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IMPROVED SYNTHESES OF CHLORODICYCLOPENTADIENYL DERIVATIVES OF SCANDIUM(III), TITANIUM(III) AND VANADIUM(III)

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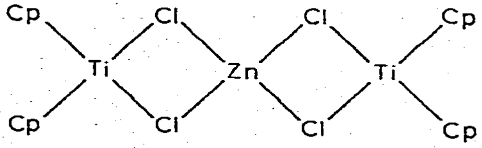
Summary

An improved synthesis of chlorodicyclopentadienyl derivatives of scandium(III), titanium(III) and vanadium(III) has been developed by the reaction of thallium cyclopentadienide with the appropriate anhydrous metal trihalides.

Cyclopentadienyl (Cp) derivatives of titanium(IV) have received considerable attention since they serve as model compounds for the study of Ziegler—Natta-type polymerization catalysts [1]. Although dicyclopentadienyl complexes of titanium(III) have also been studied in considerable detail, a simple preparation of Cp_2TiCl(I) is not available. In polar organic solvents such as methanol, tetrahydrofuran, and acetone Cp_2TiCl_2 will react with finely divided zinc to give the adduct II [2]. Cp_2TiCl can be obtained from this complex in very low yield by pyrolysis [3]. Green and Lucas [4] have recently found that the zinc complex may be partially decomposed with diethyl ether to give Cp_2TiCl in about 50% yield. Reid and Wailes [5] described the preparation of Cp_2TiCl in 78% yield from $TiCl_3$ and $MgCp_2$. The main drawback to the latter reaction is the preparation of $MgCp_2$.



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We have now found a very simple procedure using commercially available starting materials that readily yields large quantities of Cp_2TiCl in a few hours. The procedure simply involves the reaction of two molar equivalents of TlCp with $TiCl_3$ in boiling tetrahydrofuran (eq. 1). It is important to use freshly sublimed TlCp.

$$TiCl_3 + 2\,TlCp \xrightarrow{THF} Cp_2TiCl + 2\,TlCl \qquad (1)$$

The TlCl is filtered from the reaction mixture and washed with hot THF. The THF is removed from the combined filtrate and washings by rotary evaporation [6] giving Cp_2TiCl as a green-brown crystalline compound. If precautions are taken to rigorously exclude air and moisture during the entire synthesis, the Cp_2TiCl obtained is analytically pure and may be used without further purification.

Reaction 1 is easily extended to scandium and vanadium. The addition of two molar equivalents of TlCp to VCl_3 in THF gave Cp_2VCl in >90% yield. This represents an improvement over the previous methods of reacting VCl_4 with NaCp in a 1 : 3 ratio [6,7] and reacting Cp_2V with HCl [7,8], $PhCH_2Cl$ [8] or CH_3Cl [8].

The reaction of two equivalents of TlCp with anhydrous $ScCl_3$ in THF gives a clear colorless solution with a precipitate of TlCl. The solution was filtered and the solvent removed by rotary evaporation to give large white crystals that may be recrystallized from toluene and ether. The NMR and analytical data indicate that a THF molecule is coordinated to give $Cp_2ScCl(THF)$. The compound can be sublimed but retains the coordinated THF. The high resolution mass spectrum, however, showed a parent ion for $[Cp_2ScCl]_2$ (Calculated mass 420.006; observed mass 420.001). $[Cp_2ScCl]_2$ as previously prepared by Coutts and Wailes [9] from the reaction of Cp_2Mg with $ScCl_3$ in THF was obtained as a yellow-green crystalline solid whose X-ray crystal structure has been determined [10]. The reason for the stability of the THF complex obtained by the present process is not obvious but it does provide a more convenient route to the Cp_2ScCl moiety.

Several attempts to prepare $[CpTiCl_2]_x$ by the reaction of one equivalent of TlCp with $TiCl_3$ or $TiCl_3(THF)_3$ in THF gave only a mixture of Cp_2TiCl and $TiCl_3(THF)_3$. These results may well indicate that the reaction between TlCp and $TiCl_3$ is kinetically controlled (i.e., $k_2 \gg k_1$).

$$TlCp + TiCl_3 \xrightarrow{k_1} CpTiCl_2 \xrightarrow[TlCp]{k_2} Cp_2TiCl$$

The $CpTiCl_2$ that is initially produced must react with the remaining TlCp faster than $TiCl_3$ reacts with TlCp.

Experimental

Tetrahydrofuran was refluxed over $LiAlH_4$, distilled under nitrogen, and stored over sodium. All other solvents were dried by passing them through columns containing molecular sieves (Linde 4A) and were sparged with nitrogen before use.

Thallium cyclopentadienide was purchased from Strem Chemicals and sublimed at 10^{-4} mmHg and 150°C.

All anhydrous metal chlorides were purchased from Research Organic/Inorganic Chemicals Corporation.

All manipulations of air-sensitive materials were performed in a Vacuum-Atmospheres Corporation dry box (Model HE 43-2).

Microanalyses were performed by our Physical and Analytical Division and by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

A. Preparation of Cp_2TiCl

$TiCl_3$ (20.0 g, 0.130 mol) was suspended in 300 ml of tetrahydrofuran in a 1-liter round-bottom flask. The suspension was magnetically stirred and solid TlCp (69.9 g, 0.260 mol) was added over a period of about 10 min. The titanium trichloride rapidly dissolved to give a green-brown solution. When all the TlCp had been added, the mixture was refluxed for 1 h and filtered into a 1-liter round-bottom flask. The TlCl was washed with THF until the washings were colorless. The THF was removed from the filtrate and washings by rotary evaporation (Note: the complex is extremely sensitive to air and moisture so that care must be taken to flush the rotaty evaporator with nitrogen while transferring the flask to and from the evaporator). As the THF was removed, small green-brown crystals were formed. When the crystals were dry, the solid was scraped from the flask to give 27.2 g of an analytically pure sample, m.p. 285—288°C. (lit. [5] 282—283°C). Yield 98%.

Anal. found: C, 56.30; H, 4.85; Cl, 16.68. $C_{10}H_{10}ClTi$ calcd.: C, 56.22; H, 4.72; Cl, 16.59%.

B. Preparation of Cp_2VCl

To a magnetically stirred suspension of VCl_3 (10.3 g, 0.065 mol) in 300 ml of THF was added TlCp (35.52 g, 0.132 mol). The mixture was then refluxed for 2 h to give a deep blue solution and a precipitate of TlCl. The TlCl was filtered off and washed until the washings were colorless. The THF was then removed from the filtrate and washings by rotary evaporation to give metallic blue crystals. The compound was dissolved in the minimum amount of dichloromethane, filtered through a fine frit to remove some insoluble white solid, and then the dichloromethane was removed by rotary evaporation to give pure Cp_2VCl, m.p. 194—198°C (lit. [8] 206—207°C).

The compound is extremely sensitive to air and moisture both in the solid state and in solution. It may be easily sublimed at 10^{-4} mmHg, 100°C to give dark-blue needles. The yield was 13.0 g (91.5%). Anal. found: C, 55.28; H, 4.59; Cl, 16.43. $C_{10}H_{10}ClV$ calcd.: C, 55.45; H, 4.65; Cl, 16.37%).

C. Preparation of $Cp_2ScCl \cdot THF$

A suspension of $ScCl_3$ (9.0 g, 59.48 mmol) and TlCp (32.04 g, 0.118 mol) in 500 ml of THF was refluxed for 2 h to give a clear, colorless solution and a precipitate of TlCl. The solution was filtered and the TlCl was washed with THF. The solvent was removed from the filtrate and washings by rotary evaporation to give white crystals of $Cp_2ScCl \cdot THF$ (14.3 g, 85%). The compound may be recrystallized from toluene, and ether, m.p. 303—307°C.

Anal. found: C, 58.33; H, 6.35; O, 6.53. $C_{10}H_{18}ClOSc$ calcd.: C, 59.48;

H, 6.42; O, 5.66%. NMR (C_6D_6/TMS): $\delta(C_5H_5)$ 6.25; $\delta(OCH_2)$ 3.52; $\delta(O{-}C{-}CH_2)$ 131 ppm.

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