Synthesis and *X*-Ray Crystal Structure of a Novel Paramagnetic Organotitanium(III) Compound, Cyclopentadienyl-bis[*o*-(*NN*-dimethylaminomethyl)phenyl]titanium

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Summary The reaction of Li-*o*-$C_6H_4CH_2NMe_2$ (2 equiv.) with $[(C_5H_5)TiCl_2]_x$ in ether gives the novel, air-sensitive, paramagnetic complex $(C_5H_5)Ti(o\text{-}C_6H_4CH_2NMe_2)_2$ (**1**), whose crystal structure has been determined; (**1**) reacts with CO_2 and exchanges the cyclopentadienyl hydrogens with D_2.

ORGANOMETALLIC complexes of titanium are of considerable interest in view of their role in Ziegler–Natta type olefin polymerizations.[1] Numerous organodicyclopentadienyl derivatives of Ti^{III} have been prepared;[2] however, most of these complexes are only marginally stable at room temperature. Organometallic complexes of Ti^{III} containing one cyclopentadienyl group are expected to be less stable and possibly more reactive. We now report the preparation, *X*-ray structure, and reactions of the first σ-bonded organometallic complex of Ti^{III} containing only one cyclopentadienyl group.

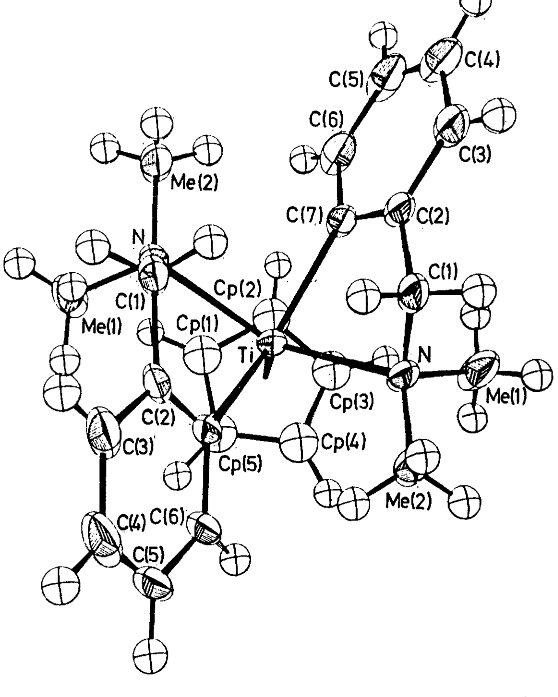

FIGURE 1. Complex (**1**): arbitrary temperature factors for the C_5H_5 carbon atoms and all hydrogen atoms.

The addition of Li-*o*-$C_6H_4CH_2NMe_2$[3] (2 equiv.) to a well stirred solution of $[(C_5H_5)TiCl_2]_x$[4] in ether at room temperature under N_2 immediately gave a dark green solution. After several minutes, the stoicheiometric amount of LiCl produced was filtered off and some solvent was evaporated off. Dark green crystals were formed, which were filtered off and washed with pentane. The compound is extremely air- and moisture-sensitive and elemental analyses were hard to reproduce, although they were close† to the formulation $(C_5H_5)Ti(C_6H_4CH_2NMe_2)_2$ (**1**). The magnetic moment of (**1**) in benzene, determined by Evan's method,[5] is 1·7 B.M. which is very close to the spin-only value of 1·73 B.M. expected for a d^1-system.[6] The electronic [λ_{max} (C_6H_6) 574 (ε 268) and 705 (shoulder; ε 211) nm] and e.s.r. spectra (*g* 1·979) are also typical of Ti^{III}.

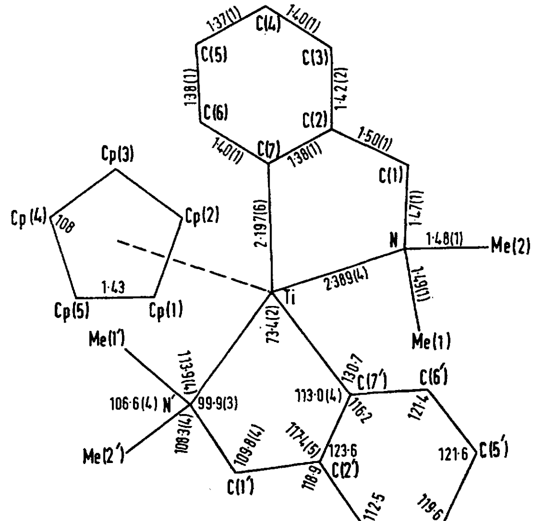

FIGURE 2. Complex (**1**): idealized drawing showing interatomic distances and angles. Unless shown the angle errors are *ca.* 0·6°. Ti–C(C_5H_5), 2·38(1); Ti–CNT (centroid of C_5H_5 ring), 2·05(1) Å; ∠N–Ti–N′, 123·9(2); N–Ti–C(7′) 83·8(2); N–Ti–CNT, 118·1(2); C(7)–Ti–C(7′); 130·5(2); C(7)–Ti–CNT, 114·8(2); Ti–N–Me(2), 119·2(3); C(1)–N–Me(1), 108·1(4)°.

The crystal structure was determined to establish the stereochemistry of the molecule. *Crystal data:* $(C_5H_5)Ti(C_6H_4CH_2NMe_2)_2$, monoclinic, space group *C*2/*c* assumed, $a = 16{\cdot}143(5)$, $b = 7{\cdot}889(3)$, $c = 16{\cdot}347(4)$ Å, $\beta = 100{\cdot}63(6)°$, $Z = 4$, $D_c = 1{\cdot}24$ g cm^{-3}. The structure was solved by heavy atom methods using 1382 reflections [$F_0 > 1{\cdot}5\,\sigma(F_0)$] which were corrected for absorption effects (μ 4·41 cm^{-1}). The assumption of space group *C*2/*c* requires an 180° orientational disorder of the C_5H_5 ring which was included in the refinement as a rigid body (C–C = 1·43,

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† Several analyses gave the correct C:H:N:Ti ratio; however, the results varied, probably owing to the high reactivity of the compound.

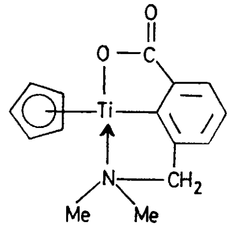
C–H = 1·0 Å) perpendicular to, and centred on, the 2-fold axis. Hydrogen atoms were placed in calculated positions; R = 0·11.

The molecular conformation is shown in Figure 1 and bond distances and angles are given in Figure 2. Individual distances and angles are similar to those observed for other complexes. The 5-membered ring formed by the bidentate aminomethylphenyl ligand is characterized by a 127·9° fold between the Ti, C(1)–C(7) plane and the Ti, N, C(1) plane. A dihedral angle of 112·4° is observed between the two bidentate ligands as defined by the Ti, N, and C(7) atoms. The Ti, C(1)–C(7) atoms are planar to 0·09 Å with N 0·94 Å out of this plane. The Ti–N distance is very long for a single bond.

It is noteworthy that the two bidentate dimethylaminomethylphenyl ligands adopt roughly a *trans*-configuration about titanium.

Although the molecule has only a 15-electron configuration and therefore would be expected to form an adduct with a suitable donor ligand, we have found no interaction with either trimethylphosphine or pyridine.‡ With D_2 gas (100 °C; benzene) the compound exchanges five hydrogen atoms per molecule (determined by mass spectroscopy), presumably those of the C_5H_5 group.[7]

Compound (**1**) reacts slowly with CO_2 (30 lb in^{-2}) at 85 °C in toluene to give a red-brown crystalline precipitate (**2**) in low yield, showing a strong sharp i.r. band at 1710 cm^{-1}, to which we tentatively assign the structure shown. Vol'pin and his co-workers[8] have reported a similar reaction between $(C_5H_5)_2TiPh_2$ and CO_2 to give an *ortho* carboxylated derivative.



(2)

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‡ There was no evidence of a colour change or shift in the e.s.r. resonance of (**1**) when an excess of ligand was added.

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