

Structural flexibility of titanocene diselenolene complexes: Combined structural and VT NMR investigations

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Abstract

A comparative investigation on five different Cp₂Ti(diselenolene) complexes, i.e. Cp₂Ti(Se₂C₂Z₂) (Z = -CO₂Me), Cp₂Ti[Se₂C₂Z(CF₃)], Cp₂Ti(bds) (bds = 1,2-benzene-diselenato), Cp₂Ti(dsit) (dsit = 1,3-dithiole-2-thione-4,5-diselenato) and Cp₂Ti(ddds) (ddds = 5,6-dihydro-1,4-dithiine-2,3-diselenato) is performed based on structural and variable-temperature NMR data. Preparation of Cp₂Ti[Se₂C₂Z(CF₃)] involves the reaction of Cp₂TiSe₅ with an excess of methyl-4,4,4-trifluorotetrolate while Cp₂Ti(bds) is obtained from the bds²⁻ diselenolate and Cp₂TiCl₂. Their X-ray crystal structures have been determined, showing that Cp₂Ti(bds) is not isostructural with the sulfur analog Cp₂Ti(bdt). Similarly the structures of Cp₂Ti(dsit) and Cp₂Ti(Se₂C₂Z₂) were also determined from single crystal X-ray diffraction. All complexes exhibit a strong folding of the metallacycle along the Se···Se hinge, ranking from 47.8° in Cp₂Ti(Se₂C₂Z₂) to 52.3° in Cp₂Ti(ddds). VT NMR investigations on Cp₂Ti[Se₂C₂Z(CF₃)] and Cp₂Ti(ddds), complementing earlier results on the other complexes, show that the largest activation energies and associated folding angles are observed with the most electron rich diselenolenes (ddds, bds), a behavior closely related to that observed earlier in dithiolene complexes.

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1. Introduction

Heteroleptic dithiolene complexes, which involve dithiolene ligand and other ligands such as diimines have been extensively investigated for their luminescence and photo-physical properties [1]. Similar mixed complexes associating dithiolene and cyclopentadienyl ligands, formulated as [Cp_nM(dithiolene)_m], can be classified into four main categories (Chart 1), according to the ratio of Cp and dithiolene ligands: [Cp₂M(dithiolene)] (Cp/dithiolene ratio = 2:1 complex), [CpM(dithiolene)₂] (1:2 complex), [CpM(dithiolene)₂] (bimetallic 1:1 complex), and [CpM(dithiolene)] (1:1 complex) [2].

These complexes have proven particularly attractive for the stabilization of open shell species [3], with their peculiar magnetic properties in the solid state associated with the topology of the intermolecular overlaps, through dithiolene/dithiolene, dithiolene/Cp but also Cp/Cp interactions [4]. Another striking feature of these complexes lies in their structural flexibility, nicely illustrated in the Cp₂M(dithiolene) series. Indeed, as shown in Chart 2, the d⁰ Cp₂Ti(dithiolene) complexes exhibit a strong distortion [2] of the TiS₂C₂ metallacycle with a folding along the S···S hinge which can reach values up to 50° while the d² CpMo(dithiolene) complexes are essentially non-folded (θ = 0°) [5,6].

The intermediate d¹ complexes, either neutral species [7] with M = V or Nb or cationic ones [6,8] with M = Mo or W adopt folded structures with intermediates folding angles between 0° and 35°, depending subtly on the nature

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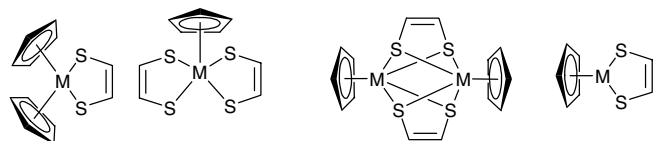


Chart 1.

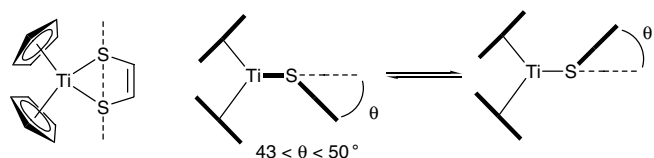


Chart 2.

of the metal, the dithiolene ligand and also the counter ion [3]. This behavior of the d^0 titanocene complexes had been rationalized some years ago by Lauher and Hoffmann [9] who showed that a stabilizing interaction between the empty a_1 orbital of the Cp_2Ti fragment with the HOMO of the dithiolene ligand (a π orbital of b_1 symmetry in C_{2v} conformation) was only possible by a symmetry lowering to the C_2 conformation with associated folding of the TiS_2C_2 metallacycle. We have also shown that the largest folding angles were associated with the most electron-rich dithiolene ligands [10], whose fragment orbital had an energy closest to that of the Cp_2Ti fragment orbital. Similarly, based on this model, the d^2 Cp_2Mo (dithiolene) complexes could be predicted to be unfolded ($\theta \approx 0^\circ$), as indeed experimentally observed [5,6].

A natural extension of this work concerns the analogous diselenolene complexes. Comparisons have been reported in the radical d^1 [Cp_2Mo (dithiolene/diselenolene)]⁺ complexes [6b] as well as in the d^7 [$CpNi$ (dithiolene/diselenolene)] series [4], showing closely related behaviors, but with a recurrent tendency for a stronger folding of the metallacycles. We wanted to investigate if similar effects were also observed in the d^0 titanocene complexes where these folding angles reach their largest values [11]. We describe here a comparative investigation on five different Cp_2Ti (diselenolene) complexes, i.e. $Cp_2Ti(Se_2C_2Z_2)$ ($Z = -CO_2Me$) [12], $Cp_2Ti[Se_2C_2Z(CF_3)]$, $Cp_2Ti(bds)$ ($bds = 1,2$ -benzenediselenato) [13,14], $Cp_2Ti(dsit)$ ($dsit = 1,3$ -dithiole-2-thione-4,5-diselenato) [11], and $Cp_2Ti(dddS)$ ($dddS = 5,6$ -dihydro-1,4-dithiine-2,3-diselenato) [15,16] (see Chart 3).

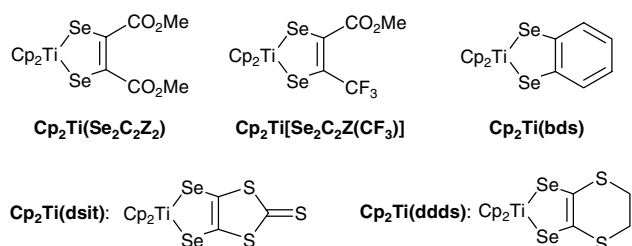


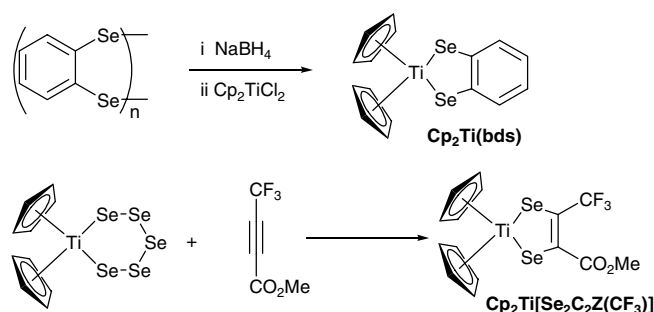
Chart 3.

Among them, four complexes were already described but three were not structurally characterized and one had not been investigated by VT NMR. We describe here original preparations of $Cp_2Ti[Se_2C_2Z(CF_3)]$ and $Cp_2Ti(bds)$, their X-ray crystal structures together with those of $Cp_2Ti(Se_2C_2Z_2)$ and $Cp_2Ti(dsit)$ and original VT NMR investigations on $Cp_2Ti[Se_2C_2Z(CF_3)]$ and $Cp_2Ti(dddS)$, affording an extensive series which interestingly covers now a broad spectrum, from electron “poor” diselenolenes with the electron-withdrawing CO_2Me or CF_3 groups to the electron-rich $dddS$ ligand.

2. Results and discussion

2.1. Synthesis and electrochemical properties

$Cp_2Ti(dddS)$ and $Cp_2Ti(dsit)$ were prepared as previously described from the reaction of titanocene dichloride with the corresponding diselenolene [15,11]. The earlier preparation of $Cp_2Ti(bds)$ was based on a straightforward, albeit time-consuming, preparation of bds^{2-} [17]. We choose to prepare the bds^{2-} ligand from the $NaBH_4$ reduction of the poly(*o*-diselenobenzene) [18], itself obtained from Na_2Se_2 and *o*-dibromobenzene in DMF at $140^\circ C$ [19]. This procedure had been successfully used for the preparation of the anionic square planar $[M(bds)_2]^-$ complexes ($M = Ni, Co, Cu$). Thus, direct reaction of the $NaBH_4$ reduction product with Cp_2TiCl_2 afforded $Cp_2Ti(bds)$ in good yield. The preparation of $Cp_2Ti[Se_2C_2Z_2]$, as described by Rauchfuss involves the reaction of Cp_2TiSe_5 with activated alkynes such as dimethyl acetylenedicarbonylate [12]. We used a similar strategy to prepare $Cp_2Ti[Se_2C_2Z(CF_3)]$ from the reaction of Cp_2TiSe_5 with an excess (4 equiv.) of methyl-4,4,4-trifluorotetrolate [20] (Scheme 1). All complexes are air-stable solid compounds with a dark green color. Note that CH_2Cl_2 solutions slowly decompose upon standing. The ^{77}Se NMR spectra were measured for those complexes not characterized earlier. One absorption was observed for $Cp_2Ti(bds)$ and $Cp_2Ti(dddS)$ at 967.7 and 1034.5 ppm, respectively, downfield of that of neat Me_2Se , while two lines at 697.2 and 697.6 ppm were found for $Cp_2Ti[Se_2C_2Z(CF_3)]$ in accordance with the presence of two different ^{77}Se nuclei. These values compare favorably



Scheme 1.

Table 1
Cyclic voltammetry data vs. Fc^+/Fc

	$E^{1/2}$ (red)	E_p (ox)	Reference
$\text{Cp}_2\text{Ti}(\text{Se}_2\text{C}_2\text{Z}_2)$	−1.32 (−1.20 vs. Ag^+/Ag)	+0.57 nc	This work [12]
$\text{Cp}_2\text{Ti}(\text{Se}_2\text{C}_2\text{ZCF}_3)$	−1.36	+0.70	This work
$\text{Cp}_2\text{Ti}(\text{dsit})$	−1.21 (−0.62 vs. SCE)	+0.51	This work [11]
$\text{Cp}_2\text{Ti}(\text{bds})$	−1.44	+0.27	This work
$\text{Cp}_2\text{Ti}(\text{ddds})$	−1.48	+0.21	This work

with those reported for $\text{Cp}_2\text{Ti}(\text{Se}_2\text{C}_2\text{Z}_2)$ (1001 ppm) [12] and $\text{Cp}_2\text{Ti}(\text{dsit})$ (855 ppm) [11].

Cyclic voltammetry experiments (Table 1) performed in CH_2Cl_2 show for every complex a reversible reduction wave corresponding the $\text{Ti}^{\text{IV}}/\text{Ti}^{\text{III}}$ process, together with irreversible oxidation waves. As already observed with the corresponding sulfur analogs, the reduction potential is influenced by the nature of the diselenolene ligand, within the following electrochemical series starting with the most anodic reduction potential $\text{Se}_2\text{C}_2\text{Z}_2 \approx \text{Se}_2\text{C}_2\text{Z}(\text{CF}_3) > \text{dsit} > \text{bds} \approx \text{ddds}$ and indicating that the most electron-withdrawing substituents on the diselenolene moiety favor indeed the one-electron reduction. A similar ranking was also observed in the corresponding titanocene dithiolene complexes [10].

2.2. Structural determinations

Several X-ray crystal structures determinations of titanocene diselenolene complexes have been reported to date, most of them, however, with alkylated cyclopentadienyl rings such as EtMe_4Cp or MeCp [11]. We will restrict here our comparisons with the less alkylated derivatives which do not introduce any steric effect in the folding process of the metallacycle. This leaves only two described examples, $(\text{MeCp})_2\text{Ti}(\text{dsit})$ [11] and $\text{Cp}_2\text{Ti}(\text{ddds})$ [16] with folding angles of 52.4° and 52.7° , respectively. We describe in the following the X-ray crystal structure determinations of $\text{Cp}_2\text{Ti}(\text{bds})$, $\text{Cp}_2\text{Ti}(\text{dsit})$, $\text{Cp}_2\text{Ti}(\text{Se}_2\text{C}_2\text{ZCF}_3)$ and Cp_2Ti

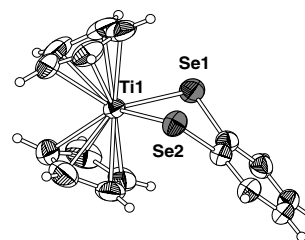


Fig. 1. ORTEP view of $\text{Cp}_2\text{Ti}(\text{bds})$. Thermal ellipsoids at 50% probability level.

($\text{Se}_2\text{C}_2\text{Z}_2$), thus affording a complete series of diselenolene derivatives from electron releasing to electron withdrawing groups. The structural molecular characteristics of the complexes such as the bond distances and the folding angle within the TiSe_2C_2 metallacycles are collected in Table 2.

$\text{Cp}_2\text{Ti}(\text{bds})$ crystallizes in the orthorhombic system, space group $Pbca$, with one molecule in general position in the unit cell (Fig. 1). Note that it is not isostructural with the corresponding dithiolene complex $\text{Cp}_2\text{Ti}(\text{bdt})$ [21], at variance with the $\text{Cp}_2\text{Ti}(\text{ddds})/\text{Cp}_2\text{Ti}(\text{dddt})$ complexes which are isostructural [16]. Of particular note is the longer $\text{C}=\text{C}$ bond within the metallacycle when compared with the other complexes, a likely consequence of the fused benzene ring, already observed in various bdt and bds complexes [4a]. The folding angle of the TiSe_2C_2 metallacycle amounts to $50.0(1)^\circ$, that is notably larger than the corresponding folding angle of the TiS_2C_2 metallacycle in $\text{Cp}_2\text{Ti}(\text{bdt})$, reported at 46° . $\text{Cp}_2\text{Ti}(\text{dsit})$ crystallizes in the monoclinic system, space group $P2_1$, with one molecule in general position in the unit cell (Fig. 2). Again, it is not isostructural with its sulfur analog, $\text{Cp}_2\text{Ti}(\text{dmit})$ [10] but adopts also a folded structure of the TiSe_2C_2 metallacycle with a folding angle of $49.84(8)^\circ$, to be compared with $\text{Cp}_2\text{Ti}(\text{dmit})$ [$47.4(3)^\circ$]. $\text{Cp}_2\text{Ti}(\text{Se}_2\text{C}_2\text{Z}_2)$ crystallizes in the triclinic system, space group $P\bar{1}$ with one molecule in general position in the unit cell (Fig. 3). Besides the characteristic features of the metallacycle, we also observe that one ester group (with O3 and O4 oxygen atoms) is coplanar

Table 2
Bond distances and folding angle in the TiSe_2C_2 metallacycles

	Ti–Se (Å)	Se–C (Å)	C=C (Å)	θ ($^\circ$)	Reference
$\text{Cp}_2\text{Ti}(\text{Se}_2\text{C}_2\text{Z}_2)$	2.5326(7)	1.880(4)	1.362(5)	47.77(9)	This work
	2.5680(6)	1.899(3)			
$\text{Cp}_2\text{Ti}(\text{Se}_2\text{C}_2(\text{CF}_3)\text{Z})$	2.5430(8)	1.903(4)	1.355(5)	48.36(6)	This work
	2.5782(8)	1.892(4)			
$\text{Cp}_2\text{Ti}(\text{bds})$	2.5639(12)	1.909(6)	1.407(8)	50.0(1)	This work
	2.5459(11)	1.908(6)			
$\text{Cp}_2\text{Ti}(\text{dsit})$	2.5697(17)	1.884(6)	1.372(7)	49.84(8)	This work
	2.5743(17)	1.878(6)			
$(\text{MeC}_5\text{H}_4)_2\text{Ti}(\text{dsit})$	2.564(5)	1.883(15)	1.365(14)	52.45	[11]
	2.569(13)	1.897(11)			
$\text{Cp}_2\text{Ti}(\text{ddds})$ molecule A	2.5433(10)	1.902(5)	1.370(7)	52.7(1)	[16]
	2.5478(9)	1.895(5)			
$\text{Cp}_2\text{Ti}(\text{ddds})$ molecule B	2.5408(9)	1.895(5)	1.359(7)	52.7(1)	
	2.5456(9)	1.900(5)			

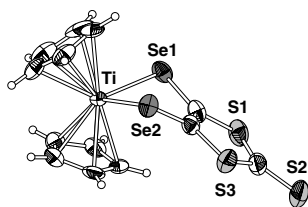


Fig. 2. ORTEP view of $\text{Cp}_2\text{Ti}(\text{dsit})$. Thermal ellipsoids at 50% probability level.

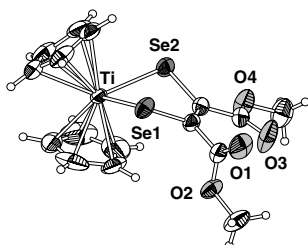


Fig. 3. ORTEP view of $\text{Cp}_2\text{Ti}(\text{Se}_2\text{C}_2\text{Z}_2)$. Thermal ellipsoids at 50% probability level.

with the Se_2C_2 diselenolene mean plane while the other is almost perpendicular. A similar arrangement is also observed in the corresponding dithiolene complex, crystallized as the methylcyclopentadienyl derivative, $(\text{MeCp})_2\text{Ti}(\text{S}_2\text{C}_2\text{Z}_2)$ [12]. Note also that the folding angle of the TiSe_2C_2 metallacycle amounts to $47.77(9)^\circ$, again larger than the similar angle in the corresponding sulfur analog (44°). Finally, the most unsymmetrical derivative, $\text{Cp}_2\text{Ti}[\text{Se}_2\text{C}_2\text{Z}(\text{CF}_3)]$ crystallizes in the monoclinic system, space group $C2/c$ with one molecule in general position in the unit and a folding angle of the metallacycle found at $48.36(6)^\circ$ (Fig. 4). Note also the role of the CF_3 group which hinders the $-\text{CO}_2\text{Me}$ moiety to be coplanar with the diselenolene moiety.

2.3. VT NMR experiments

The large folding angle of the TiSe_2C_2 metallacycles in the various complexes described above is associated in solution to an inversion process which is observable by variable-temperature NMR. Indeed, the two cyclopentadienyl rings, discernable at low temperatures as two singlets due to the slow exchange between the two folded conformations, exchange rapidly at higher temperatures, affording an averaged symmetrical situation with coalescence of the

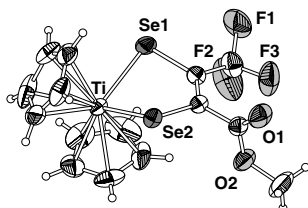


Fig. 4. ORTEP view of $\text{Cp}_2\text{Ti}[\text{Se}_2\text{C}_2\text{Z}(\text{CF}_3)]$. Thermal ellipsoids at 50% probability level.

two signals. The evaluation of the coalescence temperature T_c and $\Delta\nu$ value in the low exchange limit allows for the calculation of the activation energy ΔG_c^\ddagger at T_c , according to the following equations:

$$k_c = 2^{-1/2}\pi\Delta\nu \quad \Delta G_c^\ddagger = -RT_c \ln(hk_c/k_B T_c)$$

We have reported in Table 3 the VT NMR characteristics of the five complexes, together with the folding angle (θ) values deduced from the X-ray crystal structure determinations.

We observe that the ΔG_c^\ddagger values evolve with the nature of the diselenolene with the largest activation energies associated the most electron-rich diselenolenes. This evolution also parallels that of the folding angles of the TiSe_2C_2 metallacycles, the largest folding angles being associated with the largest activation energies. A very similar behavior was observed with the corresponding dithiolene complexes with activation energies which are also very close to those measured in the dithiolene complexes.

3. Summary

In conclusion, the combined structural, electrochemical and kinetic studies of these series of titanocene diselenolene complexes demonstrate that they behave almost identically to their dithiolene congeners. The even larger folding angles observed in the diselenolene complexes are most probably attributable to a Ti–Se bond length larger than the Ti–S one, allowing for a stronger folding before the diselenolene bumps into the cyclopentadienyl ligand. Indeed, we observe essentially no evolution of the Cp–Ti–Cp angle (Table 3) when going from the dithiolene to the diselenolene complexes, indicating that the Cp_2Ti fragment is not modified. This assumption is also based on the observation of even larger folding angles of the metallacycles in those species incorporating only one cyclopentadienyl or cyclooctadienyl moiety, as reported in for example in $[\text{CpTi}(\text{dmit})_2]^-$ [10], $[\text{Cp}^*\text{M}(\text{dmit})]^{-1,0}$ ($\text{M} = \text{Mo}, \text{W}$) [23] or $[(\text{cot})\text{U}(\text{dddt})_2]^{2-,1-}$ [24]. It demonstrates unambiguously that the strongly favored folding of the metallacycle due to electronic interactions is essentially limited in these $\text{Cp}_2\text{M}(\text{diselenolene})$ complexes by the steric requirements of the cyclopentadienyl ligands. On the other hand, the inversion movement associated with this folding depends on the electronic nature of the diselenolene, since with similar folding angles, strongly differing activation energies are observed, from 50 to 67 kJ mol^{-1} when going from the electron-poor $\text{Se}_2\text{C}_2\text{Z}_2$ to the electron-rich ddds diselenolene ligand.

4. Experimental

4.1. Syntheses

Nuclear magnetic resonance spectra were recorded at 500.04 for ^1H , 470.28 for ^{19}F and 57.287 MHz for ^{77}Se

Table 3

Folding angle (θ) values and VT NMR data for the diselenolene complexes and comparison with the analogous dithiolene complexes (*in italics*)

Complex	θ ($^\circ$)	Cp–Ti–Cp ($^\circ$)	Solvent	T_c ($^\circ\text{C}$)	ΔG_c^\ddagger (kJ mol^{-1})	Reference
$\text{Cp}_2\text{Ti}(\text{Se}_2\text{C}_2\text{Z}_2)$	47.77(9)	132.6	CD_2Cl_2	–27	51.5	[12]
<i>$\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_2\text{Z}_2)$</i>	44 ^a	132.4 ^a	<i>CD_2Cl_2</i>	–34	49.7	[12]
$\text{Cp}_2\text{Ti}[\text{Se}_2\text{C}_2\text{Z}(\text{CF}_3)]$	48.36(6)	133.0	CDCl_3	+27	54.3	This work
<i>$\text{Cp}_2\text{Ti}[\text{S}_2\text{C}_2\text{Z}(\text{CF}_3)]$</i>	–	–	–	–	–	–
$\text{Cp}_2\text{Ti}(\text{bds})$	50.0(1)	132.5	Toluene- d_8	–9	57.0	[14]
<i>$\text{Cp}_2\text{Ti}(\text{bdt})$</i>	46 ^b	131.9 ^b 132.3	CS_2	+10	58.5	[22]
$\text{Cp}_2\text{Ti}(\text{dsit})$	49.84(8)	132.3	CDCl_3	+28	60.0	[11]
<i>$\text{Cp}_2\text{Ti}(\text{dmit})$</i>	47.4(3) ^c	132.2 ^c	<i>CDCl_3</i>	+30	60.0	[10]
$\text{Cp}_2\text{Ti}(\text{ddd}s)$	52.7(1) ^d	133.5, 132.5 ^d	Toluene- d_8	+55	67.1	This work
<i>$\text{Cp}_2\text{Ti}(\text{ddd}t)$</i>	49.2, 51.2(2) ^e	131.5, 132.3 ^e	<i>CDCl_3</i>	+53	67.0	[10]

^a From Ref. [12].^b From Ref [21].^c From Ref [10].^d From Ref [16].^e From Ref. [10].

NMR. $\text{Cp}_2\text{Ti}(\text{ddd}s)$ [15], $\text{Cp}_2\text{Ti}(\text{Se}_2\text{C}_2\text{Z}_2)$ [12] and $\text{Cp}_2\text{Ti}(\text{dsit})$ [11] were prepared from published procedures.

4.1.1. Preparation of $\text{Cp}_2\text{Ti}(\text{bds})$

To a suspension of *o*-poly(diselenobenzene) [18,19] (1.17 g, 5 mmol) in dry MeOH (50 mL) was added NaBH_4 (0.76 g, 20 mmol) in small successive quantities. After complete dissolution, Cp_2TiCl_2 (0.62 g, 2.5 mmol) is added and the reaction mixture stirred for 1 h. Evaporation of the solvent and chromatography on SiO_2 (CH_2Cl_2 :petrol ether

2:1) afforded a dark green solid, further recrystallized from CH_2Cl_2 /petrol ether to afford $\text{Cp}_2\text{Ti}(\text{bds})$ as dark green crystals (0.62 g, 60% based on Cp_2TiCl_2). $^{77}\text{Se}\{^1\text{H}\}/\text{Me}_2\text{Se}$ ext (in CDCl_3) δ : 967.7. Anal. Calc. for $\text{C}_{16}\text{H}_{14}\text{TiSe}_2$: C, 46.66; H, 3.23. Found: C, 46.50; H, 3.15%.

4.1.2. Preparation of $\text{Cp}_2\text{Ti}[\text{Se}_2\text{C}_2\text{Z}(\text{CF}_3)]$

Cp_2TiSe_5 (4.124 g, 7.23 mmol) and methyl-4,4,4-trifluorotetrolate (4.4 g, 29 mmol, 5 equiv.) were warmed under reflux in toluene (50 mL) for 2 h. The solution was filtered

Table 4

Crystallographic data

Compound	$\text{Cp}_2\text{Ti}(\text{dsit})$	$\text{Cp}_2\text{Ti}(\text{bds})$	$\text{Cp}_2\text{Ti}(\text{Se}_2\text{C}_2\text{Z}_2)$	$\text{Cp}_2\text{Ti}[\text{Se}_2\text{C}_2\text{Z}(\text{CF}_3)]$
Formula	$\text{C}_{13}\text{H}_{10}\text{S}_3\text{Se}_2\text{Ti}$	$\text{C}_{16}\text{H}_{14}\text{Se}_2\text{Ti}$	$\text{C}_{16}\text{H}_{16}\text{O}_4\text{Se}_2\text{Ti}$	$\text{C}_{15}\text{H}_{13}\text{F}_3\text{O}_2\text{Se}_2\text{Ti}$
Formula weight	468.21	412.09	478.11	488.07
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1$	$Pbca$	$P\bar{1}$	$C2/c$
a (\AA)	7.881(5)	12.9507(11)	7.8083(3)	25.268(2)
b (\AA)	8.492(5)	14.8016(11)	9.8415(3)	8.1430(5)
c (\AA)	11.856(5)	15.1847(13)	12.3385(5)	16.2567(13)
α ($^\circ$)	90.0	90.0	71.738(3)	90.0
β ($^\circ$)	105.002(5)	90.0	81.510(3)	90.521(10)
γ ($^\circ$)	90.0	90.0	79.709(2)	90.0
V (\AA^3)	766.4(7)	2910.8(4)	881.64(6)	3344.9(4)
Z	2	8	2	8
d_{calc} (Mg m^{-3})	2.029	1.881	1.801	1.938
Diffraction	Stoe-IPDS	Stoe-IPDS	Kappa-CCD	Stoe-IPDS
Temperature (K)	293(2)	293(2)	293(2)	293(2)
μ (mm^{-1})	5.697	5.572	4.629	4.898
θ Range ($^\circ$)	1.78–26.05	2.48–26.02	2.20–27.50	2.51–25.87
Measured reflections	10479	15714	22862	12511
Independent reflections	2961	2833	4007	3210
R_{int}	0.0761	0.0917	0.0411	0.0682
$I > 2\sigma(I)$ reflections	2297	1723	2989	2177
Absorption corrections	Multi-scan	Multi-scan	Multi-scan	Multi-scan
$T_{\text{max}}, T_{\text{min}}$	0.3326, 0.5369	0.6465, 0.1932	1.0, 0.7194	0.3482, 0.3987
Refined parameters	172	172	209	208
$R(F)$ with $[I > 2\sigma(I)]$	0.0306	0.0439	0.0391	0.0325
$wR(F^2)$ (all data)	0.0613	0.1207	0.1187	0.0706
Maximum and minimum $\Delta\rho$ (e \AA^{-3})	+0.51 and –0.96	+0.61 and –0.62	+0.74 and –0.87	+0.46 and –0.36

while hot, concentrated and chromatographed in silica gel with CH_2Cl_2 elution, affording the title compound as green crystals after evaporation (1.63 g, 50%). ^1H NMR (CDCl_3) δ , 3.85 (s, 3H, Me), 6.15 (bs, 10H, Cp). ^{19}F NMR (CDCl_3) δ , 59.03. $^{77}\text{Se}\{^1\text{H}\}/\text{Me}_2\text{Se}$ ext (CDCl_3) δ , 697.2, 697.6. Anal. Calc. for $\text{C}_{15}\text{H}_{13}\text{F}_3\text{O}_2\text{TiSe}_2$: C, 36.93; H, 2.68. Found: C, 36.19; H, 2.49%.

4.2. Electrochemistry

Cyclic voltammetry were performed in CH_2Cl_2 containing $^n\text{Bu}_4\text{NPF}_6$ 0.05 M as electrolyte. A platinum disk and platinum wire were used as working and counter electrode, respectively, together with an Ag^+/Ag reference, at a scan rate of 100 mV s^{-1} . Ferrocene was added at the end of the experiment.

4.3. Crystallography

Crystals were mounted at the end of a glass fiber with Aradilte™ glue. Data were collected on a Stoe Imaging Plate Diffraction System (IPDS) with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The crystal data are summarized in Table 4. Structures were solved by direct methods (SHELXS-97) and refined (SHELXL-97) [25] by full-matrix least-squares methods using the WinGX chain of programs [26]. Numerical absorption corrections were applied for all structures. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and not refined.

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Appendix A. Supplementary material

CCDC 646564, 646565, 646566 and 646567 contain the supplementary crystallographic data for $\text{Cp}_2\text{Ti}(\text{bds})$, $\text{Cp}_2\text{Ti}(\text{dsit})$, $\text{Cp}_2\text{Ti}[\text{Se}_2\text{C}_2(\text{CO}_2\text{Me})_2]$ and $\text{Cp}_2\text{Ti}[\text{Se}_2\text{C}_2(\text{CF}_3)(\text{CO}_2\text{Me})]$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax:

(+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.06.040](https://doi.org/10.1016/j.jorganchem.2007.06.040).

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