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Monocyclopentadienyl titanium complexes supported by functionalized carboxylate ligands

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ABSTRACT

The reaction of $[TiCp^*Cl_3]$ with $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COOH)]$ in the presence of NEt_3 yields $[TiCp^*\{(OOC–C_5H_4)FeCp\}_3]$ (**1**), ($Cp = \eta^5\text{-}C_5H_5$). The alkyl complex $[TiCp^*Me_3]$ reacts with $[FeCp(\eta^5\text{-}C_5H_4–CH_2COOH)]$ or anthranilic acid rendering the tris-carboxylate titanium complexes $[TiCp^*\{(OOCCH_2–C_5H_4)FeCp\}_3]$ (**2**) and $[TiCp^*\{(OOCC_6H_4NH_2)_3]$ (**3**), respectively. Complex **3** can be protonated with triflic acid to render $[TiCp^*\{(OOCC_6H_4NH_2)_3].HOTf$ (**4**). The reaction of $[TiCp^*Me_3]$ with anthranilic acid in a 1:2 M ratio yields the alkyl carboxylate derivative $[TiCp^*Me\{(OOCC_6H_4NH_2)_2]$ (**5**). Complex **5** reacts with ^tBuNC to render the iminoacyl complex $[TiCp^*(\eta^2\text{-}MeCN^tBu)\{(OOCC_6H_4NH_2)_2]$ (**6**). The reaction of $[TiCp^*Cl_3]$ with the ferroceneacetic acid, gives $[TiCp^*Cl_2\{(OOCCH_2–C_5H_4)FeCp\}]$ (**7**). The $[TiCp^*Cl]_2(\mu\text{–}O)[(OOC–C_5H_4)_2Fe]$ (**8**) can be obtained by reaction of $[TiCp^*Cl_3]$ with $[Fe(\eta^5\text{-}C_5H_4–COOH)_2]$ in the presence of a base. The molecular structures of **1** and **8** have been established by X-ray diffraction methods.

1. Introduction

Titanium is a metal used on a wide range of materials supporting medical applications. It is therefore of great interest to investigate simple complexes that could act as structural models of the intricate interaction between titanium biological molecules with which it comes in contact. In this sense, carboxylate and amine functions are ubiquitous in biological molecules and therefore it is important to study their titanium coordination chemistry [1].

Moreover, carboxylates [2] are versatile ligands because appropriate substitution patterns allow substantial changes on the steric and electronic properties of the metal center and on account of that are common groups in systems of catalytic utility. In addition, they offer a great variety of coordination modes and this makes them interesting in the construction of molecular architectures [3,4].

We have focused our work on the synthesis and study of titanium carboxylates with amino or ferrocene functions. In spite of the extensive work on the symmetrical and unsymmetrical ferrocenyl ligands [5] the chemistry of monocyclopentadienyl derivatives of titanium with this type of ligand remains practically unexplored.

The ferrocene backbone provides for a relatively rigid coordination environment and it is known that the incorporation of an electron rich transition metal in the complex can stabilize electron deficient and cationic early transition metal complexes [6].

We report here our results on the preparation and structural characterization of a series of monocyclopentadienyl titanium complexes containing functionalized carboxylate ligands.

2. Results and discussion

The titanium derivative $[TiCp^*Cl_3]$ reacts with ferrocenecarboxylic acid $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COOH)]$ in the presence of NEt_3 in toluene at room temperature rendering the tris-carboxylate titanium complex $[TiCp^*\{(OOC–C_5H_4)FeCp\}_3]$ (**1**) (Scheme 1). In this complex three carboxylate chelate moieties from three ferrocenyl ligands are coordinated to a titanium center.

Complex **1** has been characterized by the usual spectroscopic techniques. The ^1H NMR spectrum shows a singlet signal at 2.06 ppm corresponding to the Cp^* group, two multiplet signals at 4.00 and 4.90 ppm corresponding to the carboxylic cyclopentadienyl moiety and a singlet at 4.38 ppm assigned to the Cp group bonded to the iron atom. The ^{13}C NMR data are also in agreement with the coordination of the carboxylate groups as depicted in Scheme 1.

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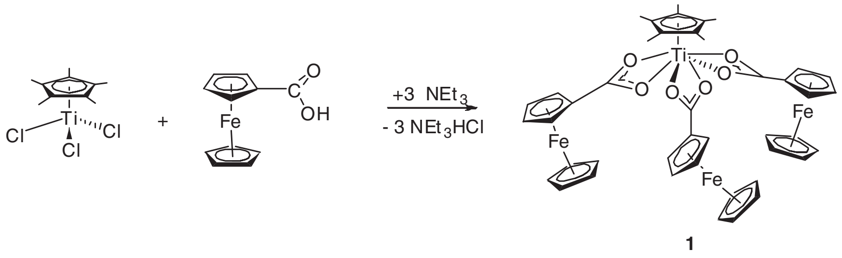


Scheme 1.

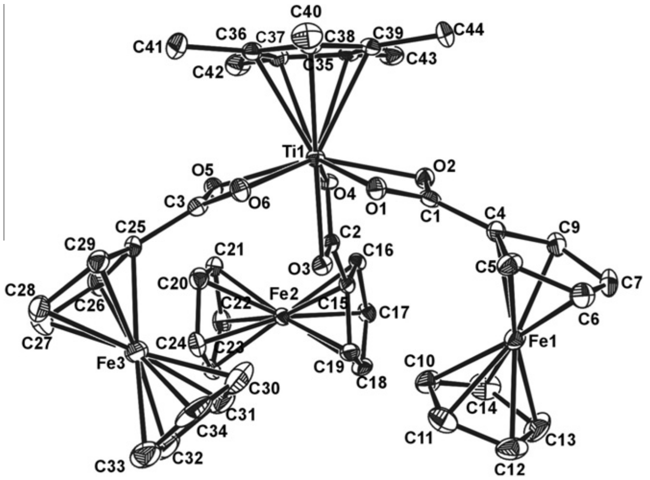


Fig. 1. Perspective ORTEP (30%) of the molecular structure of complex **1**.

Table 1
Selected bond lengths [Å] and angles [°] for **1** and **8**.

1		**8**	
Bond distances			
Ti(1)–O(4)	2.071(3)	Ti(1)–O(3)	1.819(1)
Ti(1)–O(6)	2.121(3)	Ti(1)–O(1)	2.107(1)
Ti(1)–O(1)	2.123(3)	Ti(1)–O(2)	2.143(1)
Ti(1)–O(3)	2.189(3)	Ti(1)–Cl(1)	2.3193(7)
Ti(1)–O(2)	2.195(3)	Ti(1)–C(9)	2.355(2)
Ti(1)–O(5)	2.203(3)	C(1)–O(2)	1.271(3)
		C(1)–O(1)	1.277(3)
		C(1)–C(2)	1.462(3)
Bond angles			
C(2)–O(4)–Ti(1)	93.1(3)	O(2)–C(1)–O(1)	117.3(2)
C(2)–O(3)–Ti(1)	87.9(2)	O(2)–C(1)–C(2)	123.6(2)
C(1)–O(2)–Ti(1)	89.4(3)	O(1)–C(1)–C(2)	119.2(2)
C(1)–O(1)–Ti(1)	92.9(3)	Ti(1)–O(3)–Ti(1)[a]	132.1(1)
O(6)–Ti(1)–O(1)	74.3(1)	O(1)–Ti(1)–O(2)	61.59(6)
O(4)–Ti(1)–O(3)	61.4(1)	O(3)–Ti(1)–Cl(1)	97.04(3)
O(4)–Ti(1)–O(6)	132.3(1)	O(1)–Ti(1)–Cl(1)	134.41(5)
O(4)–Ti(1)–O(1)	130.4(1)		

[a] Symmetry operation used to generated the atom: $-x + 2, y, -z + 1/2$.

In order to accurately establish the structure of complex **1** we have carried out its characterization by X-ray diffraction methods. An ORTEP of **1** is shown in Fig. 1, and some selected bond distances and angles are summarized in Table 1. The structure consists of discrete molecules separated by van der Waals distances. The titanium atom is bonded to the cyclopentadienyl ring in a η^5-mode and to three carboxylate groups in a bidentate fashion.

The geometry around the metal center can be described as a distorted pentagonal pyramid. The Ti–O bond distances range from 2.071(3) to 2.203(3) Å and compare well with that found in the tris-carboxylate titanium derivative [TiCp*(O_2CPh)$_3$] [7].

The synthesis of carboxylate derivatives can also be achieved by reaction of metal-alkyl complexes with the corresponding carboxylic acid [8]. In this way, the titanium alkyl derivatives [TiCp*Me_3] reacts with ferroceneacetic or anthranilic acid, at room temperature, to yield the tri carboxylate compounds **2** or **3**, respectively (Scheme 2).

This procedure can also be used to prepare complex **1**, by reaction of [TiCp*Me_3] with [Fe(η^5-C_5H_5)(η^5-C_5H_4COOH)].

Complexes **2** and **3** are air stable and have also three chelate carboxylate moieties. They have been characterized by the usual spectroscopic techniques. As an example the ^{1}H NMR of **2** shows singlet signals at 1.89 ppm and 3.32 ppm assigned to the Cp* ligand and to the methylene moieties, respectively. The aromatic protons of the ferrocenyl ligands appear at 3.93, 4.00 and 4.19 ppm.

Compound **3** is interesting in several ways, both because the anthranilate group can behave as a N and O donor ligand and can therefore can be a good model of the interaction between titanium with biological molecules, and also because it has NH_2R moieties that can be easily protonated to yield cationic derivatives.

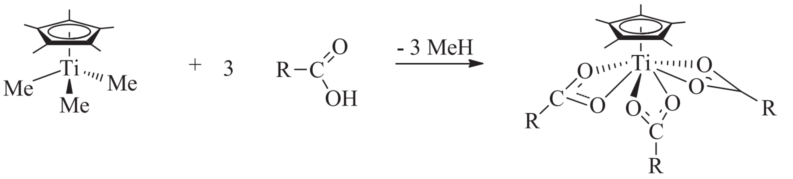
In this way, compound **3** reacts with triflic acid to yield a new complex, **4**, that has been characterized by the usual analytical and spectroscopic techniques (Scheme 3).

The ^{1}H NMR spectrum of compound **4** shows a broad signal at 5.95 ppm that is assigned to the seven protons of the amine and ammonium groups. The ^{13}C NMR spectrum indicates that all the three aromatic rings are in the same chemical environment. The spectrum shows only one signal, at 187.4 ppm, corresponding to the carboxylate moieties. All this data could indicate that there is a rapid proton transfer between all the three anthranilate groups in the NMR time scale. A VTNMR experiment shows that even at 223 K the proton transfer process is rapid in the NMR time scale.

As we have seen, the reaction of [TiCp*Me_3] with the corresponding carboxylic acid is a good synthetic procedure for the preparation of tricarboxylate derivatives. However, because of the high polarity of the Ti–C bonds and the acidity of carboxylic acids normally it is not possible to carry out the protonolysis reaction of the Ti–Me bonds in a stepwise manner in order to isolate the carboxylate alkyl complex. Probably the lack of an appropriate synthetic procedure of such derivatives has prevented a systematic study of the reactivity of the Ti–C bond in complexes with carboxylate groups as ancillary ligands.

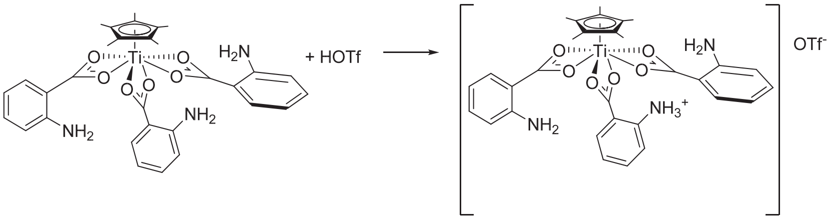
The reaction of [TiCp*Me_3] with anthranilic acid in a 1:2 M ratio, in pentane at low temperature, yields the corresponding dicarboxylate compound **5** (Scheme 4) along with small amounts of **3** (ca. 5%). In contrast, complexes **1** or **2** were the only isolated products when different molar ratios of [TiCp*Me_3] and ferrocenecarboxylic or ferroceneacetic acid, respectively, were employed.

Complex **5** has been isolated as an air sensitive orange solid, soluble in CH_2Cl_2 and THF and less soluble in pentane. It has been spectroscopically characterized.



R = $(CH_2\text{-}C_5H_4)$FeCp (**2**), $C_6H_4NH_2$ (**3**)

Scheme 2.



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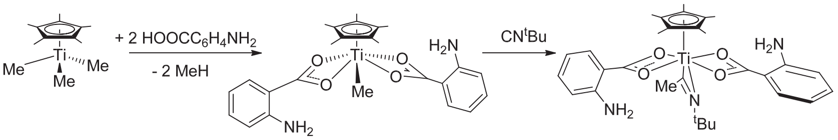
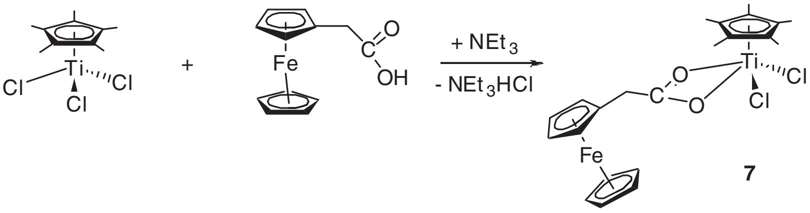
Scheme 3.



Scheme 4.



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Scheme 5.

Firstly, we have carried out the reaction of **5** with *tert*-butylisocyanide in a 1:1 M ratio to yield an air sensitive orange solid which was identified as complex **6** (See Scheme 4).

The ^{1}H NMR spectrum shows singlet signals at 1.53, 1.93 and 2.49 ppm which are assigned to the *tert*-butyl group, the Cp* ligand and the inserted methyl moiety, respectively. In addition, the spectrum shows a broad signal at 5.68 ppm corresponding to the amine protons and three multiplet signals due to the aromatic protons. Furthermore, ^{13}C NMR shows, among others, two singlet signals at 227.3 and 179.4 ppm which we assign to the iminoacyl carbon atom and to the carboxylic groups of the anthranilate ligands. All those data suggest that complex **6** has reacted with *tert*-Butylisocyanide to yield a rather symmetric compound. In order to know the orientation of the imine fragment a NOESY experiment was carried out. The response in the ^{1}H NOESY-1D experiment from the Cp* ligand upon irradiating the methyl groups of iminoacyl fragment indicate that in solution the orientation depicted in Scheme 4 is preferred.

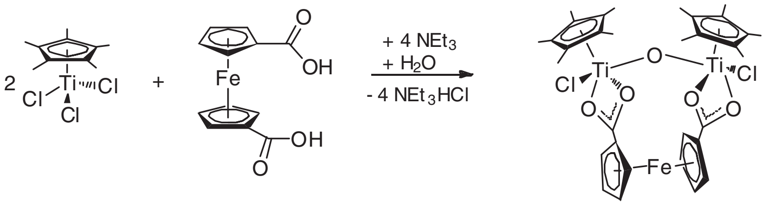
Finally, in order to prepare chloro-carboxylate derivatives we have studied the reaction of the starting compound $[TiCp^*Cl_3]$ with ferroceneacetic acid in the presence of NEt_3 at room temperature in 1:1 M ratio, we have found the mono-carboxylate titanium complex $[TiCp^*Cl_2\{(OOCCH_2–C_5H_4)FeCp\}]$ (**7**) is produced (Scheme 5). Complex **7** has been characterized by ^{1}H and ^{13}C NMR as well as by elemental analysis and IR spectroscopy.

The ^{1}H NMR spectrum of complex **7** shows two singlet signals at 2.01 and 3.07 ppm assigned to the Cp* group and to the methylene protons of the ferrocenyl ligand. The resonances of the cyclopentadienyl protons appear as multiplet absorptions at 3.85, 3.90, and 4.00 ppm.

The reaction of the starting compound $[TiCp^*Cl_3]$ with $[Fe(\eta^5\text{-}C_5H_4–COOH)_2]$ in a 2:1 M ratio in the presence of NEt_3, proceeds in toluene, at room temperature, to yield the heterometallic complex $[TiCp^*Cl]_2(\mu\text{-}O)[(OOC–C_5H_4)_2Fe]$ (**8**) (Scheme 6), in which two titanium centers are connected throughout an oxo bridging ligand. Compound **8** is also obtained if the reaction of $[TiCp^*Cl_3]$ with $[Fe(\eta^5\text{-}C_5H_4–COOH)_2]$ is carried out in a 1:1 M ratio.

Probably, the presence of the oxo group is the result of a hydrolysis process due to some residual moisture in the solvent. The formation of oxo-containing derivatives by reaction of early transition metal complexes with carboxylic acids is not unusual. In this way, the use of organic carboxylic acids to modify the reactivity of titanium alkoxides has led to the isolation of a variety of complex molecules containing titanium oxo-alkoxide cores coordinated by carboxylate ligands [9].

Complex **8** has been characterized by NMR and IR spectroscopy as well as by elemental analysis and X-ray diffraction. The ^{1}H NMR spectrum shows the resonance corresponding to the Cp* ligand at 2.12 ppm while those assigned to the carboxylate cyclopentadienyl



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Scheme 6.

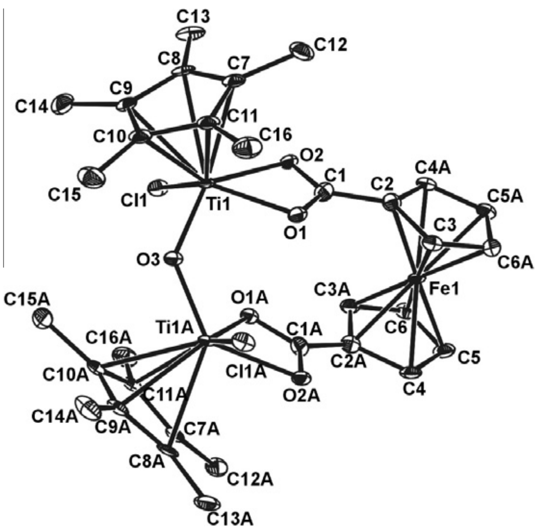

Fig. 2. Perspective ORTEP (30%) of the molecular structure of complex **8**.

group appear at 3.67, 3.82, 4.77 and 4.82 ppm. The ratio of the integrals is consistent with the proposed stoichiometry while the number of signals indicates that the four protons in each carboxylate cyclopentadienyl ligand are unequivalent. The ^{13}C NMR spectrum is in agreement with the proposed disposition. Both titanium atoms in complex **8** are chiral centers and the ^{1}H NMR spectrum shows that only the SS and/or the RR isomers are isolated. Formation of the SR isomer is, probably prevented by the rigid nature of the bridging carboxylate ligand.

The coordination mode of the ferrocenyl ligand has been confirmed by an X-ray diffraction study. An ORTEP of **8** is shown in Fig. 2, and some selected bond distances and angles are summarized in Table 1.

The structure consists of discrete trimetallic molecules separated by van der Waals distances. The structure around the two titanium atoms in the molecule is that of a pseudo-square pyramidal geometry. The ferrocene dicarboxylate moiety is bridging the two titanium centers. Furthermore, each of the two titanum atoms is bonded to a Cp* group, to a chlorine atom and to an oxo bridging ligand.

It is noteworthy that the rigid nature of the bridging ferrocene carboxylate ligand imposes some specific structural parameters. The Ti–O bond distance (Ti(1)–O(3), 1.8195(11) is within the range expected for μ-oxo–dititanium bridging systems [10] and the Ti–O–Ti bond angle (132.11(14)°) is wider than that found in di-μ-oxo–dititanium complexes but it is in the range expected for dinuclear derivatives bridged only through an oxo ligand [8,11]. The Ti(1)–O(1) and Ti(1)–O(2) bond distances (2.107(2) and 2.143(2) Å, respectively) are somewhat longer than those in **1** but are within the range expected for bidentate carboxylate titanium derivatives [7].

The Ti(1)–Ti(1)[a] distance (3.3258(1) Å) is short and it falls into the range observed for dinuclear oxo bridged titanium systems [8,11,12]. Besides, the X-ray data indicate that the crystals are a racemic mixture of both RR and SS isomers.

All complexes reported in this paper show IR bands for which Δ ν_{as}(COO)–ν_{s}(COO) values are in agreement with a bidentate coordination of the carboxylate group to the titanium center [13].

3. Conclusion

In conclusion, we report in this paper the synthesis of a series of complexes containing monocyclopentadienyl titanium units with different functionalized carboxylate moieties. We have seen that although the NH_2 moiety of the anthranilate group does interact with the titanium center it can play a role on the reactivity of the complex because it acts as basic center that can be protonated to yield cationic derivatives. We have also been able to synthesize a methyl carboxylate complex and we have studied the reactivity of the Ti–Me bond with ^{t}BuNC. Studies in order to know how the redox state of the iron affects the electron density at the titanium atom are underway.

4. Experimental section

4.1. General procedures

The preparation and handling of described compounds was performed with rigorous exclusion of air and moisture under nitrogen atmosphere using standard vacuum line and Schlenk techniques. All solvents were dried and distilled under a nitrogen atmosphere.

The following reagents were prepared by literature procedures: [TiCp*Me$_3$] [14] and [TiCp*Cl$_3$] [15]. The commercially available compounds were used as received from Aldrich.

^{1}H and ^{13}C NMR spectra were recorded on a 200 Mercury Varian or on a 400 Avance Bruker Fourier Transform Spectrometers. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in units of parts per million relative to $SiMe_4$.

IR spectra were recorded in the region 4000–400 cm^{-1} with a Nicolet Magna-IR 550 spectrophotometer.

4.2. Synthesis

4.2.1. Synthesis of [TiCp*{(OOC–C$_5$H$_4$)FeCp}$_3$] (**1**)

To a solution of [TiCp*Cl$_3$] (0.235 g, 0.81 mmol) in 10 mL of toluene were added ferrocenecarboxylic acid (0.560 g, 2.43 mmol) and 0.339 mL (2.43 mmol) of NEt_3 at room temperature, and the mixture was stirred for 18 h. After that, the solvent was evaporated and the residue washed with pentane (8 mL), yielding complex **1** as an orange solid (0.364 g, 52%). IR (KBr, cm^{-1}): 1540 (vs $\nu_{as(COO)}$), 1465 (vs $\nu_{s(COO)}$), Δ = 75 cm^{-1}. ^{1}H NMR (C_6D_6, rt): δ 2.06 (s, 15 H, Cp*), 4.00 (s, 6 H, CH), 4.38 (s, 15 H, CH), 4.9 (s, 6 H, CH). $^{13}C\{^{1}H\}$NMR (C_6D_6, rt): 11.6 (Cp*), 70.2 (CH), 70.5 (CH), 71.3

(CH), 77.0 (C_{ipso}), 134.9 (Cp*), 187.9 (COO). *Anal.* Calc. for $C_{43}H_{42}Fe_3O_6Ti$: C, 59.34; H, 4.86. Found: C, 59.47; H, 4.95%.

4.2.2. Synthesis of [TiCp{(OOCCH$_2$–C$_5$H$_4$)FeCp}$_3$] (**2**)*

To a mixture of [TiCp*Me_3] (0.205 g, 0.89 mmol) and ferroceneacetic acid (0.657 g, 2.67 mmol) was added toluene (7 mL) at room temperature and the mixture was stirred for 3 h. After that, the solvent was evaporated and the residue washed with pentane to yield a yellow solid, which was characterized as **2** (0.589 g, 72 %). IR (KBr, cm^{-1}): 1545 (vs $\nu_{as(COO)}$), 1469 (vs $\nu_{s(COO)}$), $\Delta = 76\ cm^{-1}$. ^1H NMR (C_6D_6, rt): δ 1.89 (s, 15 H, Cp*), 3.32 (s, 6 H, CH_2), 3.93 (m, 6 H, CH), 4.00 (m, 15 H, CH), 4.19 (m, 6 H, CH). $^{13}C\{^1H\}$NMR (C_6D_6, rt): 11.5 (Cp*), 38.0 (CH_2), 67.9 (CH), 69.2 (CH), 80.6 (C_{ipso}), 131.0 (Cp*), 187.3 (COO). *Anal.* Calc. for $C_{46}H_{48}Fe_3O_6Ti$: C, 60.56; H, 5.30. Found: C, 60.66; H, 5.43%.

4.2.3. Synthesis of [TiCp{(OOCC$_6$H$_4$NH$_2$)$_3$] (**3**)*

To a mixture of [TiCp*Me_3] (0.230 g, 1.01 mmol) and anthranilic acid (0.414 g, 3.02 mmol) was added dichloromethane (5 mL) at room temperature, and the mixture was stirred for 3 h. After that, the solvent was evaporated and the residue washed with pentane to yield a yellow crystalline solid, which was characterized as **3** (0.560 g, 94 %). IR (KBr, cm^{-1}): 1568 (m, $\nu_{as(COO)}$), 1469 (s, $\nu_{s(COO)}$), $\Delta = 99\ cm^{-1}$. ^1H NMR ($CDCl_3$, rt): δ 2.12 (s, 15 H, Cp*), 5.61 (br, 6 H, NH_2), 6.57 (m, 3 H, Ar), 6.62 (m, 3 H, Ar), 7.21 (m, 3 H, Ar), 7.88 (m, 3 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): 11.6 (Cp*), 112.6 (C_{ipso}), 116.1 (Ar), 116.3 (Ar), 129.0 (Cp*), 131.5 (Ar), 133.8 (Ar), 149.9 (C_{ipso}), 182.5 (COO). *Anal.* Calc. for $C_{31}H_{33}O_6N_3Ti$: C, 62.94; H, 5.62, N, 7.10. Found: C, 62.58; H, 5.70, N, 7.01%.

4.2.4. Synthesis of [TiCp{(OOCC$_6$H$_4$NH$_2$)$_3$]·HOTf (**4**)*

To a solution of compound **3** (0.235 g, 0.39 mmol) in CH_2Cl_2, at room temperature, was added HOTf (35 μL, 0.39 mmol) and the mixture was stirred for 3 h. After that, the solvent was evaporated and the residue washed with Et_2O to yield a red crystalline solid, which was characterized as **4** (0.155 g, 53 %). IR (KBr, cm^{-1}): 1567 (vs $\nu_{as(COO)}$), 1485 (vs $\nu_{s(COO)}$), $\Delta = 82\ cm^{-1}$. ^1H NMR (CD_2Cl_2, rt): δ 2.06 (s, 15 H, Cp*), 5.95 (br, 7 H, NH_2), 6.74 (m, 4 H, Ar), 6.84 (m, 2 H, Ar), 7.29 (m, 1 H, Ar), 7.44 (m, 2 H, Ar), 7.85 (m, 1 H, Ar), 7.97 (m, 2 H, Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, rt): 12.1 (Cp*), 116.7 (C_{ipso}), 117.3 (Ar), 131.1 (Cp*), 131.4 (Ar), 136.9 (Ar), 152.3 (C_{ipso}), 187.4 (COO). *Anal.* Calc. for $C_{32}H_{34}F_3N_3O_9STi$: C, 51.82; H, 4.62, N, 5.66. Found: C, 51.29; H, 4.83, N, 5.48%.

*4.2.5. Synthesis of [TiCp*Me{(OOCC$_6$H$_4$NH$_2$)$_2$] (**5**)*

To a solution of [TiCp*Me_3] (0.310 g, 1.37 mmol) in 10 mL of pentane at −40 °C was added anthranilic acid (0.375 g, 2.74 mmol). The mixture was allowed to reach the room temperature and then was added toluene (2 mL) at room temperature. The mixture was stirred for 3 h. After that, the solvents were filtered and the residue washed with pentane to yield an orange solid, which was characterized as **5** (0.450 g, 70 %). IR (KBr, cm^{-1}): 1528 (m, $\nu_{as(COO)}$), 1441 (s, $\nu_{s(COO)}$), $\Delta = 87\ cm^{-1}$. ^1H NMR ($CDCl_3$, rt): δ 0.91 (s, 3 H, Me), 2.03 (s, 15 H, Cp*), 5.67 (br, 4 H, NH_2), 6.66 (m, 4 H, Ar), 7.26 (m, 2 H, Ar), 7.88 (m, 2 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): 11.6 (Cp*), 68.9 (Me), 111.4 (C_{ipso}), 116.1 (Ar), 116.4 (Ar), 128.0 (Cp*), 131.6 (Ar), 134.4 (Ar), 150.6 (C_{ipso}), 182.3 (COO).

4.2.6. Synthesis of [TiCp(^{2}-MeCN^{t}Bu){(OOCC$_6$H$_4$NH$_2$)$_2$] (**6**)*

To a solution of compound **5** (0.321 g, 0.67 mmol) in 8 mL of CH_2Cl_2 at room temperature was added ^{t}BuNC (0.057 g, 0.67 mmol). The mixture was stirred for 1 h. After that, the solvent was evaporated under vacuum and the residue washed with pentane to yield an orange solid, which was characterized as **5** (0.181 g, 48 %). IR (KBr, cm^{-1}): 1512 (s, $\nu_{as(COO)}$), 1445 (s, $\nu_{s(COO)}$), $\Delta = 67\ cm^{-1}$. ^1H NMR ($CDCl_3$, rt): δ 1.53 (s, 9 H, ^{t}Bu), 1.93 (s, 15 H, Cp*), 2.49 (s, 3 H, Me), 5.68 (br, 4 H, NH_2), 6.62 (m, 4 H, Ar), 7.21 (m, 2 H, Ar), 7.86 (m, 2 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): 11.4 (Cp*), 17.5 (Me), 29.7 (^{t}Bu), 62.2 (^{t}Bu), 114.2 (C_{ipso}), 115.8 (Ar), 116.0 (Ar), 121.7 (Cp*), 131.2 (Ar), 132.8 (Ar), 149.7 (C_{ipso}), 179.4 (COO), 227.3 (CN). *Anal.* Calc. for $C_{30}H_{39}O_4N_3Ti$: C, 65.10; H, 7.09; N, 7.59. Found: C, 65.08; H, 6.98, N, 7.26%.

*4.2.7. Synthesis of [TiCp*Cl$_2${(OOCCH$_2$–C$_5$H$_4$)FeCp}] (**7**)*

To a solution of [TiCp*Cl_3] (0.246 g, 0.85 mmol) in 10 mL of toluene were added ferroceneacetic acid (0.211 g, 0.85 mmol) and 0.118 mL (0.85 mmol) of NEt_3 at room temperature, and the mixture was stirred for 16 h. After filtration, the solvent was evaporated

Table 2
Crystal data and structure refinement for **1** and **8**·C_7H_8.

	1	**8**·C_7H_8
Molecular formula	$C_{43}H_{42}Fe_3O_6Ti$	$C_{39}H_{45}Cl_2FeO_5Ti_2$
Formula weight	870.22	816.30
Temperature (K)	200(2)	100(2)
Wavelength (Å)	0.71073	1.54178
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
a (Å)	10.8864(8)	11.0151(2)
b (Å)	10.4805(7)	30.7297(7)
c (Å)	33.068(2)	11.3000(2)
β (°)	98.765(3)	101.852(1)
Volume (Å^3)	3728.8(4)	3743.4(1)
Z	4	4
Density (calculated) (g/cm^3)	1.550	1.448
Absorption coefficient (mm^{-1})	1.399	8.264
$F(0\,0\,0)$	1792	1692
Crystal size (mm^3)	0.42 × 0.14 × 0.11	0.25 × 0.22 × 0.12
Theta range for data collection (°)	1.25–26.39	2.88–70.38
Index ranges	$-13 \leqslant h \leqslant 13$	$-13 \leqslant h \leqslant 13$
	$-12 \leqslant k \leqslant 13$	$-37 \leqslant k \leqslant 34$
	$-41 \leqslant l \leqslant 41$	$-12 \leqslant l \leqslant 13$
Reflections collected	32461	9139
Independent reflections	7626 [$R_{(int)} = 0.0949$]	3521 [$R_{(int)} = 0.0395$]
Data/restraints/parameters	7626/0/483	3521/0/312
Goodness-of-fit on F^2	0.990	0.993
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0563$	$R_1 = 0.0383$
	$wR_2 = 0.1226$	$wR_2 = 0.0995$
Largest difference in peak and hole	0.629 and −0.591	0.524 and −0.566

and the residue washed with pentane (7 mL) to yield complex **7** as an orange solid (0.200 g, 47%). IR (KBr, cm^{-1}): 1542 (m, $\nu_{as(COO)}$), 1469 (vs $\nu_{s(COO)}$), $\Delta = 73\ cm^{-1}$. ^1H NMR (C_6D_6, rt): δ 2.01 (s, 15 H, Cp*), 3.07 (s, 2 H, CH_2), 3.85 (m, 2 H, CH), 3.90 (s, 5 H, CH), 4.00 (m, 2 H, CH). $^{13}C\{^1H\}$ NMR (C_6D_6, rt): 12.4 (Cp*), 35.0 (CH_2), 68.1 (CH), 69.0 (CH), 69.1 (CH), 79.9 (C_{ipso}), 176.1 (COO). *Anal.* Calc. for $C_{22}H_{26}Cl_2FeO_2Ti$: C, 53.15; H, 5.27. Found: C, 53.13; H, 5.27%.

4.2.8. Synthesis of $[TiCp^*Cl]_2(\mu\text{-}O)[(OOC–C_5H_4)_2Fe$ (**8**)

To a solution of $[TiCp^*Cl_3]$ (0.320 g, 1.10 mmol) in 5 mL of toluene were added 1,1′-ferrocenedicarboxylic acid (0.151 g, 0.55 mmol) and 0.306 mL (2.20 mmol) of NEt_3, and the mixture was stirred at room temperature for 4 h. After filtration, the solvent was removed under vacuum and the solid washed with pentane (2 mL) yielding complex **8** as a red crystalline solid (0.250 g, 55%). IR (KBr, cm^{-1}): 1531 (vs $\nu_{as(COO)}$), 1455 (vs $\nu_{s(COO)}$), $\Delta = 76\ cm^{-1}$. ^1H NMR (C_6D_6, rt): δ 2.12 (s, 30 H, Cp*), 3.67 (m, 2 H, CH), 3.82 (m, 2 H, CH), 4.77 (m, 2 H, CH), 4.82 (m, 2 H, CH). $^{13}C\{^1H\}$NMR (CD_2Cl_2): 11.2 (Cp*), 69.7 (CH), 70.1 (CH), 71.1 (CH), 72.5 (CH), 130.9 (Cp*), 185.7 (COO). *Anal.* Calc. for $C_{39}H_{46}Cl_2O_5FeTi_2$: C, 57.31; H, 5.67. Found: C, 57.63; H, 5.87%.

4.3. X-ray Crystallography for **1** and $\mathbf{8{\cdot}C_7H_8}$

A summary of crystal data collection and refinement parameters for all compounds are given in Table 2. Single crystals of a orange block of **1** was placed in a Bruker-Nonius X8 APEXII CCD area-detector diffractometer, equipped with a graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). X-ray data were collected at 200 K, with a combination of three runs at different φ and ω scans. A red single crystal of $\mathbf{8{\cdot}C_7H_8}$ with prismatic shape was mounted on a glass fibber and transferred to a Bruker SMART 6K CCD area-detector three-circle diffractometer with a Rotating Anode (Cu Kα radiation, $\lambda = 1.54178$ Å) generator equipped with Goebel mirrors at settings of 50 kV and 110 mA. X-ray data were collected at 100 K, with a combination of five runs at different φ and ω scans. For both compounds the substantial redundancy in data allows semi-empirical absorption corrections (SADABS) [16] to be applied using multiple measurements of symmetry-equivalent reflections. The raw intensity data frames were integrated with the SAINT [17] program, which also applied corrections for Lorentz and polarization effects.

The software package SHELXTL [18] was used for space group determination, structure solution and refinement. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct method (SHELXS-97) [19], completed with difference Fourier syntheses, and refined with full-matrix least-squares using SHELXL-97 [20] minimizing $\omega(F_0^2 - F_c^2)^2$. Weighted R factors (R_w) and all goodness of fit S are based on F^2; conventional R factors (R) are based on F. All non-hydrogen atoms were refined with anisotropic displacement parameters.

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References

[1] (a) E.Y. Tshuva, J.A. Ashenhurst, Eur. J. Inorg. Chem. (2009) 2203;
(b) E.Y. Tshuva, D. Peri, Coord. Chem. Rev. 253 (2009) 2098;
(c) H. Shimizu, T. Habu, Y. Takada, K. Watanabe, O. Okuno, T. Okabe, Biomaterials 23 (2002) 2275.;
(d) A. Moroni, C. Faldini, M. Rocca, S. Stea, S. Giannini, J. Orthop. Trauma 16 (2002) 257;
(e) M. Oka, Orthop. Sci. 6 (2001) 448;
(f) T.M. Klapötke, H. Köpf, I.C. Tornieporth-Oetting, P.S. White, Organometallics 13 (1994) 3628.

[2] Y. Dang, Coord. Chem. Rev. 135 (1994) 93.

[3] C. Oldhan, Carboxylates, squarates and related species, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, Pergamon Press, Oxford, 1987;
(b) B.-H. Ye, M.-L. Tong, X.-M. Chen, Coord. Chem. Rev. 249 (2005) 545.

[4] (a) E. Mieczyńska, A.M. Trzeciak, J.J. Ziółkowski, T. Lis, J. Chem. Soc. Dalton Trans. (1995) 105;
V.G. Kessler, Chem. Commun. (1985) 1213;
(c) C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. Chem., Int. Ed. 43 (2004) 1466;
(d) S.L. Castro, W.E. Streib, J.C. Huffmann, G. Christou, Chem. Commun. (1996) 2177;
(e) K. Gigant, A. Rammal, M. Henry, J. Am. Chem. Soc. 123 (2001) 11632;
(f) O. Mamula, M. Lama, H. Stoeckli-Evans, S. Shova, Angew. Chem., Int. Ed. 45 (2006) 4940;
(g) N. Guillou, C. Livage, G. Férey, Eur. J. Inorg. Chem. (2006) 4963;
(h) H. Tian, Q.-X. Jia, Y.-Q. Wang, Y. Ma, E.-Q. Gao, J. Mol. Struct. 933 (2009) 8.

[5] (a) A. Togni, T. Hayashi, Soc. Rev. 33 (2004) 313;
(c) T.M. Miller, K.J. Ahmed, M.S. Wrighton, Inorg. Chem. 28 (1989) 2347;
(d) K. Mach, J. Kubišta, I. Císařová, P. Štěpnička, Acta Crystallogr., Sect. C 58 (2002) m116;
(e) J. Kühnert, P. Ecorchard, H. Lang, Eur. J. Inorg. Chem. (2008) 5125;
(f) H.-M. Gau, C.-C. Schei, L.-K. Liu, L.-H. Luh, J. Organomet. Chem. 435 (1992) 43;
(g) L.C. Francesconi, D.R. Corbin, A.W. Clauss, D.N. Hendrickson, G.D. Stuky, Inorg. Chem. 20 (1981) 2078.

[6] A. Shafir, J. Arnold, J. Am. Chem. Soc. 123 (2001) 9212.

[7] P. Gómez-Sal, B. Royo, P. Royo, R. Serrano, I. Sáez, S. Martinez-Carreras, J. Chem. Soc., Dalton Trans. (1991) 1575.

[8] R. Fandos, B. Gallego, A. Otero, C. Pastor, A. Rodríguez, M.J. Ruiz, P. Terreros, Dalton Trans. 15 (2006) 2683.

[9] (a) T.J. Boyle, R.P. Tyner, T.M. Alam, B.L. Scott, J.W. Ziller, B.G.J. Potter, J. Am. Chem. Soc. 121 (1999) 12104;
(b) S. Doeuff, Y. Dromzee, F. Taulelle, C. Sanchez, Inorg. Chem. 28 (1989) 4439;
(c) A. Bailey, M. Shang, T.P. Fehlner, Inorg. Chem. 39 (2000) 4374.

[10] (a) Y. Qian, J. Huang, X. Chen, G. Li, X. Jin, Q. Yang, Polyhedron 13 (1994) 1105;
(b) T.J. Clark, T.A. Nile, D. McPhail, A.T. McPhail, Polyhedron 8 (1989) 1804.

[11] R. Fandos, C. Hernández, A. Otero, A. Rodríguez, M.J. Ruiz, P. Terreros, J. Chem. Soc., Dalton Trans. (2002) 11.

[12] (a) F. Bottomley, I.J.B. Lin, P.S. White, J. Am. Chem. Soc. 103 (1981) 704;
(b) J. Okuda, E. Herdtweck, Inorg. Chem. 30 (1991) 1516.

[13] M. Mena, M.A. Pellinghelli, P. Royo, R. Serrano, A. Tiripicchio, J. Chem. Soc., Chem. Commun. (1986) 1118.

[14] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.

[15] (a) A.M. Cardoso, R.J.H. Clark, S.J. Moorhouse, J. Chem. Soc., Dalton Trans. (1980) 1156;
(b) G. Hidalgo, M. Mena, F. Palacios, P. Royo, R. Serrano, J. Organomet. Chem. 340 (1988) 37.

[16] G.M. Sheldrick, SADABS Version 2004/1, A Program for Empirical Absorption Correction, University of Göttingen, Göttingen, Germany, 2004.

[17] SAINT+ v7.12a, Area-Detector Integration Program, Bruker-Nonius AXS, Madison, Wisconsin, USA, 2004.

[18] SHELXTL-NT Version 6.12, Structure Determination Package, Bruker-Nonius AXS, Madison, Wisconsin, USA, 2001.

[19] G.M. Sheldrick, SHELXS-97, Program for structure solution, Acta Crystallogr., Sect. A 46 (1990) 467.

[20] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, 1997.