Titanocene complexes of the *N*-methyl and *N*-phenyl-1,3-thiazoline-2-thione-4,5-dithiolates and 4,5-diselenolate ligands

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ABSTRACT

Cp$_2$Ti(dithiolene) and Cp$_2$Ti(diselenolene) complexes containing the *N*-methyl-1,3-thiazoline-2-thione-4,5-dithiolate ligand (Me-thiazdt), the *N*-phenyl-1,3-thiazoline-2-thione-4,5-dithiolate ligand (Ph-thiazdt) and the *N*-methyl-1,3-thiazoline-2-thione-4,5-diselenolate ligand (Me-thiazds) have been synthesized. Three approaches have been developed in order to generate the dithiolene or the diselenolene ligands which were reacted with Cp$_2$TiCl$_2$ to form the corresponding heteroleptic complexes. Their X-ray crystal structures, UV–Vis absorption spectra as well as their redox properties, determined by cyclic voltammetry have been investigated and discussed. Variable-temperature ^{1}H NMR experiments have been performed in order to determine the activation energies of the chelate ring inversion.

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1. Introduction

Mixed cyclopentadienyl/dithiolene complexes such as Cp$_2$M(dithiolène) [1] (M = Ti [2,3] Zr and Hf [3], V [4], Nb [5], Mo [6] and W [6,7]), exhibit different geometries according to the metal, the nature and the redox state of the ligand. Among these complexes, the metal which focused the most the attention is Titanium. Indeed, these diamagnetic complexes, Cp$_2$Ti(dithiolene) first described by Köpf and Schmidt more than 40 years ago [8] are usually obtained in good yields, are air stable and can be considered as inorganic protected forms of the air-sensitive 1,2-dithiolate. Rauchfuss et al. reported later a series of Cp$_2$Ti(diselenolene) analogues exhibiting similar properties [9]. All these heteroleptic complexes exhibit an out-of-plane deformation of the metallacycle with a folding around the SS axis of about 43° < θ < 50°, as represented in Chart 1 [10]. This folding has been attributed to the stabilizing interaction of metal and sulfur orbitals and the lowering of the total energy of the system [10,11].

In continuation of our studies on metal complexes involving *N*-methyl-1,3-thiazoline-2-thione-4,5-dithiolate, [M(Me-thiazdt)$_2$]$^{n-}$, or *N*-methyl-1,3-thiazoline-2-thione-4,5-diselenolate, [M(Me-thiazds)$_2$]$^{n-}$ (Zn, Ni and Pd) [12], we have investigated heteroleptic metal complexes containing both cyclopentadienyl and dithiolene or diselenolene moieties substituted with a thiazole backbone such as Cp$_2$M(R-thiazdt) or Cp$_2$M(R-thiazds). Our goal was to compare the properties of these hitherto unknown derivatives with their

sulfur analogues Cp$_2$Ti(dmit) and Cp$_2$Ti(dsit) and to determine the influence of the thiazole skeleton. It is interesting to note that only one other example of a metal dithiolene complex involving R-thiazdt has been reported to date, as its CpCo complex, that is CpCo(R-thiazdt) (R = Me, Ph, CH$_2$Ph) obtained by a four step lengthy synthesis [13].

2. Results and discussion

2.1. Synthesis of Cp$_2$Ti(R-thiazdt) and Cp$_2$Ti(R-thiazds)

In the literature, the main route employed for the synthesis of Cp$_2$Ti(dmit) is the use of the 1,3-dithiole-2-thione-4,5-dithiolate (dmit) either under the tetraethylammonium salt of its zinc complex [14] or the sodium or potassium salt [2,3] generated from 4,5-bis(benzoylthio)-1,3-dithiole-2-thione. The dithiolene reacts further with the organometallic precursor, Cp$_2$TiCl$_2$ through the substitution of the chlorines by thiolates. The selenium analogue, Cp$_2$Ti(dsit), synthesized first by Olk et al. was also prepared according to a similar strategy [15,16]. The cesium salt of the 1,3-dithiole-2-thione-4,5-diselenolate (dsit), generated from the 4,5-bis(benzoylseleno)-1,3-dithiole-2-thione, was reacted with Cp$_2$TiCl$_2$ to afford Cp$_2$Ti(dsit). Here, three different chemical approaches have been investigated for the synthesis of the target molecules. First, Cp$_2$Ti(R-thiazdt) complexes were synthesized starting from the thiazole-2-thione derivatives **1a** [17] (R = Me) and **1b** [18] (R = Ph) as shown in Scheme 1. This strategy consists in generating the dilithiated species from the thiazole-2-thione derivatives in the presence of LDA, followed by the addition of
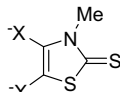
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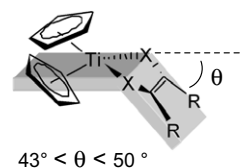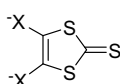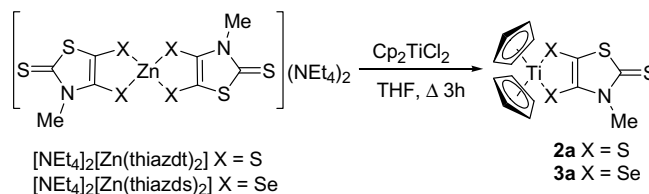
Chart 1.
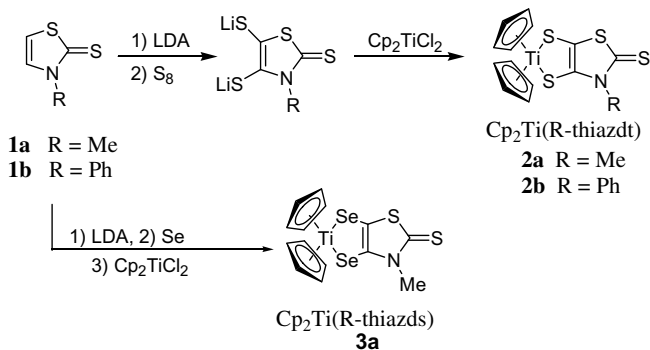
Scheme 1.

Scheme 3.

sulfur. While the formation of the dithiolate from **1a** was already described by us during our investigation on the formation of homoleptic complexes [12], we investigated also the possibility of forming the dithiolate species from other *N*-substituted thiazole cores such as **1b**. The generated dithiolate reacts in situ with the organometallic complex, Cp$_2$TiCl$_2$. The corresponding Cp$_2$Ti(R-thiazdt), **2a** (R = Me) and **2b** (R = Ph), were isolated as green crystals in 10% and 30% yields, respectively, after purification on column chromatography and recrystallization in chloroform. A similar approach was used to prepare the corresponding diselenolene analogue, Cp$_2$Ti(R-thiazds). Actually, using this strategy, we were able to isolate the Cp$_2$Ti(Me-thiazds) **3a** as blue crystals in only 10% yield.

Considering the low yield obtained for **2a** and **3a** by this direct route, we considered a second strategy which consists in starting from an organic dithiolate or diselenolate hidden form (Scheme

2), the *N*-methyl-bis(cyanoethylthio)-1,3-thiazoline-2-thione **4** and *N*-methyl-bis(cyanoethylseleno)-1,3-thiazoline-2-thione **5** where the two thiolate and selenolate functions are protected by cyanoethyl groups. These derivatives have been prepared earlier from [NEt$_4$]$_2$[Zn(Me-thiazdt)$_2$] and [NEt$_4$]$_2$[Zn(Me-thiazds)$_2$] [12]. Herein, we present another direct route from the thiazole-2-thione **1a** as described in Scheme 2. After the treatment of **1a** at low temperature with LDA and the chalcogen sulfur or selenium, 3-bromo-propionitrile was added to the medium. Work up of the reaction leads to compounds **4** and **5**, easily isolated after column chromatography in 60% and 43% yield, respectively. Deprotection of the thiolate and selenolate functions was realized in basic medium using cesium hydroxide, addition of Cp$_2$TiCl$_2$ allowed us to isolate the dithiolene complexes **2a** and **3a** in an improved 40% yield.

The last approach towards target molecules consists in the heating to reflux of the inorganic dithiolate or diselenolate hidden form, the tetraethylammonium salt of the dithiolate zinc complex [19], [NEt$_4$]$_2$[Zn(thiazdt)$_2$] or diselenolate zinc complex [NEt$_4$]$_2$[Zn(thiazds)$_2$] [12] in the presence of 2 equiv of Cp$_2$TiCl$_2$ during 3 h (Scheme 3). Using this strategy, we were able to isolate **2a** in 74% yield and **3a** in 67% yield. The advantages of this approach lies in the fact that the corresponding complexes are easier to purify by a quick filtration on silica gel column and are obtained in higher yields.

2.2. X-ray structure analysis

Crystals of the heteroleptic complexes **2a**, **2b** and **3a** were isolated after recrystallization in chloroform. Cp$_2$Ti(Me-thiazdt) **2a** and Cp$_2$Ti(Me-thiazds) **3a** crystallize in the orthorhombic system, space group *Pna*2$_1$ and are isostructural. Cp$_2$Ti(Ph-thiazdt) **2b** crystallizes in the monoclinic system, space group *P*2$_1$/*c*. X-ray molecular structures for the three complexes are given in Fig. 1.

All these heteroleptic complexes exhibit the same structural trends: a fully planar thiazole core and a non planar metallacycle
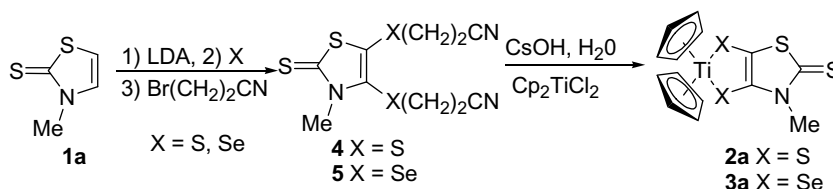
Scheme 2.
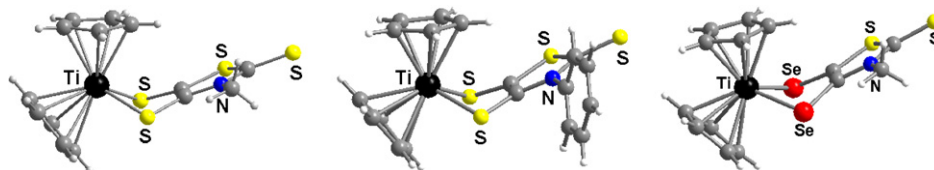
Fig. 1. Molecular structures of Cp$_2$Ti(R-thiazdt) **2a** (left), **2b** (middle) and Cp$_2$Ti(Me-thiazds) **3a** (right).

Table 1
Significant bond lengths [Å] and angles [°], with X = S or Se

Compound	Ti–X (Å)	X–C (Å)	C=C (Å)	X–Ti–X (°)	θ (°)[a]
Cp$_2$Ti(Me-thiazdt) **2a**	2.4336(10) 2.4516(10)	1.714(4) 1.722(3)	1.386(5)	85.30(4)	48.34(13)
Cp$_2$Ti(Ph-thiazdt) **2b**	2.4195(6) 2.4486(6)	1.7199(18) 1.7274(18)	1.377(3)	86.005(18)	50.41(7)
Cp$_2$Ti(dmit) [2]	2.434(3) 2.430(41)	1.733(12) 1.718(8)	1.357(15)	84.40(2)	47.45(39)
Cp$_2$Ti(Me-thiazds) **3a**	2.5680(12) 2.5799(12)	1.879(6) 1.879(6)	1.357(8)	85.21(4)	48.19(21)
Cp$_2$Ti(dsit) [16]	2.5697(17) 2.5743(17)	1.884(6) 1.878(6)	1.372(7)	84.62(3)	49.84(8)

[a] See Chart 1 for the definition of θ.

folded along the S···S axis for the Cp$_2$Ti(R-thiazdt) or the Se···Se axis for Cp$_2$Ti(Me-thiazds). Selected bond lengths and folding angles are listed in Table 1 together with their dithiole analogues, Cp$_2$Ti(dmit) and Cp$_2$Ti(dsit) for comparison. The bond lengths, Ti···X and X···C (X = S, Se), in the metallacycles of **2a**–**b** and **3a** are very close to the ones observed in the corresponding Cp$_2$Ti-(dmit) and Cp$_2$Ti(dsit) complexes. The ligand bite angles, S–Ti–S (85.30(4)° for **2a** and 86.005(18)° for **2b**) or Se–Ti–Se (85.21(4)° for **3a**) are in the same range as the ones observed for the dithiole analogues [2,16]. The phenyl ring mean plane in **2b** forms an angle with the thiazole core mean plane of 61.3(2)°. The folding angles (θ) within the metallacycle of complexes **2a**–**b** and **3a** are in the range of the folding angles observed for Cp$_2$Ti(dmit) and Cp$_2$Ti-(dsit) indicating that the nature of the heterocycle, thiazole or dithiole has no significant influence on the geometry of the metallacycle TiS$_2$C$_2$ (or TiSe$_2$C$_2$) of these heteroleptic complexes.

2.3. Electrochemical properties

The redox behaviour of Cp$_2$Ti(R-thiazdt) **2a**–**b** and Cp$_2$Ti(R-thiazds) **3a** has been studied by cyclic voltammetry in dichloromethane solution with 0.1 M nBu$_4$NPF$_6$ as supporting electrolyte. The data are collected in Table 3 and are given in V vs. SCE together with the redox potentials of the sulfur Cp$_2$Ti(dmit) and selenium Cp$_2$Ti(dsit) analogues which were re-examined in the same experimental conditions for comparison. All these complexes are neutral and stable upon air atmosphere and exhibit very similar cyclic voltammograms as the one shown in Fig. 2. On the anodic scan, an irreversible oxidation wave appears while on the cathodic scan, a reversible reduction wave is observed. The oxidation wave is attributed to the oxidation of the dithiolene or diselenolene ligand and the irreversibility of the process is a consequence of the decoordination of the oxidized ligand from the complex. Indeed, theoretical analysis performed by Dahl et al. have shown that

Table 3
Variable-temperature ^{1}H NMR data

Complex	θ (°)	Solvent	T_C (°C)	$\Delta\nu$ (Hz)	$\Delta G^{\neq}$ (kJ mol^{-1})
Cp$_2$Ti(Me-thiazdt) **2a**	48.34(13)	CD$_3$CN	+53	302	60.6
Cp$_2$Ti(Ph-thiazdt) **2b**	50.41(7)	CD$_3$CN	+50	236	60.6
Cp$_2$Ti(dmit) [2]	47.45(39)	CDCl$_3$	35	84	60.0
Cp$_2$Ti(Me-thiazds) **3a**	48.19(21)	CD$_3$CN	42	290	58.5
Cp$_2$Ti(dsit) [16]	49.84(8)	CDCl$_3$	+28	100	60.0
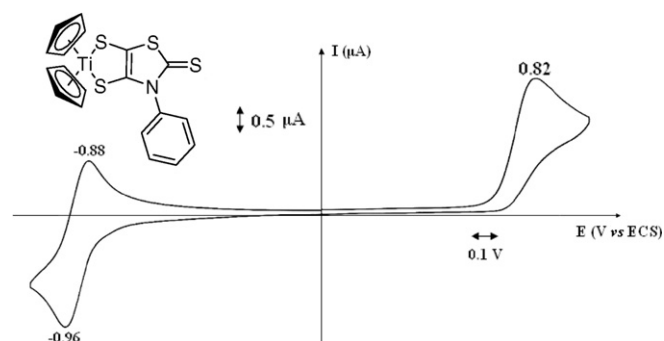
Fig. 2. Cyclic voltammogram of complex Cp$_2$Ti(Ph-thiazdt) **2b**, scanning rate 100 mV/s.

removal of electron from the HOMO of such complexes, which is strongly metal ligand bonding, severely weakens the metal ligand interaction [20]. The reversible reduction process observed corresponds to the reduction of the metal Ti$^{(IV)}$/Ti$^{(III)}$.

We also observe that the oxidation of the N-phenyl substituted thiazole derivative **2b** occurs at a more positive potential (+40 mV) than that of the N-methyl one **2a**. This indicates a small electron withdrawing influence of the phenyl ring on the heterocycle. Contrariwise, the nature of the coordinating chalcogen atom (S vs. Se) does not modify the oxidation potential of the complex. It can also be noticed on both series, dithiolene and diselenolene, that the oxidation of the thiazole derivatives is observed at a lower potential than the oxidation of the dithiole derivative indicating that the most electron rich ligand is the thiazdt over dmit and thiazds over dsit. This is also consistent with the reduction potentials observed for the Ti$^{(IV)}$/Ti$^{(III)}$ process. Indeed, the electron releasing effect of the thiazole core compared with the dithiole one induces a negative shift of the redox potentials indicating that the metal is then more difficult to reduce in Cp$_2$Ti(thiazdt) **2a**–**b** (−0.92 V vs. SCE) than in Cp$_2$Ti(dmit) (−0.82 V vs. SCE). Similar observations can be made in the diselenolene series.

Table 2
Redox potentials[a] in V vs. SCE and UV–Vis absorption band and extinction coefficient of Cp$_2$Ti(R-thiazdt) **2a**–**b**, Cp$_2$Ti(Me-thiazds) **3a**, Cp$_2$Ti(dmit) and Cp$_2$Ti(dsit)

Complex	E^a (Ti^{IV}/Ti^{III})	E_{pa}	λ_{max} (nm) (ε [M^{-1} cm^{-1}])
Cp$_2$Ti(Me-thiazdt) **2a**	−0.92	+0.78	653 (7600), 493 (5010), 347 (21420)
Cp$_2$Ti(Ph-thiazdt) **2b**	−0.92	+0.82	643 (8620), 489 (4550), 346 (15820)
Cp$_2$Ti(dmit)	−0.82	+0.96	639 (5300), 490 (3400), 425 (9100), 290 (21700) [3]
Cp$_2$Ti(Me-thiazds) **3a**	−0.86	+0.78	702 (6940), 505 (4180), 353 (21770)
Cp$_2$Ti(dsit)	−0.79	+0.96	

[a] determined in CH$_2$Cl$_2$ by cyclic voltammetry using nBu$_4$PF$_6$ as supporting electrolyte, Pt working electrode, scan rate 100 mV/s.

2.4. ^1H NMR experiments

As demonstrated from the X-ray structure analysis, the metalla-cycles of **2a**–**b** and **3a** are non planar in the solid state with a torsion angle between 48° and 50°. Room temperature ^1H NMR investigation in CDCl$_3$ or in CD$_3$CN shows that the two cyclopentadienyl groups are indeed not equivalent due to different surroundings and two singlets are observed. Variable temperature ^1H NMR experiments performed in CD$_3$CN provided activation energies for the ring inversion process. Indeed, upon raising the temperature, coalescence of the two signals appears on the spectra at T_c (coalescence temperature), as shown in Fig. 3, due to a rapid inversion process as suggested by Köpf on other Cp$_2$Ti(dithiolene) [21]. Determination of T_c and the use of Eyring equation [22] allowed us to determine the activation energy $\Delta G^{\neq}$. The data (θ, T_c, $\Delta G^{\neq}$) for the complexes **2a**–**b** and **3a** are collected in Table 3 together with those of Cp$_2$Ti(dmit) and Cp$_2$Ti(dsit) for comparison. It can be noticed that the nature of the heterocycle ring, thiazole or dithiole does not influence the value of the activation energy for the inversion process, as also the nature of the chalcogen atom coordinated to the metal.

2.5. UV–Vis–NIR spectra

Absorption spectra of the titanocene complexes **2a**–**b** and **3a** are measured in dichloromethane. The absorption maxima and extinction coefficients are collected in Table 2. The three complexes exhibit similar absorption spectra with absorption bands in the UV–Vis region as the one shown for **2b**, Cp$_2$Ti(Ph-thiazdt), in Fig. 4.

These bands are assigned to ligand metal transitions (LMCT). It can be observed that, among the different dithiolene ligands, either the substitution of a methyl group for a phenyl group or the substi-
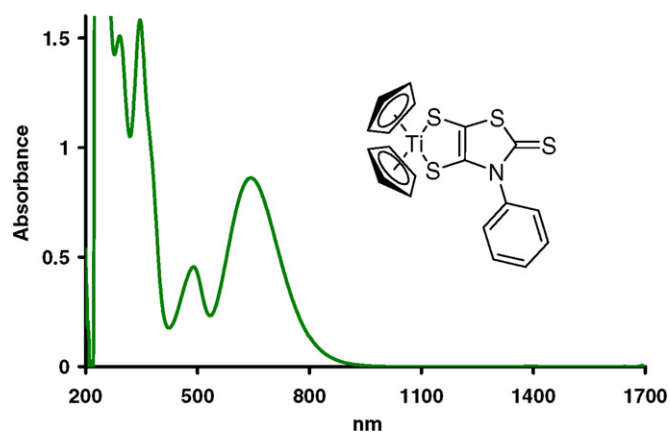

Fig. 4. UV–Vis–NIR absorption spectrum of **2b** Cp$_2$Ti(Ph-thiazdt) (CH$_2$Cl$_2$, C = 10^{-4} M).

tution of the thiazole ring for a dithiole ring do not modify significantly the absorption spectra. A bathochromic shift of about 50 nm can be noticed for Cp$_2$Ti(Me-thiazds) when compared with Cp$_2$Ti(Me-thiazdt).

3. Conclusion

In summary, we have synthesized a novel family of heteroleptic complexes involving bis(cyclopentadienyl)titanocene dithiolene or diselenolene on a thiazole backbone and have shown that it was possible to insert different substituents on the nitrogen, N-Me and N-Phe. We also investigated their structural and redox properties and compared them with their dithiole analogues Cp$_2$Ti(dmit) and Cp$_2$Ti(dsit). The synthesized complexes exhibit a good stability and structural flexibility was evidenced through variable temperature ^1H NMR experiments. The nature of the heterocyclic backbone does not influence significantly the spectral and structural properties, especially the folding angles (θ) and the activation energy for the inversion process, even if the thiazole core is a better electron releasing group than the dithiole one as evidenced by the redox properties [10]. One attractive peculiarity of these complexes with a thiazole core is the presence of an anchoring point for other functionalities through the nitrogen atom. We have shown here that the synthetic strategy developed earlier for the N-Me derivatives could be successfully extended to the N-Ph one. Further work will be devoted to the preparation of other paramagnetic heteroleptic complexes as well as modification of the phenyl ring.

4. Experimental

4.1. General

All reagents were commercially available and used without further purification. CsOH · H$_2$O and selenium powder (200 mesh) were purchased from Acros organics. [NEt$_4$]$_2$[Zn(Me-thiazdt)$_2$] and [NEt$_4$]$_2$[Zn(Me-thiazds)$_2$] were synthesized according to literature procedure [12]. Tetrahydrofuran was distilled from sodiumbenzophenone. CH$_2$Cl$_2$ was distilled from P$_2$O$_5$. Chromatography was performed using silica gel Merck 60 (70–260 mesh melting points were measured using a Kofler hot-stage apparatus. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AC 300P spectrometer. Chemical shifts are reported in ppm referenced to TMS for ^1H NMR and ^{13}C NMR. For the variable temperature ^1H NMR studies, data were exploiting by using the Eyring equation [22] $\Delta G^{\neq} = -RT_c \ln(k_c h / k_B T_c)$ where k_c is equal to $2^{-1/2} \pi \Delta \nu$ and $\Delta \nu$ is the frequency difference between the two cyclopentadienyl shifts
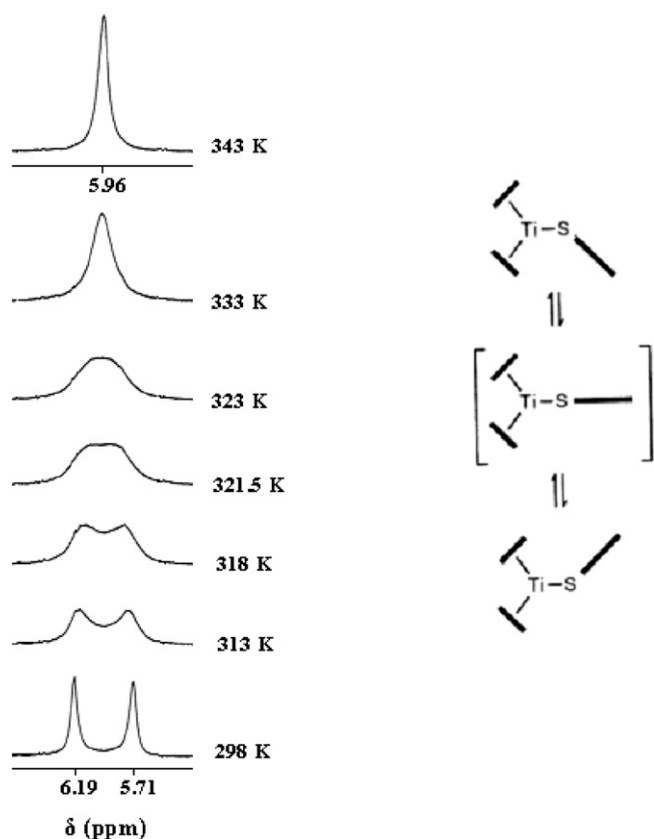

Fig. 3. Variable temperature ^1H NMR spectra of Cp$_2$Ti(Ph-thiazdt) **2b** in CD$_3$CN.

in the slow exchange limit ($T \ll T_c$). UV–Vis–NIR spectra were recorded on a Cary 5 spectrophotometer in CH_2Cl_2. Mass spectra were recorded with Varian MAT 311 instrument and a ZABSpec TOF instrument by the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Elemental analyses were performed at the Centre Régional de Mesures Physiques de l'Ouest, Rennes). Cyclic voltammetry was carried out on a 10^{-3} M solution of metal complex derivative in CH_2Cl_2 containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte. Voltammograms were recorded at 0.1 V s^{-1} on a platinum disk electrode (1 mm^2). Potentials were measured vs. saturated calomel electrode (SCE).

4.2. Synthesis and characterization

4.2.1. General procedure for the synthesis of Cp2Ti(R-thiazdt) 2a–b and Cp2Ti(Me-thiazds) 3a

Method a (Scheme 1): To a solution of thiazoline-2-thione (3.8 mmol, 0.5 g for **1a** or 0.74 g for **1b**) in dry THF (40 mL) was added a solution of LDA freshly prepared from BuLi (5.7 mmol, 3.6 mL, 1.6 M in hexane) and diisopropylamine (5.7 mmol, 0.58 g) in 15 mL of dry THF. After the mixture has been stirred for 30 min at −10 °C, S_8 (5.7 mmol, 0.18 g) for **2a–b** or Se (5.7 mmol, 0.45 g) for **3a** was added and the solution was stirred for an additional 30 min. To the medium a solution of LDA (7.6 mmol, 4.76 mL of nBuLi in hexane added to 7.6 mmol, 0.77 g of diisopropylamine in 20 mL of dry THF) was added. The reaction mixture was stirred at −10 °C for 3 h, then sulfur S_8 (0.24 g, 7.6 mmol) for **2a–b** or selenium (7.6 mmol, 0.6 g) for **3a** was added. After 30 min, Cp_2TiCl_2 (3.8 mmol, 0.95 g) was added to the medium and the reaction mixture was stirred for 15 h. The solvent was evaporated in vacuo and the residue was extracted with CH_2Cl_2. The concentrated solution was subjected to flash chromatography on silica gel using CH_2Cl_2 as the eluant. The complex was recrystallized from $CHCl_3$, filtration afforded **2a** in 10 % yield, **2b** in 30% yield and **3a** in 10% yield.

Method b (Scheme 2): The 4,5-bis (2′-cyanoethylthio)-1,3-thiazol-2-thione **4** and 4,5-bis (2′-cyanoethylseleno)-1,3-thiazol-2-thione **5** are prepared according to the method a, given above, by using 3-bromopropionitrile (1 g, 7.6 mmol) instead of Cp_2TiCl_2. After the work up of the reaction mixture, the thiazoline thione **4** and **5** were obtained in 60% and 43% yield, respectively (data are given in Ref. [12]). To a stirred solution of 1,3-thiazoline-2-thione (500 mg, 1.65 mmol for **4**), or (650 mg, 1.65 mmol for **5**) in dry THF (20 mL), under argon, was added CsOH, H_2O (610 mg, 3.65 mmol) dissolved in MeOH (6 mL). The mixture was stirred 30 min at room temperature and Cp_2TiCl_2 (410 mg, 1.65 mmol) was added. After stirring for 1 h, during which time the solution became dark blue–green, the solvent was concentrated in vacuo. The residue was chromatographied on silica gel column using CH_2Cl_2 as eluent. The complexes are obtained after recrystallization in $CHCl_3$ in 40% yield.

Method c (Scheme 3): To a stirred solution of $[NEt_4]_2[Zn(thiazdt)_2]$ (130 mg, 0.18 mmol) or $[NEt_4]_2[Zn(thiazds)_2]$ (160 mg, 0.18 mmol) in dry THF (20 mL) was added Cp_2TiCl_2 (90 mg, 0.36 mmol). The reaction mixture was stirred for 3 h to reflux under argon. The solution turn dark blue green and becomes homogeneous. The medium is then filtered on silica gel column and eluted with CH_2Cl_2 to afford **2a** (100 mg, 74 % yield) and **3a** (90 mg, 67% yield).

Compound **2a** Cp$_2$Ti(Me-thiazdt), green crystals, m.p. = 268 °C; R_f = 0.68 (CH_2Cl_2); ^{1}H NMR (CDCl$_3$, 300 MHz) δ = 3.77 (s, 3H, CH$_3$), 5.51 (s, 5H, Cp), 6.13 (s, 5H, Cp); ^{13}C NMR (CDCl$_3$, 75 MHz) δ = 36.14 (CH$_3$), 107.94 (Cp), 112.34 (Cp), 131.23 (=C), 144.56 (=C), 190.36 (C=S); HRMS calc. for C$_{14}$H$_{14}$NS$_4$^{48}Ti: 371.9489. Found: 371.9490; UV–Vis–NIR (CH$_2$Cl$_2$): λ = 653 nm (ε = 7600 L mol^{-1} cm^{-1}); 493 (ε = 5010 L mol^{-1} cm^{-1}); 347 (ε = 21420 L mol^{-1} cm^{-1}).

Compound	2a	3a	2b
Formula	C$_{14}$H$_{13}$NS$_4$Ti	C$_{14}$H$_{13}$NS$_2$Se$_2$Ti	C$_{19}$H$_{15}$NS$_4$Ti
FW (g mol^{-1})	371.39	465.19	433.46
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	Pna21	Pna21	P21/n
a (Å)	9.7661(3)	9.8377(7)	8.2138(5)
b (Å)	10.1436(7)	10.1415(8)	20.1931(13)
c (Å)	15.6116(11)	15.6379(12)	11.4373(7)
α (°)	90	90	90
β (°)	90	90	107.748(3)
γ (°)	90	90	90
V (Å^3)	1546.54(16)	1560.2(2)	1806.73(19)
T (K)	293(2)	100(2)	100(2)
Z	4	4	4
D$_{calc}$ (g cm^{-3})	1.595	1.980	1.594
μ (mm^{-1})	1.080	5.469	0.938
Total reflection	25089	7570	24435
Unique reflection (R_{int})	3297 (0.0284)	3208 (0.0532)	3974 (0.0432)
Unique reflection	2931 ($I > 2\sigma(I)$)	2948 ($I > 2\sigma(I)$)	3448 ($I > 2\sigma(I)$)
R_1, wR_2	0.0306, 0.0831	0.0394, 0.0830	0.0302, 0.0732
R_1, wR_2 (all data)	0.0427, 0.0997	0.0436, 0.0841	0.0373, 0.0767
Goodness-of-fit (GoF)	1.303	1.091	1.036

Compound **2b** Cp$_2$Ti(Ph-thiazdt), green crystals, m.p. = 270 °C, R_f = 0.68 (CH_2Cl_2); ^{1}H NMR (CDCl$_3$, 300 MHz) δ = 5.60 (s, 5H, Cp), 6.09 (s, 5H, Cp), 7.38–7.63 (m, 5H, Ph); ^{13}C NMR (CDCl$_3$, 75 MHz) δ = 107.86 (Cp), 112.34 (Cp), 128.13 (=C, Ar), 128.69 (2=C, Ar), 129.73 (2=C, Ar), 131.59 (=C), 138.52 (NC, Ar), 144.17 (=C), 191.64 (C=S); Anal. Calc. for C$_{19}$H$_{15}$NS$_4$Ti: C, 52.65; H, 3.49; N, 3.23; S, 29.59. Found: C, 52.55; H, 3.61; N, 3.29; S, 29.82%. UV–Vis–NIR (CH_2Cl_2): λ_{max} = 643 nm (ε = 8620 L mol^{-1} cm^{-1}); 489 (ε = 4550 L mol^{-1} cm^{-1}); 346 (ε = 15820 L mol^{-1} cm^{-1}).

Compound **3a** Cp$_2$Ti(Me-thiazds), blue crystals, m.p. = 250 °C, R_f = 0.67 (CH_2Cl_2). ^{1}H NMR (CDCl$_3$, 300 MHz) δ = 3.90 (s, 3H, CH$_3$), 5.65 (s, 5H, Cp), 6.23 (s, 5H, Cp); ^{13}C NMR (CDCl$_3$, 75 MHz) δ = 38.41 (CH$_3$), 108.95 (Cp), 111.95 (Cp), 125.79 (=C), 143.33 (=C), 191.40 (C=S); HRMS calc. for C$_{14}$H$_{13}$NS$_2$^{48}Ti^{80}Se$_2$: 466.8299. Found: 466.8310; HRMS Calc. for [M+H]$^+$ C$_{14}$H$_{14}$NS$_2$^{48}Ti^{80}Se$_2$: 467.8377. Found: 467.8361; UV–Vis–NIR (CH_2Cl_2): λ = 702 nm (ε = 6940 L mol^{-1} cm^{-1}); 505 (ε = 4180 L mol^{-1} cm^{-1}); 353 (ε = 21770 L mol^{-1} cm^{-1}).

4.3. Crystallography

Single-crystal diffraction data were collected on a Nonius KappaCCD diffractometer from the University of Angers for compound **2a** and on APEX II Bruker AXS diffractometer for compounds **2b** and **3a** (Centre de Diffractométrie X, Université de Rennes, France). Details of the crystallographic are given in Table 4.

Appendix A. Supplementary material

CCDC 685463, 685464 and 685465 contain the supplementary crystallographic data for **2a** Cp$_2$Ti(Me-thiazdt), **2b** Cp$_2$Ti(Ph-thiazdt) and **3a** Cp$_2$Ti(Me-thiazds). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.05.021.

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