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Journal of Organometallic Chemistry 648 (2002) 119–125

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and characterization of Cp_2Ti-containing organometallics via in situ oxidative-addition of 'Cp_2Ti' intermediate. Crystal structures of $(1\text{-}C_{10}H_7S)_2TiCp_2$, $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2S)]_2TiCp_2$ and $[\eta^2\text{-}OC(Ph){=}C(Ph)O]TiCp_2$

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Received 16 July 2001; received in revised form 12 October 2001; accepted 19 October 2001

Abstract

A simple and convenient route for synthesizing Cp_2Ti-containing compounds $(RS)_2TiCp_2$ (**1**, R = $1\text{-}C_{10}H_7$; **2**, R = $CH_2{=}CHCH_2$; **3**, R = $n\text{-}C_5H_{11}$; **4**, R = CH_2CO_2Me; **5**, R = CH_2CO_2Et; **6**, R = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2)$) and $[\eta^2\text{-}OC(Ph){=}C(Ph)O]TiCp_2$ (**7**) has been developed. This route starts from Cp_2TiCl_2 and involves an in situ oxidative-addition of the intermediate 'titanocene' with corresponding RSSR and benzil. While **7** was previously prepared by another route, **1**–**6** and one starting material $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2)]_2S_2$ (**8**) are new and have been characterized by elemental analysis, IR and ^{1}H-NMR spectroscopy, as well as by X-ray diffraction analysis for **1**, **6** and **7**. Furthermore, the electrochemical properties of **1**–**6** have been studied by cyclic voltammetry. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 'Cp_2Ti'-containing complex; Titanaheterocyclic complex; Cyclic voltammetry; Crystal structures

1. Introduction

It is known that some compounds of type $(RS)_2TiCp_2$ and titanaheterocyclic compound $[\eta^2\text{-}OC(Ph){=}C(Ph)O]TiCp_2$ can be prepared starting from Cp_2TiCl_2 through two separate steps: one step involves the preparation of $Cp_2Ti(CO)_2$, which is prepared by reduction of Cp_2TiCl_2 under a CO atmosphere [1] and the other involves reaction of $Cp_2Ti(CO)_2$ with corresponding RSSR or benzil to give $(RS)_2TiCp_2$ [2] and $[\eta^2\text{-}OC(Ph){=}C(Ph)O]TiCp_2$ [3]. Herein we report a more convenient, 'one pot' method for synthesis of such Cp_2Ti-containing organometallic compounds with satisfactory yields. This method includes reduction of Cp_2TiCl_2 with Mg [4–6] followed by in situ treatment of the intermediate 'Cp_2Ti' with the corresponding RSSR or benzil. We also report the structural characterization of all the new synthesized compounds, three crystal molecular structures and the electrochemical properties of the synthesized compounds with a general formula of $(RS)_2TiCp_2$.

2. Results and discussion

2.1. Preparation and characterization of $(RS)_2TiCp_2$ (1–6), $Cp_2Ti[\eta^2\text{-}OC(Ph){=}C(Ph)O]$ (7) and $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2)]_2S_2$ (8)

We found that freshly crushed magnesium powders or the magnesium turnings activated by 1,2-dibromoethane could reduce Cp_2TiCl_2 in THF to give a brown–green solution of the low-valent titanium(+II) intermediate 'Cp_2Ti', which reacted in situ with RSSR or benzil through an oxidative-addition process to afford a series of high-valent titanium(+IV) organo metallic compounds **1**–**7**, as shown in Scheme 1.

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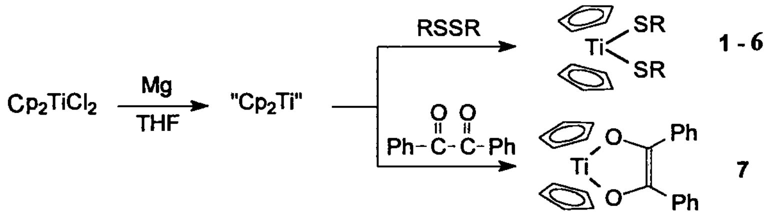
PII: S0022-328X(01)01413-9



	1	2	3	4	5	6
R	α-$C_{10}H_7$	$CH_2CH{=}CH_2$	n-C_5H_{11}	CH_2CO_2Me	CH_2CO_2Et	$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2)$

Scheme 1.

It is worthy of note that the magnesium turnings activated by 1,2-dibromoethane, when compared to the non-activated magnesium powders, can greatly accelerate the reducing process of Cp_2TiCl_2. However, both of these two forms of magnesium work well to produce the coordinatively unsaturated 'Cp_2Ti' intermediate that reacts in situ with corresponding substrates to give **1**–**7** in quite high yields.

Compounds **1**–**6** are all air-stable purple solids. Their elemental analysis and spectral data coincide very well with their structures shown in Scheme 1. For example, the ^{1}H-NMR spectra of **1**–**6** each show one singlet at 6.09–6.21 ppm for the ten protons of Cp_2Ti moieties and corresponding signals for their respective R groups. In addition, the IR spectra of **1**–**6** display absorption bands similar to those of other compounds containing Cp_2Ti groups [7], as well as the corresponding organic functionalities. Compound **7** is a known titanaheterocyclic compound [3], which was not only identified by comparison of its IR and ^{1}H-NMR spectra with those of an authentic sample, but also has been confirmed by X-ray diffraction analysis.

Although, starting materials RSSR for **1**–**5** are known [8], the starting material RSSR for preparation of **6**, i.e. $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2)]_2S_2$ (**8**) is new. We found that **8** could be prepared by an in situ reaction of NaSSNa formed from an aqueous solution of $Na_2S{\cdot}9H_2O$ and sulfur [9] with $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2NMe_3)]^+I^-$. This reaction could be formally regarded as a double nucleophilic attack of the two negatively charged S atoms in NaSSNa at the carbon atom of the methylene group of $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2NMe_3)]^+I^-$ [10] to give **8** and by-products Me_3N and NaI. Compound **8** was characterized by combustion analysis, IR and ^{1}H-NMR spectroscopy, and was further proved by the crystal molecular structure of its derivative **6**, a novel compound containing one bent titanocene and two ferrocenyl structural units.

2.2. X-ray structural analyses of 1, 6 and 7

In order to unequivocally confirm the structures of **1**, **6** and **7**, their X-ray crystal diffraction analyses were carried out. The ORTEP drawings of **1**, **6** and **7** are presented in Figs. 1–3, whereas the selected bond lengths and angles are given in Tables 1–3, respectively.

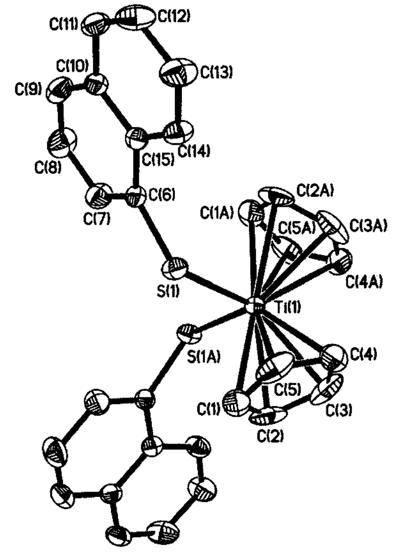


Fig. 1. ORTEP drawing of **1** with atom-labeling scheme.

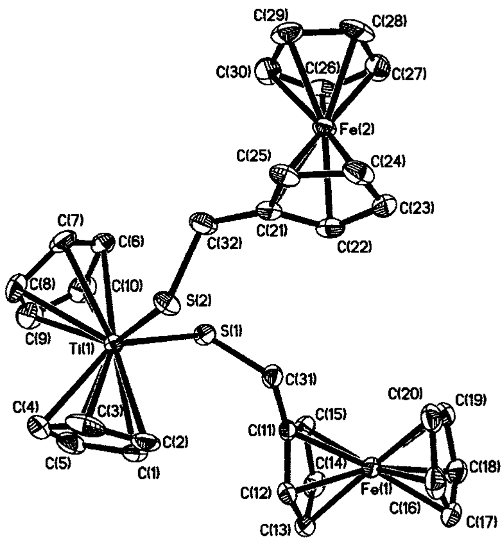


Fig. 2. ORTEP drawing of **6** with atom-labeling scheme.

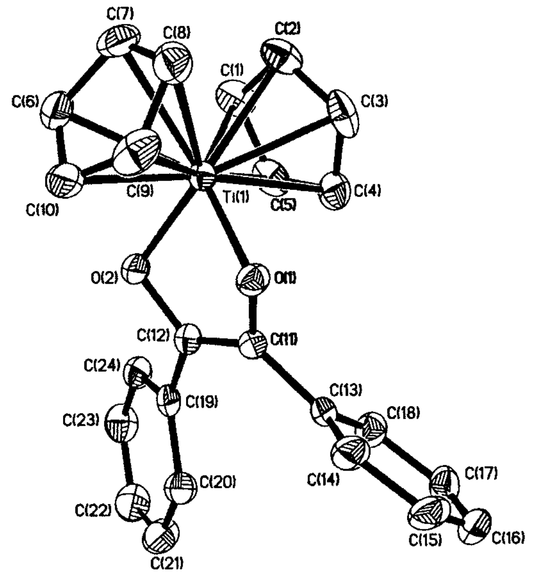


Fig. 3. ORTEP drawing of **7** with atom-labeling scheme.

Table 1
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths	
Ti(1)–C(1)	2.371(5)
Ti(1)–S(1)	2.4324(13)
S(1)–C(6)	1.771(4)
C(1)–C(2)	1.335(6)
C(6)–C(7)	1.379(6)
C(6)–C(15)	1.441(5)
C(7)–C(8)	1.424(7)
C(8)–C(9)	1.350(7)
C(9)–C(10)	1.412(6)
C(10)–C(11)	1.413(6)
C(10)–C(15)	1.427(6)
C(11)–C(12)	1.344(8)
C(12)–C(13)	1.395(7)
C(13)–C(14)	1.358(7)
C(14)–C(15)	1.410(6)
Bond angles	
C(1)–C(2)–C(3)	108.5(7)
S(1)–Ti(1)–S(1A)	100.32(7)
S(1)–C(6)–C(7)	120.2(4)
S(1)–C(6)–C(15)	120.2(3)
C(6)–C(7)–C(8)	120.1(5)
C(7)–C(8)–C(9)	121.4(5)
C(8)–C(9)–C(10)	120.9(5)
C(9)–C(10)–C(11)	122.0(4)
C(9)–C(10)–C(15)	118.8(4)
C(10)–(11)–C(12)	120.6(5)
C(11)–C(12)–C(13)	120.9(6)
C(12)–C(13)–C(14)	120.4(5)
C(13)–C(14)–C(15)	121.1(5)
C(14)–C(15)–(10)	117.8(4)
C(14)–C(15)–C(6)	122.6(4)

It can be seen from Figs. 1 and 2 that **1** contains two 1-naphthylthio ligands coordinated to titanium atom of its Cp_2Ti moiety, whereas **2** contains two ferrocenylmethylthio ligands coordinated to titanium atom of its Cp_2Ti moiety. In addition, there is a plane consisting of S(1), S(1A) and Ti(1) for **1** or S(1), S(2) and Ti(1) for **6**, which divides the Cp_2Ti moiety into two equal parts and the two Cp groups symmetrically occupy the opposite sides of the plane. It appears that due to steric effects, the two bulky groups (two 1-$C_{10}H_7$ for **1** and two (η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2$) for **6**) on S atoms keep away from each other in opposite direction. In fact, the geometry around the titanium centers of **1** and **6** is very similar to corresponding that of a simpler analog

Table 2
Selected bond lengths (Å) and bond angles (°) for **6**

Bond lengths	
Ti(1)–C(1)	2.387(4)
S(1)–Ti(1)	2.3965(13)
S(1)–C(31)	1.834(4)
C(11)–C(31)	1.503(5)
Fe(1)–C(11)	2.044(3)
Fe(1)–C(16)	2.036(4)
C(11)–C(15)	1.414(5)
C(16)–C(17)	1.412(6)
Bond angles	
C(1)–C(2)–C(3)	108.7(4)
S(1)–Ti(1)–S(2)	93.38(5)
C(31)–S(1)–Ti(1)	113.06(13)
C(32)–S(2)–Ti(1)	107.90(3)
C(12)–C(11)–(31)	126.9(3)
C(11)–C(12)–C(13)	107.9(3)
C(16)–C(17)–C(18)	108.5(4)
C(11)–C(31)–S(1)	114.4(2)

Table 3
Selected bond lengths (Å) and bond angles (°) for **7**

Bond lengths	
T(1)–O(1)	1.961(3)
Ti(1)–O(2)	1.965(3)
C(11)–C(12)	1.371(6)
O(1)–C(11)	1.336(5)
O(2)–C(12)	1.361(5)
C(11)–C(13)	1.492(6)
C(12)–C(19)	1.481(7)
Ti(1)–C(1)	2.378(6)
Ti(1)–C(6)	2.366(5)
C(13)–C(14)	1.393(7)
C(19)–C(20)	1.391(7)
Bond angles	
O(1)–Ti(1)–O(2)	81.82(13)
C(11)–O(1)–Ti(1)	104.9(3)
C(12)–O(2)–Ti(1)	105.6(3)
O(1)–C(11)–C(12)	117.0(4)
O(2)–C(12)–C(11)	115.7(4)
C(12)–C(11)–C(13)	127.7(4)
C(11)–C(12)–C(19)	128.7(4)
C(2)–C(1)–C(5)	108.1(5)
C(7)–C(6)–C(10)	108.3(6)
C(14)–C(13)–C(18)	119.2(4)
C(20)–C(19)–C(24)	117.2(5)

Table 4
Comparison of related geometric parameters in **1**, **6** and $(PhS)_2TiCp_2$

	1	**6**	$Cp_2Ti(SPh)_2$
Bond angle of S–Ti–S (°)	100.32(7)	93.38(5)	99.3(3)
Dihedral angle between two Cp (°)	48.5	49.1	47.6
Distances from Ti to centroids of two Cp (Å)	2.062 2.062	2.071 2.084	2.067 2.072
Bond lengths of two Ti–S (Å)	2.4324(13) 2.4324(13)	2.3965(13) 2.3964(13)	2.395(8) 2.424(8)

$(PhS)_2TiCp_2$ [11], and some comparable geometric parameters are listed in Table 4.

In contrast to **1** and **6**, compound **7** contains a five-membered titanaheterocycle Ti(1)O(1)O(2)C(11)C(12), which is non-planar and puckered. The dihedral angle between Ti(1)O(1)O(2) plane and O(1)O(2)C(11)C(12) plane is 145.1°. The C=C double bond length of C(11)–C(12) (1.371(6) Å) is slightly longer than the ordinary C=C double bond length (1.34 Å), probably due to the π-electron delocalization of this double bond in the five-membered heterocycle Ti(1)O(1)C(11)C(12)O(2). The distances from Ti atom to each center of the two Cp rings are 2.100 and 2.064 Å, respectively. The bond angle O(1)–Ti(1)–O(2) is 81.82(13)°. It follows that the geometry of **7** is totally similar to that of Cp_2Ti-containing titanaheterocyclic compound $Cp_2Ti[\eta^5\text{-SC(H)=C(H)S}]$ [12].

2.3. Electrochemical properties of *1–6* and *$(PhS)_2TiCp_2$*

The electrochemical properties of **1**–**6** and $(PhS)_2TiCp_2$ [13] were investigated by cyclic voltammetric techniques. Table 5 lists the electrochemical data of the Ti(IV)–Ti(III) redox pairs of **1**–**6** and $(PhS)_2TiCp_2$, obtained when scanned from 0.0 to –2.5 V.

It can be seen from Table 5 that $(PhS)_2TiCp_2$, **2**, **4** and **5** display quasi-reversible redox processes, while those of **1**, **3** and **6** are irreversible. In addition, **4** and **5** have smaller negative $E_{1/2}$ values than that of **2** containing a weaker electron-withdrawing allyl group, but have slightly larger negative $E_{1/2}$ values than that of $(PhS)_2TiCp_2$ containing a stronger electron-withdrawing phenyl group. This means that compounds $(RS)_2TiCp_2$ with stronger electron-withdrawing R groups would have $E_{1/2}$ shifted toward anodic direction, which is consistent with those observed for ferrocene derivatives [14] and bent zirconocenes $(\eta^5\text{-}C_5H_4R)_2ZrCl_2$ [15].

Finally, it is worth pointing out that the electrochemical oxidation processes of **1**–**5** and $(PhS)_2TiCp_2$ are all irreversible when scanned from 0.0 to + 2.0 V, but in this scanning range **6** exhibits a reversible redox process at $E_{1/2} = 0.54$ V (Fig. 4), which is caused apparently by its ferrocene groups ($E_{1/2} = 0.572$ V for free ferrocene).

3. Experimental

All reactions involving 'titanocene' were carried out under a highly purified Ar atmosphere using standard Schlenk or vacuum-line techniques. Tetrahydrofuran (THF) and dimethoxyethane were dried and deoxygenated by distillation from Na–benzophenone ketyl. $Na_2S\cdot9H_2O$, sulfur, NaOH, Et_2O, CH_2Cl_2, C_6H_{14}, petroleum ether (30–60 °C), alumina and diatomite were available commercially. Cp_2TiCl_2 [16], $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2NMe_3)^+I^-$ [17], benzil [18], tetrabutylammonium perchlorate [19] and R_2S_2 ($R = 1\text{-}C_{10}H_7$, $CH_2{=}CHCH_2$, $n\text{-}C_5H_{11}$, MeO_2CCH_2 and EtO_2CCH_2 [9,20] were prepared according to the reported proce-

Table 5
Electrochemical data of Ti(IV)–Ti(III) redox pairs of 1–6 and $(PhS)_2TiCp_2$

	$E_{1/2}$ (V)	I_{pa}/I_{pc}	E_{pa} (V)	E_{pc} (V)
$(PhS)_2TiCp_2$	− 1.18 [a]	1.02	− 1.05	− 1.31
1	Irreversible			− 1.26
2	− 1.39	0.48	− 1.28	− 1.50
3	Irreversible		− 1.35	− 1.63
4	− 1.20	0.92	− 1.13	− 1.26
5	− 1.25	0.90	− 1.10	− 1.40
6	Irreversible			− 1.47

[a] The $E_{1/2}$ value (− 1.18 V vs SCE) of $(PhS)_2TiCp_2$ is equivalent to the previously reported one (− 1.9 V vs 10^{-3} mol dm^{-3} Ag^+/Ag electrode) [13].

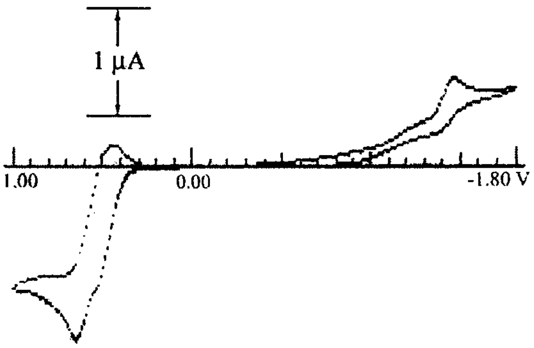


Fig. 4. Cyclic voltammogram of **6**.

dures. ^{1}H-NMR spectra were recorded on a Bruker AC-P200 spectrometer, while IR spectra were recorded on either a Bio-Rad FTS 135 or a Nicolet 560 E.S.P. spectrometer. Elemental analyses and cyclic voltammetric measurements were performed on a Elmentar Vario EL analyzer and a BAS-100B electrochemical analyzer, respectively. M.p. were determined on a Yanaco MP-500 micromelting points apparatus.

3.1. Two standard methods for preparation of intermediate 'Cp$_2$Ti'

Method (i): A 100 ml three-necked flask equipped with a magnetic stir-bar, a serum cap and an Ar inlet tube, was charged with 25 mg (1.0 mmol) of freshly crushed Mg powders, 6 ml of THF and 249 mg (1.0 mmol) of bis(η^5-cyclopentadienyl)dichlorotitanium. The mixture was stirred at room temperature (r.t.) for 1–2 h until most of Mg disappeared to give a brown-green solution of the intermediate bis(η^5- cyclopentadienyl)titanium 'Cp$_2$Ti'.

Method (ii): The same equipped flask as in Method (i) was charged with 50 mg (2.0 mmol) of fine Mg turnings, 6 ml of THF and 0.085 ml (1.0 mmol) of 1,2-$C_2H_4Br_2$. The reaction mixture was heated gently with stirring until gas ceased emitting in about 5 min and then 249 mg (1.0 mmol) of bis(η^5-cyclopentadienyl) dichlorotitanium was added. The mixture was stirred at r.t. for about 0.5 h, at which time most of the activated Mg disappeared to give a THF solution of the 'Cp$_2$Ti' intermediate. The THF solution of the 'Cp$_2$Ti' generated by either Method (i) or Method (ii) was employed immediately in the following preparations and showed no obviously different chemical behavior.

*3.1.1. Preparation of (1-$C_{10}H_7S)_2TiCp_2$ (**1**)*

To the freshly prepared solution of 'Cp$_2$Ti' through Method (ii) was added 3 19 mg (1.0 mmol) of di-1-naphthyl disulfide. The mixture turned purple immediately and was stirred at r.t. for an additional 2 h. The solvent was removed under vacuum and the residue was dissolved in CH_2Cl_2, which was filtered through a column packed with alumina. Removal of solvent afforded 483 mg (93%) of **1** as a purple solid, which was further purified by recrystallization from CH_2Cl_2–C_6H_{14}. M.p. 85–86 °C. Anal. Found: C, 72.59; H, 4.75. Calc. for $C_{30}H_{24}S_2Ti$: C, 72.57; H, 4.87%. IR (KBr disk, cm^{-1}): 3115m, 3080m, 3050m, 1582w, 1555w, 1499m, 1441m, 1375s, 1320w, 1252w, 1194w, 1135w, 1057w, 1021m, 972s, 864m, 835vs, 796vs, 722vs, 664vs, 549m. ^{1}H-NMR (CH_3COCH_3-d_6): $\delta = 6.13$ (s, 10H, 2C_5H_5), 7.10–8.45 (m, 14H, 2$C_{10}H_7$).

*3.1.2. Preparation of ($CH_2 = CHCH_2S)_2TiCp_2$ (**2**)*

To the 'Cp$_2$Ti' solution prepared through Method (ii) was added 146 mg (1.0 mmol) of diallyl disulfide. Similarly, 157 mg (48%) of **2** as a purple solid was obtained. M.p. 55–56 °C. Anal. Found: C, 59.20; H, 5.94. Calc. for $C_{16}H_{20}S_2Ti$: C, 59.25; H, 6.22%. IR (KBr disk, cm^{-1}): 3096w, 3009w, 2977w, 2930w, 2898w, 1629m, 1446m, 1427m, 1403m, 1367m, 1213m, 1020w, 1010w, 990m, 911s, 848s, 816s, 745w. ^{1}H-NMR ($CHCl_3$-*d*): $\delta = 3.63$(d, $J = 7.2$ Hz, 4H, 2CH_2), 4.87–5.06 (m, 4H, 2C=CH_2), 5.69–5.93 (m, 2H, 2CH), 6.13 (s, 10H, 2C_5H_5). When the 'Cp$_2$Ti' solution prepared through Method (i) was used, 160 mg (49%) of **2** was obtained.

*3.1.3. Preparation of (n-$C_5H_{11}S)_2TiCp_2$ (**3**)*

To the 'Cp$_2$Ti' solution prepared through Method (i) was added 206 mg (1.0 mmol) of di-*n*-pentyl disulfide. After similar workup 256 mg (67%) of **3** as a purple solid was obtained. M.p. 54–55 °C. Anal. Found: C, 62.46; H, 8.44. Calc. for $C_{20}H_{32}S_2Ti$: C, 62.48; H, 8.39%. IR (KBr disk, cm^{-1}): 3074w, 2957w, 2926m, 2856w, 1463w, 1447w, 1428w, 1361w, 1027w, 1011w, 816s. ^{1}H-NMR ($CHCl_3$-d): $\delta = 0.83$ (t, $J = 7.2$ Hz, 6H, 2CH_3), 1.16–1.59 (m, 12H, 6CH_2), 3.01 (t, $J = 7.2$ Hz, 4H, 2SCH_2), 6.09 (s, 10H, 2C_5H_5).

*3.1.4. Preparation of ($MeO_2CCH_2S)_2TiCp_2$ (**4**)*

To the 'Cp$_2$Ti' solution prepared through Method (i) was added 210 mg (1.0 mmol) of $(MeO_2CCH_2)_2S_2$. Similarly, after removal of solvent, the residue was dissolved in CH_2Cl_2–Et_2O (v/v = 1:1), which was filtered through a column packed with alumina. From the filtrate 163 mg (42%) of **4** as a dark-purple solid was obtained. M.p. 170–172 °C. Anal. Found: C, 49.20; H, 5.21. Calc. for $C_{16}H_{20}O_4S_2Ti$: C, 49.49; H, 5.19%. IR (KBr disk, cm^{-1}): 3104w, 2946w, 1740m, 1712s($\nu_{C=O}$), 1442m, 1427m, 1292s 1268s 1149m, 1113m, 1006m, 820s. ^{1}H-NMR ($CHCl_3$-*d*): $\delta = 3.64$ (s, 6H, 2CH_3), 3.68 (s, 4H, 2CH_2), 6.14 (s, 10H, 2C_5H_5).

*3.1.5. Preparation of ($EtO_2CCH_2S)_2TiCp_2$ (**5**)*

To the 'Cp$_2$Ti' solution prepared through Method (i) was added 238 mg (1.0 mmol) of $(EtO_2CCH_2)_2S_2$. Similarly, after removal of solvent, the residue was dissolved in Et_2O, which was filtered through a column packed with alumina. From the filtrate 247 mg (59%) of **5** as a red-purple solid was obtained. M.p. 144–145 °C. Anal. Found: C, 51.80; H, 5.92. Calc. for $C_{18}H_{24}O_4S_2Ti$: C, 51.92; H, 5.81%. IR (KBr disk, cm^{-1}): 3125w, 3078m, 2999w, 2936w, 1720s($\nu_{C=O}$), 1464m, 1436m, 1412m, 1389m, 1361m, 1278s 1196m, 1117s 1034s, 1015m, 845m, 822s. ^{1}H-NMR ($CHCl_3$-d): $\delta = 1.26$ (t, $J = 7.4$ Hz, 6H, 2CH_3), 3.73 (s, 4H, 2SCH_2), 4.14 (q, $J = 7.4$ Hz 4H, 20CH_2), 6.21 (s, 10H, 2C_5H_5).

3.1.6. Preparation of $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2S)]_2TiCp_2$ (**6**)

To the 'Cp_2Ti' solution prepared through Method (i) was added 462 mg (1.0 mmol) of $[C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2)]_2S_2$. Similarly, after removal of solvent, the residue was dissolved in CH_2Cl_2, which was filtered through a column packed with diatomite. From the filtrate 516 mg (81%) of **6** as a dark-purple solid was obtained. M.p. 170–174 °C. Anal. Found: C, 59.98; H, 5.02. Calc. for $C_{32}H_{32}Fe_2S_2Ti$: C, 60.03; H, 5.04%. IR (KBr disk, cm^{-1}): 3094m, 2909w, 2825w, 1758w, 1463w, 1439m, 1411w, 1368w, 1249m, 1233m, 1205m, 1105s, 1020s, 1000s, 925m, 814vs. ^{1}H-NMR ($CHCl_3$-d): $\delta = 3.96$ (s, 4H, $2CH_2$), 4.10–4.14 (m, 18H, $2C_5H_5 + 2C_5H_4$), 6.15 (s, 10H, $2C_5H_5$).

3.1.7. Preparation of $[\eta^2\text{-}OC(Ph){=}C(Ph)O]TiCp_2$ (**7**)

To the 'Cp_2Ti' solution prepared using Method (i) was added 210 mg (1.0 mmol) of benzil and the reaction mixture turned dark-green immediately, which was stirred for additional 2 h. After solvent was removed under vacuum, the residue was dissolved in 20 ml of C_6H_6. The solution was washed with 15 ml × 3 of anaerobic water, then was dried over anhydrous Na_2SO_4. Removal of Na_2SO_4 and solvent gave 370 mg (95%) of **7** as air-sensitive, dark-green crystals. Further purification was performed by recrystallization from CH_2Cl_2–C_6H_{14}. M.p. > 250 °C (Ar sealed tube). IR (KBr disk, cm^{-1}): 3079s 2927s 2854w, 1679s 1595s 1538w, 1492w, 1447s 1211s 1176w, 1153w, 1070w, 1016s, 927s 817vs 698s 643s 412s. ^{1}H-NMR (CH_3COCH_3-d_6): $\delta = 6.14$ (s, 10H, $2C_5H_5$), 7.19–7.31 (m, 10H, Ph).

3.1.8. Preparation of $[(\eta\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2)]_2S_2$ (**8**)

To a 100 ml flask with a reflux condenser and a magnetic stir-bar were added 0.51 g (2.1 mmol) of $Na_2S{\cdot}9H_2O$, 0.070 g (2.2 mmol) of sulfur, 0.10 g (0.25 mmol) of NaOH and 20 ml of water. The mixture was refluxed for 10 min, and the resulting orange-yellow solution was slowly added to another 100 ml flask containing 30 ml of an aq. solution of 1.65 g (4.28 mmol) $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2NMe_3)]^+I^-$ under stirring. The reaction mixture was refluxed for an additional 1 h. After the reaction mixture was cooled to r.t., it was extracted with Et_2O. The organic layer was separated and dried over anhydrous Na_2SO_4. After removal of Na_2SO_4 and solvent, the residue was chromatographed on a column packed with alumina. Elution with CH_2Cl_2–petroleum ether (v/v = 3:5) afforded a brown band, from which was isolated 0.342 g (35%) of **8** as an orange solid. The product was further purified by recrystallization from C_6H_6–C_6H_{14}. M.p. 129–130 °C. Anal. Found: C, 57.18; H, 4.69. Calc. for $C_{22}H_{22}Fe_2S_2$: C, 57.17; H, 4.80%. IR (KBr disk, cm^{-1}): 3090m, 2980w, 2916w, 2852w, 2250w, 1733w, 1467w, 1409s 1370w, 1239s 1208s 1122m, 1105s 1061m, 1037s 1023s, 999s 927m, 865m, 816vs. ^{1}H-NMR ($CHCl_3$-d): $\delta = 3.50$ (s, 4H, $2CH_2$), 4.14–4.23 (m, 18H, $2C_5H_5 + 2C_5H_4$).

3.2. X-ray structural determinations of **1**, **6** and **7**

Single-crystals of **1**, **6** and **7** suitable for X-ray diffraction were grown from their CH_2Cl_2–C_6H_{14} solution at −20 °C. A crystal was mounted to a glass fiber (for **1** or **6**) or sealed in a capillary (for **7**) and placed on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). With the SHELXS-97 and SHELXL-97 package the structures were solved by direct method and the final refinement was performed by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for non-hydrogen atoms. Crystal collection data for **1**, **6** and **7** are summarized in Table 6.

3.3. Cyclic voltammetric measurements of **1**–**6** and $(PhS)_2TiCp_2$

The electrochemical measurements were performed at 20 °C by using a BAS-100B electrochemical analyzer, with a Pt rod ($\varphi = 1$ mm) as working electrode, a Pt wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference. The Pt working electrode surface was polished with 0.05 μm Al_2O_3, sonicated in distilled water, and air-dried immediately before use. Anaerobic dimethoxyethane and tetrabutylammonium perchlorate were used as solvent and supporting electrolyte (0.10 mol dm^{-3}), respectively. All the potential values are quoted relative to SCE. Under the present experimental conditions, the one-electron oxidation of ferrocene occurs at $E_{1/2} = +0.572$ V. The sample solutions (5×10^{-3} mol dm^{-3}) were placed in a single-compartment electrochemical cell and bubbled with highly purified nitrogen for 15 min before measurement. The current–potential curves were recorded at scan rate 100 mV s^{-1}.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 166554 for **1**, 166555 for **6** and 155227 for **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 6
Crystal data and structure refinements for **1**,**6** and **7**

	1	**6**	**7**
Empirical formula	$C_{30}H_{24}S_2Ti$	$C_{32}H_{32}Fe_2S_2Ti$	$C_{24}H_{20}O_2Ti$
Formula weight	496.51	640.30	388.30
Crystal size (mm)	$0.50\times0.30\times0.10$	$0.30\times0.20\times0.10$	$0.40\times0.35\times0.10$
Temperature (K)	298(2)	293(2)	293(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbcn*	$P\bar{1}$	$P2_1/c$
a (Å)	7.942(2)	11.423(5)	11.735(6)
b (Å)	13.378(3)	11.669(5)	7.585(4)
c (Å)	23.119(6)	12.902(6)	21.887(11)
α (°)	90	90.655(8)	90
β (°)	90	114.890(7)	99.691(9)
γ (°)	90	114.919(6)	90
V (Å^3)	2456.4(11)	1377.1(11)	1920.4(17)
Z	4	2	4
D_{calc} (mg m^{-3})	1.343	1.544	1.343
Absorption coefficient (mm^{-1})	0.535	1.495	0.461
$F(000)$	1032	660	808
Reflections collected	9370	5812	6787
Independent reflections	2171 ($R_{int}=0.0870$)	4861 ($R_{int}=0.0235$)	3019 ($R_{int}=0.0677$)
Observed reflections	1330	3595	1934
Absorption correction	SADABS	SADABS	SADABS
Max/min transmission	0.9485 and 0.7758	0.8649 and 0.6626	0.9553 and 0.8371
Goodness-of-fit on F^2	1.047	0.998	1.020
Final R indices [$I>2\sigma(I)$]	$R_1=0.0534$, $wR_2=0.1161$	$R_1=0.0376$, $wR_2=0.0865$	$R_1=0.0664$, $wR_2=0.1432$
R indices (all data)	$R_1=0.1055$, $wR_2=0.1370$	$R_1=0.0579$, $wR_2=0.0964$	$R_1=0.1160$, $wR_2=0.1668$
Largest difference peak and hole (e Å^{-3})	0.320 and -0.346	0.467 and -0.279	0.768 and -0.242

Acknowledgements

We are grateful to the National Natural Science Foundation of China and the State Key Laboratory of Structural Chemistry for financial support of this work.

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