CRYSTAL AND MOLECULAR STRUCTURE
OF \((\pi-C_6H_5)_2Ti(C_6H_4CO_2)\) — PRODUCT OF THE FIXATION
OF CARBON DIOXIDE BY A TRANSITION METAL COMPLEX

G. G. Aleksandrov and Yu. T. Struchkov

A complete investigation of the \((\pi-C_6H_5)_2Ti(C_6H_4CO_2)\) complex, obtained by reaction of \((\pi-C_6H_5)_2Ti(C_6H_5)_2\) with carbon dioxide, was carried out. The structure was interpreted by the
heavy-atom method and refined by the method of least squares within the isotropic approximation up to \(R=0.13\). It is shown that the CO\(_2\) molecule enters in the ortho position (with respect
to the C—Ti bond) of one of the phenyl rings of the starting complex in the form of a carboxylate
group formed by an intramolecular O—Ti bond with closing of the five-membered metallo cycle
and displacement of the second phenyl group. The metallo cycle is planar with Ti—O of 1.95 Å
and Ti—C of 2.20 Å. The \(\pi\)-cyclopentadienyl rings are not parallel (two-face angle 134°), and the
Ti—C distances (cyclopentadienyl) are the usual ones (2.39 Å).

INTRODUCTION

The problem of the reaction of carbon dioxide with transition metal complexes has become an extremely
timely and interesting one, at least in two respects: 1) in the hydrogenation of carbon dioxide, catalyzed by transi-
tion metal complexes, it is possible to obtain derivatives of formic acid, formaldehyde, and other organic deriv-
atives; 2) the carbon dioxide molecule can affect either the catalyst activity or its selectivity and stereospecificity.

The fact that carbon dioxide complexes with the transition metal will be formed in these catalytic reactions
is not excluded [1-4]. It was possible that one example of such complexes is product I, recently obtained by Vol'pin
and co-workers in the reaction of bis(\(\pi\)-cyclopentadienyl) diphenyltitanium with carbon dioxide [5]:

\[
(C_6H_5)_2TiPh_2 + CO_2 \xrightarrow{80-90°C} \text{xylene} (C_6H_5)_2Ti(Ph)(CO_2) + C_6H_6
\]

The red crystals of I are diamagnetic, stable to air, melt at 192-195°C, are soluble in acetone and alcohol,
and slightly soluble in benzene. In the IR spectrum, in addition to the usual absorption bands of the phenyl and
cyclopentadienyl groups, there are absorption bands at 880, 1130, 1280, 1620, and 1660 cm\(^{-1}\). The NMR spectrum
contains proton signals of the phenyl (6.5-7.58 ppm) and cyclopentadienyl rings (6.45 ppm) in the ratio 4:10.

In order to objectively establish the manner of coordination of the CO\(_2\) molecule with the transition metal
atom, we carried out a complete x-ray diffraction investigation of I.

EXPERIMENTAL

Crystals of I have the shape of elongated prisms and are rhombic. The elementary cell parameters were de-
termined with a DRON-1 diffractometer, * and the densities were measured by the method of hydrostatic suspension
in Thoulet's solution:

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Systemization of the extinctions unambiguously determines the Pbca space group.

Scannings of the hkl0-hkl7 layer lines with a total of ~ 800 independent reflections were obtained with a Weissenberg, equally inclined, x-ray diffractometer in unfiltered copper radiation. Transverse h0l -hkl scannings were used to reduce the intensities of the different layer lines to the general scale. In converting the intensities to structural factors, the Lorentz and polarization factors were taken into account, a correction for expansion and compression of the strains was introduced, and the absorption factor was disregarded (the crystal dimensions did not exceed 0.10x 0.15x 0.5 mm, and the crystal was elongated along the c-axis of rotation).

**Interpretation and Refinement of the Structure**

The coordinates of the Ti atom were found from the three-dimensional Patterson function, during which $x_{Ti} \approx \frac{1}{4}$ and $y_{Ti} \approx \frac{1}{2}$. This pseudo-special position of the heavy atom led to pseudoperiodicity ($b' = b/2$) and to the appearance of pseudoplanarity of the mirror image with $x = \frac{1}{4}$ in the first three-dimensional synthesis of the electron density calculated with signs determined from the coordinates of the titanium atom ($R = 0.60$). Splitting of the maxima with halving of their heights somewhat hindered interpretation of this series. However, we were able to localize ten carbon atoms of the two cyclopentadienyl residues which form a wedge-shaped sandwich at the titanium atom on the basis of literature data on the structure of the dicyclopentadienyl-titanium fragment. Consideration of these atoms lowered the $R$ factor to 0.46 and, by eliminating the pseudoplanarity of the symmetry in the second synthesis of the electron density, made it possible to localize in it another six light atoms which form the benzene ring. Finally, a third synthesis (signs with respect to Ti + 16 C, $R = 0.35$) exposed another three maxima which, according to crystallochemical considerations, corresponded satisfactorily to the $\text{O}_3\text{C}_3$ fragment. At this stage, $R = 0.28$ when $B_{tot} = 3.0 \text{Å}^2$. The null-differential synthesis (subtraction of all the previously localized atoms: Ti + 17 C + 2 O) did not contain maxima of appreciable height.

The structure was refined by the method of least squares within the completely matrix isotropic approximation with weights according to Cruickshank [6]. Additional geometrical conditions according to Waser [7] were considered in the initial stages of refining: the equality of the lengths of the chemically equivalent bonds was fixed (additional conditions were not imposed on the CO$_2$ fragment). The additional conditions were removed in the final stages of refining.

*The calculations were accomplished according to programs set up by B. L. Tamopol'skii, V. I. Andrianov, and Z. Sh. Safina (Institute of Chemical Physics, Academy of Sciences of the USSR).

**TABLE 1. Atomic Coordinates and Individual Temperature Factors**

<table>
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<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_p$, Å$^2$</th>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_p$, Å$^2$</th>
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<tr>
<td>Ti</td>
<td>0.2606 (2)</td>
<td>0.4786 (2)</td>
<td>0.3025 (3)</td>
<td>3.70 (5)</td>
<td>C (15)</td>
<td>0.384 (3)</td>
<td>0.571 (1)</td>
<td>0.471 (2)</td>
<td>4.5 (3)</td>
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<tr>
<td>O (1)</td>
<td>0.244 (1)</td>
<td>0.425 (1)</td>
<td>0.321 (1)</td>
<td>4.2 (2)</td>
<td>C (16)</td>
<td>0.263 (1)</td>
<td>0.624 (1)</td>
<td>0.476 (2)</td>
<td>4.9 (3)</td>
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<tr>
<td>O (2)</td>
<td>0.288 (1)</td>
<td>0.319 (1)</td>
<td>0.632 (1)</td>
<td>4.5 (3)</td>
<td>C (17)</td>
<td>0.272 (1)</td>
<td>0.641 (1)</td>
<td>0.374 (2)</td>
<td>3.8 (4)</td>
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<tr>
<td>C (1)</td>
<td>0.371 (1)</td>
<td>0.368 (1)</td>
<td>0.391 (1)</td>
<td>4.0 (3)</td>
<td>H (2)</td>
<td>0.453 (1)</td>
<td>0.366 (1)</td>
<td>0.246 (1)</td>
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</tr>
<tr>
<td>C (2)</td>
<td>0.434 (1)</td>
<td>0.334 (1)</td>
<td>0.317 (1)</td>
<td>4.4 (3)</td>
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<td>0.234 (1)</td>
<td>0.281 (1)</td>
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<tr>
<td>C (3)</td>
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<td>0.257 (1)</td>
<td>0.336 (1)</td>
<td>4.7 (3)</td>
<td>H (4)</td>
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<td>0.168 (1)</td>
<td>0.444 (1)</td>
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<tr>
<td>C (4)</td>
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<td>0.221 (1)</td>
<td>0.429 (1)</td>
<td>4.5 (3)</td>
<td>H (5)</td>
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<td>0.216 (1)</td>
<td>0.574 (1)</td>
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<tr>
<td>C (5)</td>
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<td>0.503 (1)</td>
<td>4.8 (3)</td>
<td>H (6)</td>
<td>0.227 (1)</td>
<td>0.489 (1)</td>
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<tr>
<td>C (6)</td>
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<td>0.320 (1)</td>
<td>0.478 (1)</td>
<td>4.9 (3)</td>
<td>H (9)</td>
<td>0.242 (1)</td>
<td>0.316 (1)</td>
<td>0.247 (1)</td>
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<td>C (7)</td>
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<td>0.355 (1)</td>
<td>0.550 (1)</td>
<td>4.6 (3)</td>
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<td>0.130 (1)</td>
<td>0.306 (1)</td>
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<tr>
<td>C (8)</td>
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<td>0.463 (1)</td>
<td>0.235 (1)</td>
<td>4.3 (3)</td>
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<td>0.468 (1)</td>
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<td>0.370 (1)</td>
<td>0.275 (1)</td>
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<td>H (12)</td>
<td>0.104 (1)</td>
<td>0.594 (1)</td>
<td>0.287 (1)</td>
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<tr>
<td>C (10)</td>
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<td>0.365 (1)</td>
<td>0.360 (1)</td>
<td>4.2 (3)</td>
<td>H (13)</td>
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<td>0.605 (1)</td>
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<tr>
<td>C (11)</td>
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<td>0.452 (1)</td>
<td>0.371 (1)</td>
<td>4.2 (3)</td>
<td>H (14)</td>
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<tr>
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<td>0.514 (1)</td>
<td>0.296 (1)</td>
<td>4.7 (3)</td>
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<td>0.547 (1)</td>
<td>0.332 (1)</td>
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<td>0.602 (1)</td>
<td>0.309 (1)</td>
<td>4.8 (3)</td>
<td>H (16)</td>
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<td>C (14)</td>
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<td>0.559 (1)</td>
<td>0.370 (2)</td>
<td>4.5 (3)</td>
<td>H (17)</td>
<td>0.213 (1)</td>
<td>0.677 (1)</td>
<td>0.351 (1)</td>
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</tr>
</tbody>
</table>

†The number of H atoms coincides with the number of C atoms bonded to them.