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SYNTHESIS AND PROPERTIES OF A THERMALLY STABLE METHYLTITANIUM(IV) COMPOUND: CYCLOPENTADIENYLMETHYLDICHLOROTITANIUM(IV)

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Summary

η^5-$C_5H_5Ti(CH_3)Cl_2$ and η^5-$C_5H_5Ti(C_2H_5)TiCl_2$ have been synthesized. The reactivity of the methyl compound is much greater than that of the closely related sandwich compound, $(\eta^5$-$C_5H_5)_2Ti(CH_3)Cl$, but the thermal stability is comparable.

The thermal instability of alkyltitanium(IV) compounds is well known. However the stability is greater for those compounds having no hydrogen on a carbon β to the metal, notably methyl and neopentyl compounds [1]. The presence of η^5-cyclopentadienyl ligands on the titanium also appears to increase stability and many of the better characterized alkyltitanium compounds have cyclopentadienyl ligands [2].

Among the compounds combining both these characteristics, the most frequently studied are two dicyclopentadienyl compounds, $(C_5H_5)_2Ti(CH_3)_2$ * and $(C_5H_5)_2Ti(CH_3)Cl$. Monocyclopentadienyl derivatives have been studied less frequently. Although $(C_5H_5)Ti(CH_3)_3$ has been examined [3–5] and is known to be, by the standards of alkyltitanium chemistry, moderately stable, $(C_5H_5)Ti(CH_3)Cl_2$ has not been reported except for a brief reference to the NMR spectrum [6]. On the basis of what is known about the thermal decomposition of these related compounds it appeared likely that $(C_5H_5)Ti(CH_3)Cl_2$ would be exceptionally stable and it has proven to be so.

Preparation

The compound can be prepared by treating $(C_5H_5)TiCl_3$ with $(CH_3)_3Al$, CH_3Li or CH_3MgCl but the reagent which leads most readily to isolating pure product is $(CH_3)_2Zn$. Preparations with this reagent are simplified by the insolubility of $ZnCl_2$

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* Throughout this paper, (C_5H_5) implies $(\eta^5$-$C_5H_5)$.

in benzene or alkanes, and by the fact that no $(C_5H_5)Ti(CH_3)_2Cl$ is detected even in the presence of a 10/1 excess of $(CH_3)_2$ Zn. Despite the latter fact, only a small excess of $(CH_3)_2Zn$ should be used since a large excess leads to formation of soluble CH_3ZnCl with consequent complications in isolating the product. Both $(C_5H_5)TiCl_3$ and $(C_5H_5)Ti(CH_3)Cl_2$ are reactive with water and therefore care must be taken throughout the preparation if formation of $[(C_5H_5)TiCl_2]_2O$ is to be avoided.

$(C_5H_5)TiCl_3$ was prepared using a minor variation of the method of Gorsich [7]. A mixture of about 16 g of $(C_5H_5)_2TiCl_2$ (65 mmol) and 20 g of $TiCl_4$ (100 mmol) was refluxed for 48 h in 300 ml of dry toluene under a nitrogen atmosphere. The volatiles were then removed by pumping and the resulting brown solid was purified by sublimation. The $(CH_3)_2Zn$ was prepared as described previously [8].

In a typical preparation of $(C_5H_5)Ti(CH_3)Cl_2$, 2.35 g of $(C_5H_5)TiCl_3$ (10.7 mmol) and 50 ml of degassed, sodium-dried benzene were added to a 100 ml round bottom flask under an atmosphere of dry nitrogen, and the flask swirled until all of the solid had dissolved. A Schlenk separating funnel was then used to add a solution (0.429 ml of $(CH_3)_2Zn$ in 10 ml of benzene) drop by drop with continuous stirring. After standing for ten to fifteen minutes, the zinc chloride can be separated by filtration. The solvent is evaporated under vacuum and the dark orange solid residue transferred to a sublimation vessel. The yield of sublimed material is typically over 60%, based on $(C_5H_5)TiCl_3$. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, Tennessee, U.S.A. The actual and theoretical values, in mole percentages, are as follows. Found: C, 36.28; H, 4.05; Ti, 23.97; Cl, 35.70. $C_6H_8TiCl_2$ calcd.: C, 36.23; H, 4.05; Ti, 24.08; Cl, 35.64%.

All three deuterated analogues (d_3, d_5 and d_8) were prepared by the same method. $(CD_3)_2Zn$ (Merck, Sharpe and Dohme Canada, 99.5% isotopic purity) was purchased. $(C_5D_5)TiCl_3$ was prepared by refluxing 5.0 g of C_5D_5Tl (18 mmol) and 2.9 ml of $TiCl_4$ (26 mmol) in 50 ml dry toluene under nitrogen for twelve hours. The volatiles were removed by pumping and the product purified by sublimation under vacuum. Yield was 60% based on $TiCl_4$.

C_5D_5Tl was prepared by the method of Cross et al. [9], with minor variations. Typically, 9.1 g of sodium (400 mmol) was cut directly into a 250 ml 3-neck flask under dry nitrogen. The flask was cooled in powdered dry ice and 100 g of D_2O (Merck, Sharpe and Dohme Canada, 99.8% isotopic purity) was added cautiously from a dropping funnel, the resulting D_2 being vented in a slow stream of nitrogen. Freshly cracked cyclopentadiene (2.9 ml, 35 mmol) was syringed into the resulting NaOD solution, the latter having been cooled first. The flask was then sealed and shaken vigorously for five hours. The flask was opened under nitrogen and 6.75 g of Tl_2SO_4 (29 mmol) was added rapidly. The flask was resealed and shaken for an additional hour. The buff solid was filtered, washed with distilled water, and dried overnight over H_2SO_4. Sublimation gave pale yellow crystals in 80% yield based on Tl_2SO_4. Isotopic purity was 93.2%.

$(C_5H_5)Ti(C_2H_5)Cl_2$ has been prepared by a completely analogous route using $(C_2H_5)_2Zn$ (Texas Alkyls). It is a red liquid crystallizing at about 20°C to give dark red crystals. However, adequate purity has not yet been achieved.

Properties

(i) General properties

The compound $(C_5H_5)Ti(CH_3)Cl_2$ is an orange to yellow-orange crystalline solid

TABLE 1

PROTON NMR DATA AT 25°C

Compound	Solvent	Concentration (mol l^{-1})	C_5H_5	CH_3	CH_2
$C_5H_5Ti(CH_3)Cl_2$	$CDCl_3$	0.2	6.71	1.93	–
$C_5H_5Ti(CH_3)Cl_2$	CCl_4	0.2	6.67	1.83	–
$C_5H_5Ti(CH_3)Cl_2$	C_6D_6	0.2	5.87	1.74	–
$C_5H_5Ti(CH_3O)Cl_2$	C_6D_6	0.2	6.09	3.76	–
$[C_5H_5TiCl_2]_2O$	C_6D_6	0.1	6.35	–	–
$C_5H_5Ti(C_2H_5)Cl_2$	C_6D_6	0.2	5.88	1.45	2.27

at room temperature, the color depending on the size and aggregation of the crystals. Its volatility is sufficient to permit sublimation at room temperature at reduced pressure. It is soluble in benzene, tetrachloromethane, trichloromethane and tetrahydrofuran, but is only modestly soluble in alkanes.

The ^1H and ^{13}C spectra each exhibit a single cyclopentadienyl resonance and a single methyl resonance. Some chemical shifts measured on a Bruker CXP-200 NMR spectrometer for 0.2 mol l^{-1} solutions at 25°C are listed in Table 1. The IR spectrum in benzene solution shows very strong bands at 415, 495 and 820 cm^{-1}, and bands of medium intensity at 1380 and 1430 cm^{-1}.

(ii) Reactions with oxygen and water

The compound is reactive with both water and oxygen and must be handled in an inert atmosphere. A small amount of water added to a benzene solution of the compound reacted quickly to produce CH_4 and $[(C_5H_5)TiCl_2]_2O$. Methane was identified by mass spectrometry and by ^1H NMR spectroscopy. $[(C_5H_5)TiCl_2]_2O$ was characterized by its NMR spectrum. There are also minor NMR resonances in the region of the hydrogen spectrum where cyclopentadienyltitanium resonances occur. The identification of $[(C_5H_5)TiCl_2]_2O$ was reinforced by preparing it separately by an established method [7] and showing that the NMR resonances superimpose. This oxygen bridged dititanium species is identical to that produced by the reaction of water with $(C_5H_5)TiCl_3$ [7] and is analogous to the compound produced by the reaction of water with $(C_5H_5)_2Ti(CH_3)Cl$ [10]. However whereas $(C_5H_5)Ti(CH_3)Cl_2$ reacts quickly, the formation of $[(C_5H_5)_2TiCl]_2O$ is slow, and $(C_5H_5)_2Ti(CH_3)Cl$ can be dissolved in cold water without significant reaction taking place [11].

Oxygen, dried over P_2O_5, was introduced into a tube containing a benzene solution of the compound, the O_2/Ti ratio being around 0.5. Shaking the tube brought about complete and rapid conversion of the compound to $(C_5H_5)Ti(CH_3O)Cl_2$. Again, this compound was synthesized separately by established methods [7] and the NMR resonances were shown to coincide exactly.

(iii) Reaction with HCl

Dry HCl bubbled through a benzene solution produced CH_4 and $(C_5H_5)TiCl_3$ in stoichiometric amounts. Mass spectrometry was used to identify the first and ^1H NMR to characterize the second. Similarly DCl produced CH_3D and $(C_5H_5)TiCl_3$. These reactions took several hours to reach completion at room temperature.

TABLE 2

VOLATILE PRODUCTS OF THERMAL DECOMPOSITION OF $CpTiMeCl_2$ AT 340 K

State	Products (yield (%))
Solid	CH_4 (99.5), C_2H_6 (0.5)
0.2 mol l^{-1} in C_6D_6	CH_4 (95), C_2H_6 (5)
0.2 mol l^{-1} in CCl_4	CH_4 (70), CH_3Cl (25), C_2H_6 (5)

Reaction with crystalline $(C_5H_5)Ti(CH_3)Cl_2$ was even slower, with only traces of CH_3D detected by mass spectrometry after four weeks exposure of the crystals to DCl gas.

(iv) Reaction with halogens

Reaction with iodine or bromine added to benzene solution was rapid and gave a quantitative yield of methyl iodide or methyl bromide. ^1H NMR was used to monitor the reaction. The other product is a cyclopentadienyltitanium trihalide, with a complete range of mixed halides in each case.

(v) Thermal stability

Pure crystalline $C_5H_5Ti(CH_3)Cl_2$ stored under a nitrogen atmosphere in the dark at ambient temperature showed no detectable decomposition even after four years. Several weeks were required for complete decomposition at 373 K.

Decomposition in benzene or hexane solution is more rapid. Thermal decomposition was complete in a matter of months above 70°C. Photodecomposition in ordinary laboratory light took place in a few weeks at ambient temperature. Both modes of decomposition involved some abstraction of solvent hydrogen from benzene and from hexane.

The volatile products of thermal decomposition are shown in Table 2. It is noteworthy that decomposition gave predominantly methane in all cases in contrast to the decomposition of CH_3TiCl_3 [13] which yields much ethane in the same solvent at the same temperature.

Much of the published work on cyclopentadienyltitanium compounds is on the η^5-dicyclopentadienyl compounds. Comparison of the properties of monocyclopentadienyl compounds with those of the η^5 compounds, and with those of the alkyltitanium halides, is of interest in uncovering the role of cyclopentadienyl rings in determining properties. The ready reactivity of $CH_3Ti(C_5H_5)Cl_2$ with oxygen, water and other reactants is much more like that of CH_3TiCl_3 [12] than it is like that of the inert and slow-to-react $CH_3Ti(C_5H_5)_2Cl$ [11]. On the other hand, its thermal stability, especially in the crystalline state, is similar to and indeed exceeds that of $CH_3Ti(C_5H_5)_2Cl$ whereas crystalline CH_3TiCl_3 decomposes rapidly at room temperature. Studies of the thermal decomposition of $(C_5H_5)Ti(CH_3)Cl_2$ and of related compounds are continuing.

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