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Preparation of the substituted salicylato of titanocene derivatives by the liquid–liquid interfacial reaction

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Abstract

The reaction of Cp_2TiCl_2 with several substituted salicylic acids in $H_2O + CHCl_3$ medium was discussed in detail. By interfacial reaction (methods 1–3), ten titanocene derivatives were prepared, respectively. The compounds were characterized by elemental analysis, UV–vis, IR and ^{1}H-NMR. Based on the UV–vis spectrum, the following mechanism of reaction was proposed: first, Cp_2TiCl_2 in the organic phase interfacially with water in the aqueous phase to form its hydrolysate (such as $[Cp_2Ti(OH)(OH_2)]^+$). When 5-sulfosalicylic acid (H_2Ssal) is present in the reaction system, the hydrolysate transforms itself into $[Cp_2Ti(Ssal)]^+$ and the reaction is prompted. The resulting species undergoes an interfacial interaction with substituted salicylic acid to form the final complexes, which stay in the organic phase. Then the 'Cp_2Ti' species return to the organic phase.

Keywords: Titanocene; Salicylic acid; Interfacial reaction; Synthesis

1. Introduction

Titanocene derivatives have attracted considerable interest because of the fact that these compounds act as catalysts in organic synthesis [1,2], anti-tumor activity drugs [3,4] and even as antioxidative agents [5]. However, most of titanocene derivatives are prepared in anhydrous organic solvent [1–3,5,6].

Syntheses of titanium complexes in the presence of water are still comparatively scarce [7]. In part, this is due to the limited stability of titanocene dichloride (Cp_2TiCl_2) in aqueous solution [8], as well as in two-phase systems [9,10]. Recently, we used Cp_2TiCl_2 in a reaction with the sodium salt of substituted salicylic acid to give the types $Cp_2Ti(Sal)$ and $Cp_2Ti(HSal)_2$. However, the reaction is strongly affected by some factors, such as temperature, pH value of aqueous solution, concentration of substituted salicylic acid and the ratio of reaction species [11]. In this paper, we are interested in preparing some substituted salicylato titanocene derivatives in a $H_2O/CHCl_3$ medium. In order to obtain more information about this method, we use three different approaches to probe into the reaction behavior of Cp_2TiCl_2 in two phases. It is found that water played an important role in the interfacial reaction, and to a certain degree, it is used as HCl-receiver to help in forming the resulting products. Additionally, 5-sulfosalicylic acid can prompt the reaction between Cp_2TiCl_2 and some substituted salicylic acids.

2. Results and discussion

2.1. The action of water

Water plays an important role in the interfacial reaction. No reaction phenomena were observed when Cp_2TiCl_2 mixed with the substituted salicylic acid in chloroform. However, the reaction clearly occurs in the presence of water. In the absence of water, the UV–vis spectrum gives a very intense band of Cp_2TiCl_2 at 522 nm in $CHCl_3$ (Figs. 1–3(b)). A characteristic absorption band of the complex **1** at 602 nm in $CHCl_3$ was

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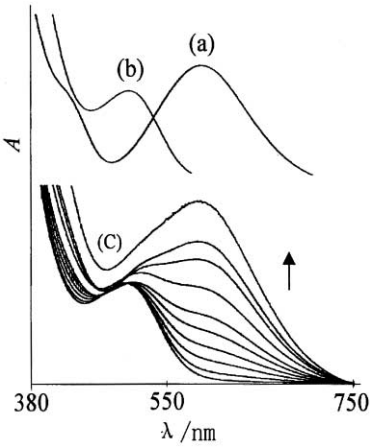


Fig. 1. UV–vis spectrum (in $CHCl_3$ layer) of the process of the reaction between Cp_2TiCl_2 and thiosalicylic acid $H_2O + CHCl_3$. (a) UV–vis spectrum of complex **1** in $CHCl_3$. (b) UV–vis spectrum of Cp_2TiCl_2 in $CHCl_3$. (c) Process of the reaction.

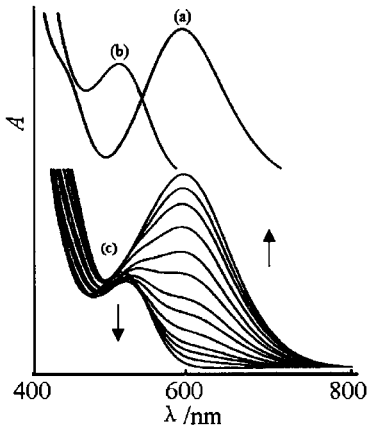


Fig. 2. UV–vis spectrum (in $CHCl_3$ layer) of the process of the reaction between Cp_2TiCl_2 and sodium thiosalicylato in $H_2O + CHCl_3$. (a) UV–vis spectrum of complex **1** in $CHCl_3$. (b) UV–vis spectrum of Cp_2TiCl_2 in $CHCl_3$. (c) Process of the reaction.

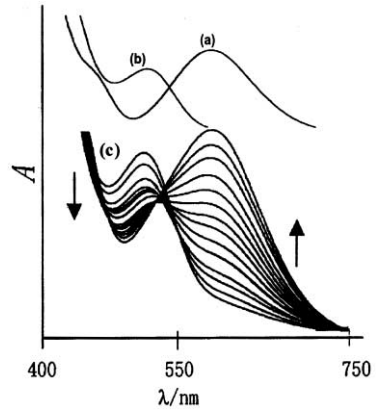
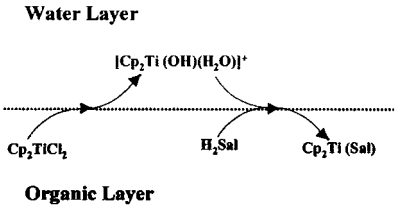


Fig. 3. UV–vis spectrum (in $CHCl_3$ layer) of the process of the reaction between Cp_2TiCl_2, 5-sulfosalicylic acid and thiosalicylic acid $H_2O + CHCl_3$. (a) UV–vis spectrum of complex **1** in $CHCl_3$, (b) UV–vis spectrum of Cp_2TiCl_2 in $CHCl_3$. (c) Process of the reaction.



Scheme 1. Formation of $Cp_2Ti(Sal)$ from Cp_2TiCl_2 and H_2Sal in $H_2O + CHCl_3$. H_2Sal: substituted salicylic acid.

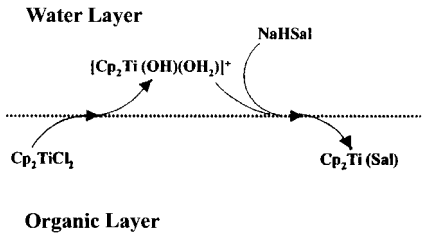
illustrated in Figs. 1–3(a). Thiosalicylic acid has no characteristic absorption band in the range of 380–800 nm. Hence, in the presence of water, the dynamic process of the reaction between Cp_2TiCl_2 with thiosalicylic acid in $CHCl_3$ was monitored by the UV–vis spectrum shown in Figs. 1–3(c).

As seen in Fig. 1(c), the characteristic absorption of Cp_2TiCl_2 can be easily found and does not seem to change much in the earlier stage of the reaction while that of the complex **1** increases gradually. In the midterm of the reaction, there is a slight red-shift for the characteristic absorbance of Cp_2TiCl_2. Finally, the absorption band of the product continually increases when that of Cp_2TiCl_2 disappears. These results suggest that the reaction occurs through an interfacial action in the presence of water, and the red-shift of the spectrum is possibly related to the characteristic absorption bands of Cp_2TiCl_2 and the product. This spectrum nature implies no intermediate species in the organic phase. Thus the formation of the product is carried out by the interfacial reaction. For the purpose of obtaining more information about it, the UV–vis spectrum of the reaction is detected in water phase. To the result, we observe the characteristic absorption of Cp_2TiCl_2 at ca. 243 nm. In fact, Cp_2TiCl_2 in water undergoes a series of hydrolytic actions to form the various cationic species, such as $[Cp_2Ti(OH)(OH_2)]^+$ and $[Cp_2Ti(OH_2)_2]^{2+}$, which are stable in acid solution [8,12,13]. Therefore, the interfacial reaction mechanism is divided by two steps: the first step is that the 'Cp_2Ti' species transforms itself from organic phase into water phase to form the aquocomplex cations of titanocene; and then the 'Cp_2Ti' species, which reacted with thiosalicylic acid in organic layer to form the final complex, returns itself to organic phase from water phase (see Scheme 1).

Similarly to Fig. 1, Fig. 2(c) shows the characteristic absorption changes of the reaction of Cp_2TiCl_2 with sodium thiosalicylate in organic layer ($CHCl_3$). Obviously, in the earlier stage of the reaction, the corresponding absorbance of the Cp_2TiCl_2 decreases more clearly than that of Fig. 1, indicating that Cp_2TiCl_2 transforms into the water phase. After that, similar spectral trends are observed accounting for a similar mechanism (see Scheme 2) for method 1 and method 2.

However, the reaction of method 2 (30 min) is clearly faster than that of method 1 (about 2 h).

The difference between them is that there are different species of thiosalicylic acid in the reaction systems: in the former case, there is a strongly coordinating anion — sodium thiosalicylate — in the water phase, and in the latter case, thiosalicylic acid itself stays in the organic phase. This result suggests that these reactions are possibly related to the ligand ion, and obviously the latter reaction occurs with more difficulty with the withdrawal of hydrogen atom from the neutral molecule than the former reaction. Therefore, water, similar to Et_3N [6,14,15], is used as an HCl-receiver in both cases. The formation of the complexes are expressed by the following chemical equations:



Scheme 2. Formation of $Cp_2Ti(Sal)$ from Cp_2TiCl_2 and NaHSal in $H_2O + CHCl_3$. NaHSal: sodium substituted salicylate.

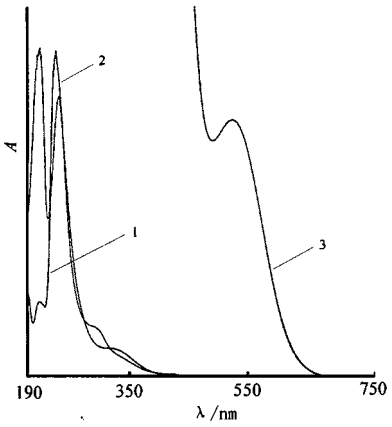


Fig. 4. UV–vis spectrum of Cp_2TiCl_2 (**1**), 5-sulfosalicylic acid (**2**) and aquocomplex **II** (**3**) in water.

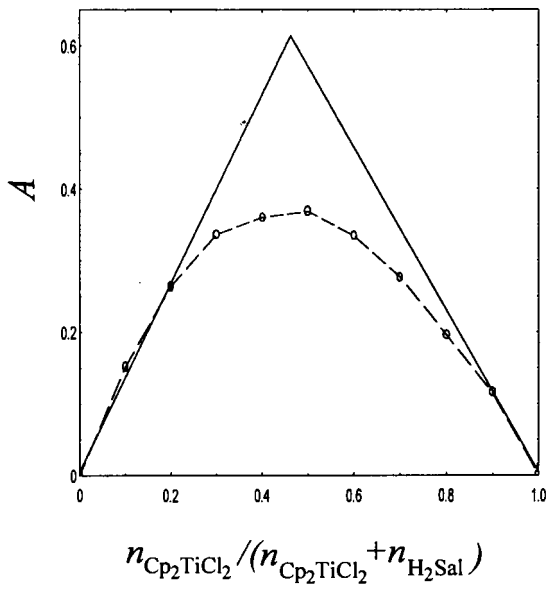


Fig. 5. The curve of continuous variations of aquocomplex **II** (1:1).

$$Cp_2TiCl_2 + 2H_2O \overset{pH<3.5,\ CHCl_3}{\rightleftharpoons} \underset{\mathbf{I}}{[Cp_2Ti(OH)(OH_2)]^+} + H^+ + 2Cl^-$$

$$\underset{\mathbf{I}}{[Cp_2Ti(OH)(OH_2)]^+} + H_2Sal \overset{H_2O/CHCl_3}{\rightleftharpoons} \underset{\mathbf{1-8}}{Cp_2Ti(Sal)} + 2H_2O + H^+$$

$$\underset{\mathbf{I}}{[Cp_2Ti(OH)(OH_2)]^+} + NaHSal \overset{H_2O/CHCl_3}{\rightleftharpoons} \underset{\mathbf{1-9}}{Cp_2Ti(Sal)} + 2H_2O + Na^+$$

H_2Sal, thiosalicylic acid (**1**); salicylic acid (**2**); 5-chlorosalicylic acid (**3**); 5-bromosalicylic acid (**4**); 5-nitro salicylic acid (**5**); 3,5-dinitrosalicylic acid (**6**); 3-hydroxy-2-naphthoic acid (**7**); 1-hydroxy-2-naphthoic acid (**8**); alizarin yellow G-G (**9**); 5-nitrosalicylic acid (**10**).

2.2. The action of 5-sulfosalicylic acid

Addition of 5-sulfosalicylic acid to an aqueous solution of Cp_2TiCl_2 results in the color change from red to dark red, and the pH value from 1.0 to about 0.5, indicating that the reaction has occurred. Fig. 4 shows the electronic absorption of Cp_2TiCl_2 (**1**), 5-sulfosalicylic acid (**2**) and their product (**3**) in aqueous solution, respectively. In the range of 190–750 nm, it is to be noticed that a characteristic electronic absorption band at 528.6 nm appears; that Cp_2TiCl_2 or 5-sulfosalicylic acid does not have the characteristic absorption band in this range confirmed that a new aquocomplex forms when Cp_2TiCl_2 is mixed with 5-sulfosalicylic acid. However, we have not as yet isolated the expected titanocene complex. By the method of continuous variations, the constitution of the aquocomplex is determined (see Fig. 5). The result illustrates this aquocomplex similar to containing Cp_2TiCl_2 and 5-sulfosalicylic acid with a 1:1 molar ratio.

In an attempt to obtain the aquocomplex, we tested its reaction with $K_2[HgI_4]$ in an aqueous solution to give the complex $[Cp_2Ti(Ssal)]_2[HgI_4]\cdot 4H_2O$, which was isolated as a light-yellow solid and characterized by elemental analyses, IR and TG and DTA, respectively. This result suggests that the aquocomplex contains the cationic species of $[Cp_2Ti(Ssal)]^+$ (**II**).

When treating Cp_2TiCl_2 with thiosalicylic acid in the presence of 5-sulfosalicylic acid in $H_2O + CHCl_3$ (method 3), complex **1** is obtained faster and more

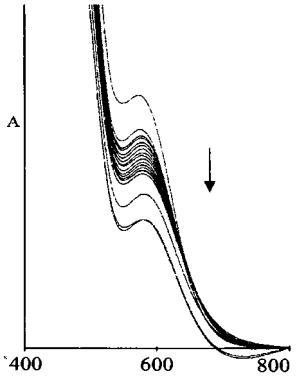
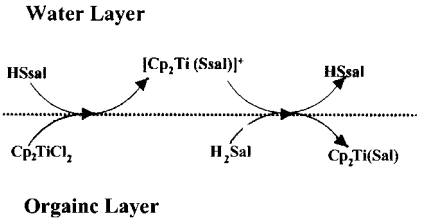


Fig. 6. UV–vis spectrum (in water layer) of the process of the reaction between aquocomplex **II** and thiosalicylic acid $H_2O + CHCl_3$.



Scheme 3. Formation of $Cp_2Ti(Sal)$ from Cp_2TiCl_2, H_2Sal and HSsal in $H_2O/CHCl_3$. H_2Sal: substituted salicylic acid; HSsal: 5-sulfosalicylic acid.

easily (in only 5 min) than in the case of methods 1 or 2. In Fig. 3(c), we have found the characteristic absorption band of Cp_2TiCl_2 which does not shift in the beginning then it decreases most clearly in the case of methods 1–3, and it frequently disappears. In the meantime, the characteristic absorption band of the product is increasing. Obviously, the reason this reaction is facile is the presence of 5-sulfosalicylic acid. In this case, Cp_2TiCl_2 in organic layer previously reacts with water as described above, next its hydrolyzate interacts with 5-sulfosalicylic acid to form the aquocomplex **II**, and then the species of **II** reacts with thiosalicylic acid in organic phase to form the final complex. Thus the characteristic absorption band of Cp_2TiCl_2 declines rapidly due to the fast formation of **II**. For this reason, the formation of the final complex is speeded up compared to methods 1 and 2. To understand this behavior better, we detected the UV–vis spectrum of the similar reaction of an aqueous solution containing **II** with thiosalicylic acid in $CHCl_3$ (see Fig. 6). As expected, the characteristic absorption band of **II** goes down obviously. In this case, when monitored in organic layer by UV–vis spectrum, we found only the characteristic absorption band of complex **1** and it is increasing correspondingly. This observation is consistent with the decline of Cp_2TiCl_2 in the organic layer and it confirmed that the reaction of Cp_2TiCl_2 with thiosalicylic acid has to occur through the interface of two phases.

As mentioned above, the procedure of the synthetic complex is proposed below: the first step is that Cp_2TiCl_2 possibly transfers its hydrolyzate, $[Cp_2Ti(OH)(OH_2)]^+$, from the organic phase into the water phase, and then the hydrolyzate interacts with 5-sulfosalicylic acid in water to turn into $[Cp_2Ti(Ssal)]^+$. Finally, the species of $[Cp_2Ti(Ssal)]^+$ reacts with the substituted salicylic acid in the organic phase to form the final complex. Therefore, similarly to methods 1 and 2, the preparation of complexes undergoes an interfacial interaction from organic phase to water phase, and then from water phase to organic phase (see Scheme 3). So the reaction may be presented below:

$$[\underset{\mathbf{I}}{Cp_2Ti(OH)(OH_2)}]^+ + HSSal \overset{H_2O/CHCl_3}{\rightleftharpoons} [\underset{\mathbf{II}}{Cp_2Ti(Ssal)}]^+ + 2H_2O$$

$$[\underset{\mathbf{II}}{Cp_2Ti(Ssal)}]^+ + H_2Sal \overset{H_2O/CHCl_3}{\rightleftharpoons} \underset{\mathbf{1-8}}{Cp_2Ti(Sal)} + HSsal + H^+$$

HSsal = 5-sulfosalicylic acid; H_2Sal = salicylic acid and its derivatives.

3. Conclusions

It is easy to find some differences in the different approaches. First, compared with method 1, 5-sulfosalicylic acid is found in method 3. Second, the cationic species is different such as $[Cp_2Ti(OH)(OH_2)]^+$, $[Cp_2Ti(Ssal)]^+$. Third, for method 3, the rapid color change in the water phase also indicates that the formation of the cationic species is easier and the higher concentration of **II** in the water phase possibly becomes rate determining. In this case, 5-sulfosalicylic acid can be considered as catalyst. It is interesting for method 2 that the reaction speed is clearly increased by the presence of anion ligand in water phase as well as by the change of the cationic species for method 3. However, for the three different approaches, the preparations of these complexes undergo a similar reaction procedure — the interfacial reaction, which seems to be similar to the corresponding mechanism in an ion reaction.

4. Experimental

All the chemicals and reagents used were of analytical grade, bis(cyclopentadienyl)titanium(IV) dichloride was prepared by the method described in the literature [16]. Elemental analyses for C, H and N were performed by Perkin–Elmer Model 2400. IR spectra were recorded on a Mattson FT-IR using KBr pellets. ^{1}H-NMR spectra were determined using an AC-80 in

CD_3COCD_3 (with TMS as internal standard) at a sweep with of 80 MHz. UV–vis spectra were recorded on an UV-260 spectrometer. Absorbance data were recorded on a WFZ-800D2 UV–vis spectrophotometer. Thermogravimetric analysis was performed by model PE-TGA7.

4.1. Reaction of Cp_2TiCl_2 with water

Water (20 ml) was added (the pH of which was adjusted below 3.5 by adding hydrochloric acid) to a solution containing 1.0 mmol Cp_2TiCl_2 in 30 ml $CHCl_3$, and the mixture was stirred for 2 h. The orange–red aqueous layer was separated; the solvent was removed under reduced pressure. The solid product determined by m.p. 286–287°C and IR [17], was Cp_2TiCl_2 and the yield obtained was 80%.

4.2. Reaction of Cp_2TiCl_2 with 5-sulfosalicylic acid

A mixture of 1.0 mmol Cp_2TiCl_2, 1.1 mmol 5-sulfosalicylic acid and 10 ml water was stirred for 30 min at room temperature (r.t.). A dark red solution was obtained (pH 0.5–1.0) and the solvent was removed under reduced pressure. The residue was washed with diethyl ether and recrystallised from acetone–hexane, leaving 0.24 mg (95%) of Cp_2TiCl_2.

Water (10 ml) containing 1.1 mmol of 5-sulfosalicylic acid was added to a solution containing 1.0 mmol Cp_2TiCl_2 in 30 ml $CHCl_3$, and the mixture was stirred for 5 min. The aqueous layer turned deep red and then separated, the solvent was removed under reduced pressure. The residue was washed with diethyl ether and recrystallised from acetone–hexane, leaving 0.23 mg (90%) of Cp_2TiCl_2.

4.3. Constitute of Aquocomplex *II*

The electronic spectra of Cp_2TiCl_2, 5-sulfosalicylic acid and aquocomplex **II**, which was obtained by reaction of Cp_2TiCl_2 with an aqueous solution, were recorded on a UV-260 spectrophotometer with a 1 cm quartz cell in water in the range of 750–190 nm. The UV–vis of Cp_2TiCl_2 shows two intense bands at 243 and 208 nm (see 1 of Fig. 4), 5-sulfosalicylic acid at 301 and 226 nm (see **2** of Fig. 4) and aquocomplex **II** only shows a very intense band at 528.6 nm in the visible range (see **3** of Fig. 4).

An aqueous solution of 0.002 mmol l^{-1} Cp_2TiCl_2 (the pH of which was adjusted below 3.5 by adding hydrochloric acid) and an aqueous solution of 0.002 mmol l^{-1} 5-sulfosalicylic acid were prepared, mixed containing Cp_2TiCl_2 with a 0, 0.1, 0.2,..., 1.0 molar fraction, respectively, and then recorded on a WFZ-800D2 UV–vis spectrophotometer at 528.6 nm. A continuous variations curve was given by molar fraction of Cp_2TiCl_2 and absorbances of aquocomplex **II** (see Fig. 5).

An aqueous solution of 24 ml $K_2[HgI_4]$ (0.05 mmol l^{-1}) was added to a solution of 20 ml aquocomplex **II** (0.05 mmol l^{-1}). The mixture was stirred about 3 h and filtered. Then the light-yellow precipitates were obtained, which were washed with water, diethyl ether, respectively, and dried in vacuum. The yield was 58%. light–yellow solid, m.p. >300°C; Anal. Calc. For $C_{34}H_{34}I_4O_{16}S_2HgTi_2$: C, 25.98; H, 2.42; Ti, 6.10. Found: C, 26.12; H, 2.18; Ti, 5.96%. IR: 3100, 1604, 1545, 1460, 1320, 1280, 1020, 830, 735 cm^{-1}. By TG and DTA, the resulting complex contains four water moleculars.

4.4. Electronic spectrum of process of reaction

The electronic spectra of Cp_2TiCl_2 and thiosalicylato biscyclopentadienyl–titanium(IV) (complex **1**) were recorded on a UV-260 spectrophotometer with a 1 cm quartz cell in chloroform in the range of 750–380 nm. The UV–vis of them shows a very intense band at 522 nm (see (b) of Figs. 1–3) and 602 nm (see (a) of Figs. 1–3), respectively.

A chloroform solution (A) of 0.001 mmol l^{-1} Cp_2TiCl_2 and thiosalicylic acid and an aqueous solution of 0.003 mmol l^{-1} 5-sulfosalicylic acid (B) were prepared. The solution of 0.5 ml B (or 1.0 ml water) was added to a quartz cell containing 3.5 ml A, and the mixture was stirred by blowing N_2. Then the electronic spectra of the organic layer were monitored in the range of 800–380 nm at intervals of 10, 5 and 5 min, respectively (see Figs. 1–3).

A solution of 0.001 mmol l^{-1} aquocomplex **II** was prepared. Using the above method, the electronic spectra of the water layer were monitored in the range of 800–380 nm at intervals of 5 min (see Fig. 6).

4.5. Preparation of salicylato derivatives of bis(cyclopentadienyl)titanium(IV) (*1*–*9*) from Cp_2TiCl_2

4.5.1. Method 1: [($Cp_2TiCl_2 + H_2Sal$)/($CHCl_3 + H_2O$)] (*1*–*8*)

A solution of Cp_2TiCl_2 (2.0 mmol) and 2.2 mmol substituted salicylic acid in 30 ml $CHCl_3$ was added to 10 ml water. The mixture was stirred for about 1.5–2 h (1 h for compound **8**) at r.t. The organic layer was separated and washed with an aqueous solution of saturated sodium carbonate and water, respectively, and dried with anhydrous magnesium sulfate and filtered. The filtrate was evaporated to dryness under vacuum. The solid product was recrystallised with dichloromethane–hexane. The complexes **1**–**8** were obtained by this method.

4.5.2. Method 2: [$Cp_2TiCl_2/CHCl_3 + NaHSal/H_2O$] (**1**–**9**)

Substituted salicylic acid (2.2 mmol) and NaOH (2.2 mmol) were dissolved in 100 ml of water (the pH of which was adjusted 3.0–5.0 by adding diluent HCl or NaOH). The aqueous solution was added to a solution of 2.0 mmol Cp_2TiCl_2 in 30 ml $CHCl_3$. The mixture was stirred for about 30 min at r.t. The following steps were the same as method 1. The complexes **1**–**9** were obtained by this method.

sub24.5.3. Method 3: [($Cp_2TiCl_2 + H_2Sal$)/ $CHCl_3 + H_2Ssal/H_2O$] (**1**–**8**)

A solution of 2.0 mmol Cp_2TiCl_2 and 2.2 mmol substituted salicylic acid in 30 ml $CHCl_3$ was added to 2.0 mmol of 5-sulfosalicylic acid in 10 ml of water. The mixture was stirred for about 5 min at r.t.. The following steps were the same as method 1. The complexes **1**–**8** were obtained by this method.

1: dark-green solid, m.p. 168–170°C; Anal. Calc. for $C_{17}H_{14}O_2STi$: C, 61.83; H, 4.23. Found: C, 61.90; H, 4.21%. ^{1}H-NMR: δ 6.48 (10H, s, $2 \times C_5H_5$), 7.22–8.42 (4H, m, $4 \times$ ArH); IR: 3105, 1613, 1429, 1291, 1017, 823 cm^{-1}; $\lambda_{max}(CHCl_3)$:242 (log ε 4.5), 378 (log ε 2.8), 602 (log ε 3.1) nm.

2: dark-brown solid, m.p. 185–187°C; Anal. Calc. for $C_{17}H_{14}O_3Ti$: C, 64.99; H, 4.49. Found: C, 64.61; H, 4.45%. ^{1}H-NMR: δ 6.54 (10H, s, $2 \times C_5H_5$), 6.61–8.10 (4H, m, $4 \times$ ArH); IR: 3106, 1621, 1450, 1325, 1014, 818 cm^{-1}; $\lambda_{max}(CHCl_3)$: 244 (log ε 4.9), 526 (log ε 3.3) nm.

3: purple–brown solid, m.p. 214–216°C; Anal. Calc. for $C_{17}H_{13}ClO_3Ti$: C, 58.56; H, 3.76. Found: C, 58.51; H, 3.73%. ^{1}H-NMR: δ 6.57 (10 H, s, $2 \times C_5H_5$), 6.64–8.00 (3H, m, $3 \times$ ArH); IR: 3096, 1618, 1403, 1306, 1017, 820 cm^{-1}; $\lambda_{max}(CHCl_3)$: 245 (log ε 4.6), 444 (log ε 3.0), 532 (log ε 2.8) nm.

4: purple–brown solid, m.p. 208–210°C; Anal. Calc. for $C_{17}H_{13}BrO_3Ti$: C, 51.94; H, 3.33. Found: C, 51.86; H, 3.36%. ^{1}H-NMR: δ 6.57 (10 H, s, $2 \times C_5H_5$), 6.68–8.13 (3H, m, $3 \times$ ArH); IR: 3096, 1619, 1403, 1302, 1017, 820 cm^{-1}; $\lambda_{max}(CHCl_3)$: 245 (log ε 4.8), 444 (log ε 3.3), 531 (log ε 3.2) nm.

5: dark-red solid, m.p. 230–232°C; Anal. Calc. for $C_{17}H_{13}NO_5Ti$: C, 56.85; H,3.65; N,3.90. Found: C, 56.60; H, 3.73; N, 3.50%. ^{1}H-NMR: δ 6.64 (10 H, s, $2 \times C_5H_5$), 6.78–8.78 (3H, m, $3 \times$ ArH); IR: 3099, 1619, 1566, 1427, 1314, 1020, 830, 751 cm^{-1}; $\lambda_{max}(CHCl_3)$: 324 (log ε 4.2), 356 (log ε 4.2), 521 (log ε 2.8) nm.

6: dark-red solid, m.p. 238–240°C; Anal. Calc. for $C_{17}H_{12}N_2O_7Ti$: C, 50.51; H, 2.97; N, 6.93. Found: C, 50.37; H, 2.86; N, 6.68%. ^{1}H-NMR: δ 6.67 (10 H, s, $2 \times C_5H_5$), 8.88–9.44 (2H, m, $2 \times$ ArH); IR: 3116, 1657, 1536, 1368, 1329, 1017, 832, 747 cm^{-1}; $\lambda_{max}(CHCl_3)$: 243 (log ε 4.5), 326 (log ε 4.2), 522 (log ε 2.6) nm.

7: dark-purple solid, m.p. 199–200°C; Anal. Calc. for $C_{21}H_{16}O_3Ti$: C, 69.25; H, 4.43. Found: C, 69.04; H, 4.39%. ^{1}H-NMR: δ 6.58 (10H, s, $2 \times C_5H_5$), 7.01–8.65 (6H, m, $2 \times$ ArH); IR: 3021, 1633, 1442, 1342, 1015, 825 cm^{-1}.

8: dark-purple solid, m.p. 219–221°C; Anal. Calc. for $C_{21}H_{16}O_3Ti$: C, 69.25; H, 4.43. Found: C, 68.75; H, 4.34%. ^{1}H-NMR: δ 6.60 (10H, s, $2 \times C_5H_5$), 7.26–8.23 (6H, m, $2 \times$ ArH); IR: 3075, 1620, 1443, 1397, 1020, 815cm^{-1}.

9: red–brown solid, m.p. 230–232°C; Anal. Calc. For $C_{23}H_{17}N_3O_5Ti$: C, 59.61; H, 3.76; N, 9.07. Found: C, 59.06; H, 3.92; N, 8.91. ^{1}H-NMR: δ 6.50 (10H, s, $2 \times C_5H_5$), 6.74–8.71 (7H, m, $2 \times$ ArH); IR: 3090, 1621, 1542, 1466, 1410, 1350, 1020, 830 cm^{-1}; $\lambda_{max}(CHCl_3)$: 243 (log ε 4.7), 388 (log ε 4.0) nm.

4.6. Preparation of bis(cyclopentadienyl)titanium(IV) di(5-nitrosalicylate) (**10**)

Using the above methods 1–3, respectively, the reactions were carried out in 20 ml of chloroform at r.t., the ratio of Cp_2TiCl_2 to 5-nitrosalicylic acid was 1:2. And the mixtures were stirred for 3 h and filtered. Then the orange–yellow precipitates were obtained, washed with water, diethyl ether and a small amount of chloroform, respectively, and dried in vacuum. The solid products were recrystallised with dichloromethane–hexane. The yields were 61, 70 and 56%, respectively. Orange–yellow solid, m.p. 194–195°C; Anal. Calc. for $C_{23}H_{17}N_3O_5Ti$: C, 53.15; H, 3.35; N, 5.17. Found: C, 53.45; H, 3.35; N, 4.90. ^{1}H-NMR: δ 6.68 (10H, s, $2 \times C_5H_5$), 6.86–8.90 (6H, m, $6 \times$ ArH), 12.66 (2H, $+ D_2O$ disappearing); IR: 3200, 1640, 1566, 1427, 1372, 1020, 830, 751 cm^{-1}; $\lambda_{max}(CHCl_3)$: 242 (log ε4.8), 303 (log ε4.6), 511 (log ε2.8) nm.

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