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# Vanadocene and niobocene dihalides containing electron-withdrawing substituents in the cyclopentadienyl rings: Synthesis, characterization and cytotoxicity

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ABSTRACT

The first example of the group V metallocene dihalides substituted in the cyclopentadienyl rings with electron-withdrawing substituents is reported. This study includes synthesis and spectroscopic characterization of the series of vanadocene and niobocene compounds functionalized in the cyclopentadienyl rings with the ester groups. Structures of $(\eta^5\text{-}C_5H_4COOPh)_2VCl_2$, $(\eta^5\text{-}C_5H_4COOMe)_2VBr_2{\cdot}CH_2Cl_2$, $(\eta^5\text{-}C_5H_4COOPh)_2NbCl_2$, $(\eta^5\text{-}C_5H_4COOMe)_2NbBr_2$ and $(\eta^5\text{-}C_5H_4COOEt)_2NbBr_2$ were determined by X-ray diffraction analysis. Cytotoxic activity toward human leukemia cells MOLT-4 was established *in vitro* for all newly prepared metallocene compounds.



## 1. Introduction

Design of the metal-based anticancer drug superior or at least complement to cisplatin become the challenge of the inorganic chemists in last few decades [1–5]. The bent metallocenes $Cp_2MCl_2$ (Cp = $\eta^5$-$C_5H_5$; M = group IV–VI metal) were the first class of the organometallic compounds to be systematically investigated for this purpose [6] and remain under comprehensive scrutiny up to now. The early stage of the investigation have shown that the bis-cyclopentadienyl complexes of Ti(IV) [7], V(IV) [8], Nb(IV) [9], Nb(V) [10], Mo(IV) [11] and Mo(VI) [10] are active toward Ehrlich ascites tumor cells while complexes of the other metals from group IV, V and VI are much less active or inactive [12]. This rule seems to be more general. It may be applied also for other cancer cell lines and for substituted derivatives with only few exceptions [13,14].

The first stage of the scrutiny was focused mainly on titanocene dichloride that has passed though the preclinical and phase I clinical trials [15]. However, the phase II trials have concluded that this agent is not effective in patients with metastatic breast cancer [16] and metastatic renal-cell carcinoma [17]. These objections together with other weak points of titanocene dichloride (*e.g.*, complex hydrolytic behavior) led to design of the modified titanocene, vanadocene and molybdenocene compounds. The preclinical studies on *cis*-platin resistant tumor cell lines are proving that the cytotoxicity of the titanocene complexes could be enhanced through the substitution in the cyclopentadienyl ring. Promising results were obtained mainly for aminoalkyl [18–20], methoxycarbonyl [21] and methoxybenzyl functionalized compounds [22]. So far, only few studies have been focused in metallocene containing other metal than titanium. The high cytotoxicity was found only in case of the vanadocene [23–27] and molybdenocene compounds [28] containing methoxy-benzyl substituted cyclopentadienyl rings.

Our focus on the modification and the application of the group V metallocene compounds follows our previous studies attended in leukemia therapy [23,29,30] and corresponds with our long-standing interest in the chemistry of metallocene compounds [31,32]. The introduction of the ester group in the cyclopentadienyl rings was chosen due to promising biological properties of the titanocene analogues with similar structure pattern [21]. Furthermore, this study brings the first example of the group V metallocene dihalides modified with strong electron withdrawing groups in the cyclopentadienyl ligands and describes their effect on the structure and EPR spectra.

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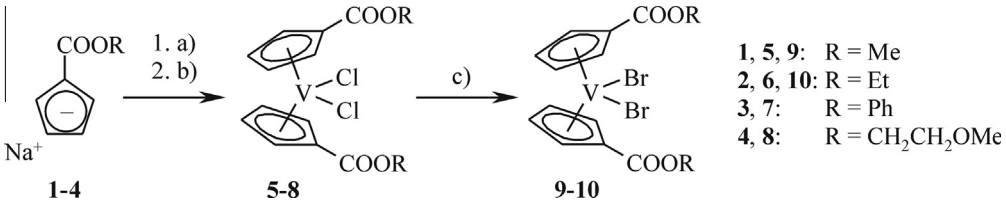



**Scheme 1.** Synthesis of vanadocene complexes. (a) $VCl_3(THF)_3$/THF; (b) $PCl_3/Et_2O$; (c) $BBr_3/CH_2Cl_2$.

## 2. Results and discussion

### 2.1. Synthesis of vanadocene and niobocene complexes

Ester-substituted vanadocene dichlorides ($\eta^5$-$C_5H_4COOR)_2VCl_2$ (**5**: R = Me, **6**: R = Et, **7**: R = Ph, **8**: R = $CH_2CH_2OMe$) were prepared by the reaction of $VCl_3(THF)_3$ with appropriate substituted sodium cyclopentadienide (**1–4**), see Scheme 1. The putative monochloride intermediates ($\eta^5$-$C_5H_4COOR)_2VCl$ were not isolated but their appearance was described previously for several *ansa*-vanadocene analogues [33]. The synthesis of the ring-substituted and *ansa*-bridged vanadocene dichlorides has been optimized previously [23,33–35]. It was shown that reactions of Grignard reagents Cp′MgCl (Cp′ = substituted Cp) with $V(acac)_3$ or $V(acac)_2Cl(THF)$ are giving the vanadocene complexes in much higher yield than reaction of lithium or sodium cyclopentadienides with $VCl_3(THF)_3$. Unfortunately, this modification of the procedure could not be applied for ester-substituted vanadocenes because the starting ($C_5H_4$-COOR)MgCl is not accessible due to pronounced reactivity of the Grignard reagents with carboxylic acid esters.

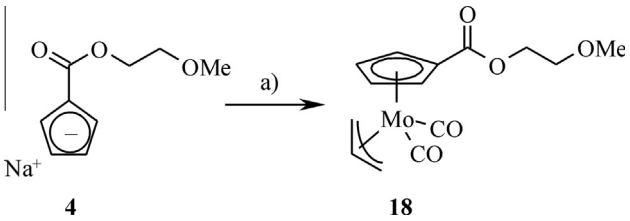
The complexes **5** and **6** were further used for preparation of the dibromide complexes ($\eta^5$-$C_5H_4COOMe)_2VBr_2$ (**9**: R = Me, **10**: R = Et). The ligand-exchange reaction was done in dichloromethane using the boron tribromide (Scheme 1). This protocol was chosen for ester-functionalized vanadocene complexes mainly due to mild reaction conditions and fast reaction rate [35].

Niobocene dichloride complexes ($\eta^5$-$C_5H_4COOR)_2NbCl_2$ (**11**: R = Me, **12**: R = Et, **13**: R = Ph, **14**: R = $CH_2CH_2OMe$) were prepared by the reaction of $NbCl_4(THF)_2$ with appropriate substituted sodium cyclopentadienide (**1–4**), see Scheme 2. This method is a modification of the protocol developed for the unsubstituted niobocene dichloride [36]. The dibromide complexes **15** and **16** were prepared similarly as the vanadocene analogues by reaction of niobocene dichlorides (**11** and **12**) with boron tribromide.

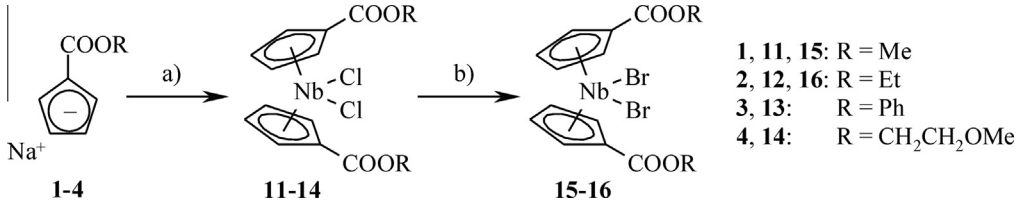
Synthesis of the starting compounds **1–3** was done according to literature procedures [37–39]. The cyclopentadienide **4** was prepared according to Scheme 3. Base-catalyzed transesterification [40,41] of dimethyl carbonate with 2-methoxy-ethanol gives bis(2-methoxyethyl) carbonate (**17**). Following reaction with sodium cyclopentadienide gives compound **4** in medium yield. The infrared spectrum of the compound **4** shows strong band of the CO stretching at 1641 $cm^{-1}$ that proves the attachment of ester group. The assembly of substituted cyclopentadienide was further evidenced by spectroscopic characterization of the molybdenum(II) complex [($\eta^3$-$C_3H_5$)($\eta^5$-$C_5H_4COOCH_2CH_2OMe$)$Mo(CO)_2$] (**18**) that was prepared by reaction of the compound **4** with [($\eta^3$-$C_3H_5$)$Mo(CO)_2(NCMe)_2Cl$], see Scheme 4.

### 2.2. Spectroscopic characterization of vanadocene and niobocene complexes

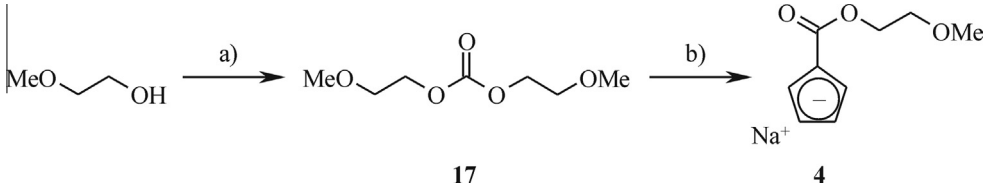
The infrared spectra of the vanadocene complexes **5–10** and niobocene complexes **11–16** show characteristic band of C=O stretching at 1720–1751 $cm^{-1}$; see Table 1. These high wavenumbers indicate low delocalization of the $\pi$-electrons from C=O group that is compatible with expected $\eta^5$-coordination mode. The starting




**Scheme 4.** Synthesis of compounds **18**. (a) [($\eta^3$-$C_3H_5$)$Mo(CO)_2(NCMe)_2Cl$]/THF.




**Scheme 2.** Synthesis of niobocene complexes **15** and **16**. (a) $NbCl_4(THF)_2$/THF; (b) $BBr_3/CH_2Cl_2$.




**Scheme 3.** Synthesis of cyclopentadienide **4**. (a) $(MeO)_2CO$, NaOMe ; (b) NaCp/THF.

**Table 1**
Wavenumbers of the CO stretching bands ($cm^{-1}$) of the metallocene complexes.

| | ν(C=O) | | ν(C=O) |
|---|---|---|---|
| **5** | 1722, 1732 | **11** | 1721, 1732 |
| **6** | 1718, 1726 | **12** | 1716, 1726 |
| **7** | 1751 | **13** | 1735, 1742 |
| **8** | 1716, 1726 | **14** | 1713, 1728 |
| **9** | 1724 | **15** | 1723 |
| **10** | 1720 | **16** | 1720 |

cyclopentadienides **1**–**4** show this band at considerably lower wavenumbers (~1640 $cm^{-1}$) due higher contribution of the structure with negative charge on oxygen atom. The C=O stretching band of the alkyl esters **5**, **6**, **8**, **11** and **12** (1721–1727 $cm^{-1}$) was found at lower wavenumbers than in the case of the phenyl ester analogues (**7**: 1751 $cm^{-1}$, **13**: 1738 $cm^{-1}$) [note: averaged values from $\nu_s$(C=O) and $\nu_a$(C=O) are given when the C=O stretching modes are coupled]. It is a result of electron withdrawing properties of the phenyl group that enhances the contribution of the double bond C=O. The exchange of chlorides with bromides has only minor effect on the frequency of the C=O stretching. This substitution cause the decrease of the wavenumbers about 1–3 $cm^{-1}$.

The EPR spectra of the vanadocene and niobocene complexes were measured in dichloromethane at room temperature. The vanadocene complexes (**5**–**10**) show eight-line hyperfine coupling (HFC) corresponding to the nuclear spin value of $^{51}V$ ($I = 7/2$; 99.8%). The niobocene complexes (**11**–**16**) give ten-line spectra due to interaction with $^{93}Nb$ (100%; 9/2). The isotropic HFC constants ($|A_{iso}|$) and isotropic *g*-factors of the compounds **5**–**16** are listed in the Table 2.

The isotropic HFC constants of ester-substituted vanadocene dichlorides (**5**–**8**: $|A_{iso}| = 67.9–68.0 \times 10^{-4}$ $cm^{-1}$) are lower than were reported for unsubstituted analogue $Cp_2VCl_2$ ($|A_{iso}| = 69.7 - \times 10^{-4}$ $cm^{-1}$ [35]). It is an effect of the electron withdrawing substituent in the Cp ring that weakens the bonds Cp–V and strengthens the bonds V–Cl. This interpretation arise from previous studies showing that the unpaired electron is localized in the orbital antibonding to V–Cl bonds [42,43]. The higher covalency of the bonds V–Cl therefore increases the delocalization of the spin density that results in lower $|A_{iso}|$ values. As expected the vanadocene dibromide complexes **9** and **10** have considerably lower $|A_{iso}|$ constant and higher $g_{iso}$ than chloride analogues **5** and **6**, respectively. It reflexes high delocalization of unpaired electron on the bromides and agrees with data obtained for unsubstituted analogues (*cf.* EPR data of $Cp_2VCl_2$ and $Cp_2VBr_2$ in Table 2).

Similar effects of the substitution were observed for niobocene dihalide complexes **11**–**16**. Furthermore, the substitution of the niobocene complexes with ester group in the cyclopentadienyl ring induces an observable increase of the $g_{iso}$ parameter (*cf.* **11**–**14** with $Cp_2NbCl_2$ and **15**, **16** with $Cp_2NbBr_2$).

**Table 2**
Isotropic HFC constants (in $10^{-4}$ $cm^{-1}$) and isotropic *g*-factors of the metallocene complexes.

| | $\|A_{iso}\|$ | $g_{iso}$ | | $\|A_{iso}\|$ | $g_{iso}$ |
|---|---|---|---|---|---|
| $Cp_2VCl_2$[a] | 69.7 | 1.989 | $Cp_2NbCl_2$ | 107.4 | 1.979 |
| $Cp_2VBr_2$[a] | 63.6 | 2.024 | $Cp_2NbBr_2$ | 100.0 | 2.013 |
| **5** | 68.0 | 1.989 | **11** | 104.6 | 1.984 |
| **6** | 68.0 | 1.989 | **12** | 104.0 | 1.984 |
| **7** | 67.9 | 1.989 | **13** | 104.4 | 1.984 |
| **8** | 67.9 | 1.989 | **14** | 104.6 | 1.984 |
| **9** | 62.1 | 2.027 | **15** | 96.9 | 2.019 |
| **10** | 62.2 | 2.026 | **16** | 96.9 | 2.019 |

[a] The EPR data reported in [35].

### 2.3. X-ray structures of $Cp_2VBr_2$, **7**, **9**·$CH_2Cl_2$, **13**, **15** and **16**

Structures of $Cp_2VBr_2$, **7**, **9**·$CH_2Cl_2$, **13**, **15** and **16** were determined by single crystal X-ray diffraction analysis. Molecular structures of the complexes are shown in Figs. 1–3. Selected bond distances and angles are summarized in Table 3.

The complexes $Cp_2VBr_2$, **7**, **9**·$CH_2Cl_2$, **13**, **15** and **16** have typical bend metallocene structure with two $\eta^5$-bonded cyclopentadienyl rings and two halides coordinated to the central metal in the oxidation state IV. The centroids of the Cp rings and halides make distorted tetrahedron around central metal. The bond angles $Cg_1$–M–$Cg_2$ were found to be in the range 130.49(6)–132.99(8)°. The angles $X_1$–M–$X_2$ are 86.60(4)–88.26(2)°. Here reported ester-substituted vanadocene and niobocene compounds show considerably shorter bonds metal–halide than unsubstituted analogues (*cf.* **7** with

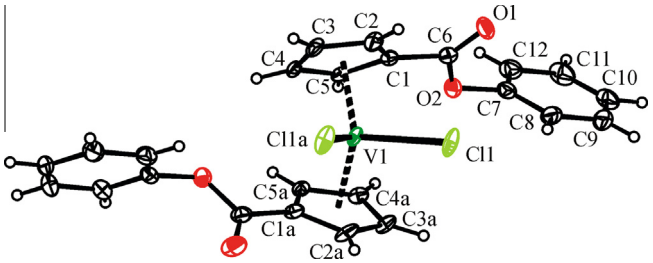



**Fig. 1.** ORTEP drawing of $(\eta^5\text{-}C_5H_4COOPh)_2VCl_2$ (**7**). The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

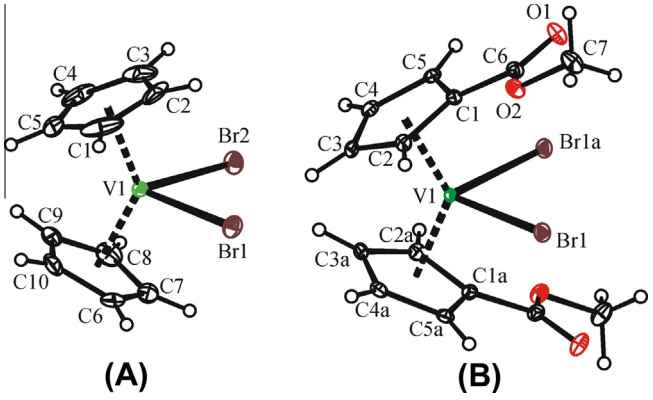



**Fig. 2.** ORTEP drawing of vanadocene complexes: (A) $Cp_2VBr_2$; (B) $(\eta^5\text{-}C_5H_4COOMe)_2VBr_2$ (**9**·$CH_2Cl_2$). The labeling schemes for all non-hydrogen atoms are shown. Thermal ellipsoids are drawn at the 30% probability level. The molecule of $CH_2Cl_2$ present in the crystal lattice of compound **9**·$CH_2Cl_2$ is omitted for clarity.

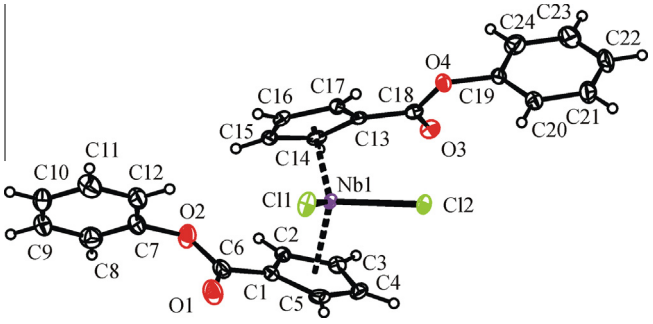



**Fig. 3.** ORTEP drawing of $(\eta^5\text{-}C_5H_4COOPh)_2NbCl_2$ (**13**). The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

**Table 3**
Structural parameters (Å, °) of vanadocene and niobocene compounds describing the coordination around the metal.[a]

| | $M–Cg_1$ | $V–Cg_2$ | $M–X_1$ | $M–X_2$ | $Cg_1–M–Cg_2$ | $X_1–M–X_2$ |
|---|---|---|---|---|---|---|
| $Cp_2VCl_2$[b] | 1.9770(13) | 1.9676(14) | 2.4108(8) | 2.4077(8) | 131.92(5) | 87.20(3) |
| $Cp_2VBr_2$ | 1.967(5) | 1.965(3) | 2.5792(12) | 2.5681(14) | 132.4(2) | 86.60(4) |
| $Cp_2NbCl_2$[c] | 2.085 | 2.090 | 2.468(4) | 2.476(3) | 131.6 | 85.5(0.1) |
| | 2.092 | 2.087 | 2.464(5) | 2.475(4) | 132.1 | 85.7(0.2) |
| **7** | 1.971(2) | 1.971(2) | 2.3886(11) | 2.3886(11) | 132.99(8) | 88.84(4) |
| **9·$CH_2Cl_2$** | 1.9861(15) | 1.9861(15) | 2.5233(5) | 2.5233(5) | 131.48(6) | 87.91(2) |
| **13** | 2.080(2) | 2.088(2) | 2.4350(13) | 2.4476(12) | 132.49(8) | 87.55(4) |
| **15** | 2.084(2) | 2.084(2) | 2.6122(4) | 2.6122(4) | 130.49(6) | 87.64(1) |
| **16** | 2.0924(15) | 2.0925(15) | 2.5908(5) | 2.5908(5) | 130.51(6) | 88.26(2) |

[a] M, metal, Cg, centroid of the cyclopentadienyl ring.
[b] The data reported in [44].
[c] Two molecules in the crystal lattice; the structural data reported in [45].

$Cp_2VCl_2$ [44], **9·$CH_2Cl_2$** with $Cp_2VBr_2$ and **13** with $Cp_2NbCl_2$ [45]). This shortening is a result of higher covalency of the bond M–X that was also evidenced by EPR spectroscopic measurements. The expected shortening of the bond Cp–M induced by strong electron-withdrawing substituent was evidenced only in case of the compound **9·$CH_2Cl_2$** (*cf.* with $Cp_2VBr_2$). The bond distances of the other ester-substituted metallocene dihalides could be hardly compared owing to low accuracy of the bond distances M–Cp in the unsubstituted compounds $Cp_2VCl_2$ [44] and $Cp_2NbCl_2$ [45] (see Fig. 4).

Ester groups are not fully conjugated with cyclopentadienyl ring. The interplanar angle between the COO group and cyclopentadienyl were found to be 18.4(6)° for **7**, 10.5(4)° for **9·$CH_2Cl_2$**, 10.8(6) and 11.4(5)° for **13**, 17.7(5)° for **15** and 11.1(4)° for **16**.

### 2.4. Cytotoxicity of vanadocene and niobocene complexes

Cytotoxic effect of vanadocene complexes **5**–**10** and niobocene complexes **11**–**16** was evaluated on human T-lymphocytic leukemia cells MOLT-4 in exponential grow phase, 24 h after the incubation with the cytostatic drugs. Table 4 summarizes the $IC_{50}$ values obtained from the standard WST-1 viability assays. The effect of the drug concentration on the viability of the leukemic cells is given as Supplementary material.

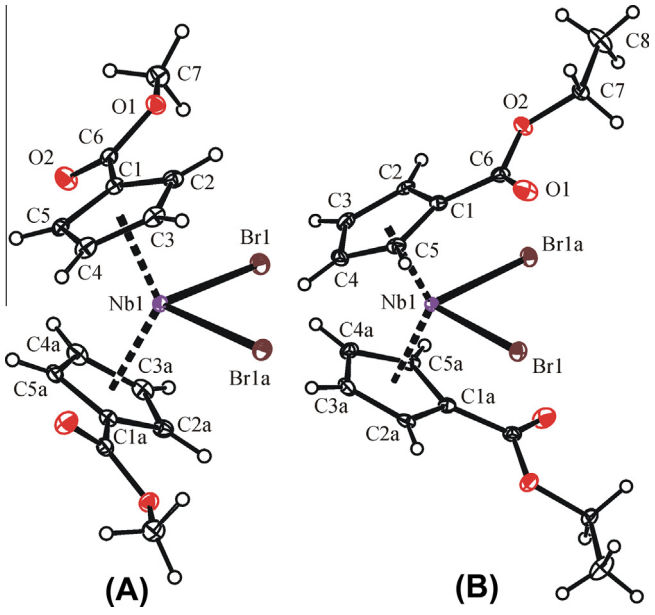



**Fig. 4.** ORTEP drawing of niobocene complexes: (A) ($\eta^5$-$C_5H_4COOMe)_2NbBr_2$ (**15**); (B) ($\eta^5$-$C_5H_4COOEt)_2NbBr_2$ (**16**). The labeling schemes for all non-hydrogen atoms are shown. Thermal ellipsoids are drawn at the 30% probability level.

**Table 4**
Cytotoxicity of the vanadocene and niobocene complexes toward MOLT-4 cells expressed as the $IC_{50}$ values (in μmol/L).

| $Cp_2VCl_2$ [a] | 70 ± 7 | $Cp_2NbCl_2$ | 49 ± 5 |
|---|---|---|---|
| $Cp_2VBr_2$ | 124 ± 7 | $Cp_2NbBr_2$ | 61 ± 10 |
| **5** | 151 ± 20 | **11** | 29 ± 5 |
| **6** | ⩾200 | **12** | 81 ± 11 |
| **7** | 117 ± 9 | **13** | 60 ± 2 |
| **8** | ⩾200 | **14** | 113 ± 5 |
| **9** | ⩾200 | **15** | ⩾200 |
| **10** | ⩾200 | **16** | ⩾200 |

[a] Data reported in [23].

It was observed that niobocene complexes display about 1.5–5 times higher cytotoxicity than vanadocene analogues. This trend was observed for parent metallocene dihalides ($Cp_2MX_2$) as well as for the ester substituted compounds (**5**–**16**). In the case of vanadocene complexes, the substitution in the cyclopentadienyl ring has rather negative effect. These compounds have $IC_{50}$ values higher than 100 μmol/L. Positive effect was observed only for ($\eta^5$-$C_5H_4COOMe)_2NbCl_2$ (**11**) that displays almost two times higher cytotoxicity ($IC_{50}$ = 29 ± 5 μmol/L) than unsubstituted analog $Cp_2NbCl_2$ ($IC_{50}$ = 49 ± 5 μmol/L). The rest of the ring-substituted niobocene compounds have similar or lower cytotoxicity than unsubstituted niobocene dichloride. The effect of the halide ligands was also evaluated. It was observed that chloride complexes show considerably higher activity than their bromide analogues. This trend was observed for both vanadocene and niobocene complexes.

## 3. Conclusions

This study has shown that vanadocene and niobocene dihalide complexes functionalized in each cyclopentadienyl ring with one ester group are stable compounds and could be prepared by standard protocols starting from $VCl_3(THF)_3$ and $NbCl_4(THF)_2$, respectively. The substitution with strong electron-withdrawing substituents causes decrease of the donor ability of the cyclopentadienyl ligand that results in the changes of the molecular and electronic structure as was evidenced by X-ray diffraction analyses and EPR spectroscopic measurements.

The cytotoxic properties of ester-substituted vanadocene and niobocene compounds were evaluated on the MOLT-4 leukemia cell line. Although the study includes only relatively small series of complexes, it could be concluded that niobocene complexes exhibit apparently higher cytotoxicity than vanadocenes. Unfortunately, introduction of the ester group in the cyclopentadienyl

ring has rather negative effect on cytotoxicity. It could be caused by lower stability of the putative active metallocene species under physiological conditions.

## 4. Experimental

### 4.1. Methods and materials

All operations were performed under nitrogen using conventional Schlenk-line techniques. The solvents were purified and dried by standard methods [46]. Previously published procedures were used for synthesis of $Cp_2VCl_2$ [47], $Cp_2NbCl_2$ [36], $NbCl_4(THF)_2$ [48], Na($C_5H_4COOMe$) (**1**) [37,38], Na($C_5H_4COOEt$) (**2**) [38] and Na($C_5H_4COOPh$) (**3**) [39]. The other starting materials were available commercially (Acros Organics).

### 4.2. Measurements

IR spectra were recorded in the 4000–400 $cm^{-1}$ region on a Nicolet Magna 6700 FT-IR spectrometer using diamond smart orbit ATR. $^1H$ NMR spectra were recorded on Bruker 400 and 500 MHz spectrometers at room temperature. $CDCl_3$ was used as obtained (Sigma–Aldrich) without further purification. Chemical shifts are given in ppm relative to TMS. The EPR spectra were recorded on Miniscope MS 300 spectrometers at X-band at ambient temperature.

### 4.3. Preparation of Na($C_5H_4COOCH_2CH_2OMe$) (**4**)

Freshly monomerized cyclopentadiene (5.1 mL; 60.7 mmol) was added dropwise to the suspension sodium sand (1.52 g; 66.1 mmol) in THF (150 mL). When the addition was completed, the reaction mixture was stirred for 30 min at the room temperature. The excess of sodium was filtered off and the pink solution of sodium cyclopentadienide was treated with bis(2-methoxyethyl) carbonate (**17**, 10.6 g; 59,6 mmol). The reaction mixture was stirred under reflux overnight. The volatiles were removed under vacuum and the solid residuum was treated with diethyl ether (100 mL). The suspension was transferred on the glass frit and the product was filtered off, washed with diethyl ether (3 × 30 mL) and dried under vacuum to give white powder. Yield: 7.04 g (37 mmol, 63%). *Anal.* Calc. for $C_9H_{11}NaO_3$: C: 56.84; H, 5.83. Found: C, 56.72; H, 5.89%. IR($cm^{-1}$, ATR): 1641 s [$\nu$(CO)].

### 4.4. Preparation of ($\eta^5$-$C_5H_4COOMe$)$_2VCl_2$ (**5**)

$VCl_3$ (1.06 g; 6.7 mmol) was suspended in THF (40 mL) and stirred at 60 °C for 3 h. The pink suspension was cooled on 0 °C and treated with suspension of Na($C_5H_4COOMe$) (**1**; 2.01 g; 13.8 mmol) in THF (30 mL). The reaction mixture was stirred at room temperature overnight. Celite (5 g) was added to brown suspension and the solvent was vacuum evaporated. The solid residuum was transferred on the extraction frit and extracted with diethyl ether. The extract was treated with an excess of $PCl_3$ (1 mL) and stirred at room temperature overnight. The green precipitate was separated, washed with diethyl ether (3 × 20 mL) and hexane (20 mL) and vacuum dried to give the product as a green powder. Yield: 0.41 g (1.1 mmol, 17%). *Anal.* Calc. for $C_{14}H_{14}Cl_2O_4V$: C, 45.68; H, 3.83. Found: C, 45.52; H, 3.89%. EPR($CH_2Cl_2$): $g_{iso}$ = 1.989, $|A_{iso}|$ = 73.3 G. IR(ATR, $cm^{-1}$): 1732 vs [$\nu$(CO)], 1722 vs [$\nu$(CO)].

### 4.5. Preparation of ($\eta^5$-$C_5H_4COOEt$)$_2VCl_2$ (**6**)

The steps of synthesis followed the procedure for compound **5**. Reagents: $VCl_3$ (1.12 g; 7.1 mmol), Na($C_5H_4COOEt$) (**2**; 2.29 g; 14.3 mmol), $PCl_3$ (1 mL). Yield: 0.59 g (1.5 mmol, 21%). *Anal.* Calc. for $C_{16}H_{18}Cl_2O_4V$: C, 48.51; H, 4.58. Found: C, 48.29; H, 4.65%. EPR($CH_2Cl_2$): $g_{iso}$ = 1.989, $|A_{iso}|$ = 73.2 G. IR(ATR, $cm^{-1}$): 1718 s [$\nu$(CO)].

### 4.6. Preparation of ($\eta^5$-$C_5H_4COOPh$)$_2VCl_2$ (**7**)

The steps of synthesis followed the procedure for compound **5**. Reagents: $VCl_3$ (0.94 g; 6.0 mmol), Na($C_5H_4COOPh$) (**3**; 2.51 g; 12.1 mmol), $PCl_3$ (1 mL). Yield: 0.43 g (0.9 mmol, 15%). *Anal.* Calc. for $C_{24}H_{18}Cl_2O_4V$: C, 58.56; H, 3.69. Found: C, 58.31; H, 3.73%. EPR($CH_2Cl_2$): $g_{iso}$ = 1.989, $|A_{iso}|$ = 73.2 G. IR(ATR, $cm^{-1}$): 1751 s [$\nu$(CO)]. Single crystals of **7** suitable for X-ray analysis were obtained by careful overlayering of the $CH_2Cl_2$ solution with double volume of hexane.

### 4.7. Preparation of ($\eta^5$-$C_5H_4COOCH_2CH_2OMe$)$_2VCl_2$ (**8**)

The steps of synthesis followed the procedure for compound **5**. Reagents: $VCl_3$ (1.00 g; 6.3 mmol), Na($C_5H_4COOCH_2CH_2OMe$) (**4**; 2.46 g, 12.9 mmol), $PCl_3$ (1 mL). Yield: 0.32 g (0.7 mmol, 11%). *Anal.* Calc. for $C_{18}H_{22}Cl_2O_6V$: C, 47.39; H, 4.86. Found: C, 47.17; H, 4.93%. EPR($CH_2Cl_2$): $g_{iso}$ = 1.989, $|A_{iso}|$ = 73.1 G. IR(ATR, $cm^{-1}$): 1716 s [$\nu$(CO)].

### 4.8. Preparation of ($\eta^5$-$C_5H_4COOMe$)$_2VBr_2$ (**9**)

($\eta^5$-$C_5H_4COOMe$)$_2VCl_2$ (**5**; 48 mg; 0.13 mmol) was dissolved in $CH_2Cl_2$ and treated with $BBr_3$ (22 mg; 0.09 mmol). The reaction mixture was stirred 0.5 h. The volatiles were evaporated under vacuum. The crude product was recrystallized from mixture $CH_2Cl_2$/hexane and dried in vacuum to give the product as a green powder. Yield: 0.41 mg (0.09 mmol, 68%). *Anal.* Calc. for $C_{14}H_{14}Br_2O_4V$: C, 36.79; H, 3.09. Found: C, 36.92; H, 3.05%. EPR($CH_2Cl_2$): $g_{iso}$ = 2.027, $|A_{iso}|$ = 65.7 G. IR(ATR, $cm^{-1}$): 1724 vs [$\nu$(CO)]. Single crystals of **9**·$\mathbf{CH_2Cl_2}$ suitable for X-ray analysis were obtained by careful overlayering of the $CH_2Cl_2$ solution with double volume of hexane.

### 4.9. Preparation of ($\eta^5$-$C_5H_4COOEt$)$_2VBr_2$ (**10**)

The steps of synthesis followed the procedure for compound **9**. Reagents: ($\eta^5$-$C_5H_4COOEt$)$_2VCl_2$ (**6**; 42 mg; 0.11 mmol), $BBr_3$ (18 mg; 0.07 mmol). Yield: 37 mg (0.08 mmol, 72%). *Anal.* Calc. for $C_{16}H_{18}Br_2O_4V$: C, 39.62; H, 3.74. Found: C, 39.38; H, 3.82%. EPR($CH_2Cl_2$): $g_{iso}$ = 2.026, $|A_{iso}|$ = 65.8 G. IR(ATR, $cm^{-1}$): 1720 s [$\nu$(CO)].

### 4.10. Preparation of ($\eta^5$-$C_5H_4COOMe$)$_2NbCl_2$ (**11**)

Suspension of Na($C_5H_4COOMe$) (**1**; 0.84 g; 5.8 mmol) in THF (30 mL) was added to suspension of $NbCl_4(THF)_2$ (1.03 g, 2.7 mmol) in THF (30 mL) precooled at 0 °C. The reaction mixture was stirred overnight. The solvent was evaporated under vacuum. Celite (5 g) was added to the brown suspension and the solvent was vacuum evaporated. The solid residuum was transferred on the extraction frit and extracted with $CH_2Cl_2$. The extract was treated with hexane. The precipitate was filtered off, washed with ether and hexane and vacuum dried to give the product as brown powder. Yield: 0.40 g (1.0 mmol, 36%). *Anal.* Calc. for $C_{14}H_{14}Cl_2NbO_4$: C, 41.01; H, 3.44. Found: C, 40.78; H, 3.39. EPR($CH_2Cl_2$): $g_{iso}$ = 1.984, $|A_{iso}|$ = 113.1 G. IR(ATR, $cm^{-1}$): 1732 s [$\nu$(CO)], 1721vs [$\nu$(CO)].

**Table 5**
Crystallographic data for $Cp_2VBr_2$, **7**, **9**·$CH_2Cl_2$, **13**, **15** and **16**.

| Compound | $Cp_2VBr_2$ | **7** | **9**·$CH_2Cl_2$ | **13** | **15** | **16** |
|---|---|---|---|---|---|---|
| Formula | $C_{10}H_{10}VBr_2$ | $C_{24}H_{18}O_4VCl_2$ | $C_{14}H_{14}O_4VBr_2$, $CH_2Cl_2$ | $C_{24}H_{18}O_4NbCl_2$ | $C_{14}H_{14}O_4NbBr_2$ | $C_{16}H_{18}O_4NbBr_2$ |
| Crystal system | orthorhombic | monoclinic | monoclinic | monoclinic | monoclinic | orthorhombic |
| Space group | $P2_12_12_1$ | $C2/c$ | $P2/c$ | $P2_1/c$ | $C2/c$ | $Pbcn$ |
| $a$ (Å) | 6.8880(3) | 27.4670(2) | 10.8410(6) | 6.5570(5) | 20.0123(5) | 11.8000(5) |
| $b$ (Å) | 12.1511(8) | 6.4942(5) | 6.8750(2) | 30.1549(16) | 7.2540(3) | 6.9130(7) |
| $c$ (Å) | 12.5510(6) | 13.3931(3) | 12.0651(6) | 11.2610(12) | 14.4631(3) | 20.7381(8) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 90 | 117.383(5) | 98.538(5) | 105.304(7) | 133.240(2) | 90 |
| $\gamma$ (°) | 90 | 90 | 90 | 90 | 90 | 90 |
| $Z$ | 4 | 4 | 2 | 4 | 4 | 4 |
| $\mu$ ($mm^{-1}$) | 8.500 | 0.749 | 5.368 | 0.839 | 6.023 | 5.451 |
| $D_x$ ($g\,cm^{-3}$) | 2.156 | 1.541 | 2.024 | 1.652 | 2.167 | 2.069 |
| Crystal size (mm) | 0.51 × 0.32 × 0.04 | 0.18 × 0.10 × 0.05 | 0.26 × 0.22 × 0.16 | 0.38 × 0.21 × 0.03 | 0.36 × 0.24 × 0.19 | 0.35 × 0.22 × 0.04 |
| Crystal color | green | light green | dark green | grey | dark green | dark violet |
| Crystal shape | plate | needle | block | plate | plate | plate |
| $\theta$ range (°) | 2.33–27.49 | 1.67–27.49 | 1.90–27.50 | 2.31–27.50 | 2.79–27.49 | 3.42–27.49 |
| $h\ k\ l$ range | −8/8, −15/15, −15/16 | −35/29, −8/7, −16/17 | −14/14, −8/8, −15/14 | −8/7, −39/38, −14/12 | −22/25, −9/8, −18/18 | −13/15, −7/8, −26/22 |
| No. of reflections measured | 9720 | 7073 | 12427 | 16935 | 5821 | 6583 |
| No. of unique reflections; $R_{int}$[a] | 2377, 0.1751 | 2420, 0.0874 | 2023, 0.0500 | 4895, 0.0725 | 1747, 0.0485 | 1926, 0.0404 |
| No. of observed reflections [$I > 2\sigma(I)$] | 2123 | 1541 | 1812 | 4035 | 1586 | 1623 |
| No. of parameters | 118 | 141 | 110 | 280 | 96 | 105 |
| $S$[b] all data | 1.148 | 1.126 | 1.090 | 1.170 | 1.126 | 1.116 |
| $R$[c], $wR$[c] | 0.0422, 0.1019 | 0.0631, 0.0851 | 0.0300, 0.0698 | 0.0517, 0.1097 | 0.0267, 0.0614 | 0.0310, 0.0635 |
| $\Delta\rho$ max., min. [e $Å^{-3}$] | 0.481, −0.597 | 0.441, −0.541 | 0.481, −0.597 | 1.031, −0.848 | 0.558, −0.820 | 0.500, −0.811 |

[a] $R_{int} = \Sigma|Fo^2 - F_{o,mean}{}^2|/\Sigma F_o{}^2$.
[b] $S = [\Sigma(w(F_o{}^2 - F_c{}^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data.
[c] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$for observed data, $wR(F^2) = [\Sigma(w(F_o{}^2 - F_c{}^2)^2)/(\Sigma w(F_o{}^2)^2)]^{½}$ for all data.

### 4.11. Preparation of ($\eta^5$-$C_5H_4COOEt)_2NbCl_2$ (**12**)

The steps of synthesis followed the procedure for compound **11**. Reagents: $NbCl_4(THF)_2$ (1.14 g, 3.0 mmol), Na($C_5H_4COOEt$) (**2**; 1.03 g, 6.4 mmol). Yield: 0.54 g (1.2 mmol, 41%). *Anal.* Calc. for $C_{16}H_{18}Cl_2NbO_4$: C, 43.86; H, 4.14. Found: C, 43.52; H, 4.23%. EPR($CH_2Cl_2$): $g_{iso}$ = 1.984, $|A_{iso}|$ = 112.2 G. IR(ATR, $cm^{-1}$): 1716 s [$\nu$(CO)].

### 4.12. Preparation of ($\eta^5$-$C_5H_4COOPh)_2NbCl_2$ (**13**)

The steps of synthesis followed the procedure for compound **11**. Reagents: $NbCl_4(THF)_2$ (1.27 g, 3.4 mmol), Na($C_5H_4COOPh$) (**3**; 1.41 g, 6.8 mmol). Yield: 0.68 g (1.3 mmol, 38%). *Anal.* Calc. for $C_{24}H_{18}Cl_2NbO_4$: C, 53.96; H, 3.40. Found: C, 53.85; H, 3.52%. EPR($CH_2Cl_2$): $g_{iso}$ = 1.984, $|A_{iso}|$ = 122.7 G. IR(ATR, $cm^{-1}$): 1736 s [$\nu$(CO)]. Single crystals of **13** suitable for X-ray analysis were obtained by careful overlayering of the $CH_2Cl_2$ solution with double volume of hexane.

### 4.13. Preparation of ($\eta^5$-$C_5H_4COOCH_2CH_2OMe)_2NbCl_2$ (**14**)

The steps of synthesis followed the procedure for compound **11**. Reagents: $NbCl_4(THF)_2$ (0.83 g, 2.2 mmol), Na($C_5H_4COOCH_2CH_2$-OMe) (**4**; 0.85 g, 4.5 mmol). Yield: 0.35 g (0.7 mmol, 32%). *Anal.* Calc. for $C_{18}H_{22}Cl_2NbO_6$: C, 43.40; H, 4.45. Found: C, 43.02; H, 4.49%. EPR($CH_2Cl_2$): $g_{iso}$ = 1.984, $|A_{iso}|$ = 112.9 G. IR(ATR, $cm^{-1}$): 1713 s [$\nu$(CO)].

### 4.14. Preparation of ($\eta^5$-$C_5H_4COOMe)_2NbBr_2$ (**15**)

The steps of synthesis followed the procedure for compound **9**. Reagents: ($\eta^5$-$C_5H_4COOMe)_2NbCl_2$ (**11**; 50 mg; 0.12 mmol), $BBr_3$ (20 mg; 0.08 mmol). Yield: 41 mg (0.08 mmol, 67%). *Anal.* Calc. for $C_{14}H_{14}Br_2NbO_4$: C, 33.70; H, 2.83. Found: C, 33.48; H, 2.75%. EPR($CH_2Cl_2$): $g_{iso}$ = 2.019, $|A_{iso}|$ = 102.9 G. IR(ATR, $cm^{-1}$): 1724 s [$\nu$(CO)]. Single crystals of **15** suitable for X-ray analysis were obtained by careful overlayering of the $CH_2Cl_2$ solution with double volume of diethyl ether.

### 4.15. Preparation of ($\eta^5$-$C_5H_4COOEt)_2NbBr_2$ (**16**)

The steps of synthesis followed the procedure for compound **9**. Reagents: ($\eta^5$-$C_5H_4COOEt)_2NbCl_2$ (**12**; 43 mg; 0.10 mmol), $BBr_3$ (16 mg; 0.06 mmol). Yield: 36 mg (0.07 mmol, 69%). *Anal.* Calc. for $C_{16}H_{18}Br_2NbO_4$: C, 36.46; H, 3.44. Found: C, 36.12; H, 3.48%. EPR($CH_2Cl_2$): $g_{iso}$ = 2.019, $|A_{iso}|$ = 102.8 G. IR(ATR, $cm^{-1}$): 1720s [$\nu$(CO)]. Single crystals of **16** suitable for X-ray analysis were obtained by careful overlayering of the $CH_2Cl_2$ solution with double volume of hexane.

### 4.16. Preparation of ($MeOCH_2CH_2O)_2CO$ (**17**)

NaOMe (0.38 g; 8.7 mmol) was added to a round bottom flask containing a mixture of 2-methoxyethanol (76 g; 1.00 mol) and dimethyl carbonate (45 g; 0.50 mol). The flask was equipped with a dephlegmator and the reaction mixture was heated under reflux overnight. Methanol was slowly distilled off from the mixture and the reaction was terminated with addition of water. The emulsion was transferred into the separatory funnel and extracted with pentane (3 × 50 mL). The combined organic layers were dried with magnesium sulfate and the volatiles were vacuum evaporated on rotavapor. The crude product was vacuum distilled (4 mm Hg, 103 °C) to give colorless liquid. Yield: 26 g (146 mmol, 29%). *Anal.* Calc. for $C_7H_{14}O_5$: C, 47.19; H, 7.92. Found: C, 46.96; H, 7.95%. $^1H$ NMR($CDCl_3$, 20 °C): $\delta$ 4.31 (t, $J(^1H,^1H)$ = 4.8 Hz, 4H, $MeOCH_2CH_2$), 3.64 (t, $J(^1H,^1H)$ = 4.8 Hz, 4H, $MeOCH_2CH_2$), 3.41 (s, 6H, $OCH_3$).

### 4.17. Synthesis of [($\eta^3$-$C_3H_5$)($\eta^5$-$C_5H_4COOCH_2CH_2OMe$)Mo(CO)$_2$] (**18**)

Cyclopentadienide **4** (270 μL, 3.22 mmol) was dissolved in THF, cooled at −80 °C and treated with [($\eta^3$-$C_3H_5$)Mo(CO)$_2$(NCMe)$_2$Cl] (1.0 g, 3.22 mmol). The reaction mixture was stirred at room tem-

perature overnight. After that, the volatiles were vacuum evaporated and the residuum was extracted with hot hexane. The yellow powder of the product was obtained after recrystallization from the mixture ether/hexane at −20 °C. Yield: 835 mg (72%, 2.32 mmol). *Anal.* Calc. for $C_{22}H_{20}MoO_3$: C, 46.68; H, 4.48. Found: C, 46.56; H, 4.52%. $^1$H NMR ($CDCl_3$, 400 MHz, 25 °C, $\delta$ ppm): 5.76 (t, $J(^1H,^1H)$ = 2.3 Hz, 2H, $C_5H_4$), 5.38 (t, $J(^1H,^1H)$ = 2.3 Hz, 2H, $C_5H_4$), 4.33 (s-br, 2H, $CH_2CH_2OMe$), 3.92 (s-br, 1H, $C_3H_5$), 3.60 (s-br, 2H, $CH_2CH_2OMe$), 3.38 (s, 3H, $CH_2CH_2OCH_3$), 2.82 (s-br, 2H, $C_3H_5$), 1.03 (s-br, 2H, $C_3H_5$). FTIR (ATR, $cm^{-1}$): 3101 m [$\nu$(CH, Cp)], 3088 m [$\nu$(CH, Cp)], 1941vs [$\nu_a$(CO)], 1858vs [$\nu_s$(CO)], 1704s [$\nu$(CO, COOR)].

### 4.18. Synthesis of $Cp_2VBr_2$

The steps of synthesis followed the procedure for compound **9**. Reagents: $Cp_2VCl_2$ (49 mg; 0.19 mmol), $BBr_3$ (33 mg; 0.13 mmol). Yield: 41 mg (0.12 mmol, 64%). *Anal.* Calc. for $C_{10}H_{10}Br_2V$: C, 35.23; H, 2.96. Found: C, 35.27; H, 2.94. EPR($CH_2Cl_2$): $g_{iso}$ = 2.024, $|A_{iso}|$ = 67.2 G. Single crystals suitable for X-ray analysis were obtained by diffusion diethyl ether vapors into $CH_2Cl_2$ solution of $Cp_2VBr_2$.

### 4.19. Synthesis of $Cp_2NbBr_2$

The steps of synthesis followed the procedure for compound **9**. Reagents: $Cp_2NbCl_2$ (43 mg; 0.15 mmol), $BBr_3$ (25 mg; 0.10 mmol). Yield: 42 mg (0.11 mmol, 72%). *Anal.* Calc. for $C_{10}H_{10}Br_2Nb$: C, 31.37; H, 2.63. Found: C, 31.32; H, 2.58%. EPR($CH_2Cl_2$): $g_{iso}$ = 2.013, $|A_{iso}|$ = 106.4 G.

### 4.20. Crystallography

The X-ray data for crystals of $Cp_2VBr_2$, **7**, **9**·$CH_2Cl_2$, **13**, **15** and **16** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å), a graphite monochromator, and the $\phi$ and $\chi$ scan mode. Data reductions were performed with DENZO-SMN [49]. The absorption was corrected by integration methods [50]. Structures were solved by direct methods (Sir92) [51] and refined by full matrix least-square based on $F^2$ (SHELXL97) [52]. Crystallographic data are summarized in the Table 5.

Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H)$ = 1.2 $U_{eq}$ (pivot atom) or of 1.5 $U_{eq}$ for the methyl moiety with C–H = 0.96, 0.97, and 0.93 Å for methyl, methylene and hydrogen atoms in Cp ring, respectively.

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## Appendix A. Supplementary material

CCDC 907623–907628 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.03.018.

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