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Synthesis of mono- and dinuclear cyclopentadienyl–aryloxy titanium(IV) complexes

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Abstract

This paper reports the reactivity of monocyclopentadienyl titanium complexes $[Ti(C_5R_5)Cl_3]$ (R = H or Me) with phenol and hydroquinones to afford mono- and dinuclear aryloxy derivatives, respectively. The reaction of hydroquinones $HO(C_6H_2XY)OH$ (X = Y = H, Me; X = H, Y = Me) with $[Ti(C_5H_5)Cl_3]$ gave red–orange microcrystalline solids of the corresponding dinuclear complexes $[\{Ti(C_5H_5)Cl_2\}_2\{\mu\text{-}O(C_6H_2XY)O\}]$ (X = Y = H (**1**); X = H, Y = Me (**2**); X = Y = Me (**3**)) in high yields. However, their dilithium salts $Li_2[O(C_6H_2XY)O]$ must be used in the treatment with $[Ti(C_5Me_5)Cl_3]$ to produce the expected dinuclear derivatives $[\{Ti(C_5Me_5)Cl_2\}_2\{\mu\text{-}O(C_6H_2XY)O\}]$ (X = Y = H (**4**); X = H, Y = Me (**5**); X = Y = Me (**6**)) as red–orange microcrystals in high yields too. Reaction of $[Ti(C_5R_5)Cl_3]$ with 4-allyl-2-methoxyphenol (commonly called eugenol) $[C_6H_3(OH)(OMe)(C_3H_5)]$ or its lithium salt led to the monoaryloxy complexes $[Ti(C_5R_5)Cl_2\{OC_6H_3(OMe)(C_3H_5)\}]$ (R = H (**7**), Me (**8**)). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Aryloxy derivatives; Cyclopentadienyl complexes

1. Introduction

An area of current interest is the synthesis of metallodendrimers in which the metal has been attached to the surface for generating new inorganic/organic hybrid macromolecules with interesting advantages over both homogeneous and heterogeneous catalysis [1]. On the other hand, cyclopentadienyl Group 4 metal derivatives are a family of well-defined homogeneous olefin polymerisation catalysts [2], which are very attractive for their attachment over a dendritic surface, as model systems for heterogenisation of such complexes on, i.e. silica supports. As a part of our current research, we are interested in the synthesis of monocyclopentadienyl–aryloxy derivatives of titanium attached to a dendrimeric base for two reasons. First, there are several examples for the synthesis of molecular Cp–aryloxy complexes of titanium and their use as olefin polymerisation catalysts [3], showing that these complexes are relatively easy to synthesise and as catalysts could be compared with hybrid half-metallocene analogues [4]. And second because substituted aryloxy ligands could be suitable groups to attach the metal complex to a dendrimeric base, i.e. phenyl ether [5] or carbosilane [6] dendrimers.

In this paper, we wish to present the synthesis and characterisation of new mono- and dinuclear cyclopentadienyl titanium derivatives containing aryloxy ancillary ligands in their coordination environment, as models and starting point for the synthesis of peripheral metal–dendrimers.

2. Results and discussion

2.1. Synthesis of dinuclear complexes

Reactions of $[Ti(C_5R_5)Cl_3]$ (R = H or Me) with hydroquinones or their dilithium salts have been studied. The reaction of $HO(C_6H_2XY)OH$ (X = Y = H, Me; X = H, Y = Me) with two equivalents of $[Ti(C_5H_5)Cl_3]$ in diethyl ether at room temperature (r.t.) gave red orange microcrystalline solids of dinuclear complexes $[\{Ti(C_5H_5)Cl_2\}_2\{\mu\text{-}O(C_6H_2XY)O\}]$ (X = Y = H (**1**);

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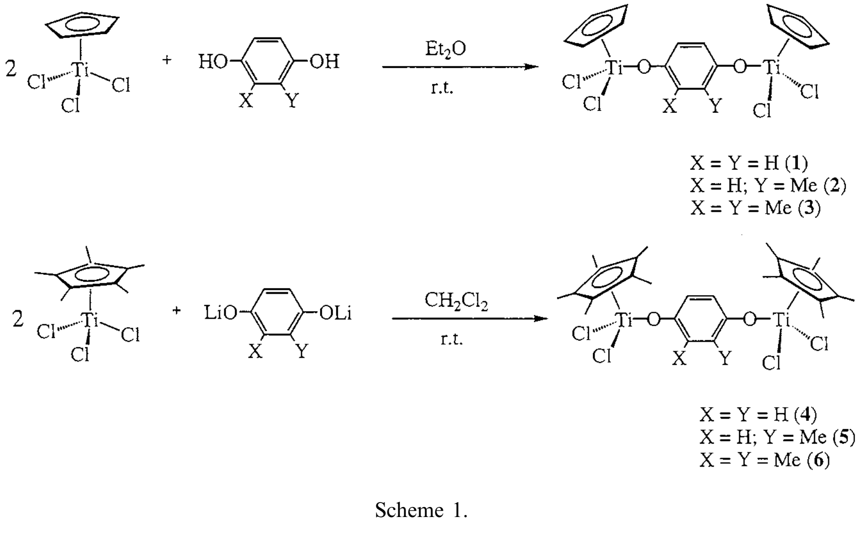
X = H, Y = Me (**2**); X = Y = Me (**3**)) (Scheme 1) in high yields. Complexes **1**–**3** are insoluble in hydrocarbon solvents and in diethyl ether, but scarcely soluble in THF and chlorinated solvents. Solubility is slightly increased on going from the unsubstituted derivative **1** to the dimethyl substituted aryloxy complex **3**. Compounds **1**–**3** are thermally stable but moisture sensitive, decomposing slowly to the well known oxo complex [{Ti(C_5H_5)Cl_2}$_2$(μ-O)] [7] in the presence of traces of water.

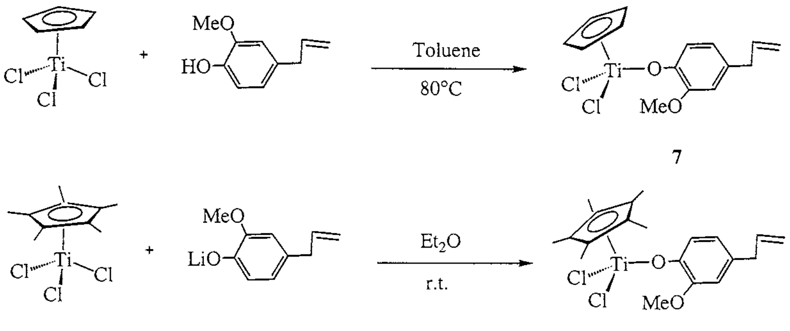
For compound [Ti(C_5Me_5)Cl_3] no reaction was observed with the hydroquinones in analogous conditions, whereas at 100°C they gave, in all cases, mixtures of the predicted complexes with unreacted starting materials. Moreover, treatment above this temperature led to decomposition of the organotitanium compounds. A more suitable procedure consists in the treatment of [Ti(C_5Me_5)Cl_3] with the dilithium salt of the hydroquinones Li_2[O(C_6H_2XY)O] (X = Y = H, Me; X = H, Y = Me) [8] in a molar ratio 2:1 in dichloromethane at r.t., affording the expected dinuclear derivatives [{Ti(C_5Me_5)Cl_2}$_2${μ-O(C_6H_2XY)O}] (X = Y = H (**4**); X = H, Y = Me (**5**); X = Y = Me (**6**)) (Scheme 1) as red–orange microcrystals in high yields. C_5Me_5 derivatives **4**–**6** present higher thermal stabilities and solubilities in the common solvents than complexes **1**–**3** containing the unsubstituted cyclopentadienyl ring. However, they are likewise moisture sensitive and undergo hydrolysis. For instance, complex **4** produced the mononuclear compound [Ti(C_5Me_5)Cl_2{O(C_6H_4)OH}] by selective hydrolysis of the Ti–O bond (^{1}H-NMR evidence) [9]. Subsequent hydrolysis of this intermediate led to the well known oxo complex [{Ti(C_5Me_5)Cl_2}$_2$(μ-O)] [10].

The IR and NMR data and analytical composition for complexes **1**–**6** (see Section 4) are consistent with the structures depicted in Scheme 1.

The IR spectra of the new aryloxy complexes contain bands due to the ν(C–O) at ca. 1215 cm^{-1} and the ν(Ti–O) at ca. 900 cm^{-1}, which are in the range reported for related derivatives [3c,11,12]. ^{1}H-NMR spectra show a singlet for the protons of the two C_5H_5 ligands in complexes **1** and **3** and for the methyl groups of the two C_5Me_5 rings in compounds **4** and **6**. Nevertheless, **2** and **5** exhibit two singlets attributed to the non-equivalent 'Ti(C_5H_5)Cl_2' or 'Ti(C_5Me_5)Cl_2' units bonded to the aryloxy bridging ligands. A relevant feature is that C_5H_5 or C_5Me_5 signals are almost unmodified on going from the non-substituted to the disubstituted aryloxy compounds (δ 6.78–6.75 for **1**–**3** or δ 2.20–2.18 for **4**–**6** in $CDCl_3$), indicating that alkyl substitution on the phenyl ring does not induce significant changes in the electronic density of the metal centre. For the protons of the aryloxy ligands, a singlet due to the four equivalent hydrogen atoms for complexes **1** and **4** (δ 6.92 and δ 6.85, respectively) and another singlet attributed to the two equivalent protons for complexes **3** and **6** (δ 6.81 and δ 6.72, respectively) are observed. These resonance patterns are comparable to those shown by the analogous derivatives [{MoTp(NO)X}$_2${μ-O(C_6H_4)O}] [13] or [{MoTp(O)-Cl}$_2${μ-N(C_6H_4)N}] [14], and are expected for homodinuclear bonding to the corresponding diphenoxide ligands. However, for compounds **2** and **5** a complex spin system is observed as a consequence of asymmetric substitution on the diphenoxide [O(C_6H_3Me)O]$^{2-}$ unit. The most interesting feature in their ^{13}C{^{1}H}-NMR spectra is the almost identical chemical shift of the *ipso* carbons bonded directly to the oxygen atoms that are recorded at the narrow range of δ 164.6–164.1 for **2**–**3** and δ 160.8–159.3 for **4**–**6**. For pentamethylcyclopentadienyl complexes, these signals appear at higher field than those observed for compounds **2** and **3**, as the result of the presence of a more electron-donating ligand [15].



Scheme 1.



7

8

Scheme 2.

Reactions of homodinuclear complexes with different alkylating reagents have been studied. Attempts to prepare tetraalkyl derivatives by treatment of complexes **1** or **6** with LiMe, MeMgCl or $AlMe_3$ were unsuccessful. In contrast, these processes seem to be appropriated for more sterically encumbered aryloxy systems [16]. It is interesting to note that the reaction of complex **1** or **6** with two equivalents of $AlMe_3$ in toluene at r.t. gave a mixture of previously reported monometallic derivatives $[Ti(C_5R_5)MeCl_2]$ (R = H, Me) [17,18] and $[Ti(C_5R_5)Me_3]$ (R = H, Me) [19,20] as unique organotitanium species. These results are probably due to the lack of steric hindrance around the Ti–O bond [3a,3b,16] and to the high affinity of aluminium alkyls for oxo functionalities [21].

2.2. Synthesis of mononuclear complexes

Treatment of $[Ti(C_5H_5)Cl_3]$ with one equivalent of 4-allyl-2-methoxyphenol (commonly called eugenol) $[C_6H_3(OH)(OMe)(C_3H_5)]$ in toluene at 80°C afforded the aryloxy complex $[Ti(C_5H_5)Cl_2\{OC_6H_3(OMe)(C_3H_5)\}]$ (**7**) (Scheme 2) as red microcrystals in 80% yield. However, the reaction with $[Ti(C_5Me_5)Cl_3]$ in analogous conditions was not completed, recovering always large amounts of starting materials. A ^{1}H-NMR experiment carried out in a sealed tube shown that a mixture of $[Ti(C_5Me_5)Cl_3]$ and eugenol in $CDCl_3$ at 100°C for 12 h, yielded almost quantitatively the complex $[Ti(C_5Me_5)Cl_2\{OC_6H_3(OMe)(C_3H_5)\}]$ (**8**) when the spectrum was registered keeping such temperature. In contrast, upon cooling the tube at r.t., the reverse reaction took place, leading quantitatively to the starting substrates. In a NMR tube scale, compound **8** can be isolated by means of heating and subsequent removal of the concomitant HCl under vacuum. Unfortunately, this procedure is not appropriated for **8** in a large scale synthesis. A more convenient method consists in the reaction of $[Ti(C_5Me_5)Cl_3]$ with the lithium salt $[Li\{OC_6H_3(OMe)(C_3H_5)\}]$ [8] that gave **8** as an orange solid in 90% yield. Complexes **7** and **8** are thermally stable but moisture sensitive, slightly soluble in alkanes and very soluble in the rest of the common solvents.

The structures proposed for the new complexes **7** and **8** are shown in Scheme 2 and their spectroscopic and analytical data collected in Section 4.

Once more, the IR spectra of the new monoaryloxy complexes contain bands due to the ν(C–O) at ca. 1270 cm^{-1} and the ν(Ti–O) at ca. 890 cm^{-1}, similar to those found in the dinuclear systems prepared above and other related derivatives [3c,11,12]. The ^{1}H-NMR spectra of complexes **7** and **8** show the singlet attributed to the cyclopentadienyl and pentamethylcyclopentadienyl ligands, and one resonance for the corresponding carbon atoms of the rings are observed in their ^{13}C-NMR spectra. Regarding to the eugenolate moiety, the presence of three different substituents makes all the phenyl proton and carbon atoms chemically non-equivalent. Thus, a set of complex signals for the phenyl ring protons in the ^{1}H-NMR and six resonances for the corresponding carbon atoms in the ^{13}C-NMR are detected. The *ipso* carbon bonded to the Ti–O unit appears at δ 157.4 for compound **7** and slightly shifted to higher field for complex **8** (δ 153.6), again due to the different electrodonating properties of the C_5H_5 and C_5Me_5 rings, and both shifted downfield from the resonance of the free eugenol (δ 143.7). The chemical shift of the *ipso*-C atom bonded to the OMe group is located at δ 150.0 for both complexes, moved 3 ppm downfield from the free alcohol. This observation is in agreement with the lack of interaction with the metal centre [22]. Analogously to this, the ^{1}H- and ^{13}C-NMR spectra of the allyl fragment in complexes **7** and **8** are consistent with neither intra- nor intermolecular interactions with the titanium metal [22,23].

2.3. Electrochemical studies

Cyclic voltammograms have been recorded for complexes **1**–**6** versus the Cp_2Fe/Cp_2Fe^+ couple at a plat-

Table 1
Cyclic voltammetric data for mono- and dinuclear aryloxy complexes in THF/$[Bu_4N][PF_6]$

Complex	E^c (V) vs. Cp_2Fe/Cp_2Fe^+
1	-1.38 [a]
2	-1.50 [a]
3	-1.40 [a]
4	-1.34 [a]
5	-1.52 [a]
6	-1.54 [a]
7	-1.68 [b]
$[Ti(C_5H_5)Cl_3]$	-0.86

[a] Reduction potentials since the couple is irreversible.

[b] Partially reversible process.

inum electrode in a THF solution using $[Bu_4N][PF_6]$ as supporting electrolyte. They all show two irreversible overlapped reduction waves. We assume that the irreversible reductions are metal centred and the resulting radical anions are very reactive and decompose rapidly. The dinuclear derivatives undergo two one-electron reduction processes, although it is difficult to distinguish from a single two-electron transfer when the separation between the two redox waves is so short [13,14,24]. The reduction peaks are broad and poorly defined and the results are summarised in Table 1 for a scan rate of 200 mV s^{-1}. Comparing these data with that of the $[Ti(C_5H_5)Cl_3]$, replacement of one chlorine atom by an aryloxy ligand makes the reduction potential more negative by a value of ca. 0.50–0.60 V. It has been proposed that the formal potentials for the Ti^{IV}/Ti^{III} couples are insensitive to the substituents of the phenyl ring in aryloxy complexes [25,26]. In our case, the slightly different results could be attributed to both the overlapping processes and some degree of interaction between the metal centres. Identical rationalisation have been described for other homodinuclear systems containing Group 5 metals [13,14]. A cyclic voltammogram has also been carried out for compound **7** which, under analogous conditions, exhibits a reversible wave at potential -1.68 V. The reversibility decreases as scan rate decreases. These results show that the titanium metal centre in **7** is slightly more electron rich than in the related homodinuclear complexes **1**–**6**.

3. Conclusions

Treatment of $[Ti(C_5H_5)Cl_3]$ with hydroquinones cleanly afforded new homodinuclear aryloxy complexes $[\{Ti(C_5H_5)Cl_2\}_2\{\mu\text{-}O(C_6H_2XY)O\}]$ without the use of their dilithium salts or auxiliary amines for chloro abstraction, while in the case of $[Ti(C_5Me_5)Cl_3]$, their dilithium salts must be used for the synthesis of the corresponding complexes $[\{Ti(C_5Me_5)Cl_2\}_2\{\mu\text{-}O(C_6H_2XY)O\}]$. These simple procedures would be a key step for the attachment of the titanium complex on phenyl ether dendrimers via HCl elimination or lithiation/transmetallation sequences. Analogous reaction with eugenol or its lithium salt afforded $[Ti(C_5R_5)Cl_2\{OC_6H_3(OMe)(C_3H_5)\}]$ (R = H or Me) in high yield. The synthesis of such complexes containing pendant allyl groups would allow their introduction on the surface of organosilicon dendrimers containing Si–H bonds via hydrosilylation reactions.

4. Experimental

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or a dry box. Solvents were previously dried and freshly distilled under argon: tetrahydrofuran and diethyl ether from sodium benzophenone, toluene from sodium, hexane from sodium–potassium alloy, and methylene chloride over P_2O_5. Unless otherwise stated, reagents were obtained from commercial sources and used as received. $[Ti(C_5H_5)Cl_3]$ [27] and $[Ti(C_5Me_5)Cl_3]$ [28] were prepared according to reported methods.

IR spectra were recorded in Nujol mulls between CsI pellets over the range 4000–200 cm^{-1} on a Perkin–Elmer 583 spectrophotometer. ^1H- and ^{13}C-NMR spectra were recorded on a Varian Unity VXR-300 or Varian Unity 500 Plus instruments. Chemical shifts (δ ppm) were measured relative to residual ^1H and ^{13}C resonances for chloroform-d_1 used as solvent. C, H and N analyses were carried out with a Perkin–Elmer 240 C microanalyzer. Cyclic voltammetry measurements were carried out under dry argon using distilled and dried THF as solvent. $[Bu_4N][PF_6]$ (0.2 M) was used as supporting electrolyte. A three-platinum-electrode cell and ferrocene as internal reference were used. Measurements were made using an AMEL 553 Potentiostat, an AMEL 567 wave generator and recorded on an AMEL 863 recorder.

4.1. Synthesis of *$[\{Ti(C_5H_5)Cl_2\}_2\{\mu\text{-}O(C_6H_4)O\}]$* (**1**)

A solution of $[Ti(C_5H_5)Cl_3]$ (1.00 g, 4.56 mmol) in Et_2O (50 ml) was slowly cannulated into a solution of hydroquinone (0.25 g, 2.3 mmol) in Et_2O (20 ml). An orange solid precipitated and the mixture was stirred overnight at r.t. Then, the solution was filtered off through Celite, and the solid was dried under vacuum affording **1** as an orange microcrystalline solid (0.92 g, 85% yield). Complex **1** can be purified by washing with several small portions of toluene. Anal. Calc. for $C_{16}H_{14}Cl_4O_2Ti_2$: C, 40.39; H, 2.97. Found: C, 40.44; H, 2.98%. IR (Nujol, CsI): 1629 (w), 1225 (s), 1096 (w), 1020 (m), 909 (s), 486 (m), 438 (s), 419 (m), 389 (m). ^1H-NMR ($CDCl_3$): δ 6.92 (s, 4H, C_6H_4), 6.78 (s, 10H,

C_5H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 120.9 (C_5H_5), 119.2 (C_6H_4). C_{ipso} not observed.

4.2. Synthesis of $[\{Ti(C_5H_5)Cl_2\}_2\{\mu\text{-}O(C_6H_3Me)O\}]$ (**2**)

This complex was obtained by the same procedure described for **1**, starting from $[Ti(C_5H_5)Cl_3]$ (0.71 g, 3.2 mmol) and methylhydroquinone (0.20 g, 1.6 mmol) giving **2** as a red solid (0.63 g, 80% yield). For further purification, it was washed with CH_2Cl_2. Anal. Calc. for $C_{17}H_{16}Cl_4O_2Ti_2$: C, 41.68; H, 3.29. Found: C, 41.85; H, 3.34%. IR (Nujol, CsI): 1592 (w), 1212 (s), 1011 (m), 904 (s), 467 (m), 437 (s), 388 (w). ^1H-NMR ($CDCl_3$): δ 6.89 (m, 2H, C_6H_3), 6.77 (s, 5H, C_5H_5), 6.76 (s, 5H, $C_5H'_5$), 6.73 (m, 1H, C_6H_3), 2.27 (s, 3H, CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 164.6, 164.2 (C_{ipso}, C_6H_3), 120.9 (C_5H_5), 120.8 ($C_5H'_5$), 120.5, 120.3, 119.9, 116.8 (C_6H_3), 16.9 (CH_3).

4.3. Synthesis of $[\{Ti(C_5H_5)Cl_2\}_2\{\mu\text{-}O(C_6H_2Me_2)O\}]$ (3)

This complex was obtained by the same procedure described for **1**, starting from $[Ti(C_5H_5)Cl_3]$ (0.63 g, 2.9 mmol) and 2,3-dimethylhydroquinone (0.20 g, 1.4 mmol) to give **3** as a red solid (0.60 g, 82% yield)). For further purification it was washed with toluene. Anal. Calc. for $C_{18}H_{18}Cl_4O_2Ti_2$: C, 42.90; H, 3.60. Found: C, 43.03; H, 3.65%. IR (Nujol, CsI): 1592 (w), 1212 (s), 1108 (m), 1011 (m), 904 (s), 467 (m), 438 (s), 389 (w). ^1H-NMR ($CDCl_3$): δ 6.81 (s, 2H, C_6H_2), 6.75 (s, 10H, C_5H_5), 2.21 (s, 6H, CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 164.1 (C_{ipso}, C_6H_2), 120.7 (C_5H_5), 120.4, 117.5 (C_6H_2), 13.3 (CH_3).

4.4. Synthesis of $[\{Ti(C_5Me_5)Cl_2\}_2\{\mu\text{-}O(C_6H_4)O\}]$ (4)

A solution of $[Ti(C_5Me_5)Cl_3]$ (0.80 g, 2.8 mmol) in methylene chloride (30 ml) was added to 1.4 mmol of the dilithium salt of hydroquinone [8]. The reaction mixture was stirred for 12 h and then filtered through Celite to remove LiCl. The resulting orange solution was evaporated under reduced pressure and cooled to −40°C, to give **4** as orange microcrystals (0.77 g, 90% yield). Anal. Calc. for $C_{26}H_{34}Cl_4O_2Ti_2$: C, 50.72; H, 5.52. Found: C, 50.46; H, 5.51%. IR (Nujol, CsI): 1550 (w), 1223 (s), 1089 (w), 1023 (m), 909 (s), 481 (m), 446 (m), 339 (w). ^1H-NMR ($CDCl_3$): δ 6.85 (s, 4H, C_6H_4), 2.20 (s, 30H, C_5Me_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 160.8 (C_{ipso}, C_6H_4), 133.1 (C_6H_4), 120.1 (C_5Me_5), 13.0 ($C_5\mathit{Me}_5$).

4.5. Synthesis of $[\{Ti(C_5Me_5)Cl_2\}_2\{\mu\text{-}O(C_6H_3Me)O\}]$ (5)

This complex was prepared by a similar procedure to that described above for complex **4**, starting from $[Ti(C_5Me_5)Cl_3]$ (0.42 g, 1.4 mmol) and 0.7 mmol of the dilithium salt of methylhydroquinone [8]. Complex **5** was isolated as orange microcrystals (0.4 g, 90% yield). Anal. Calc. for $C_{27}H_{36}Cl_4O_2Ti_2$: C, 51.46; H, 5.71. Found: C, 52.06; H, 5.97%. IR (Nujol, CsI): 1589 (w), 1221 (s), 1102 (m), 1005 (w), 901 (s), 467 (m), 435 (m), 413 (m). ^1H-NMR ($CDCl_3$): δ 6.81–6.73 (m, 3H, C_6H_3), 2.20 (s, 15H, C_5Me_5), 2.19 (s, 15H, $C_5Me'_5$), 2.17 (s, 3H, CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 160.7, 159.6 (C_{ipso}, C_6H_3), 132.9, 132.7, 132.3, 129.3 (C_6H_3), 121.1 (C_5Me_5), 120.7 ($\mathit{C}_5Me'_5$), 16.8 (CH_3), 13.0 ($C_5\mathit{Me}_5$), 12.9 ($C_5\mathit{Me}'_5$).

4.6. Synthesis of $[\{Ti(C_5Me_5)Cl_2\}_2\{\mu\text{-}O(C_6H_2Me_2)O\}]$ (6)

This complex was prepared by a similar procedure to that described for **4**, starting from $[Ti(C_5Me_5)Cl_3]$ (0.38 g, 1.3 mmol) and 0.65 mmol of the dilithium salt of dimethylhydroquinone [8]. Complex **6** was isolated as an orange solid (0.38 g, 90% yield). Anal. Calc. for $C_{28}H_{38}Cl_4O_2Ti_2$: C, 52.20; H, 5.90. Found: C, 51.42; H, 5.93%. IR (Nujol, CsI): 1600 (w), 1246 (s), 1095 (m), 1021 (w), 921 (s), 462 (s), 418 (s), 391 (m). ^1H-NMR ($CDCl_3$): δ 6.72 (s, 2H, C_6H_2), 2.18 (s, 30H, C_5Me_5), 2.16 (s, 6H, CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 159.3 (C_{ipso}, C_6H_2), 132.6, 132.1 (C_6H_2), 118.4 (C_5Me_5), 13.1 (CH_3), 12.9 ($C_5\mathit{Me}_5$).

4.7. Synthesis of $[Ti(C_5H_5)Cl_2\{O[C_6H_3(OMe)(CH_2CH{=}CH_2)]\}]$ (7)

A solution of $[Ti(C_5H_5)Cl_3]$ (1.00 g, 4.56 mmol) in toluene (40 ml) was slowly added to a solution of eugenol (0.75 g, 4.56 mmol) in toluene (20 ml). The mixture was heated at 80°C for 5 h and subsequently stirred overnight at r.t. Then, the solvent was removed at reduced pressure, to obtain a red oil. The product was washed with hexane to leave **7** as red microcrystals (1.26 g, 80% yield). Anal. Calc. for $C_{15}H_{16}Cl_2O_2Ti$: C, 51.91; H, 4.65. Found: C, 52.36; H, 4.83%. IR (Nujol, CsI): 1593 (w), 1277 (s), 1228 (s), 1031 (m), 889 (s), 452 (m), 413 (s). ^1H-NMR ($CDCl_3$): δ 6.92 (m, 1H, C_6H_3), 6.74 (s, 5H, C_5H_5), 6.72–6.65 (m, 2H, C_6H_3), 5.90 (m, 1H, $CH_2\text{–}C\mathit{H}{=}CH_2$), 5.07 (m, 2H, $CH_2\text{–}CH{=}C\mathit{H}_2$), 3.86 (s, 3H, OMe), 3.34 (m, 2H, $C\mathit{H}_2\text{–}CH{=}CH_2$); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 157.4 (C_{ipso} bonded to –OTi), 150.0 (C_{ipso} bonded to –OMe), 137.1 (C_{ipso} bonded to $-C_3H_5$), 137.0 ($CH_2\text{–}\mathit{C}H{=}CH_2$), 121.1 ($C_5H_5$), 120.5, 119.1 ($C_6H_3$), 116.2 ($CH_2\text{–}CH{=}\mathit{C}H_2$), 113.2 ($C_6H_3$), 56.4 (OMe), 40.1 ($\mathit{C}H_2\text{–}CH{=}CH_2$).

4.8. Synthesis of $[Ti(C_5Me_5)Cl_2\{O[C_6H_3(OMe)\text{-}(CH_2CH{=}CH_2)]\}]$ (8)

4.8.1. Method A

A solution of $[Ti(C_5Me_5)Cl_3]$ (0.35 g, 1.2 mmol) in diethyl ether (20 ml) was added over a diethyl ether solution (10 ml) of the lithium salt of eugenol [8]. The reaction mixture was stirred overnight and then filtered leading to an orange solution that was evaporated to dryness to give complex **8** as an oily orange solid (0.45 g, 90% yield).

4.8.2. Method B

In a sealed NMR tube was placed a solution of $[Ti(C_5Me_5)Cl_3]$ (0.015 g, 0.066 mmol) in chloroform-d_1 and eugenol (10 μl, 0.066 mmol). The reaction mixture was heated at 100°C during 2 h, then the inert atmosphere of the tube was replaced by vacuum, in order to remove the HCl formed, and the tube was heated to 100°C for an additional 30 min, to give **8** in quantitative yield. Anal. Calc. for $C_{20}H_{26}Cl_2O_2Ti$: C, 57.57; H, 6.24. Found: C, 57.09; H, 6.02%. ^{1}H-NMR ($CDCl_3$): δ 6.90 (m, 1H, C_6H_3), 6.69–6.62 (m, 2H, C_6H_3), 5.87 (m, 1H, $\mathrm{CH_2C}\mathit{H}\mathrm{{=}CH_2}$), 5.04 (m, 2H, $\mathrm{CH_2CH{=}C}\mathit{H}_2$), 3.80 (s, 3H, OMe), 3.33 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH{=}CH_2}$), 2.18 (s, 15H, C_5Me_5). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 153.6 (C_{ipso} bonded to –OTi), 150.0, (C_{ipso} bonded to –OMe), 137.8 (C_{ipso} bonded to $-C_3H_5$), 137.4 ($\mathrm{CH_2{-}}\mathit{C}\mathrm{H{=}CH_2}$), 135.6, 132.7 ($C_6H_3$), 120.3 ($\mathit{C}_5\mathrm{Me}_5$), 115.8 ($\mathrm{CH_2{-}CH{=}}\mathit{C}\mathrm{H_2}$), 113.2 ($C_6H_3$), 56.3 (OMe), 40.0 ($\mathit{C}\mathrm{H_2{-}CH{=}CH_2}$), 12.7 ($\mathrm{C_5}\mathit{Me}_5$).

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