_2$  (**7**) (1.855 (2) and 1.750 (2) Å) is caused by the distribution of  $\pi$ -bonding between two oxygen atoms in **1a** vs. being concentrated in one Ti-O bond in complexes **6** and **7**. In compound **8**, the Ti-O bond is even longer (1.92 Å), but the Ti is bonded to less electronegative groups and thus has a lower electron demand (less contracted d orbitals) than compounds **1a**, **6**, or **7**.

One particularly unusual feature in the structure of **1a** is the exceedingly short C=C bond length, 1.306 (5) Å. This bond is 0.03 Å shorter than an isolated C=C double bond and is 0.04–0.08 Å shorter than the C=C bond lengths in the other two enolate structures shown in Figure 3. Our structure solution showed no indication of abnormalities in the thermal parameters. Thus, we feel that the short C=C distance obtained for **1a** is real. Conju-

gation of the C=C double bond with an oxygen lone pair would be expected to increase the C=C and shorten the C-O bonds as shown by the resonance forms, **10a** and **10b**.



The C-O length, 1.329 (4) Å, is in the range for similar bonds in structures **8** and **9**, so that extensive conjugation of the C=C bond with oxygen is not indicated. A carbon attached to an oxygen will develop a positive charge due to electron withdrawal by oxygen in the  $\sigma$ -framework. This increased charge on carbon may then contract the carbon  $p_\pi$  orbital and cause a shortening of the C=C bond. At the same time,  $\pi$ -conjugation will work to increase the C=C length. Thus, it may well be impossible to cleanly rationalize the C=C distance in these complexes. Note that the complexes in Figure 3 display a range of substitution patterns and the C=C bond lengths vary from 1.31 to 1.39 Å.

**Conclusions.** Simple metal enolate complexes are readily prepared by the metathesis reaction of metal halides and enolate ions. The enolates of titanocene and zirconocene are oxygen bonded and display no tendency to form ketene complexes by  $\beta$ -elimination. Preliminary experiments involving  $\text{LiOC}_2\text{H}_3$  and  $\text{L}_2\text{NiCl}_2$ ,  $\text{L}_2\text{PtCl}_2$ , and  $\text{L}_2(\text{CO})\text{RhCl}$  (L = phosphine) suggest that the *initially* formed product is oxygen bonded, but these complexes rapidly precipitate insoluble powders in much the same way that  $\text{Cp}_2\text{Zr}(\text{OC}_2\text{H}_3)_2$  does. Increasing the substitution on the  $\beta$ -carbon may prevent this type of polymerization but is also expected to decrease the likelihood of M-C bonded enolates. Further work in this area is planned.

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**Registry No.** **1a**, 92220-58-1; **1b**, 92241-00-4; **2**, 92241-01-5; **3a**, 92241-02-6; **4**, 92241-03-7;  $\text{Cp}_2\text{TiCl}_2$ , 1271-19-8;  $\text{LiOC}_2\text{H}_3$ , 2180-63-4;  $\text{LiOCHMe}_2$ , 4111-45-9;  $\text{Cp}_2\text{TiClMe}$ , 1278-83-7;  $\text{Cp}_2\text{ZrCl}_2$ , 1291-32-3;  $\text{Cp}_2\text{ZrMeCl}$ , 1291-45-8.

**Supplementary Material Available:** Table III, thermal parameters, Table Vb, bond distances and angles involving hydrogen, and Table VI, listing of  $F_o$  and  $F_c$  (5 pages). Ordering information is given on any current masthead page.