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Unusual reactivity of tritylcyclopentadienylmetal derivatives. Molecular structure of $Ph_3CC_5H_4SnMe_3$ and $Ph_3CC_5H_4TiCl_3$

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Abstract

The preparative synthetic routes to tritylcyclopentadienyl metal derivatives of sodium, tin and titanium have been studied. Molecular structures of $Ph_3CC_5H_4SnMe_3$ (3) and $Ph_3CC_5H_4TiCl_3$ (4) have been defined. The Cl–Ph agostic interaction in the structure of **4** provides an unprecedented low reactivity of **4** to nucleophiles of different natures.

Keywords: Tin; Titanium

1. Introduction

Cyclopentadienes with bulky substituents are usually applied in the syntheses of a numerous of transition metal π complexes, which are interesting as potential catalysts [1–6].

In the present work we have investigated the influence of the highly crowded triphenylmethyl substituent on the reactivities of sodium, tin and titanium cyclopentadienyl metal derivatives.

2. Results

As we have found previously [6], triphenylmethylcyclopentadiene reacts with NaH in tetrahydrofuran (THF), yielding $Ph_3CC_5H_5Na$ (**1**), which was isolated as crystalline solid. In this work we have used **1** without any special purification and analysis. Treatment of **1** with Me_3SiCl, Me_3SnCl or $TiCl_4$ in molar ratio 1:1 gives $Ph_3CC_5H_4SiMe_3$ (**2**) [6], $Ph_3CC_5H_4SnMe_3$ (**3**) and $Ph_3CC_5H_4TiCl_3$ (**4**) respectively. Bright-yellow crystalls of **4** have also been prepared by the reactions of **2** or **3** with $TiCl_4$ in toluene. In the last case, the yield of **4** is almost quantitative (Scheme 1). Synthesis of **2** [6], **3** and **4** through the sodium salt **1** is the best way to prepare these compounds to date.

The reactivity of **4** has been investigated through reactions with cyclopentadienyl and tritylcyclopentadienyl metal derivatives. An interaction of **4** with $C_5H_5SnMe_3$ gives the brick-red microcrystalline monosubstituted titanocene **6**, albeit with a poor yield. This compound dissolves a little in almost all solvents and it does not hydrolyse even in water. We tried to prepare another biscyclopentadienyl complex **5** with two bulky substituents. The reaction of **4** with **1** or **3** was examined under various conditions but, in all cases, only the starting reagents were observed. Moreover, the interaction of **4** with **1** does not provide Ti(IV)–Ti(III) reduction, which is usual for unsubstituted derivatives (Section 3.1).

The molecular structures of **3** and **4** have been defined by X-ray diffraction (Figs. 1 and 2). We have found that Me_3Sn moiety of **3** occupies exclusively the allylic σ-bonded position in the cyclopentadiene ring (but in a solution the fast 1,5-$SnMe_3$ elementotropic shifts are known to occur [7]). This situation is very similar to that of **2**, the crystal structure of which has been defined earlier [6], but in this case the Sn–C(5)–C(4) angle is 106.2(4)°, the Sn–C(5)–C(6) bond angle is 108.7(4)° and the bond lengths between carbon atoms in the substituted Cp ring indicate the coordination

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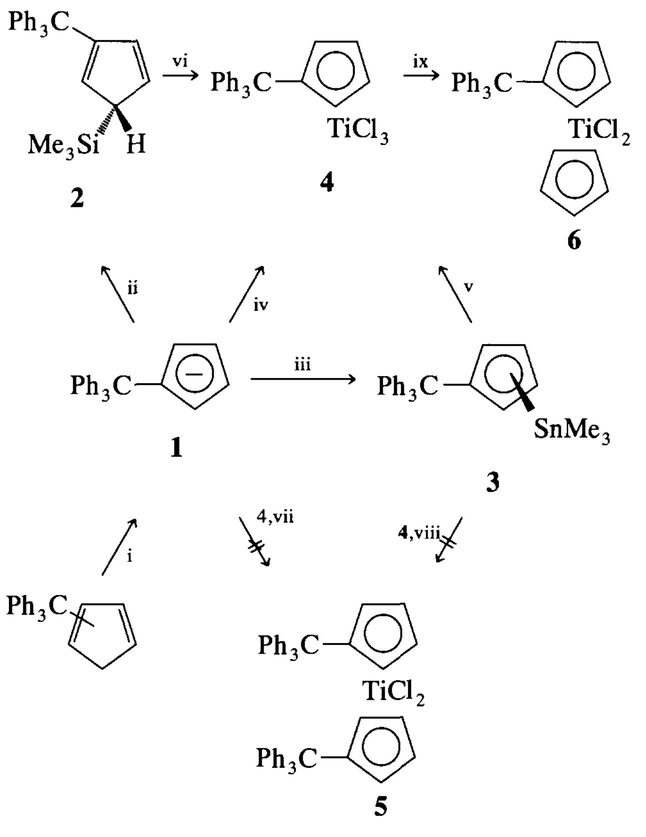

Scheme 1. Reagents and conditions: i, NaH (four equivalents), 5 h, 60°C, THF, 100%; ii, Me_3SiCl, 24 h, 100°C, toluene, 76%; iii, Me_3SnCl, 1 h, 25°C, toluene, 59%; iv, $TiCl_4$, 30 min, 25°C, toluene, 68%; v, $TiCl_4$, 24 h, 25°C, toluene, 97%; vi, $TiCl_4$, 24 h, 25°C, toluene, 75%; vii, 96 h, 100°C, toluene; viii, 48 h, 100°C, toluene; ix, $C_5H_5SnMe_3$, 150 h, 50°C, toluene, then recrystallized from THF, 35%.

lability of this molecular moiety. The steric requirements leave the substituents in a maximally distant arrangement.

The structure of **4** shows η^5 coordination of the $TiCl_3$ moiety to the trityl-substituted cyclopentadienyl ring, which is akin to the structure of unsubstituted half-sandwich $CpTiCl_3$ [8]. The structure of **4** is exemplified by normal tetrahedral angles of the central carbon atom and C–C distances in C_5 and Ph rings. The important peculiaruty in the molecular structure of **4** is the agostic contact between the Cl(1) atom and the Ph(C(21)–C(26)) ring with a 3.418 Å distance of Cl(1) to the C(21)–C(26) bond. It is interesting that the Ti–Cl(1) bond is much shorter than the two other bonds (Ti–Cl(2) and Ti–Cl(3)). This interaction was found in effect for the first time.

Average deviations of the carbon atoms from the Ph(C(21)–C(26)) plane (0.016 Å) are much greater than in the Ph(C(11)–C(16)) (0.001 Å) and Ph(C(31)–C(36)) (0.005 Å) rings. The distortion arising from the Cl–Ph interaction leads to changes in the values of the C–C1–Cp(centroid) angle (168.5°) and the (C(1),C(2),C(5))–(C(2),C(3),C(4),C(5)) plane angle (178.1°).

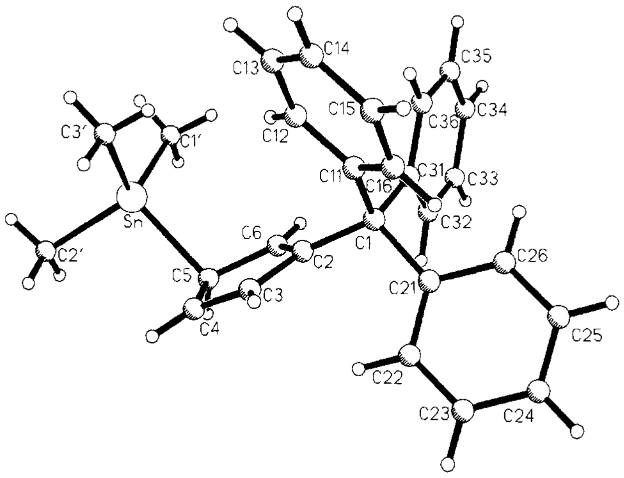

Fig. 1. Molecular structure of $Ph_3CC_5H_4SnMe_3$ (**3**), as determined by a single-crystal X-ray diffraction study. Selected bond lengths and angles are as follows: Sn–C(1'), 2.109(8) Å; Sn–C(2'), 2.127(9) Å; Sn–C(3'), 2.120(10) Å; Sn–C(5), 2.194(6) Å; C(1)–C(2), 1.543(7) Å; C(1)–C(11), 1.545(8) Å; C(1)–C(21), 1.547(7) Å; C(1)–C(31), 1.548(8) Å; C(2)–C(3), 1.441(8) Å; C(2)–C(6), 1.355(7) Å; C(3)–C(4), 1.359(7) Å; C(4)–C(5), 1.471(9) Å; C(5)–C(6), 1.482(8) Å; C(1')–Sn–C(2'), 112.0(4)°; C(1')–Sn–C(3'), 109.5(4)°; C(1')–Sn–C(5), 108.7(3)°, C(2')–Sn–C(5), 112.0(3)°; C(2')–Sn–C(3'), 110.1(4)°; C(2')–Sn–C(5), 104.5(3)°; C(1)–C(2)–C(3), 123.0(5)°; C(1)–C(2)–C(6), 128.4(5)°; C(3)–C(2)–C(6), 108.5(5)°; C(2)–C(3)–C(4), 109.7(5)°; C(3)–C(4)–C(5), 108.5(5)°; C(4)–C(5)–C(6), 104.1(5)°; C(2)–C(6)–C(5), 109.1(5)°.

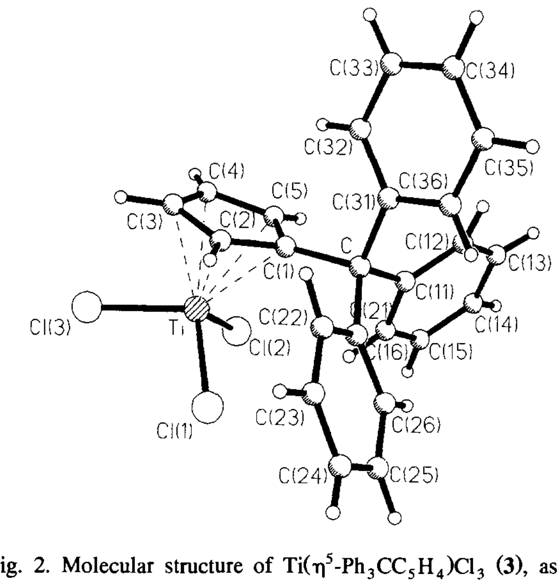

Fig. 2. Molecular structure of $Ti(\eta^5\text{-}Ph_3CC_5H_4)Cl_3$ (**3**), as determined by a single-crystal X-ray diffraction study. Selected bond lengths and angles are as follows: Ti–Cl(1), 2.205(3) Å; Ti–Cl(2), 2.212(3) Å; Ti–Cl(3), 2.236(7) Å; Ti–C(1), 2.443(6) Å; Ti–C(2), 2.382(7) Å; Ti–C(3), 2.332(8) Å; Ti–C(4), 2.292(8) Å; Ti–C(5), 2.363(7) Å; Ti–Cp(centroid), 2.037 Å; Cl(1)–C(21), 3.459 Å; Cl(1)–C(26), 3.522 Å; C(1)–C(2), 1.410(10) Å; C(1)–C(5), 1.417(9) Å; C(2)–C(3), 1.390(10) Å; C(3)–C(4), 1.400(10) Å; C(4)–C(5), 1.420(10) Å; Cl(1)–(C(21)–C(26)), 3.418 Å; Cl(1)–Ti–Cl(2), 106.3(1)°; Cl(1)–Ti–Cl(3), 102.8(1)°; Cl(2)–Ti–Cl(3), 100.2(1)°; C(1)–C(2)–C(3), 109.1(6)°; C(2)–C(3)–C(4), 108.2(7)°; C(3)–C(4)–C(5), 107.9(7)°; C(1)–C(5)–C(4), 108.1(6); C(2)–C(1)–C(5), 106.7(5)°; C–C(1)–Cp(centroid), 169.5(5)°.

An essential decrease in the reactivity of tritylcyclopentadienyltin and tritylcyclopentadienyltitanium derivatives on comparison with unsubstituted compounds has been found. Because of the presence of the highly crowded trityl substituent all these compounds show an unusual stability with respect to oxidation and hydrolisis: one can handle **4** in the open air for hours. Structural investigation of **3** and **4** showed strong interactions between tritylcyclopentadienylmetal and cyclopentadienylmetal moieties to exist; this explains their chemical properties.

3. Experimental details

3.1. Spectroscopic data

3: ^{1}H NMR (Varian VXR-400 spectrometer; THF-d_8): δ 7.30–7.05 (m, 15H, Ph-ring CH); 6.22, 5.19 (m, m, 2H, 2H, $\overline{AA'XX'}$, Cp-ring CH, $J_{\mathrm{SnH}} = 45$ Hz); 0.080 (s, 9H, $-CH_3$, $J_{\mathrm{SnH}} = 54$ Hz) ppm.

4: ^{1}H NMR (toluene-d_8): δ 7.39–6.97 (m, 15H, Ph-ring CH); 6.396, 6.257 (t, t, 2H, 2H, $\overline{AA'BB'}$, Cp-ring CH) ppm.

6: ^{1}H NMR ($CDCl_3$): δ 7.31–7.19, 7.03–6.98 (m, m, 15H, Ph-ring CH); 6.651, 6.690 (t, t, 2H, 2H, $\overline{AA'BB'}$, Ph_3CCp-ring CH); 6.244 (s, 5H, Cp-ring CH) ppm.

3.2. Crystal data

These were collected at room temperature on an Enraf–Nonius CAD4 diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The structures were solved by the direct method (SHELXS 86) [9] and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined anisotropically.

Colourless crystals of **3** grown from a toluene solution of the compound, were of the triclinic space group $P\bar{1}$; $a = 10.371(5)$, $b = 11.417(10)$ and $c = 11.710(5)$ Å; $\alpha = 71.85(5)$, $\beta = 64.59(4)$ and $\gamma = 70.65(6)$°; $V = 1158(1)$ Å^3; $Z = 2$; $D_c = 1.3512$ g cm^{-3}; $\mu = 1.11$ mm^{-1}; $F(000) = 480.00$. A total of 2614 unique reflections were recorded, leaving 2610 ($F > 2\sigma$) for solution and refinement. The final agreement factors were $R = 0.0407$, $R_w = 0.0427$ and a goodness of fit of 0.961.

Bright-yellow crystals of **4** grown from a toluene solution of the compound, were of the monoclinic space group $P2/n$; $a = 13.162(2)$, $b = 10.254(3)$ and $c = 16.497(3)$ Å; $\beta = 105.20(1)$°; $V = 2148(6)$ Å^3; $Z = 4$; $D_c = 0.8594$ g cm^{-3}; $\mu = 0.78$ mm^{-1}; $F(000) = 948.00$. A total of 1739 unique reflections were recorded, leaving 1727 ($F > 2\sigma$) for solution and refinement. The final agreement factors were $R = 0.0461$, $R_w = 0.0482$ and a goodness of fit of 1.630.

Atomic coordinates, bond lengths and angles, and thermal parameters are available from the authors.

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