

Hydrolytic Studies on $(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_3$; X-Ray Structure of $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}(\mu\text{-O})]_3$ containing a Ti_3O_3 Ring

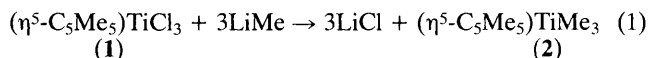
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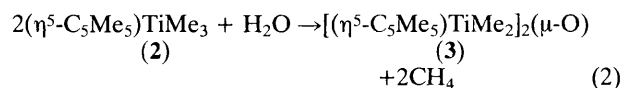
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Successive hydrolysis of $(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_3$ (**2**) gives first $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2]_2(\mu\text{-O})$ (**3**) and then $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}(\mu\text{-O})]_3$ (**4**); the crystal structure of (**4**) reveals a Ti_3O_3 ring.

Mono- and di-cyclopentadienyl titanium halides are known to hydrolyse their Ti-Cl bonds, and in the dicyclopentadienyl case one of the cyclopentadienyl (cp) rings is sometimes lost, with subsequent formation of dimeric¹ and tetrameric² complexes which have been structurally characterized. We have recently isolated and characterized several very reactive mono-pentamethylcyclopentadienyl titanium trialkyls and α -hydrogen agostic interactions have been proposed for $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{CH}_2\text{Ph})_3$ in the light of the X-ray crystallographic data.³ The methyl derivative is cleanly obtained according to equation (1).



Controlled hydrolysis of benzene or hexane solutions of (**2**) leads to the formation of the dimer (**3**)[†] with evolution of methane, equation (2).



When one equivalent, or a slight excess, of water is added to (**2**) a different yellow crystalline product (**4**)[‡] is obtained; its ¹H n.m.r. spectrum shows one C_5Me_5 signal and two other

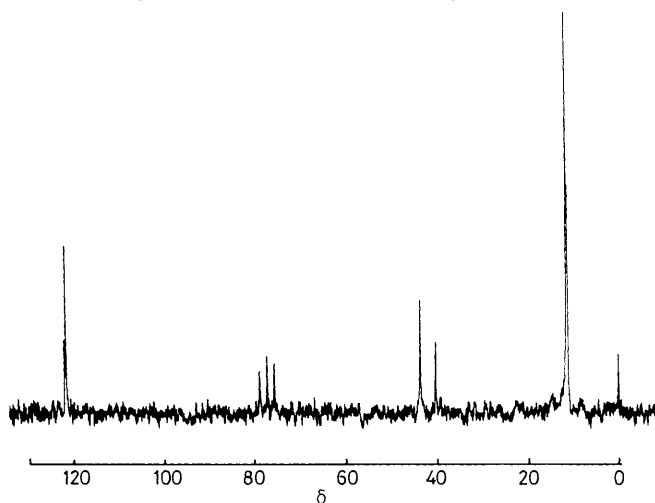


Figure 1. $^{13}\text{C}\{^1\text{H}\}$ N.m.r. spectrum of compound (**4**) in CDCl_3 .

[†] (**3**): Yellow crystals: i.r. ν (Ti-O-Ti) 800 (vs. br.) cm^{-1} ; ¹H n.m.r. (C_6D_6) δ 1.91 (s, 30H, C_5Me_5) and 0.66 (s, 12H, TiMe); $^{13}\text{C}\{^1\text{H}\}$ n.m.r. (C_6D_6) 122.09 (s, C_5Me_5), 52.35 (s, TiMe), and 11.86 (s, C_5Me_5); satisfactory analytical data were obtained.

[‡] (**4**): i.r. ν (Ti-O-Ti) 790 (vs) cm^{-1} ; ¹H n.m.r. (C_6D_6) δ 1.97 (s, 45H, C_5Me_5), 0.79 (s, 6H, Ti-Me), and 0.55 (s, 3H, Ti-Me); $^{13}\text{C}\{^1\text{H}\}$ n.m.r. (CDCl_3) 121.57 (s, C_5Me_5), 121.28 (s, C_5Me_5), 43.61 (s, Ti-Me), 40.17 (s, Ti-Me), 11.48 (s, C_5Me_5), and 11.27 (s, C_5Me_5); satisfactory analytical data were obtained.

signals at δ 0.79 and 0.55 corresponding to methyl groups bonded to Ti, with relative intensities 15:2:1. The $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectrum demonstrates nevertheless that there are non-equivalent C_5Me_5 groups in an approximate ratio of 2:1 as judged by the relative intensity of the ring and methyl carbon signals (in spite of the unreliable integration for $^{13}\text{C}\{^1\text{H}\}$ signals; see Figure 1). This suggested a trimeric structure containing two geometrically different types of methyl and cyclopentadienyl groups, which the X-ray analysis confirmed. The molecular structure of (**4**),[§] depicted in Figure 2, shows a 'titanyl' trimer $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O})\text{Me}]_3$ in which three $(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}$ units are linked through three oxygen bridges forming a Ti_3O_3 ring. The Ti-O distances range from 1.816(6) to 1.830(6) Å with a mean value of 1.823 Å which is considerably shorter than the typical Ti-O single bond distances of ca. 2.0 Å,^{2b} thus indicating partial double bond

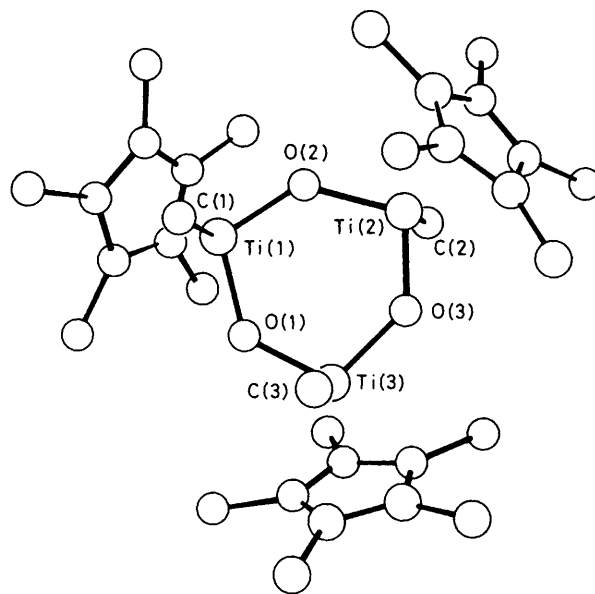


Figure 2. Molecular structure of $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}(\mu\text{-O})]_3$; selected bond lengths (Å) and angles ($^\circ$): Ti(1)-O(1) 1.827(6), Ti(1)-O(2) 1.816(6), Ti(2)-O(2) 1.824(6), Ti(2)-O(3) 1.817(6), Ti(3)-O(3) 1.827(5), Ti(3)-O(1) 1.830(6); O(1)-Ti(1)-O(2) 105.2(2), Ti(1)-O(2)-Ti(2) 133.6(3), O(2)-Ti(2)-O(3) 106.0(2), Ti(2)-O(3)-Ti(3) 133.5(3), O(3)-Ti(3)-O(1) 104.8(2), Ti(3)-O(1)-Ti(1) 131.6(3).

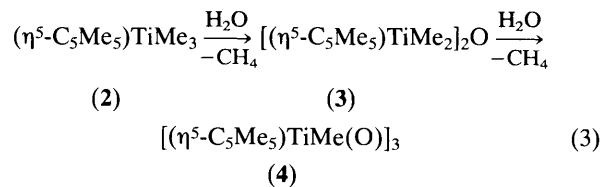
[§] Crystal data: $\text{C}_{33}\text{H}_{54}\text{O}_3\text{Ti}_3$, $M = 642.48$, monoclinic, space group $P2_1/a$, $a = 23.062(1)$, $b = 8.9449(2)$, $c = 16.957(1)$ Å, $\beta = 90.91(1)^\circ$, $U = 3497.6(3)$ Å³, $Z = 4$, $D_c = 1.22$ g cm^{-3} , $F(000) = 1368$, $\mu(\text{Cu-K}\alpha) = 59.46$ cm^{-1} . Data were recorded on a Phillips 1100 4-circle diffractometer using graphite monochromated $\text{Cu-K}\alpha$ radiation; θ range 2–65 $^\circ$; 3491 unique observed [$I > 2\sigma(I)$] absorption corrected reflections, $R = 0.089$, $R_w = 0.096$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

character. The O-Ti-O angles are between 104.8(2) and 106.0(2)°, in the same range as reported for the tetramers.² The Ti-O-Ti angles vary from 131.6(3) to 133.5(3)° and are the most acute yet observed. The Ti₃O₃ ring is nearly planar with the exception of O(1) which deviates 0.332(6) Å from the plane defined by the other five atoms. Two of the Me groups bonded to Ti and one C₅Me₅ ring are situated above the Ti₃O₃ ring and the other Me group and two C₅H₅ rings below, thus explaining the results from the n.m.r. spectra.

Compound (4) is the first example of a Ti₃O₃ ring; to our knowledge, only two related cases of M₃O₃ rings, incorporating the cp₂M moiety, have been structurally characterized to date.⁴

A sequential ¹H n.m.r. study of the hydrolysis of (2) shows that the transformations in equation (3) occur. Trimer (4) is



obtained by hydrolysis of (3) in contrast to the previously reported monomer → dimer → tetramer sequence for cpTiCl₃.^{2b}

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References

- 1 P. Corradini and G. Allegra, *J. Am. Chem. Soc.*, 1959, **80**, 5510; U. Thewalt and D. Schomburg, *J. Organomet. Chem.*, 1977, **127**, 169; U. Thewalt and B. Keibel; *ibid.*, 1978, **150**, 59.
- 2 A. C. Skapski and P. G. H. Troughton, *Acta Crystallogr., Sect. B*, 1970, **26**, 716; J. L. Petersen, *Inorg. Chem.*, 1980, **19**, 181.
- 3 M. Mena, M. A. Pellinghelli, P. Royo, R. Serrano, and A. Tiripicchio, *J. Chem. Soc. Chem. Commun.*, 1986, 1118.
- 4 G. Fachinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, 1979, **101**, 1765; B. Statte, V. Bätzel, R. Boese, and G. Schmid, *Chem. Ber.*, 1978, **111**, 1603.