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Preliminary communication

The formation and properties of mono-cyclopentadienyltitanium dichloride complexes containing trimethylphosphine and isonitrile ligands: molecular structure of $(\eta^5\text{-}C_5H_5)TiCl_2(PMe_3)_2$

Abbas Razavi, Daniel T. Mallin, Roberta O. Day*, Marvin D. Rausch*
Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003 (U.S.A.)

and Helmut G. Alt
Laboratorium für Anorganische Chemie, Universität Bayreuth, D-8580 Bayreuth (Bundesrepublik Deutschland)

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Abstract

Reduction of $CpTiCl_3$ in THF solution by magnesium in the presence of either excess trimethylphosphine or 2,6-dimethylphenylisonitrile at ca. $-30\,^\circ C$ produces the titanium(III) complexes $CpTiCl_2(PMe_3)_2$ and $CpTiCl_2(CNC_6H_3Me_2)_2$, respectively, in good yields. The X-ray structure of $CpTiCl_2(PMe_3)_2$ is reported.

We have recently demonstrated that the reduction of the metallocene dichlorides Cp_2MCl_2 (M = Ti, Zr) in THF solution in the presence of trimethylphosphine leads to the corresponding complexes $Cp_2M(PMe_3)_2$ in good yields [1–3]. The titanium analog $Cp_2Ti(PMe_3)_2$ has been shown to undergo a wide variety of substitution reactions via displacement of the PMe_3 substituents [1–7], and the titanium(III) complex $Cp_2TiCl(PMe_3)$ has been obtained by partial reduction of Cp_2TiCl_2 in the presence of PMe_3 and $HgCl_2$ [8]. Magnesium-promoted reductions of Cp_2MCl_2 in the presence of 2,6-dimethylphenylisonitrile likewise afford the diamagnetic bis(isonitrile) complexes $Cp_2M(CNC_6H_3Me_2)_2$ in high yields [9].

We now report that the reduction of $CpTiCl_3$ by magnesium in the presence of either excess PMe_3 or $CNC_6H_3Me_2$ at ca. $-30\,^\circ C$ generates the titanium(III) complexes $CpTiCl_2(PMe_3)_2$ (**1**) and $CpTiCl_2(CNC_6H_3Me_2)_2$ (**2**), respectively, in good yields. The compositions of **1** and **2** have been established by means of elemental analysis as well as by their infrared and mass spectra, and the structure of

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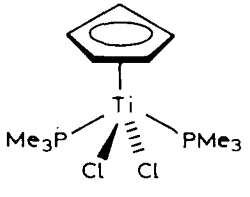
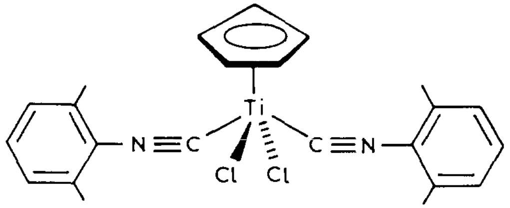
1 has been unequivocally determined by means of a single-crystal X-ray diffraction analysis. It is important that the reaction temperatures be held at ca. −30 °C during the reduction process, since treatment of Cp_2TiCl_2 in THF with magnesium in the presence of PMe_3 at room temperature leads to the formation of the titanium(II) product $Cp_2Ti(PMe_3)_2$ in good yield, apparently via a disproportionation process [10]. We postulate that the reduction proceeds via the intermediate formation of $(CpTiCl_2)_2$ (or its THF adduct) followed by ligand coordination to form **1** or **2**, since similar compounds have been previously formed by direct reactions of $(CpTiCl_2)_2$ with certain phosphines [11] and isonitriles [12] in toluene or THF solution. The new complexes **1** and **2** are highly air-sensitive both in the solid state and in solutions in organic solvents.



(**1**)



(**2**)

The molecular structure of **1** is shown in Fig. 1, together with important bond distances and angles. The molecule has a "piano stool" geometry with a non-crystallographic mirror plane passing through the Ti and Cl atoms and carbon atom C(3). The plane of the Cp ring and the planes Ti,Cl(1),Cl(2) and Ti,P(1),P(2) are all nearly mutually orthogonal with dihedral angles ranging from 89.6 to 89.9 °.

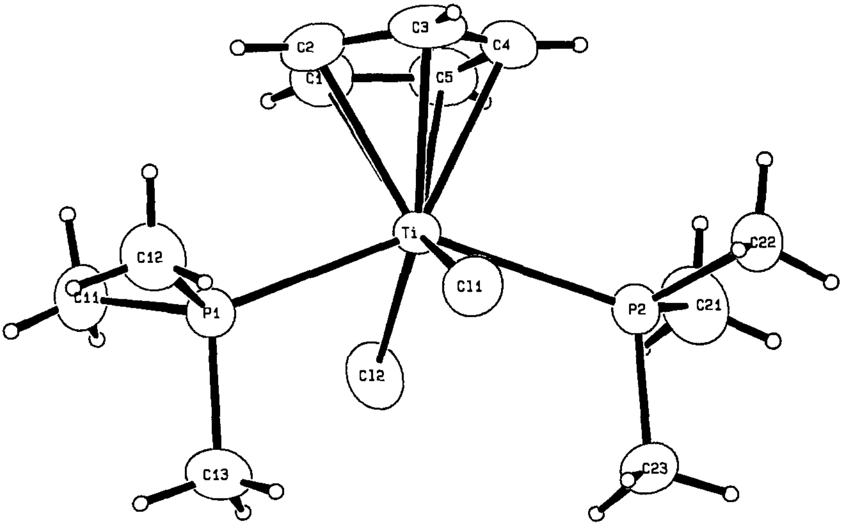


Fig. 1. ORTEP plot of $CpTiCl_2(PMe_3)_2$ (**1**) with thermal ellipsoids at the 30 percent probability level. Hydrogen atoms are represented by spheres of arbitrary radius. Bond lengths (Å): Ti–P(1) 2.602(1), Ti–P(2) 2.598(1), Ti–Cl(1) 2.394(1), Ti–Cl(2) 2.403(1), Ti–Cent 2.039. Bond angles (deg.): P(1)–Ti–P(2) 138.94(3), Cl(1)–Ti–Cl(2) 124.08(3), P–Ti–Cl (avg.) 80.54(2), P–Ti–Cent (avg.) 110.53, Cl–Ti–Cent (avg.) 117.96. Cent = center of Cp ring.

The Ti–P distances in **1** are not significantly different from that (2.599(2) Å) in the related Ti^{III} compound $Cp_2TiCl(PMe_3)$ [8], but are significantly longer than those found in the Ti^{II} compounds $Cp_2Ti(PMe_3)(CO)$ [8] (2.544(1) Å) and $Cp_2Ti(PMe_3)_2$ [1] (2.524(4) Å, 2.527(3) Å). An argument can thus be made for Ti–P back-bonding in the Ti^{II} compounds.

The Ti–Cl distances in **1** are somewhat longer (0.03 Å) than those found in Cp_2TiCl_2 [13] (avg. 2.364(2) Å), which is consistent with the higher oxidation state of the latter compound, but are considerably shorter (0.08 Å) than that (2.482(2) Å) in $Cp_2TiCl(PMe_3)$. The latter observation may perhaps be explained by the greater degree of apparent coordinative unsaturation in **1**.

1 is both isostructural and isomorphous with its vanadium analog, $CpVCl_2(PMe_3)_2$ [14]. An atom at (x, y, z) in **1** in $P2_1/c$ has a counter atom at approximately $(z, \frac{1}{2}-y, \frac{1}{2}+x)$ in the V compound which was reported in the alternate setting $P2_1/a$. The V–P bond lengths (avg. 2.509(1) Å) are roughly 0.09 Å shorter than the corresponding bond lengths in **1**, while the distance from the metal atom to the center of the Cp ring is approximately 0.07 Å shorter in the V compound. These observations are in keeping with the smaller size of the V atom [15]. In contrast, the M–Cl bond lengths are comparable in the two compounds (avg. V–Cl 2.403(1) Å).

Preliminary studies indicate that **1** may undergo various substitution reactions involving replacement of the PMe_3 substituents. The reaction chemistry of **1** as well as possible catalytic applications are under present investigation.

Experimental

All operations were performed under an argon atmosphere using Schlenk techniques. Hexane and toluene were dried over CaH_2 and tetrahydrofuran (THF) was dried over sodium/benzophenone; all solvents were freshly distilled before use. PMe_3 [16] and $CpTiCl_3$ [17] were prepared by literature methods, whereas 2,6-dimethylphenylisonitrile was obtained from Fluka Chemical Co.

Preparation of $CpTiCl_2(PMe_3)_2$ (1). To a 300 ml Schlenk flask was added 3.16 g (14.4 mmol) of $CpTiCl_3$ and 100 ml of THF. The yellow solution was cooled in a dry-ice/isopropanol bath to ca. −50 °C, and 1.00 g (41.1 mmol) of Mg and 4.0 ml (40 mmol) of PMe_3 were added. Upon addition, the solution turned orange. The mixture was allowed to warm slowly until the color began to change to blue-green (ca. −30 °C) and was maintained at this temperature for ca. 4 h. The blue-green solution was decanted from excess Mg into a Schlenk tube and the THF was removed in vacuo. The resulting residue was extracted with hexane and the extracts were filtered and cooled to −20 °C, giving 3.30 g (68%) of $CpTiCl_2(PMe_3)_2$ as green crystals, m.p. 144–146 °C dec. (Ar). ESR ($C_6H_5CH_3$) $g = 1.9821$ (t, a_P 25.0 G). IR (C_6H_6): 2965, 2905, 1415, 1295, 1255, 1005, 945, 798, and 728 cm^{-1}. Anal. Found: C, 39.25; H, 6.70; Cl. 21.26. $C_{11}H_{23}Cl_2P_2Ti$ calcd.: C, 39.31; H, 6.90; Cl, 21.10%.

Preparation of $CpTiCl_2(CNC_6H_3Me_2)_2$ (2). $CpTiCl_3$ (0.42 g, 1.9 mmol) was added to 100 ml of THF and the solution was cooled to ca. −50 °C. 2,6-Dimethylphenylisonitrile (0.56 g, 4.2 mmol) and Mg (0.25 g, 10 mmol) were added. The solution was allowed to warm slowly until the color changed to lime-green at ca. −20 °C, and was maintained at this temperature for 2 h. The THF was decanted and removed in vacuo. The residue was extracted with toluene and the green extracts were concentrated and cooled to −20 °C, resulting in 0.58 g (68%) of product. ESR ($C_6H_5CH_3$): $g = 1.9869$. IR (THF): ν(NC) 2160(s), 2265(w) cm^{-1} MS: m/e 315 ($M^+ - CNC_6H_3Me_2$), 183 ($CpTiCl_2^+$), 148 ($CpTiCl^+$), 131 ($CNC_6H_3Me_2^+$). Anal. Found: C, 62.12; H, 4.99; Cl, 16.27; N, 5.85. $C_{23}H_{23}Cl_2N_2Ti$ calcd.: C, 61.90; H, 5.20; Cl, 15.89; N, 6.28%.

X-ray data collection, solution and refinement of $CpTiCl_2(PMe_3)_2$ *(1)*

Crystal data for $CpTiCl_2(PMe_3)_2$. $C_{11}H_{23}Cl_2TiP_2$, $M = 336.06$. Monoclinic space group $P2_1/c$ (No. 14), a 13.202(4), b 10.447(3), c 12.516(3) Å, β 93.96(2)°, V 1722.1 $Å^3$, $Z = 4$, D_c 1.296 g/cm^3, $F(000) = 700$, μ(Mo-K_α) 9.7 cm^{-1}.

Polyfaceted green crystals suitable for X-ray diffraction analysis were grown from dilute hexane solution at −5 °C. The crystal used for the study (maximum dimensions 0.33 × 0.45 × 0.50 mm) was mounted in a thin walled glass capillary tube which was sealed under argon. Preliminary examination and data collection were performed with graphite monochromated Mo-K_α radiation (λ 0.71073 Å) on an Enraf–Nonius CAD4 diffractometer at an ambient temperature of 23 ± 2 °C. A total of 3022 unique reflections were measured ($+h, +k, \pm l$; θ–2θ scan mode, $2\theta_{max}$ 50°). An empirical absorption correction based on ψ scans was applied.

The structure was solved by Patterson and difference Fourier techniques and was refined by full-matrix least-squares methods (function minimized: $w(|F_0| - |F_c|)^2$, $w^{1/2} = 2F_0Lp/\sigma_I$). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included with fixed isotropic thermal parameters ("regularized" methyl group hydrogen atoms riding, positional parameters for Cp hydrogen atoms refined). The final agreement factors were $R = 0.030$ and $R_w = 0.044$ for the 2476 reflections having $I \geq 2\sigma I$.

All computations were performed on a Microvax II computer using the Enraf–Nonius SDP system of programs. Tables of atom coordinates, thermal parameters, bond lengths and angles, and observed and calculated structure factor amplitudes are available from R.O.D.

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