



Titanocene(IV) and vanadocene(IV) complexes of dicyanomethanidobenzoate

Jan Honzík^{a,*}, Jaromír Vinklár^a, Milan Erben^a, Lukáš Štrížík^a, Ivana Císařová^b, Zdeňka Padělková^a^a Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic^b Department of Inorganic Chemistry, Faculty of Natural Science, Charles University in Prague, Hlavova 2030, 128 40 Praha 2, Czech Republic

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ABSTRACT

The new titanocene and vanadocene complexes of the non-linear pseudohalides $\text{Cp}_2\text{Ti}(\text{dcmb})_2$, $\text{Cp}_2\text{VCl}(\text{dcmb})$, $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{VCl}(\text{dcmb})$ and $\text{Cp}_2\text{V}(\text{dcmb})_2$ were prepared by reaction of titanocene dichloride (Cp_2TiCl_2) and vanadocene dichlorides (Cp_2VCl_2 , $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{VCl}_2$) with dicyanomethanidobenzoic acid (dcmbH , $\text{PhC}(\text{OH})\text{C}(\text{CN})_2$). These reactions have proven that the dcmb ligand could be coordinated to the central metal by oxygen or nitrogen donor atoms. The bonding mode of the dcmb ligand reflects properties of the central metal. The strongly oxophilic titanium(IV) shows the bonding through oxygen atom while bonding through nitrogen atom was observed for less oxophilic vanadium(IV). The bonding fashion of the dcmb ligands was determined by spectroscopic methods. X-ray diffraction analysis was used for the structure determination of the compounds $\text{dcmbH}\cdot\text{H}_2\text{O}$, $\text{Cp}_2\text{Ti}(\text{dcmb})_2\cdot\text{CH}_2\text{Cl}_2$, $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{VCl}(\text{dcmb})$ and $[\text{Cp}_2\text{V}(\text{OC}(\text{Ph})\text{C}(\text{CN})\text{C}(\text{OMe})\text{NH})][\text{dcmb}]$.

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1. Introduction

Bent metallocene complexes of the type $[\text{Cp}_2\text{MCl}_2]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{M} =$ early transition metal) are currently under comprehensive investigation due to their promising catalytic [1,2] and biological activity [3,4]. Although metallocene complexes of linear pseudohalide ligands $[\text{Cp}_2\text{MX}_2]$ ($\text{X} = \text{NCO}$, NCS , NCSe , N_3 , CN) are known for long time [5–7], their analogues containing non-linear pseudohalides were described recently ($\text{X} = \text{dca}$, tcm , dcnm) [8–10]. The similarity in coordination chemistry of titanocene dichloride (Cp_2TiCl_2 ; **1a**) and vanadocene dichloride (Cp_2VCl_2 ; **2a**) is well known. The ligand-exchange reactions give pseudohalide complexes with ligands bonded through the same donor atom. The only difference was observed when the reactions are carried out in an aqueous solution. In this case, several titanocene complexes give dimers with two bis-cyclopentadienyl titanium(IV) units connected via oxygen bridging $[(\text{Cp}_2\text{TiX})_2\text{O}]$ [9,11,12].

This work is focused on coordination ability of the dicyanomethanidobenzoate (dcmb , $[\text{PhC}(\text{O})\text{C}(\text{CN})_2]^-$). It is a pseudohalide analogue of benzoate containing dicyanomethanide groups ($=\text{C}(\text{CN})_2$) instead of carbonyl oxygen ($=\text{O}$). The reactions with titanocene dichloride (**1**: Cp_2TiCl_2) and vanadocene dichlorides (**2a**: Cp_2VCl_2 , **2b**: $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{VCl}_2$) show the bonding ability of the dcmb ligand. It can be coordinated through oxygen or nitrogen atom as was proposed based on the contribution structures depicted in Scheme 1.

2. Results and discussion

2.1. Syntheses and characterization

Dicyanomethanidobenzoic acid (dcmbH) was prepared according to the procedure published elsewhere [13]. Its recrystallization from wet MeCN gives $\text{dcmbH}\cdot\text{H}_2\text{O}$ that was used for the reactions with bent metallocenes. The X-ray diffraction analysis of $\text{dcmbH}\cdot\text{H}_2\text{O}$ has shown that the dcmb is protonated at oxygen atom (see Fig. 1). The detail description of the molecular structure is given in the separate section. The infrared and Raman spectra show the bands of the $\text{C}\equiv\text{N}$ stretching at 2236 cm^{-1} ($\nu_s(\text{C}\equiv\text{N})$, IR and Raman) 2229 cm^{-1} ($\nu_s(\text{C}\equiv\text{N})$, IR) and 2228 cm^{-1} ($\nu_s(\text{C}\equiv\text{N})$, Raman). The small vibrational coupling of the $\text{C}\equiv\text{N}$ stretching (IR: $\Delta = 7\text{ cm}^{-1}$; Raman: $\Delta = 8\text{ cm}^{-1}$) is caused with nearly orthogonal orientation of the CN groups.

Aqueous solution of titanocene dichloride (**1**) reacts with $\text{dcmbH}\cdot\text{H}_2\text{O}$ giving $\text{Cp}_2\text{Ti}(\text{dcmb})_2$ (**3**) as is shown in Scheme 2. The exchange of both chlorine ligands was evidenced by spectroscopic measurement. The ^1H NMR shows singlet at 6.72 (10H, Cp) and multiplets at ~ 7.45 (d, 4H, Ph), 7.40 (t, 2H, Ph) and 7.11 ppm (t, 4H, Ph). The intensity of the signals is in the line with the proposed structure of compound **3**. The dcmb ligands are bonded through oxygen donor atoms as was proven by ^{13}C NMR spectra. The single band in the region of the cyano groups at 193.6 ppm shows that all four cyano groups of the compound **3** are equivalent.

Infrared and Raman spectra show characteristic bands of Cp_2Ti moiety such as C–H stretching (IR, Raman: $\sim 3100\text{ cm}^{-1}$), Cp ring breathing (Raman: 1130 cm^{-1}), Cp ring tilting (Raman: 269 cm^{-1})

* Corresponding author. Fax: +420 46603 7068.

E-mail address: jan.honzicek@upce.cz (J. Honzík).

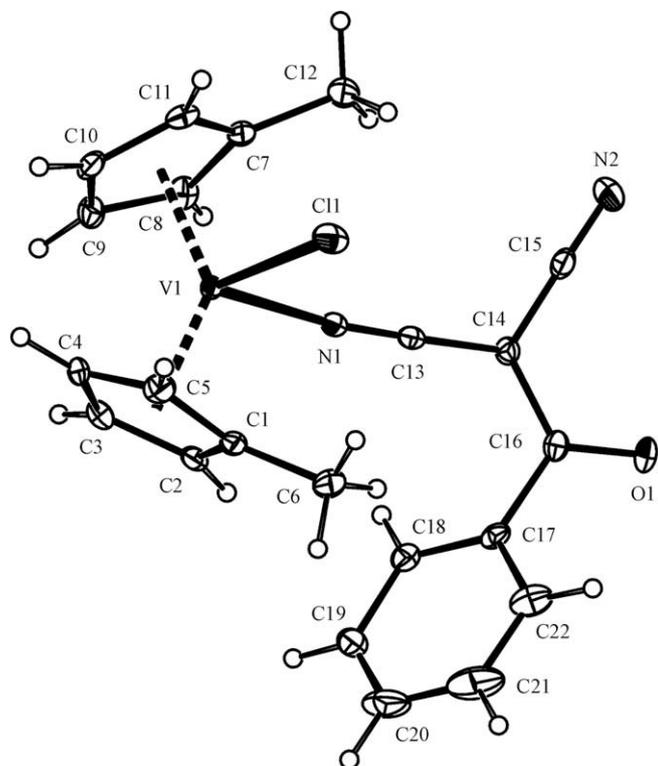


Fig. 3. ORTEP drawing of $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{VCl}(\text{dcmb})$ (**4b**) with atom numbering (ellipsoids: 30% probability). Selected bond lengths (Å) and angles ($^\circ$): V1–N1 2.046(2), V1–Cl1 2.3680(9), Cg(C1–C5)–V1 1.9691(15), Cg(C7–C11)–V1 1.9709(14), C16–O1 1.233(3), C13–N1 1.145(3), C15–N2 1.145(4), C13–C14 1.400(4), C14–C15 1.424(4), C14–C16 1.426(4), C17–C16 1.494(4), N1–V1–Cl1 84.57(7), Cg(C1–C5)–V1–Cg(C7–C11) 135.03(7), V1–N1–C13 168.8(2), N1–C13–C14 177.7(3), N2–C15–C14 178.9(3), C13–C14–C15 117.4(3), C13–C14–C16 122.7(3), C15–C14–C16 119.2(3), O1–C16–C14 122.3(3), O1–C16–C17 120.1(3), C14–C16–C17 117.6(2).

Table 1
Hyperfine coupling constants and g -factors of the vanadocene complexes.

	$ A_{\text{iso}} $ (10^{-4} cm^{-1})	g_{iso}
2a	69.7	1.989
2b	69.6	1.990
4a	69.0	1.987
4b	69.1	1.987
5a	68.4	1.986
6a	67.2	1.983

ano groups coordinated to the metal atom through the nitrogen atom [9,10].

X-ray diffraction analysis of the compound **4b** has proven the proposed molecular structure with dcmb ligand bonded through the nitrogen atom (see Fig. 3).

Compounds **4a**, **4b** and **5a** are paramagnetic making their characterization by NMR spectroscopy quite difficult. However, the oxidation state of vanadium(IV) is suitable to EPR spectroscopy. The

EPR spectra of complexes **4a**, **4b** and **5a**, collected at room temperature in anhydrous CH_2Cl_2 , show the eight-line hyperfine coupling, corresponding to the nuclear spin value of ^{51}V ($I = 7/2$, 99.8%). The $|A_{\text{iso}}|$ and g_{iso} values of compounds **4a**, **4b** and **5a** were found in the range characteristic for the compounds containing $[(\text{Cp}')_2\text{V}]^{2+}$ moiety, see Table 1.

The reactivity of $\text{Cp}_2\text{V}(\text{dcmb})_2$ (**5a**) was further investigated. It was found that coordinated cyano group of the compound **5a** is activated to the nucleophilic attack by methanol. Upon this reaction, ketimate complex $[\text{Cp}_2\text{V}(\text{OC}(\text{Ph})\text{C}(\text{CN})\text{C}(\text{OMe})\text{NH})][\text{dcmb}]$ (**6a**) is formed, see Scheme 4. The EPR spectroscopic measurements proved that this reaction does not produce any other paramagnetic product. The compound **6a** gives the eight-line spectrum with $|A_{\text{iso}}| = 67.2 \times 10^{-4} \text{ cm}^{-1}$ and $g_{\text{iso}} = 1.983$ (see Table 1). The infrared spectrum shows the bands of the cyano groups at 2207, 2201, 2178 and 2152 cm^{-1} . Strong band at 3222 cm^{-1} was assigned to N–H stretching mode of ketimate moiety. The molecular structure of the compound **6a** was determined by X-ray diffraction analysis. It is described in detail in the following section.

2.2. X-ray structures of $\text{dcmbH}\cdot\text{H}_2\text{O}$, **3-CH₂Cl₂**, **4b**, and **6a**

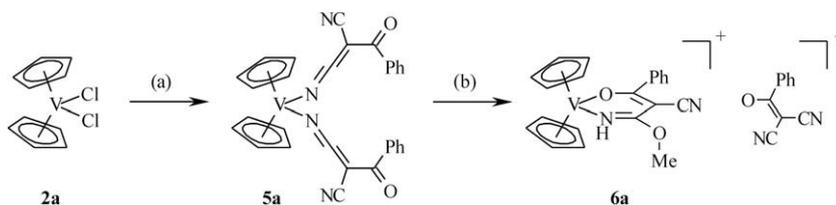
The molecular structures of $\text{dcmbH}\cdot\text{H}_2\text{O}$, **3-CH₂Cl₂**, **4b**, and **6a** are depicted in Figs. 1–4, respectively. Their crystallographic data are summarized in Table 2.

The X-ray structure of the $\text{dcmbH}\cdot\text{H}_2\text{O}$ proves that the dcmb is protonated at oxygen atom. The bond length C–O was found to be considerably longer (1.309(2) Å), and the bond lengths $\text{C}\equiv\text{N}$ are slightly shorter (1.142(3), 1.147(3) Å) than the appropriate bonds in the anionic dcmb that was found in the crystal lattice of the compound **6a** ($\text{C}=\text{O} = 1.243(2) \text{ Å}$, $\text{C}\equiv\text{N} = 1.156(2)$, 1.153(2) Å). The hydrogen bonding interactions are depicted in Fig. 5. Two hydrogen bonds were found between hydrogen atoms of water and cyano groups of dcmb. Further hydrogen bond is between hydroxyl group of dcmbH and oxygen atom of water.

The complexes **3**, **4b**, and **6a** show the typical bent metallocene structure with two η^5 -bonded cyclopentadienyl (**3**, **6a**) or methylcyclopentadienyl rings (**4b**). The two other positions around central metal are occupied with two monodentate (**3**, **4b**) or one bidentate ligand (**6a**).

The dcmb ligands in the compound **3** are bonded through oxygen atoms. The bond lengths Ti–O were found to be 1.947(2) and 1.969(2) Å. The bond angle is O–Ti–O $95.79(9)^\circ$. The distances Ti–O are longer the angle O–Ti–O is larger than those in the benzoate complex $\text{Cp}_2\text{Ti}(\text{OOCPh})_2$ (Ti–O 1.922(7), 1.930(5) Å, O–Ti–O = $91.4(3)^\circ$ [16]). The bond lengths CN vary between 1.136(4) and 1.144(5) Å. The bond lengths CO were found to be around 1.274(4) and 1.275(4) Å.

The compound **4b** has one dcmb ligand bonded to the vanadium(IV). The distance V–N was found to be 2.046(2) Å. This value is similar to pseudohalides bonded through sp -nitrogen atom ($\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{V}(\text{NCO})_2$, $\text{Cp}_2\text{V}(\text{NCS})_2$, $\text{Cp}_2\text{V}(\text{dca})_2$, $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{V}(\text{dca})_2$, (V–N $\sim 2.03\text{--}2.05 \text{ Å}$) [8,10,17,18] and shorter than in $\text{Cp}_2\text{V}(\text{N}_3)_2$ ($\sim 2.08 \text{ Å}$) that is pseudohalide bonded through sp^2 -nitrogen atom [19]. Longer distance V–N was also reported for cationic com-



Scheme 4. Preparation of compounds **5a** and **6a**: (a) water, dcmbH in CH_2Cl_2 , aqueous NaOH; (b) MeOH.

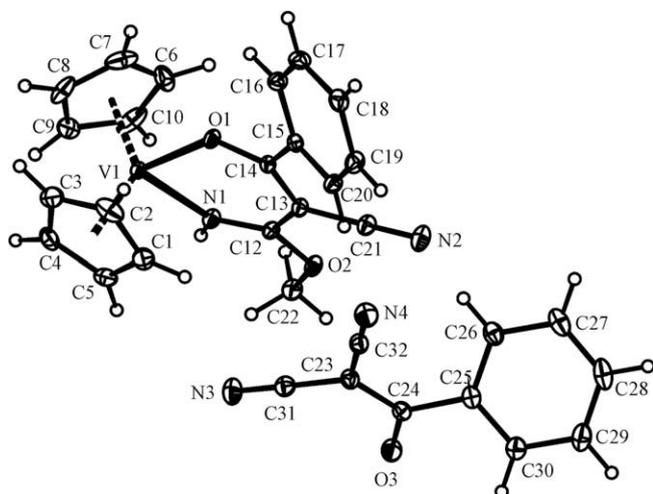


Fig. 4. ORTEP drawing of $\text{Cp}_2\text{V}(\text{OC}(\text{Ph})\text{C}(\text{CN})\text{C}(\text{OMe})\text{NH})[\text{dcmb}]$ (**6a**) with atom numbering (ellipsoids: 30% probability). Selected bond lengths (Å) and angles ($^\circ$): V1–O1 1.9895(11), V1–N1 2.0775(14), $\text{C}_g(\text{C1–C5})\text{–V1}$ 1.9702(9), $\text{C}_g(\text{C6–C10})\text{–V1}$ 1.9654(10), C14–O1 1.2848(18), C12–N1 1.290(2), C21–N2 1.147(2), C12–O2 1.3427(19), C22–O2 1.451(2), C24–O3 1.243(2), C31–N3 1.156(2), C32–N4 1.153(2), O1–V1–N1 83.92(5), $\text{C}_g(\text{C1–C5})\text{–V1}\text{–}\text{C}_g(\text{C6–C10})$ 134.10(4), V1–O1–C14 131.57(11), V1–N1–C12 129.13(12), C12–O2–C22 118.07(13), N2–C21–C13 177.8(2), N3–C31–C23 178.4(2), N4–C32–C23 179.6(2).

pounds with neutral ligands bonded through sp -nitrogen atom $[\text{Cp}_2\text{V}(\text{NCMe})\text{Cl}][\text{FeCl}_4]$ (2.087(2) Å) [20]. The bond length of the coordinated CN group (1.145(3) Å) was found to be the same as the uncoordinated one (1.145(4) Å). The bond length CO is significantly shorter (1.233(3) Å) than in the titanium compound 1.275(4) Å. It is similar to the anionic dcmb (1.243(2) Å).

Compound **6** contains vanadocene(IV) ketimate cation, while the dcmb counter anion is out of the primary coordination sphere of the vanadium. The bond length V–O (1.9895(11) Å) and bond angle V–O–C (131.57(11) $^\circ$) are similar to those in complex

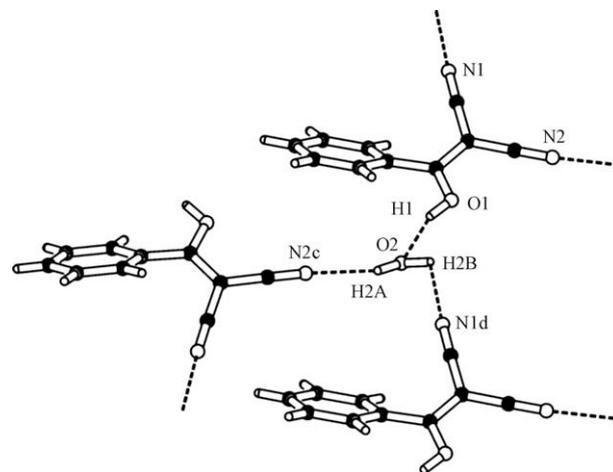


Fig. 5. Hydrogen bonds in $\text{dcmbH}\cdot\text{H}_2\text{O}$. Selected bond lengths (Å) and angles ($^\circ$): O1...O2 2.549(2), O2...N2c 2.861(3), O2...N1d 2.856(3). Operators for generating equivalent atoms: for c: $-x+2, y-1/2, -z+3/2$; for d: $x+1, y, z+1$.

$[\text{Cp}_2\text{V}(\text{acac})][\text{OTf}]$ (V–O \sim 2.00 Å; V–O–C \sim 129.7 $^\circ$) [21]. The distance V–N is significantly shorter than in compounds with neutral ligands bonded through sp^2 -nitrogen atom $[\text{Cp}_2\text{V}(\text{bpy})][\text{OTf}]_2$, $[\text{Cp}_2\text{V}(\text{phen})][\text{OTf}]_2$ (\sim 2.13–2.14 Å) and similar with those or with those with anionic univalent ligand bonded through sp^2 -nitrogen atom $\text{Cp}_2\text{V}(\text{N}_3)_2$ (\sim 2.08 Å) [19].

3. Conclusions

The coordination chemistry of the dcmb ligand was investigated using reactions of dcmbH with titanocene dichloride (**1**) and vanadocene dichlorides (**2a** and **2b**). These reactions give two types of the complexes. The reaction with titanocene dichloride (**1**) forms $\text{Cp}_2\text{Ti}(\text{dcmb})_2$ (**3**) that have both dcmb ligands bonded through the oxygen atoms. Bonding of the dcmb ligands

Table 2

Crystallographic data for $\text{dcmbH}\cdot\text{H}_2\text{O}$, **3**· CH_2Cl_2 , **4b** and **6a**.

Compound	$\text{dcmbH}\cdot\text{H}_2\text{O}$	3 · CH_2Cl_2	4b	6a
Formula	$\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2$	$\text{C}_{31}\text{H}_{22}\text{Cl}_2\text{N}_4\text{O}_2\text{Ti}$	$\text{C}_{22}\text{H}_{19}\text{ClN}_2\text{OV}$	$\text{C}_{31}\text{H}_{24}\text{N}_4\text{O}_3\text{V}$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	7.2938(9)	20.2962(13)	10.2582(8)	9.5171(3)
b (Å)	14.4572(9)	9.4628(8)	16.1031(7)	11.3965(3)
c (Å)	9.7381(16)	14.6041(9)	12.3337(9)	12.2166(3)
α ($^\circ$)	–	–	–	84.4690(15)
β ($^\circ$)	115.559(10)	93.387(9)	112.851(6)	81.1871(14)
γ ($^\circ$)	–	–	–	79.8848(16)
Z	4	4	4	2
μ (mm^{-1})	0.097	0.533	0.685	0.427
D_x (g cm^{-3})	1.349	1.426	1.464	1.424
Crystal size (mm)	$0.80 \times 0.55 \times 0.10$	$0.68 \times 0.17 \times 0.10$	$0.20 \times 0.20 \times 0.13$	$0.25 \times 0.20 \times 0.18$
Crystal color	Colourless	Yellow	Green	Green
Crystal shape	Plate	Block	Block	Plate
θ range ($^\circ$)	2.71–27.49	2.01–27.50	3.32–27.50	1.7–27.5
hkl range	–8/9, –18/18, –12/12	–26/26, –12/11, –18/16	–12/13, –20/19, –16/14	–12/12, –14/14, –15/15
No. of reflections measured	9936	24,803	17,288	11,133
No. of unique reflections; R_{int}^a	2092, 0.123	6363, 0.206	4298, 0.083	5909, 0.035
No. of observed reflections ($I > 2\sigma(I)$)	1569	4770	2942	4772
No. of parameters	127	362	244	352
S^b all data	1.084	1.116	1.095	1.008
R^c, wR^c	0.0604, 0.0860	0.0655, 0.0948	0.0528, 0.0978	0.0380, 0.1013
$\Delta\rho$, max., min. ($e \text{ \AA}^{-3}$)	0.439, –0.539	0.820, –0.652	0.331, –0.444	0.267, –0.386

^a $R_{\text{int}} = \sum |F_o^2 - F_c^2| / \sum F_o^2$.

^b $S = [\sum (w(F_o^2 - F_c^2)^2) / (N_{\text{differs}} - N_{\text{params}})]^{1/2}$ for all data.

^c $R(F) = \sum ||F_o| - F_c| / \sum |F_o|$ for observed data, $wR(F^2) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$ for all data.

through the nitrogen atoms was observed in the case of the vanadocene compounds $\text{Cp}_2\text{VCl}(\text{dcmb})$ (**4a**), $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{VCl}(\text{dcmb})$ (**4b**) and $\text{Cp}_2\text{V}(\text{dcmb})_2$ (**5a**). The bonding mode of the dcmb ligand reflects properties of the central metal. The more oxophilic titanium(IV) is bonding the dcmb ligand through oxygen atom while bonding through nitrogen atom was observed for less oxophilic vanadium(IV). Both types of the bonding were evidenced by spectroscopic measurements. The structures of the compounds **3** and **4b** were determined by X-ray diffraction analysis.

4. Experimental

4.1. Methods and materials

All reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Water was distilled and saturated with argon. Other solvents were dried by standard methods and saturated with argon. The starting materials Cp_2TiCl_2 (**1**) [22], Cp_2VCl_2 (**2a**) [22], $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{VCl}_2$ (**2b**) [23] and dcmbH [13] were prepared according to published methods. IR spectra were recorded in 4000–350 cm^{-1} region on a Perkin–Elmer 684 spectrometer in KBr pellets. Raman spectra were run on a Bruker IFS 55 equipped with FRA 106 extension at 50–3500 cm^{-1} in quartz capillaries. The EPR spectra were recorded on an ERS 221 (ZWG Berlin) spectrometer at X-band in flat cuvettes at ambient temperature.

4.2. Synthesis of dcmbH-H₂O

DcmbH (2 g, 12 mmol) was dissolved in wet MeCN. The solvent was allowed to evaporate over time to give large crystals of dcmbH-H₂O. Yield: 2.1 g (11 mmol, 95%). Anal. Calcd for $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2$: C, 63.82; H, 4.28; N, 14.89. Found: C, 63.93; H, 4.18; N, 14.95%. ¹H NMR(CD_3CN , 360 MHz): 8.78 (s-br, 1H, OH), 7.73–7.65 (m, 3H, C₆H₅), 7.57 (t, *J* = 7.6 Hz, 2H, C₆H₅). ¹³C NMR(CD_3CN , 91 MHz): 184.2 (2C, CN), 134.3 (1C, C₆H₅), 131.6 (1C_{ipso}, C₆H₅), 129.8 (2C, C₆H₅), 129.2 (2C, C₆H₅), 115.3 (1C, C=C), 113.5 (1C, C=C). IR (KBr pellet, cm^{-1}): 3408s-br, 3073w, 2236s, 2229s, 1602s, 1593s, 1564s, 1557s, 1554s, 1448s, 1387s, 1356m, 1318m, 1263w, 1226m, 1173m, 1100m, 1029m, 905m, 779s, 709s, 695s, 591m, 559m, 440w, 494w, 388m. Raman (quartz capillary, cm^{-1}): 3079(1), 3070(<1), 2236(7), 2228(8), 1602(10), 1564(2.5), 1498(<1), 1448(<1), 1387(5), 1228(1), 1162(1), 1030(1), 1003(4), 981(<1), 910(<1), 850(<1), 781(1), 712(<1), 696(<1), 686(1), 618(<1), 590(<1), 558(<1), 495(<1), 467(<1), 438(<1), 410(<1), 339(<1), 242(<1), 212(<1), 193(1), 169(3), 120(4). Single crystals suitable for X-ray diffraction analysis were obtained upon slow evaporation of the MeCN solution.

4.3. Synthesis of complex $\text{Cp}_2\text{Ti}(\text{dcmb})_2$ (**3**)

0.14 g (1.18 mmol) of dcmbH-H₂O was added to the aqueous solution of Cp_2TiCl_2 (**1**) (0.14 g; 0.56 mmol) in water (10 ml). The suspension was stirred for 1 h at room temperature. The precipitate of the product was filtered out using glass frit and dried under vacuum. The crude product was recrystallized from CHCl_3 /hexane giving orange powder of the compound **3**. Yield: 0.17 g (0.33 mmol, 59%). Anal. Calcd for $\text{C}_{30}\text{H}_{20}\text{N}_4\text{O}_2\text{Ti}$: C, 69.78; H, 3.90; N, 10.85. Found: C, 69.56; H, 3.72; N, 10.91%. ¹H NMR(CD_2Cl_2 , 360 MHz): 7.46 (d, *J* = 7.3 Hz, 4H, C₆H₅), 7.40 (t, *J* = 7.5 Hz, 2H, C₆H₅), 7.11 (t, *J* = 7.8 Hz, 4H, C₆H₅), 6.72 (s, 10H, C₅H₅). ¹³C NMR(CD_2Cl_2 , 91 MHz): 193.6 (4C, CN), 134.6 (2C_{ipso}, C₆H₅), 132.7 (2C, C₆H₅), 128.8 (4C, C₆H₅), 128.4 (4C, C₆H₅), 121.1 (10C, C₅H₅), 117.0 (1C, C=C), 116.4 (1C, C=C). IR (KBr pellet, cm^{-1}): 3121m, 2214s, 2202m, 1470vs, 1437s, 1398s, 1219m, 1014m, 837m, 781s,

710m, 696m, 627m, 557m. Raman (quartz capillary, cm^{-1}): 3134(1), 3122(1), 3115(1), 3102(1), 3069(2), 2216(10), 2206(9), 1600(6), 1500(3), 1477(2), 1438(3), 1419(6), 1364(2), 1220(2), 1177(2), 1162(1), 1130(7), 1064(1), 1033(1), 842(2), 788(1), 722(2), 688(1), 616(1), 563(1), 447(1), 414(2), 378(4), 348(1), 299(3), 269(9), 223(1), 206(4). The single crystals of **3**· CH_2Cl_2 suitable for X-ray structure analysis were prepared by careful overlaying of the CH_2Cl_2 solution with hexane at 6 °C.

4.4. Synthesis of complex $\text{Cp}_2\text{VCl}(\text{dcmb})$ (**4a**)

0.14 g (1.18 mmol) of dcmbH-H₂O was added to the aqueous solution of Cp_2VCl_2 (**2a**) (0.14 g; 0.56 mmol) in water (10 ml). The suspension was stirred for 1 h at room temperature. The precipitate of the product was filtered out using glass frit and dried under vacuum. The crude product was recrystallized from CH_2Cl_2 /hexane giving purple powder of the compound **4a**. Yield: 0.15 g (0.39 mmol, 70%). Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{ClN}_2\text{OV}$: C, 62.27; H, 3.92; N, 7.26. Found: C, 62.41; H, 3.74; N, 7.49%. EPR (CH_2Cl_2 solution): $|A_{\text{iso}}| = 69.0 \times 10^{-4} \text{ cm}^{-1}$, $g_{\text{iso}} = 1.987$. IR (Nujol mull, cm^{-1}): 3095m, 2210s, 2164s, 1728m, 1593m, 1564m, 1261m, 1155m, 1093m, 1074m, 1026m, 840m, 803m.

4.5. Synthesis of complex $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{VCl}(\text{dcmb})$ (**4b**)

0.14 g (1.18 mmol) of dcmbH-H₂O was added to the aqueous solution of $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{VCl}_2$ (**2b**) (0.16 g; 0.57 mmol in 10 ml of water). The suspension was stirred for 1 h at room temperature. The precipitate of the product was filtered on the frit and dried under vacuum. The crude product was recrystallized from CH_2Cl_2 /hexane giving purple powder of the compound **4b**. Yield: 0.17 g (0.41 mmol, 72%). Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{ClN}_2\text{OV}$: C, 63.86; H, 4.63; N, 6.77. Found: C, 63.59; H, 4.57; N, 6.51%. EPR (CH_2Cl_2 solution): $|A_{\text{iso}}| = 69.1 \times 10^{-4} \text{ cm}^{-1}$, $g_{\text{iso}} = 1.987$. IR (Nujol mull, cm^{-1}): 3084m, 2208s, 2160s, 1593s, 1564s, 1326s, 1167m, 1074m, 1028m, 908m, 854s, 791m, 704s, 552m. The single crystals suitable for X-ray structure analysis were prepared by careful overlaying of the CH_2Cl_2 solution with hexane at 6 °C.

4.6. Synthesis of complex $\text{Cp}_2\text{V}(\text{dcmb})_2$ (**5a**)

0.15 g (0.6 mmol) of Cp_2VCl_2 (**2a**) was dissolved in water (10 ml) and vigorously stirred with the solution of 0.14 g (1.2 mmol) of dcmbH-H₂O in CH_2Cl_2 (20 ml) was added. Two milliliters of carbonate free NaOH solution (0.6 mol l⁻¹) was added dropwise to this mixture. Upon the addition, the blue-green water layer turns colorless, whereas the organic layer turns to purple. The organic layer was separated and dried over MgSO_4 . The volatiles were evaporated under vacuum yielding red powder of compound **5a**. Yield: 0.24 g (0.46 mmol, 78%). Anal. Calcd for $\text{C}_{30}\text{H}_{20}\text{N}_4\text{O}_2\text{V}$: C, 69.37; H, 3.88; N, 10.79. Found: C, 69.12; H, 3.60; N, 10.98%. EPR (CH_2Cl_2 solution): $|A_{\text{iso}}| = 68.4 \times 10^{-4} \text{ cm}^{-1}$, $g_{\text{iso}} = 1.986$. IR (KBr pellet, cm^{-1}): 3112m, 2963m, 2211s, 2193s, 2167s, 1597s, 1567s, 1446m, 1328s, 1262m, 1095s, 1024s, 930m, 848m, 802s, 703s, 552m, 394m.

4.7. Synthesis of $[\text{Cp}_2\text{V}(\text{OC}(\text{Ph})\text{C}(\text{CN})\text{C}(\text{OMe})\text{NH})][\text{dcmb}]$ (**6a**)

The compound **5a** (0.10 g; 0.19 mmol) was dissolved in dry methanol and heated for 5 min under reflux. The volatiles were evaporated *in vacuo* yielding brown powder of compound **6a**. Yield: 0.09 g (0.18 mmol, 94%). Anal. Calcd for $\text{C}_{31}\text{H}_{24}\text{N}_4\text{O}_3\text{V}$: C, 67.51; H, 4.39; N, 10.16. Found: C, 67.73; H, 4.52; N, 9.84%. EPR (methanol solution): $|A_{\text{iso}}| = 67.2 \times 10^{-4} \text{ cm}^{-1}$, $g_{\text{iso}} = 1.983$. IR (KBr pellet, cm^{-1}): 3222s, 3110m, 2207s, 2201s, 2178sh, 2152sh, 1614vs, 1468s, 1436m, 1373s, 1261m, 1229m, 1218m, 1143m,

1070m, 1004m, 909w, 845m, 791m, 746w, 720w, 701w, 667w, 604m. Single crystals suitable for X-ray structure analysis were obtained by slow evaporation of methanol solution at room temperature.

4.8. Crystallography

The X-ray data for the crystals of dcmbH₂O, **3-CH₂Cl₂**, **4b** and **6a** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$), a graphite monochromator, and the φ and χ scan mode. Data reductions were performed with DENZO-SMN [24]. The absorption was corrected by integration methods [25]. Structures were solved by direct methods (SIR92) [26] and refined by full matrix least-square based on F^2 (SHELXL97) [27]. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{pivot atom})$ or of $1.5U_{\text{eq}}$ for the methyl moiety with C–H = 0.96, 0.97, 0.98 and 0.93 Å for methyl, methylene, methine and hydrogen atoms in aromatic ring, respectively, and 0.86 Å for N–H and 0.82 Å for O–H bonds.

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Appendix A. Supplementary data

CCDC 738949, 738948, 738947 and 738950 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 doi:10.1016/j.jorganchem.2009.08.037.

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