Crystal and Molecular Structure of $(C_5H_5)_2Ti(C_6H_5)_2$

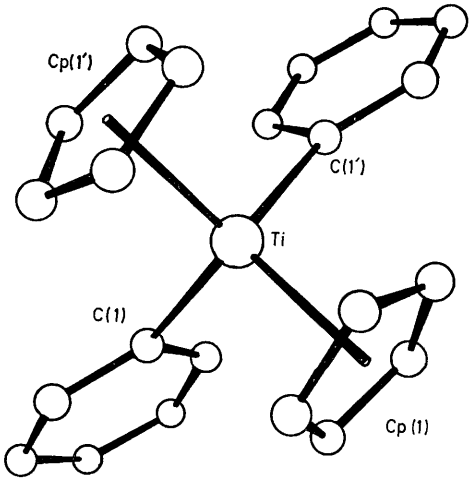
By V. KOCMAN* and J. C. RUCKLIDGE
(*Department of Geology, University of Toronto, Toronto* 181, *Canada*)
and R. J. O'BRIEN and W. SANTO
(*Department of Chemistry, University of Toronto, Toronto* 181, *Canada*)

Summary The two cyclopentadienyls in $(C_5H_5)_2Ti(C_6H_5)_2$ are π-bonded to titanium with a mean Ti–C distance of 2·31 (5) Å and the two phenyls are σ-bonded with Ti–C distance of 2·27 (1) Å.

$(C_5H_5)_2Ti(C_6H_5)_2$ WAS made according to the method of Summers and Uloth.[1] The crystals were grown from a toluene–heptane solution at −5° yielding yellow-orange, diamond shaped tabular plates which slowly decomposed under *X*-rays. The crystals are orthorhombic and systematic absences indicate two possible space groups *Cmca* and *C2cb*. The unit cell dimensions are as follows: $a = 12{\cdot}854$ (8), $b = 16{\cdot}480$ (8), $c = 8{\cdot}132$ (5) Å, $V = 1722{\cdot}6$ Å,[3] $D_m = 1{\cdot}27$ g cm^{-3}, $D_c = 1{\cdot}28$ g cm^{-3} (for $Z = 4$), μ (Cu-K_α) = 42·0 cm^{-1}, space group *C2cb* from structure analysis.

Cu-K_α data were collected on a Picker four circle automated diffractometer, scaled using standard reflections and corrected for absorption.[2] The structure was solved by the heavy-atom method and refined by full-matrix anisotropic least-squares analysis to a conventional *R* value of 0·084 for 554 observed reflections.

The molecular geometry when viewed down the two-fold axis is shown in the Figure. The two staggered cyclopentadienyl rings are π-bonded to titanium with an average Ti–C distance of 2·31 Å. Their planes are tilted at an angle of 44° which is approximately 14° smaller than the angle reported for $(C_5H_5)_2TiCl_2$ (58·5),[3] but of the same magnitude as in 1,2-dimethylallyltitanocene (48·1°).[4] The C–C bond lengths in the cyclopentadienyl rings vary from 1·28 (5) to 1·42 (5) Å with an average C–C length of 1·34 Å. This variation in C–C bond distances is similar to that found in 1,2-dimethylallyltitanocene and may be the result of librational motion or partial disorder of the ring carbons. The two phenyl rings are σ-bonded to titanium with an average Ti–C distance of 2·272 (14) Å which is similar to the Ti–C distance of the σ-cyclopentadienyl of tetracyclopentadienyltitanium [2·32 (2) Å].[5] The C–C distances of the phenyl ring varied from 1·345 (31) to 1·420 (32) Å with an average bond length of 1·390 (28) Å.



SCHEME

The arrangement of the four ligands about titanium is pseudo-tetrahedral with a C (1)–Ti–C (1′) bond angle of 97·3° (1·1) C (1)–Ti–Cp (1) (Cp = Cyclopentadienyl) (centre) angle of 102·1° and C (1)–Ti–Cp (1) (centre) angle of 106·6°.

We thank the National Research Council of Canada for financial support and for a Scholarship (to W.S.).

(*Received, July* 1*st,* 1971; *Com.* 1102.)

[1] L. Summers and R. H. Uloth, *J. Amer. Chem. Soc.*, 1954, **76**, 2278.
[2] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.
[3] N. V. Alekseev and I. A. Ronova, *J. Struct. Chem.*, 1966, **91**.
[4] R. B. Helmholdt, F. Jellinek, H. A. Martin, and A. Vos, *Rec. Trav. chim.*, 1967, **86**, 1263.
[5] J. L. Calderon, F. A. Cotton, B. G. Deboer, and J. Takats, *J. Amer. Chem. Soc.*, 1970, 3801.