

tion from structure 2. The peak at  $995\text{ cm}^{-1}$  is probably the S—O(2) stretch. This frequency is consistent with the bond length of  $1.49\text{ \AA}$  and appears to be the same as that found previously at  $1010\text{ cm}^{-1}$ , which was assigned as a C—F vibration.<sup>1</sup> If the C—H vibrations are ignored, then there should be  $3n - 6 = 6$  vibrations. The C—O stretch was not observed, but it may well be weak. The three bending vibrations are expected to have lower frequencies and it is difficult to make any certain assignments because of the large number of  $\text{Sb}_2\text{F}_{11}^-$  bands.

**Supplementary Material Available:** a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

## References and Notes

- G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Am. Chem. Soc.*, **91**, 2112 (1969).
- J. Bacon and R. J. Gillespie, *J. Am. Chem. Soc.*, **93**, 6914 (1971).
- P. E. Peterson, R. Brockington, and D. W. Vidrine, *J. Am. Chem. Soc.*, **98**, 2660 (1976).
- G. A. Olah, D. J. Donovan, and H. C. Lin, *J. Am. Chem. Soc.*, **98**, 2661 (1976).
- "International Tables for X-Ray Crystallography", Kynoch Press, Birmingham, Vol. I, 1965; Vol. IV, 1975.
- See the paragraph concerning the availability of supplementary material at the end of the paper.
- G. F. Crable and W. V. Smith, *J. Chem. Phys.*, **19**, 502 (1951).
- F. C. Milhoff and I. Hargittai, *J. Mol. Struct.*, **16**, 69 (1973).
- C. Lau, H. Lynton, J. Passmore, and P.-Y. Siew, *J. Chem. Soc., Dalton Trans.*, 2535 (1973).
- R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **41**, 2074 (1963).
- W. H. Kirchoff and E. B. Wilson, *J. Am. Chem. Soc.*, **91**, 7260 (1969).
- "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, 1965.
- J. W. Moore, H. W. Baird, and H. B. Miller, *J. Am. Chem. Soc.*, **90**, 1359 (1968).
- R. J. Gillespie, "Molecular Geometry", Van Nostrand-Reinhold, London, 1972.
- A. J. Edwards and R. J. C. Sills, *J. Chem. Soc., Dalton Trans.*, 1726 (1974).
- R. N. Wiener and E. R. Nixon, *J. Chem. Phys.*, **25**, 175 (1956).
- D. M. Byler and D. F. Shriver, *Inorg. Chem.*, **15**, 32 (1976).

# Chemistry of $\mu-(\eta^1:\eta^5\text{-Cyclopentadienyl})\text{-tris}(\eta\text{-cyclopentadienyl})\text{ditanium}(\text{Ti-Ti})$ . 1. Synthesis and Structural Studies

Guido P. Pez

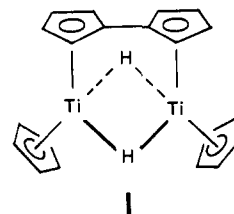
Contribution from the Chemical Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960. Received May 5, 1976

**Abstract:** The preparation of  $\mu-(\eta^1:\eta^5\text{-cyclopentadienyl})\text{-tris}(\eta\text{-cyclopentadienyl})\text{ditanium}(\text{Ti-Ti})$ ,  $(\eta\text{-C}_5\text{H}_5)_2\overline{\text{Ti}}-\mu-(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{-Ti}(\eta\text{-C}_5\text{H}_5)$ , by the low-temperature reduction of  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  with potassium naphthalene is described. Treatment of the compound with tetrahydrofuran ( $\text{C}_4\text{H}_8\text{O}$ ) leads to the formation of the crystalline adduct:  $(\eta\text{-C}_5\text{H}_5)_2\overline{\text{Ti}}-\mu-(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{-Ti}(\eta\text{-C}_5\text{H}_5)(\text{C}_4\text{H}_8\text{O})\text{-C}_4\text{H}_8\text{O}$ . The structure of this material has been determined by single-crystal x-ray diffraction methods. The molecule may be considered as two bis( $\eta\text{-cyclopentadienyl}$ )titanium units, held together by a metal-metal linkage. One of the cyclopentadienyl ligands, however, contains only four hydrogen atoms and serves to bridge the two titanium centers, in a monohapto pentahapto bonding arrangement. The Ti—Ti distance is  $3.336(4)\text{ \AA}$ . The most significant structural feature of the molecule is the high degree of coordinative unsaturation about the metal-metal bond. The tetrahydrofuran may readily be removed from the adduct by treatment with *n*-octane under vacuum to yield very pure samples of  $(\eta\text{-C}_5\text{H}_5)_2\overline{\text{Ti}}-\mu-(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{-Ti}(\eta\text{-C}_5\text{H}_5)$ . Infrared spectra of the two titanium compounds are consistent with their molecular structure, but give no indication of the unusual  $\mu-(\eta^1:\eta^5\text{-C}_5\text{H}_4)$  bonding arrangement. The 100-MHz  $^1\text{H}$  NMR spectrum of  $(\eta\text{-C}_5\text{H}_5)_2\overline{\text{Ti}}-\mu-(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{-Ti}(\eta\text{-C}_5\text{H}_5)$  in toluene consists of a single temperature-dependent broad resonance which at  $32\text{ }^\circ\text{C}$  appears at  $\delta_{\text{Me}_4\text{Si}}$  15.0 and is typical of a paramagnetic species.

The discovery of ferrocene,<sup>1</sup>  $(\eta\text{-C}_5\text{H}_5)_2\text{Fe}$ , in 1951 was quickly followed by attempts to prepare so-called metallocenes of the other transition metals. Dicyclopentadienyl compounds of V, Cr, Mn, Co, Ni in the first transition series and of Ru, Rh, Os, and Ir in the group 8 family of elements are now well known.<sup>2</sup> It has only recently been recognized, however, that simple  $(\eta\text{-C}_5\text{H}_5)_2\text{M}$  compounds of the earlier transition metals and of the lanthanide and actinide elements are not readily obtainable. Attempts to prepare such metallocenes invariably lead to complex organometallic molecules. For instance, a material commonly referred to as "niobocene" has proved to be the bridging bis( $\eta^1:\eta^5\text{-cyclopentadienyl}$ )-bis( $\eta\text{-cyclopentadienyl}$ )niobium hydride dimer:  $(\eta\text{-C}_5\text{H}_5)\text{HNb}-\mu-(\eta^1:\eta^5\text{-C}_5\text{H}_4)_2\text{-NbH}(\eta\text{-C}_5\text{H}_5)$ .<sup>3</sup> The same bridging cyclopentadienyl feature is seen in the thorium compound:  $(\eta\text{-C}_5\text{H}_5)_2\text{Th}-\mu-(\eta^1:\eta^5\text{-C}_5\text{H}_4)_2\text{-Th}(\eta\text{-C}_5\text{H}_5)_2$ .<sup>4</sup>

Many attempts have been made to synthesize discrete dicyclopentadienyltitanium(II) species. These efforts have recently been stimulated by the discovery that cyclopentadienyl compounds of low-valent titanium are able to reduce molecular

nitrogen. Titanocene,  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$  or  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}]_2$ , has been said to result from reaction of  $\text{TiCl}_2$  with cyclopentadienylsodium,<sup>5</sup> from the hydrogenolysis of  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$ ,<sup>6</sup> and from reaction of  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  with various reducing agents.<sup>7-9</sup> The main product in these syntheses is now known<sup>10,11</sup> to be  $\mu-(\eta^5:\eta^5\text{-fulvalene})\text{-di-}\mu\text{-hydrido-bis}(\eta\text{-cyclopentadienyltitanium})$  (I).



The synthesis of a "metastable titanocene",  $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2$  (II), that is active towards  $\text{N}_2$  was reported by Brintzinger and co-workers in 1971.<sup>12,13</sup> It was obtained by the decomposition of a dicyclopentadienyltitanium hydride,  $[(\text{C}_5\text{H}_5)_2\text{TiH}]_n$ .

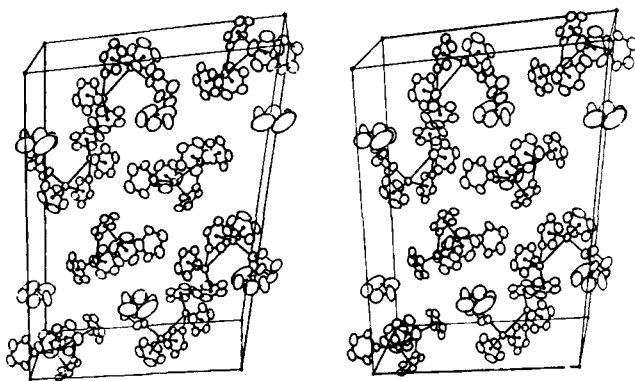
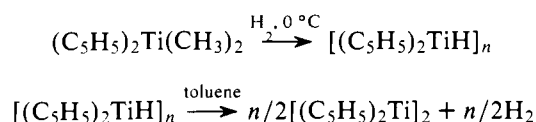


Figure 1. Stereoscopic view of crystal structure of  $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O) \cdot C_4H_8O$  (IV).



Unfortunately, however, the elemental composition and structure of this material as a dicyclopentadienyltitanium dimer were not adequately established. The synthesis of a "highly unstable" "titanocene",  $[(C_5H_5)_2Ti]_{1-2}$ , also capable of absorbing  $N_2$ , was subsequently announced by Van Tamelen et al.<sup>14</sup> Alt and Rausch have very recently reported the isolation of a "black titanocene",  $(C_5H_5)_2Ti$ , from the photolysis of  $(C_5H_5)_2Ti(CH_3)_2$ .<sup>15</sup> The relationship between these various "titanocenes" is not at all clear; no definitive proof has been presented for the existence of a bis( $\eta$ -cyclopentadienyl)titanium(II) unit in any of these materials.

We have sought to prepare stable low-valent titanium dicyclopentadienyl compounds for possible use as catalysts in chemical reactions involving nitrogen, hydrogen, and olefins. In this paper we report on the synthesis of two well-characterized metallocenes of divalent titanium, namely,  $\mu$ -( $\eta^1$ : $\eta^5$ -cyclopentadienyl)-tris( $\eta$ -cyclopentadienyl)dittitanium-(Ti-Ti), ( $\eta$ - $C_5H_5$ )<sub>2</sub>Ti- $\mu$ -( $\eta^1$ : $\eta^5$ - $C_5H_4$ )-Ti( $\eta$ - $C_5H_5$ ) (III) and its bis(tetrahydrofuran) adduct, ( $\eta$ - $C_5H_5$ )<sub>2</sub>Ti- $\mu$ -( $\eta^1$ : $\eta^5$ - $C_5H_4$ )-Ti( $\eta$ - $C_5H_5$ )( $C_4H_8O$ )· $C_4H_8O$  (IV). Chemical and catalytic properties of III and IV will be discussed in part 2 of this series.<sup>16</sup>

## Results and Discussion

**Preparation of ( $\eta$ - $C_5H_5$ )<sub>2</sub>Ti- $\mu$ -( $\eta^1$ : $\eta^5$ - $C_5H_4$ )-Ti( $\mu$ - $C_5H_5$ ) (III), and ( $\eta$ - $C_5H_5$ )<sub>2</sub>Ti- $\mu$ -( $\eta^1$ : $\eta^5$ - $C_5H_4$ )-Ti( $\eta$ - $C_5H_5$ )( $C_4H_8O$ )· $C_4H_8O$  (IV).** As noted earlier, reduction of ( $\eta$ - $C_5H_5$ )<sub>2</sub>TiCl<sub>2</sub> with sodium naphthalene<sup>7</sup> or with sodium sand at near ambient temperatures<sup>8</sup> yields mainly the fulvalene-bridged cyclopentadienyltitanium hydride I. We felt that this relatively inert substance arises from the decomposition of a highly unsaturated and reactive ( $\eta$ - $C_5H_5$ )<sub>2</sub>Ti moiety, which could perhaps be isolated by performing the reduction of ( $\eta$ - $C_5H_5$ )<sub>2</sub>TiCl<sub>2</sub> at low temperatures. We found that a very reactive metallocene,<sup>17</sup> subsequently characterized as III, could be prepared from the reaction of dicyclopentadienyltitanium dichloride with a solution of potassium naphthalene<sup>18</sup> in tetrahydrofuran at  $-80^\circ C$ . Slow warming of the reaction mixture to room temperature followed by removal of solvent and naphthalene and extraction with toluene yields  $(C_5H_5)_3(C_5H_4)Ti_2$  (III) as a black microcrystalline powder. The reaction product usually contains some 5–10% of the hydride I, and may be purified to some extent by extracting it with toluene at  $-80^\circ C$ . Very pure samples of the compound have been obtained by decomposing the bis(tetrahydrofuran) adduct IV (see below). We have not yet been able to prepare single crystals of III.

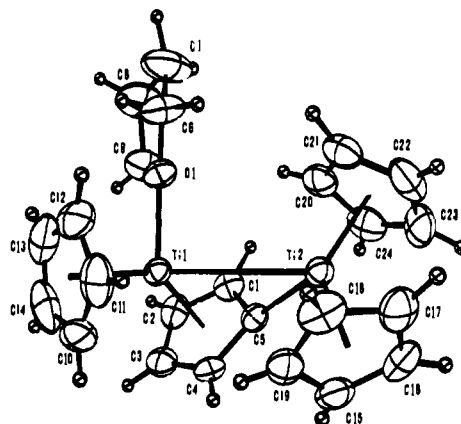


Figure 2. Molecular structure of  $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O) \cdot C_4H_8O$  (IV).

Solid  $(C_5H_5)_3(C_5H_4)Ti_2$  (III) is stable for at least several weeks when kept at room temperature under argon. Dark green solutions of III in benzene decompose to the extent of  $\sim 5\%$  over 13 days at  $23^\circ C$ . Green solutions of III in tetrahydrofuran (THF) slowly turn brown, giving over a period of several days oily brown residues, which have none of the chemical reactivity of the original material. We found, however, that by slowly evaporating THF solutions of III a crystalline bis(tetrahydrofuran) adduct  $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O) \cdot C_4H_8O$  (IV) can be isolated. The brown decomposition product remains in the mother liquor. Well-formed crystals of IV suitable for x-ray crystallography were grown by the slow diffusion of isopentane into saturated solutions of III in THF at  $5^\circ C$ .

Compound IV was characterized by elemental analyses and by single-crystal x-ray crystallography. The gross composition of III was determined from elemental microanalyses and molecular weight measurements. Its precise composition as  $(C_5H_5)_3(C_5H_4)Ti_2$  (rather than  $[(C_5H_5)_2Ti]_2$  as might be expected) has been inferred by its synthesis from crystalline  $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O) \cdot C_4H_8O$  (IV).

**Crystal and Molecular Structure of ( $\eta$ - $C_5H_5$ )<sub>2</sub>Ti- $\mu$ -( $\eta^1$ : $\eta^5$ - $C_5H_4$ )-Ti( $\eta$ - $C_5H_5$ )( $C_4H_8O$ )· $C_4H_8O$  (IV).**<sup>19</sup> The title compound is obtained from tetrahydrofuran as moderately air sensitive, brown-black prisms. The crystals were found to be monoclinic, space group  $I2/a$ , and containing eight molecules of  $Ti_2O_2C_{28}H_{35}$  per unit cell.

The crystal arrangement and molecular structure of IV are shown in Figures 1 and 2, respectively. Molecular bond distances, bond angles, and related data are presented in Tables I–III, respectively. The molecule is seen to consist of an assembly of three planar  $\eta^5$ -bound  $C_5H_5$ , cyclopentadienyl rings and one  $\eta^1$  and  $\eta^5$  bound, planar,  $C_5H_4$ , cyclopentadienyl ligand that serves to bridge the two titanium atoms. A molecule of THF is attached to the formally divalent titanium atom by coordination through oxygen. The second THF occupies a diffuse position in the crystal lattice. The arrangement of cyclopentadienyl ligands about the metal–metal bond is similar to that found in  $(\eta$ - $C_5H_5$ )(CO)M $\bar{O}$ - $\mu$ -( $\eta^5$ : $\eta^1$ - $C_5H_4$ )- $\bar{M}n(CO)_4$ .<sup>20</sup>

The molecular structure of IV contains several novel and chemically significant features. It appears to be the first example of a material which contains a bis( $\eta$ -cyclopentadienyl)titanium(II) unit, without the presence of accompanying  $\pi$ -acid ligands (as in  $(\eta$ - $C_5H_5$ )<sub>2</sub>Ti(CO)<sub>2</sub><sup>27</sup> and  $(C_5H_5)_2Ti(2,2'$ -bpy)).<sup>20b</sup> This  $(C_5H_5)_2Ti$  component is stabilized in the structure, by coordination with one molecule of THF and by a metal–metal linkage. The observed Ti–Ti bond distance of 3.336 (4) Å in IV may be compared with the value of 3.110 (7) Å in  $[(C_5H_5)(C_5H_4)TiHAl(C_2H_5)_2]_2$ ,<sup>21</sup> the corresponding value of 2.8956 Å in titanium metal ( $\alpha$ -form),<sup>22</sup> and with the

**Table I.** Table of Bond Distances (Å) for  $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O) \cdot C_4H_8O$  (IV)

Ti1-Ti2	3.336 (4)	Ti2-C5	2.19 (2)
Ti1-O1	2.26 (1)	Ti2-C15	2.39 (2)
Ti1-C1	2.34 (2)	Ti2-C16	2.40 (2)
Ti1-C2	2.37 (2)	Ti2-C17	2.41 (2)
Ti1-C3	2.37 (2)	Ti2-C18	2.39 (2)
Ti1-C4	2.32 (2)	Ti2-C19	2.38 (2)
Ti1-C5	2.32 (2)	Ti2-C20	2.37 (2)
Ti1-C10	2.38 (2)	Ti2-C21	2.39 (2)
Ti1-C11	2.38 (2)	Ti2-C22	2.42 (2)
Ti1-C12	2.37 (2)	Ti2-C23	2.40 (2)
Ti1-C13	2.40 (2)	Ti2-C24	2.39 (2)
Ti1-C14	2.39 (2)	C1-C2	1.41 (2)
O1-C6	1.46 (2)	C2-C3	1.39 (3)
O1-C9	1.45 (2)	C3-C4	1.41 (2)
C6-C7	1.48 (4)	C4-C5	1.44 (2)
C7-C8	1.46 (4)	C5-C1	1.43 (2)
C8-C9	1.47 (3)	C15-C16	1.39 (3)
C10-C11	1.36 (3)	C16-C17	1.41 (3)
C11-C12	1.36 (3)	C17-C18	1.39 (3)
C12-C13	1.34 (3)	C18-C19	1.40 (3)
C13-C14	1.37 (3)	C19-C15	1.37 (3)
C14-C10	1.39 (3)	O2-C25	1.35 (3)
C20-C21	1.40 (3)	C25-C26	1.39 (5)
C21-C22	1.39 (3)	C26-C26'	1.65 (9)
C22-C23	1.39 (3)		
C23-C24	1.40 (3)		
C24-C20	1.40 (3)	C11-H11	0.79 (18)
C1-H1	1.10 (19)	C12-H12	0.88 (20)
C2-H2	0.84 (18)	C13-H13	0.81 (19)
C3-H3	0.92 (17)	C14-H14	0.85 (18)
C4-H4	0.87 (17)	C15-H15	0.75 (17)
C6-H6,1	0.96 (19)	C16-H16	1.00 (18)
C6-H6,2	0.92 (18)	C17-H17	0.91 (18)
C7-H7,1	1.36 (21)	C18-H18	0.77 (19)
C7-H7,2	1.05 (20)	C19-H19	0.84 (17)
H8-H8,1	1.03 (19)	C20-H20	0.94 (17)
C8-H8,2	1.04 (18)	C21-H21	1.05 (18)
C9-H9,1	0.77 (18)	C22-H22	0.93 (18)
C9-H9,2	0.85 (18)	C23-H23	0.94 (18)
C10-H10	0.83 (18)	C24-H24	0.96 (18)

3.943 (2) Å Ti-Ti distance recently determined for  $[(\eta^5-C_5H_5)_2TiCl]_2$ .<sup>23</sup> In the latter there is an antiferromagnetic interaction<sup>24</sup> between the two titanium atoms, but the Ti-Ti distance is perhaps too long to be described as a metal-metal bond. In our compound, the much shorter Ti-Ti distance and the observed rigid conformation of the cyclopentadienyl rings strongly imply that there exists at least a two-electron titanium-titanium linkage. The mean distance between titanium and carbon atoms of the  $(\eta^5-C_5H_5)$  rings is 2.389 (20) Å. This value is normal for titanium metallocenes as seen for example in  $(C_5H_5)Ti(C_7H_7)$ ,<sup>25</sup>  $(C_5H_5)Ti(C_8H_8)$ ,<sup>26</sup> and  $(C_5H_5)_2Ti(CO)_2$ <sup>27</sup> which have mean reported Ti-C cyclopentadienyl distances of 2.321, 2.353, and 2.347 (9) Å, respectively. The 2.19 (2) Å separating Ti2 and the C5 carbon atom of the  $C_5H_4$  ligand is significantly less than the mean 2.389 (20) Å titanium cyclopentadienyl carbon distance and clearly shows that there is a localized  $\sigma$ -bond between the two atoms. This unusual bond is only slightly longer than the 2.13 (3) Å, partially conjugated, Ti-C linkage in tetrabenzyltitanium.<sup>28</sup> The bridging  $(\eta^1:\eta^5-C_5H_4)$  ligand is essentially planar and there is no sign of strain in the metal-carbon bonds as is seen in the Mo-Mn dimer<sup>20a</sup> cited earlier.

The molecule  $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O) \cdot C_4H_8O$  contains one hydrogen atom less than might be expected for a product obtained by the reduction of  $(C_5H_5)_2TiCl_2$  with 2 mol of potassium naphthalene. We could find no crystallographic evidence for the presence in the structure of a hydride atom attached either on titanium or onto the  $C_5$  atom of the  $C_5H_4$  li-

**Table II.** Table of Bond Angles for  $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O) \cdot C_4H_8O$  (IV) in Degrees

Ti1-Ti2-C5	43.8 (4)	C14-C10-C11	106.7 (20)
Ti2-Ti1-C5	40.9 (4)	C10-C11-C12	109.0 (21)
Ti2-Ti1-O1	96.1 (3)	C11-C12-C13	108.3 (22)
Ti1-O1-C6	125.4 (11)	C12-C13-C14	108.5 (21)
Ti1-O1-C9	124.5 (11)	C13-C14-C10	107.4 (21)
Ti1-C5-Ti2	95.3 (6)	C19-C15-C16	108.5 (17)
Ti2-C5-C1	125.6 (12)	C15-C16-C17	107.8 (18)
Ti2-C5-C4	124.2 (13)	C16-C17-C18	107.5 (18)
C6-O1-C9	108.2 (14)	C17-C18-C19	107.5 (17)
O1-C6-C7	105.1 (19)	C18-C19-C15	108.7 (17)
C6-C7-C8	106.3 (22)	C24-C20-C21	107.8 (19)
C7-C8-C9	105.7 (20)	C20-C21-C22	108.0 (19)
C8-C9-O1	107.7 (18)	C21-C22-C23	108.1 (20)
C5-C1-C2	110.9 (17)	C22-C23-C24	108.6 (19)
C1-C2-C3	107.9 (16)	C23-C24-C20	107.4 (19)
C2-C3-C4	107.6 (17)	C25-O2-C25'	114.4 (41)
C3-C4-C5	110.7 (16)	O2-C25-C26	109.7 (34)
C4-C5-C1	102.9 (14)	C25-C26-C26'	102.6 (24)
C2-C1-H1	127 (8)	C14-C10-H10	124 (14)
C5-C1-H1	122 (8)	C11-C10-H10	128 (14)
C1-C2-H2	133 (14)	C10-C11-H11	129 (15)
C3-C2-H2	119 (13)	C12-C11-H11	121 (16)
C2-C3-H3	124 (12)	C11-C12-H12	128 (12)
C4-C3-H3	128 (12)	C13-C12-H12	124 (12)
C3-C4-H4	127 (12)	C12-C13-H13	124 (15)
C5-C4-H4	122 (12)	C14-C13-H13	127 (15)
O1-C6-H6,1	112 (11)	C13-C14-H14	125 (14)
O1-C6-H6,2	108 (13)	C10-C14-H14	127 (14)
C7-C6-H6,1	114 (11)	C19-C15-H15	119 (17)
C7-C6-H6,2	106 (13)	C16-C15-H15	132 (17)
H6,1-C6-H6,2	111 (17)	C15-C16-H16	130 (10)
C6-C7-H7,1	68 (28)	C17-C16-H16	122 (10)
C6-C7-H7,2	127 (11)	C16-C17-H17	127 (12)
C8-C7-H7,1	134 (27)	C18-C17-H17	126 (12)
C8-C7-H7,2	111 (9)	C17-C18-H18	122 (15)
H7,1-C7-H7,2	106 (28)	C19-C18-H18	129 (16)
C7-C8-H8,1	127 (11)	C18-C19-H19	125 (14)
C7-C8-H8,2	104 (10)	C15-C19-H19	126 (14)
C9-C8-H8,1	106 (11)	C24-C20-H20	123 (11)
C9-C8-H8,2	123 (11)	C21-C20-H20	129 (11)
H8,1-C8-H8,2	93 (14)	C20-C21-H21	122 (10)
C8-C9-H9,1	111 (17)	C22-C21-H21	130 (10)
C8-C9-H9,2	119 (13)	C21-C22-H22	122 (11)
O1-C9-H9,1	108 (17)	C23-C22-H22	130 (11)
O1-C9-H9,2	114 (14)	C22-C23-H23	121 (11)
H9,1-C9-H9,2	95 (20)	C24-C23-H23	130 (11)
		C23-C24-H24	129 (11)
		C20-C24-H24	123 (11)

gand. When a hydrogen atom was placed at several calculated positions near  $C_5$ , the structure could not be refined. Also no hydrogen atom was found in a final difference Fourier map. Hydride atoms are visible in the x-ray structure of "niobocene" cited earlier. It is possible that a hydride atom might be located in a linear arrangement between the two metal atoms, as it is, for example, in  $Cr_2H(CO)_{10}$ ,<sup>29</sup> where the metal-metal separation is 3.41 (1) Å. However, the infrared spectra and the chemical reactivity<sup>16</sup> of IV with HCl and  $CH_3I$  are consistent with the x-ray structure and seem to exclude the possibility that there exists a metal hydride function in the molecule.

Perhaps the most striking feature of the molecule is the large degree of openness or structural unsaturation that is seen in the region bounded by atoms O1, Ti1, C11, C18, Ti2, C20 (see Figure 2). This openness results from the effect of bridging only one side of the Ti-Ti linkage with a  $(\eta^1:\eta^5-C_5H_4)$  ligand. We feel that the presence of the exposed metal-metal bond and the high degree of electron unsaturation (EAN = 31) account for the unusual reactivity of the molecule with  $N_2$ ,  $H_2$ , and olefins.<sup>16</sup>

Table III. Weighted Least-Squares Planes for  $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O) \cdot C_4H_8O$ 

Plane	Atoms in plane	Equation of plane
I	O1,C6,C7,C8,C9	$0.372x + 0.724y - 0.581z = -2.125$
II	C1,C2,C3,C4,C5	$-0.388x + 0.563y - 0.730z = -2.181$
III	C1,C2,C3,C4	$-0.399x + 0.562y - 0.725z = -2.145$
IV	C10,C11,C12,C13,C14	$0.145x + 0.911y - 0.385z = -2.510$
V	C15,C16,C17,C18,C19	$0.166x - 0.687y - 0.707z = -3.721$
VI	C20,C21,C22,C23,C24	$-0.497x - 0.804y - 0.327z = -8.169$

		Distances of Atoms from Plane ( $\text{\AA}$ )					
		Plane I	Plane II	Plane III	Plane IV	Plane V	Plane VI
O1	0.04	C1	0.01	C1	0.00	C10	0.00
C6	-0.14	C2	-0.01	C2	0.00	C11	-0.01
C7	0.18	C3	0.00	C3	0.00	C12	0.01
C8	-0.11	C4	0.01	C4	0.00	C13	-0.01
C9	0.01	C5	-0.01	C5	-0.03	C14	0.00
Ti1	-0.16	Ti2	-0.96	Ti2	-1.00	Ti1	2.08
						Ti2	-2.08
						Ti2	2.08

**Composition and Structure of  $(C_5H_5)_3(C_5H_4)Ti_2$  (III).** The gray-black material III, prepared by reduction of  $(C_5H_5)_2TiCl_2$ , gives elemental microanalyses that are in good agreement with the composition  $C_{20}H_{19}Ti_2$ . However, the definitive characterization of III depends upon its relation to the bis(tetrahydrofuran) adduct of known structure IV. Solutions of IV in *n*-octane on evaporation under vacuum at room temperature yield a gray-black residue. Tetrahydrofuran and solvent octane are the only detectable volatile products (no  $H_2$  is evolved). The gray-black residue gives the same infrared spectrum and Debye-Scherrer x-ray diffraction pattern as compound III. In addition, the absorption spectrum and chemical properties of the two materials are very similar (though not quite identical). We conclude that the substance initially synthesized from  $(C_5H_5)_2TiCl_2$  (i.e., III) has the same gross composition and general structural features as  $(\eta-C_5H_5)_2Ti-\mu-(\eta^1:\eta^5-C_5H_4)-Ti-(\eta-C_5H_5)(C_4H_8O) \cdot C_4H_8O$  (IV) less two molecules of THF ( $C_4H_8O$ ). Compound III is thus believed to be:  $(\eta-C_5H_5)_2Ti-\mu-(\eta^1:\eta^5-C_5H_4)-Ti(\eta-C_5H_5)$ . The purest form of III is obtained as described from the crystalline THF adduct. Any small differences that we have observed in the chemical properties and absorption spectra between this material and that obtained from the reduction of  $(C_5H_5)_2TiCl_2$  may be accounted for by the presence of some 5–10% of the hydride I in the latter product.

Apparent molecular weights of  $(C_5H_5)_3(C_5H_4)Ti_2$  (III) were measured at various concentrations in benzene solutions using an isopiestic technique. The results are plotted in Figure 3. A significant variation in the apparent molecular weight of III with concentration is noted. The molecular weight varies from 313 for a 0.02 *m* solution to 417 for a 0.054 *m* solution. The formula weight of  $(C_5H_5)_3(C_5H_4)Ti_2$  is 355. There are apparently considerable deviations from Raoult's law by this system; the deviations may be caused either by formation of benzene adducts<sup>30</sup> of III or by oligomers. The molecule  $(C_5H_5)_3(C_5H_4)Ti_2$  is highly coordinatively unsaturated and might be expected to form metal-metal bonded polymeric species in concentrated solutions.

**Spectral Properties.** The infrared spectra of  $(C_5H_5)_3(C_5H_4)Ti_2$  (III) and  $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O) \cdot C_4H_8O$  (IV) have been recorded in oil mulls and are shown in Figure 4. The spectrum of III is very similar to that of ferrocene or nickelocene<sup>31</sup> and is in no way indicative of the unusual  $\mu-(\eta^1:\eta^5-C_5H_4)$  bonding arrangement in our molecule. There is in particular no observable splitting in the  $790\text{ cm}^{-1}$ ,  $\pi(C-H)$  absorption as is seen, for example, in the ir spectrum of the fulvalene-bridging dicyclopentadienyl titanium hydride I.<sup>10</sup> Infrared spectra that display only simple metallocene features

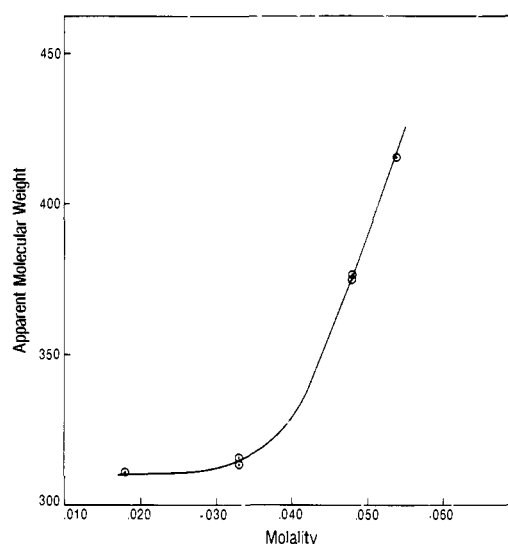
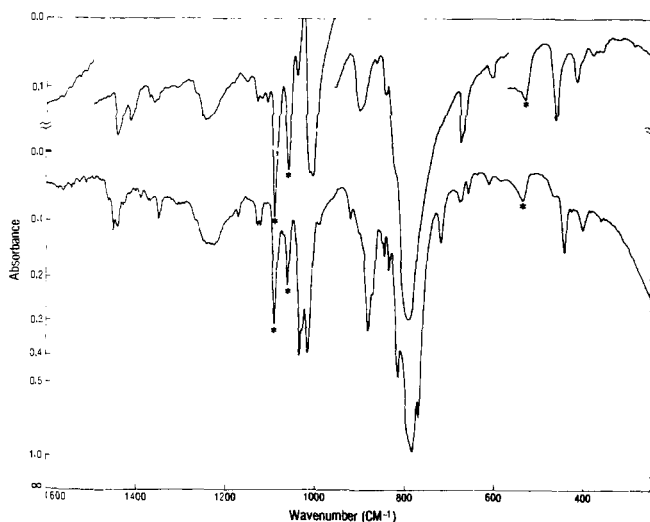


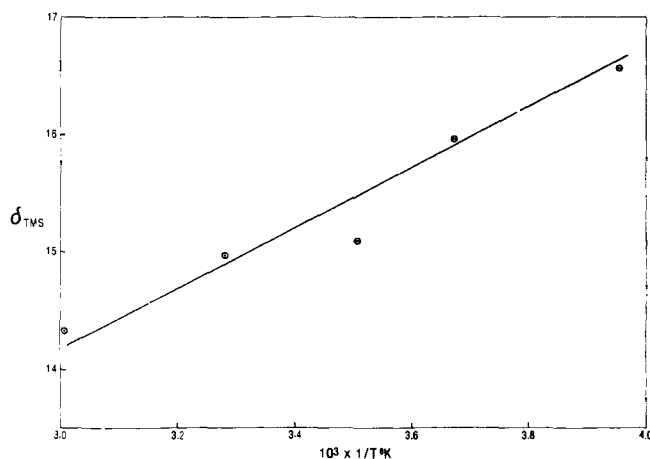
Figure 3. Dependence of apparent molecular weight of  $(C_5H_5)_3(C_5H_4)Ti_2$  (III) in benzene solutions on concentration.

thus cannot confidently be taken as evidence<sup>12–15</sup> for the absence of more complex cyclopentadienyl structures. The ir spectra of III and  $[(C_5H_5)_2Ti]_2$  (II)<sup>13</sup> are very similar, except that for II there is an additional absorption at  $\sim 1380\text{ cm}^{-1}$ . In the spectrum of the adduct IV (Figure 4), bands at 2970, 1032, and  $880\text{ cm}^{-1}$  may be ascribed to vibrations of THF. As noted earlier, the “hydride” I is often present as an impurity in III. A useful, approximate indication of the amount of hydride present may be obtained by noting the intensity of the Ti-H vibration for I which occurs at  $1223\text{ cm}^{-1}$ .<sup>10</sup> In the course of our work with III and IV we have never been able to totally eliminate the  $1223\text{-cm}^{-1}$  absorption. Even for pure crystalline IV a weak broad band is seen at  $1223\text{ cm}^{-1}$  (see Figure 4). The  $[(C_5H_5)_2Ti]_2$  (II) material apparently also shows a weak absorption at  $1230\text{ cm}^{-1}$ .<sup>13</sup> In contrast, the “titanocene” species prepared by Van Tamelen et al.<sup>14</sup> and by Alt and Rausch<sup>15</sup> are said to lack any infrared absorptions in the vicinity of  $1230\text{ cm}^{-1}$ . The observation is cited as evidence for the absence of Ti-H bonds in their compounds.

The 100-MHz proton NMR spectrum of  $(C_5H_5)_3(C_5H_4)Ti_2$  (prepared from IV) in toluene-*d*<sub>8</sub> was recorded from  $\delta_{Me_4Si} +20$  to  $-20$ . A single broad resonance occurs at  $\delta_{Me_4Si} 15.0$ ,  $32^\circ\text{C}$  (width at half-height 130 Hz). On cooling, the band broadens and moves to higher field strengths. The behavior is clearly indicative of a paramagnetic species. The NMR band positions have been measured at various temper-



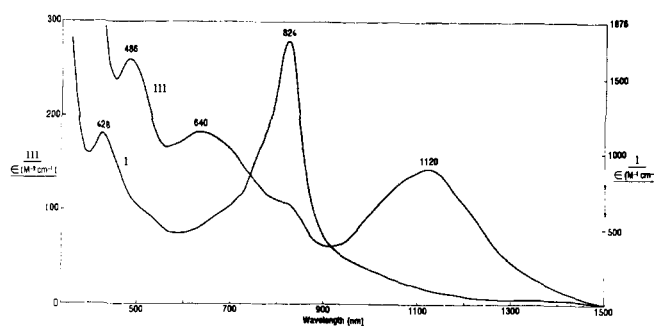
**Figure 4.** Infrared spectra of  $(C_5H_5)_3(C_5H_4)Ti_2$  (III) (upper curve) and  $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O) \cdot C_4H_8O$  (IV) (lower curve). Absorption bands of the *n*-hexadecane- $d_{34}$  mulling agent are marked with an asterisk (\*).



**Figure 5.** Variation in the chemical shift ( $\delta_{Me_4Si}$ ) of the  $^1H$  NMR signal of  $(C_5H_5)_3(C_5H_4)Ti_2$  (III) in toluene- $d_8$  with reciprocal of absolute temperature.

atures from +60 to  $-20$  °C; the data are reproduced in Figure 5, where the specific resonance  $\delta_{Me_4Si}$  is plotted vs.  $1/T$ . An apparently linear relationship is obtained which is consistent with Curie-Weiss law behavior. A least-squares fit of these data, when extrapolated to  $1/T = 0$  gives the origin of the resonance as  $\delta_{Me_4Si} \sim 7$ . This is a reasonable value for cyclopentadienyl protons; for  $(C_5H_5)_2TiCl_2$  protons for example,  $\delta_{Me_4Si}$  6.60.<sup>32a</sup> The inherent paramagnetism<sup>32b</sup> prohibits any more specific assignment of our NMR data. The "black titanocene" recently described by Alt and Rausch<sup>15</sup> is said to be diamagnetic; it shows cyclopentadienyl proton NMR signals at  $\delta_{Me_4Si}$  5–6.

Visible and near-infrared absorption spectra of solutions of  $(C_5H_5)_3(C_5H_4)Ti_2$  (III) and  $(C_5H_5)_2(C_{10}H_8)Ti_2H_2$  (I) in benzene have been recorded. These are reproduced in Figure 6. The visible spectrum of III shows two clear maxima in the visible at 486 nm ( $\epsilon$  260  $M^{-1} cm^{-1}$ ) and 640 nm ( $\epsilon$  183). In addition, there is an unusual absorption in the near-infrared at 1120 nm with  $\epsilon$  144. This band is not seen for I or for related dicyclopentadienyl dimer species such as  $[(\eta^5-C_5H_5)_2TiCl]_2$  and may arise from an intervalence transition<sup>33</sup> between the formally divalent and trivalent metal centers in  $(\eta^5-C_5H_5)_2Ti-\mu-(\eta^1:\eta^5-C_5H_4)-Ti(\eta^5-C_5H_5)$  (III). The bands at 486 and 640 nm coincide with the absorptions seen by Van Tam-



**Figure 6.** Visible and near-infrared absorption spectra of  $(C_5H_5)_2(C_{10}H_8)Ti_2H_2$  (I) and  $(C_5H_5)_3(C_5H_4)Ti_2$  (III).

elen et al. for their "highly unstable", "active titanocene", assigned the formula  $[(C_5H_5)_2Ti]_{1-2}$ .<sup>14</sup> These authors, however, make no mention of an absorption band in the near-infrared, so that a more definitive comparison is, unfortunately, not possible. The hydride I has absorption bands at 428 nm ( $\epsilon$  1130) and 824 nm ( $\epsilon$  1740). A good quantitative measure of the purity of III can be gained by comparison of the two spectra shown in Figure 6. Thus III as obtained from the crystalline bis(tetrahydrofuran) adduct IV contains less than 1% of the hydride I, as calculated from the intensity of the absorption seen at 824 nm.

## Conclusions

Reaction of  $(C_5H_5)_2TiCl_2$  with various reducing agents under near ambient conditions yields mainly  $\mu-(\eta^5:\eta^5\text{-fulvalene})\text{-di-}\mu\text{-hydrido-bis}(\eta\text{-cyclopentadienyltitanium})$  (I).<sup>10</sup> We have found that a considerably more reactive compound:  $\mu-(\eta^1:\eta^5\text{-cyclopentadienyl})\text{-tris}(\eta\text{-cyclopentadienyl})\text{dittitanium}(Ti-Ti)$ ,  $(\eta^5-C_5H_5)_2Ti-\mu-(\eta^1:\eta^5-C_5H_4)-Ti(\eta^5-C_5H_5)$  (III), can be obtained by reacting  $(C_5H_5)_2TiCl_2$  with potassium naphthalene at low temperatures in tetrahydrofuran. The substance is isolated as a gray-black solid in 45–60% yield. The low temperature reduction technique used promises to be a generally useful method for the synthesis of highly reactive, metastable organometallics.<sup>34</sup>

A crystalline material characterized by x-ray crystallography as  $(\eta^5-C_5H_5)_2Ti-\mu-(\eta^1:\eta^5-C_5H_4)-Ti(\eta^5-C_5H_5)-(C_4H_8O) \cdot C_4H_8O$  (IV) has been isolated from solutions of III in tetrahydrofuran ( $C_4H_8O$ ). The attached solvent can be removed to yield very pure specimens of III.

The most interesting structural feature of these molecules is the presence of a Ti-Ti linkage which is bridged on only one side by a  $(\eta^1:\eta^5-C_5H_4)$  ligand. As a result, there is a considerable degree of openness in the structure, on the opposite side of the Ti-Ti linkage. We feel that the presence of this exposed metal-metal bond accounts for the facile reactivity of III and IV with hydrogen, nitrogen, and olefins.<sup>16</sup>

## Experimental Section

All the organometallics used in this work are highly air sensitive and were handled with the rigid exclusion of oxygen and moisture. A Vacuum Atmospheres drybox, filled with argon gas, containing  $<5$  ppm  $O_2$  or  $H_2O$ , was used for the handling and transfer of solids. Volatile solvents and solutions were handled by standard vacuum line techniques.

"Chromatoquality" grade solvents were used when available (Matheson Coleman and Bell). Hydrocarbon solvents were purified by prolonged treatment with sodium-potassium alloy (Na/K) under argon or vacuum. Tetrahydrofuran and diethyl ether were first treated with  $LiAlH_4$  and then distilled into a flask containing Na/K alloy and anthracene. The ethers were distilled, as required from the blue radical anion solutions of Na/K-anthracene.

Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer. Mulling agents (Nujol, *n*-hexadecane- $d_{34}$  (Merck & Co. Inc., Rahway, N.J.)) were purified by treatment with Na/K followed by distillation under vacuum at 100 °C. A Cary Model 14 spectro-

photometer was used for recording the uv and visible spectra. Solutions were contained in a 2-mm pathlength quartz cell sealed onto a high-vacuum glass vessel. Proton NMR spectra were recorded on a Varian HA 100 instrument. Cyclohexane was used as an internal reference.

Titanium was determined gravimetrically as  $TiO_2$ . Carbon and hydrogen were determined by standard microanalytical procedures. A Heraeus combustion unit operating at  $1000\text{ }^\circ\text{C}$  was used in order to prevent the possible formation of metal carbides. Molecular weight measurements were carried out using a novel isopiestic technique wherein benzene solutions of the unknown are balanced in vapor pressure (to within  $\sim 10^{-3}$  Torr) against solutions of a standard solute, e.g., azobenzene, in the same solvent. The vapor pressures were monitored with an electronic capacitance manometer (Model 02, Granville Phillips, Boulder, Col.).

**(a) Preparation of  $(C_5H_5)_3(C_5H_4)Ti_2$  (III).** The synthesis depends on the reaction of  $(C_5H_5)_2TiCl_2$  with potassium naphthalene at low temperatures. A specially designed glass reactor, suitable for stirring solutions at low temperatures for extended periods of time was employed. The apparatus is shown diagrammatically in Figure 7. It consists of a 1-l. reactor which can be immersed in cold baths up to the level of the (10 mm) glass stopcock. The latter serves both as a high vacuum tap and as an entry point for charging the reactor with solids. There is a conventional paddle stirrer attached to a magnetic bar. The apparatus also has a loading vessel for solids and a filtration system (fritted disk is of 35 mm i.d. and of porosity  $10\text{--}25\ \mu$ ). A 12-mm Teflon stopcock (Kontes Glass, Vineland, N.J.) is used to isolate the material in the loading vessel.

Reagents for the synthesis were prepared as follows. Dicyclopentadienyltitanium dichloride (ROC/RIC, Sun Valley, Calif.) was outgassed at  $90\text{ }^\circ\text{C}$  under vacuum before use. Naphthalene was purified by vacuum sublimation. Potassium metal in ampules of  $>99.9\%$  purity (MSA Research Corp., Evans City, Pa.) was employed.

The low temperature reactor was charged (in an Ar atmosphere) with a mixture of solid droplets of K metal (10 g, 0.256 mol) and with naphthalene (34.4 g, 0.268 mol). Finely ground  $(C_5H_5)_2TiCl_2$  (31.8 g, 0.128 mol) was loaded into the addition vessel. The apparatus was attached to a vacuum line and THF (500 ml) was distilled into the reactor. The mixture was stirred at room temperature, until all the potassium had dissolved, and formation of the green potassium naphthalene was complete. The reactor was then immersed in liquid  $N_2$  and the  $(C_5H_5)_2TiCl_2$  slowly released onto the frozen solution. Additional THF was added (at  $-196\text{ }^\circ\text{C}$ ), so as to bring the total volume of solution to approximately 800 ml. The apparatus was then warmed to the melting point of THF and the resulting slush (at ca.  $-110\text{ }^\circ\text{C}$ ) vigorously agitated and allowed to warm to  $-80\text{ }^\circ\text{C}$ . The mixture was stirred for 3 days at  $-80\text{ }^\circ\text{C}$ ; 2 days at  $-45\text{ }^\circ\text{C}$ , and 16 h at  $-23\text{ }^\circ\text{C}$  and then rapidly warmed to room temperature. At this point the contents of the reactor were dark-green, almost black in color. Tetrahydrofuran and naphthalene were removed by pumping under vacuum at  $25\text{--}35\text{ }^\circ\text{C}$ . The remaining black residue was then extracted with 600 ml of toluene at  $-80\text{ }^\circ\text{C}$ , to yield a deep green filtrate. This was evaporated to about 100 ml and mixed with the same volume of *n*-octane. (The octane serves to precipitate the product and permits the removal of adhering toluene.) The solid remaining after evaporation of the toluene/octane mixture was subsequently washed with a further 100 ml of octane and then with 100 ml of isopentane. The final product is a gray-black, pyrophoric solid.

Anal. Calcd for  $(C_{20}H_{19}Ti_2)$ : C, 67.66; H, 5.36; Ti, 26.98. Found: C, 67.00; H, 5.55; Ti, 26.58; no traces of K, Cl. The synthesis usually yields from 10 to 14 g of III.

Powder x-ray diffraction data were obtained with a Debye-Scherrer camera using vanadium filtered chromium radiation. Samples were held in 0.5-mm quartz capillaries. The following "d" spacings ( $\text{\AA}$ ) and relative intensities were observed:  $D(I/I_1)$ : 7.28 (41), 6.56 (18), 6.19 (100), 5.29 (18), 5.15 (18), 4.88 (5), 4.59 (30), 4.39 (34), 4.29 (16), 3.95 (18), 3.63 (11), 3.42 (7), 2.97 (4), 2.56 (4), 2.49 (18), 2.35 (4), 2.29 (9), 2.24 (9), 2.09 (4), 1.94 (4).

**(b) Synthesis of Crystalline  $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O)C_4H_8O$  (IV).** An H-shaped apparatus of about 1-l. capacity, and having the two sides separated by a filter disk, was used for the synthesis. One section of the apparatus was charged with  $(C_5H_5)_3(C_5H_4)Ti_2$  (1 g) dissolved in 140 ml of THF. To the second section was added 450 ml of isopentane. The apparatus was then sealed (using Teflon stopcock valves) and left undisturbed for 10 days at  $5\text{ }^\circ\text{C}$ . Slow diffusion of isopentane into the THF resulted in the growth of well-formed crystals of IV. The

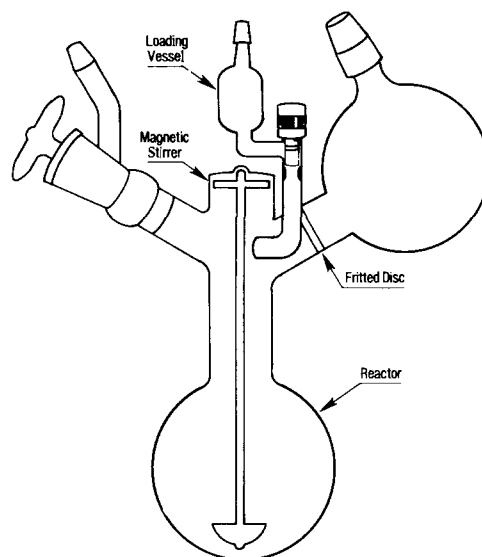


Figure 7. Apparatus for the low-temperature reduction of  $(C_5H_5)_2TiCl_2$ .

solvent was removed by gentle decantation under ambient pressure. The crystals were washed with a little isopentane and subsequently dried in a current of very pure argon. At all times a pressure of solvent (or Ar) was maintained over the crystals since vacuum pumping removes some of the bound THF. About 0.7 g of III was recovered.

Anal. Calcd for  $(C_{28}H_{35}O_2Ti_2)$ : C, 67.28; H, 7.02; Ti, 19.19. Found: C, 67.32; H, 7.10; Ti, 19.24.

The material appears to be indefinitely stable: No noticeable decomposition occurred after storing the crystals for several months at  $5\text{ }^\circ\text{C}$ , in an atmosphere of argon.

**(c) Collection of X-ray Data and Structure Determination.** For the x-ray work crystals of IV were mounted in Nujol oil in glass capillaries, under argon. Cell constants were obtained by computer centering of reflections on a Syntex P1 automatic diffractometer. Least-squares refinement of the setting angles provided the following values:  $a = 28.567(19)\text{ \AA}$ ,  $b = 8.061(2)\text{ \AA}$ ,  $c = 19.691(7)\text{ \AA}$ ,  $V = 4449(4)\text{ \AA}^3$ ,  $\lambda 0.71073$ ,  $\alpha = 90^\circ$ ,  $\beta = 101.11(2)^\circ$ ,  $\gamma = 90^\circ$ .

From the density of  $1.57 \pm 0.10\text{ g/cm}^3$  (measured by weighing the amount of isopentane displaced by 424 mg of the crystals), the number of formula units of  $Ti_2O_2C_{28}H_{35}$  per unit cell was computed to be  $8(\rho_{\text{calcd}} = 1.491\text{ g/cm}^3)$ . The systematic absences:  $h + k + l = 2n + 1$ ;  $h0l$ ,  $h + l = 2n + 1$  indicated a space group  $I2/a$ . This was confirmed by a successful refinement of the structure.

For the data collection, a prismatic crystal of dimensions  $0.30 \times 0.35 \times 0.32\text{ mm}$  was mounted on the diffractometer. Molybdenum  $K\alpha$  radiation filtered by a graphite-crystal incident-beam monochromator was employed. Data were taken in the range  $0 < 2\theta$  (Mo  $K\alpha_1$ )  $\leq 55.0^\circ$  with a scan width ranging from  $2\theta$  (Mo  $K\alpha_1$ )  $-0.6^\circ$  to  $2\theta$  (Mo  $K\alpha_2$ )  $+0.6^\circ$  (crystal at  $23 \pm 1\text{ }^\circ\text{C}$ ). A variable scan rate of  $4\text{--}24^\circ/\text{min}$  was used, so as to allow rapid data collection and good counting statistics for weak reflections. A total of 4426 independent reflections were collected. As a check on crystal and electronic stability, three representative reflections were measured periodically. There was no significant change. The data were corrected for Lorentz and polarization effects. Extinction and absorption corrections were not necessary.

The structure was solved using the Patterson method. The two titanium atoms were clearly visible in the Patterson map. Least-squares refinement of the atoms resulted in agreement factors of  $R_1 = 0.36$  and  $R_2 = 0.39$ , where  $R_1$  and  $R_2$  are defined as:

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R_2 = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}}{w = 4F_o^2 / \sigma^2(F_o^2)}$$

The remaining atoms were located in succeeding difference Fourier syntheses. The structure was refined by minimizing the function  $\sum w(|F_o| - |F_c|)^2$ . Scattering factors were taken from tables by Cromer and Waber.<sup>35</sup> Anomalous dispersion effects were included in  $F_c$ ; the values of  $\Delta f'$  and  $\Delta f''$  were those of Cromer and Liberman.<sup>36</sup>

Only the 2403 reflections having  $F_o^2 > 3\sigma(F_o^2)$  were used in the refinement. In the last cycle of least-squares refinement  $R_1$  and  $R_2$  were 0.051 and 0.062, respectively. The final Fourier map showed no peaks as high as hydrogen atoms on a previous difference Fourier map. Lists of refined positional and thermal parameters for all the atoms, and also tables of observed and calculated structure factors are available. See paragraph at end of table regarding supplementary material.

(d) **Removal of THF from  $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O)C_4H_8O$  (IV).** The compound IV (0.45 g) was ground to a fine powder and then dissolved in 300 ml of *n*-octane. Slow evaporation of the solvent, under vacuum, gave a gray-black powder (0.3 g). The infrared spectrum of the latter is identical with the product obtained from the reduction of  $(C_5H_5)_2TiCl_2$  (see Figure 4 (upper curve)), and shows no evidence of bound or solvated tetrahydrofuran. The following x-ray diffraction data were obtained for the gray-black powder (Cr radiation, 0.5 mm quartz, capillary tube):  $D(I/I_1)$ : 7.25 (40), 6.57 (13), 6.18 (100), 5.62 (4), 5.26 (18), 5.14 (15), 4.86 (9), 4.58 (24), 4.39 (32), 4.28 (8), 3.94 (22), 3.61 (4), 3.41 (6), 2.97 (3), 2.55 (8), 2.49 (13), 2.35 (5), 2.28 (6), 2.23 (13), 2.09 (12), 193 (10).

**Acknowledgments.** The author wishes to thank Mr. G. G. Miller, Mr. R. Crissey, and Mr. J. Corsi for their invaluable technical assistance. I am grateful to Mrs. R. Hogan for the elemental analyses, Mr. G. Babbit and Dr. R. Lapinsky for the NMR spectra, and Dr. P. Harget, Dr. P. Apgar, and Dr. M. Novotny for assistance with the x-ray work.

**Supplementary Material Available:** Lists of refined positional and thermal parameters for all the atoms, and also tables of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) T. J. Kealy and P. L. Pauson, *Nature (London)*, **168**, 1039 (1951).
- (2) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds", Vol. 2, Methuen, London, 1968, p 90.
- (3) L. J. Guggenberger, *Inorg. Chem.*, **12**, 294 (1973).
- (4) E. C. Baker, K. N. Raymond, T. J. Marks, and W. A. Wachter, *J. Am. Chem. Soc.*, **96**, 7586 (1974).
- (5) A. K. Fischer and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 149 (1956).
- (6) K. Clauss and H. Bestian, *Justus Liebigs Ann. Chem.*, **654**, 8 (1962).
- (7) G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Am. Chem. Soc.*, **88**, 1138 (1966).
- (8) J. J. Salzmann and P. Mosimann, *Helv. Chim. Acta*, **50**, 1831 (1967).
- (9) K. Shikata, K. Yokogawa, S. Nakao, and K. Azuma, *Kogyo Kagaku Zasshi*, **68**, 1248 (1965).
- (10) H. H. Brintzinger and J. E. Bercaw, *J. Am. Chem. Soc.*, **92**, 6182 (1970).

- (11) A. Davison and S. S. Wreford, *J. Am. Chem. Soc.*, **96**, 3017 (1974).
- (12) R. H. Marvich and H. H. Brintzinger, *J. Am. Chem. Soc.*, **93**, 2046 (1971).
- (13) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Am. Chem. Soc.*, **94**, 1219 (1972).
- (14) E. E. Van Tamelen, W. Cretney, N. Klaentschi, and J. S. Miller, *J. Chem. Soc., Chem. Commun.*, 481 (1972).
- (15) H. Alt and M. D. Rausch, *J. Am. Chem. Soc.*, **96**, 5936 (1974).
- (16) G. P. Pez and S. C. Kwan, *J. Am. Chem. Soc.*, following paper in this issue.
- (17) G. Pez, U.S. Patent 3 776 932 (1973). The patent erroneously describes III as  $[(C_5H_5)_2Ti]_2$ . An application for a reissue of this patent stating the correct structure of the material, has been submitted to the U.S. Patent Office.
- (18) Reduction of  $(C_5H_5)_2TiCl_2$  with sodium, rather than potassium, naphthalene at  $-80^\circ C$  in THF, as above, also gives III but in lower yields (ca. 20%).
- (19) The x-ray diffraction work described here was done by Jan M. Troup, Molecular Structure Corporation, College Station, Texas 77840.
- (20) (a) R. Hoxmeier, B. Deubzer, and H. D. Kaesz, *J. Am. Chem. Soc.*, **93**, 536 (1971); (b) E. O. Fischer and R. Amtmann, *J. Organomet. Chem.*, **9** P15 (1967).
- (21) (a) P. Corradini and A. Sirigu, *Inorg. Chem.*, **6**, 601 (1967); (b) F. N. Tebbe and L. J. Guggenberger, *J. Chem. Soc., Chem. Commun.*, 227 (1973).
- (22) "Handbook of Chemistry and Physics", 53d ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1972-1973, p F-180.
- (23) D. C. Sekutowski and G. D. Stucky, private communication, 1974.
- (24) R. L. Martin and G. Winter, *J. Chem. Soc.*, 4709 (1965).
- (25) J. D. Zeinstra and J. L. De Boer, *J. Organomet. Chem.*, **54**, 207 (1973).
- (26) P. A. Kroon and R. B. Heimholdt, *J. Organomet. Chem.*, **25**, 451 (1970).
- (27) J. L. Atwood, K. E. Stone, H. G. Alt, D. C. Hrnccir, and M. D. Rausch, *J. Organomet. Chem.*, **96**, C4 (1975).
- (28) I. W. Bassi, G. Allegra, R. Scordamaglia, and G. Chioccola, *J. Am. Chem. Soc.*, **93**, 3787 (1971).
- (29) L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Am. Chem. Soc.*, **92**, 7312 (1970).
- (30) Solutions of  $(C_5H_5)_3(C_5H_4)Ti_2$  in benzene or toluene cannot be evaporated to total dryness by vacuum pumping at room temperature; some of the aromatic solvent always seems to adhere to the complex. We have not been able to experimentally quantify this interaction. In solutions of III in toluene, there is no apparent exchange of the aromatic protons of  $C_6H_5CH_3$  with  $D_2$  at  $23^\circ C$ .
- (31) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2d ed, Wiley-Interscience, New York, N.Y., 1970, pp 268-271.
- (32) (a) S. A. Butter, Ph.D. Dissertation, University of Delaware, University Microfilms, Ann Arbor, Mich., 1965, p 70. (b) We made several attempts to measure the magnetic susceptibilities of III and IV with a vibrating sample magnetometer. The compounds displayed some paramagnetism, but because of their extreme chemical reactivity (towards air and the sampling devices) we were, unfortunately, unable to obtain reliable magnetic moment data.
- (33) G. M. Tom, C. Creutz, and H. Taube, *J. Am. Chem. Soc.*, **96**, 7827 (1974).
- (34) We have found that reduction of  $(C_5H_5)_2ZrCl_2$  with  $KC_{10}H_8$  at low temperatures gives a substance believed to be:  $[(\eta-C_5H_5)_2Zr-C_{10}H_8]_n$ . See G. Pez, U.S. Patent No. 3 839 381 (1974).
- (35) D. T. Cromer and J. T. Waber, "International Tables for x-ray Crystallography", Vol. 4, in preparation.
- (36) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).