

Available online at www.sciencedirect.com



Inorganica Chimica Acta

Inorganica Chimica Acta 358 (2005) 814-819

Note

www.elsevier.com/locate/ica

# Synthesis, characterization and structure of metallocene dicyanamide complexes

Jan Honzíček<sup>a</sup>, Milan Erben<sup>a</sup>, Ivana Císařová<sup>b</sup>, Jaromír Vinklárek<sup>a,\*</sup>

<sup>a</sup> The Department of General and Inorganic Chemistry, University of Pardubice, nám. Čs. legií 565, 532 10 Pardubice, Czech Republic <sup>b</sup> Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic

> Received 13 April 2004; accepted 22 September 2004 Available online 22 October 2004

### Abstract

The bis(cyclopentadienyl) complexes  $[Cp_2Ti(dca)]_2O$  and  $Cp_2V(dca)_2$  (dca = dicyanamide) have been prepared by reaction of sodium dicyanamide with aqueous solution of titanocene dichloride and vanadocene dichloride, respectively. The X-ray structure analyses of both complexes confirmed monodentate coordination of dicyanamide ligand through the terminal nitrogen atom of cyano group.

© 2004 Elsevier B.V. All rights reserved.

*Keywords:* Titanocene; Vanadocene; Pseudohalide; Dicyanamide complexes; X-ray structure; NMR spectroscopy; EPR spectroscopy; Mass spectrometry

#### 1. Introduction

The syntheses and characterization of metallocene pseudohalide complexes of  $\eta^5$ -Cp<sub>2</sub>MX<sub>2</sub> (M = Ti, V; X = NCO, NCS, NCSe, N<sub>3</sub>, CN) type have been subject of several studies [1–4]. The molecular structures of some titanocene and vanadocene complexes with linear pseudohalide ligands have been determined by X-ray diffraction analysis [5–11]. The bonding mode of the pseudohalide ligand in the other complexes was identified by spectroscopic measurements, particularly by the vibrational spectroscopy.

Although many transition metal complexes with dicyanamide ligand (dca thorough this paper) were studied, no crystal structure of complex with metals of group IV or V is known [12]. The aim of this study is to prepare new pseudohalide metallocene complexes and to deter-

E-mail address: jaromir.vinklarek@upce.cz (J. Vinklárek).

mine the bonding mode of the dicyanamide ligand in this type of complexes.

# 2. Results and discussion

The title compounds  $[Cp_2Ti(dca)]_2O$  (1) and  $Cp_2V(dca)_2$  (2) were prepared from appropriate metallocene dichlorides ( $Cp_2TiCl_2$  and  $Cp_2VCl_2$ , respectively) by a reaction with sodium dicyanamide in aqueous solution. Both complexes were characterized by elemental analysis, vibrational spectra and mass spectrometry. The <sup>1</sup>H and <sup>13</sup>C NMR spectra for diamagnetic titanocene compound 1 and fluid solution EPR spectrum for paramagnetic vanadocene complex 2 were measured. The structures of both compounds were determined by single crystal X-ray diffraction analysis.

Both Raman and infrared spectra of 1 and 2 show absorption bands typical for bent Cp<sub>2</sub>M fragment. IR bands with medium to strong intensity at  $\sim 3100 \text{ cm}^{-1}$  correspond to the stretching C–H vibrations of  $\eta^5$ -bonded Cp ring, strong Raman band at  $\sim 1130 \text{ cm}^{-1}$ 

<sup>\*</sup> Corresponding author. Tel: +420 46603 7164; fax: +420 46603 7068.

<sup>0020-1693/</sup>\$ - see front matter © 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2004.09.030

can be assigned to "ring breathing" mode and the strongest Raman band in the region  $270-285 \text{ cm}^{-1}$  is bending  $\delta_{Cp-M-Cp}$  ("ring tilting" mode). The presence of both "ring breathing" and "ring tilting" bands in Raman spectra of prepared complexes unambiguously verifies that in the bent  $Cp_2M$  the moiety remains stable [13]. The infrared spectrum of 1 contains very strong absorption band at 736 cm<sup>-1</sup>, which is characteristic for titanium(IV) compounds with Cp<sub>2</sub>Ti-O-TiCp<sub>2</sub> unit [14]. Additionally in Raman and IR spectra of 1, which was characterized as solvate with dichloromethane, the weak band at 2985 cm<sup>-1</sup> corresponding to  $v_{CH}$  vibration of CH<sub>2</sub>Cl<sub>2</sub> was found. In the infrared spectra of both compounds studied, three very intensive bands (one symmetric and two asymmetric C=N stretching vibrations of dca ligand) at  $2295 \pm 4$ ,  $2244 \pm 12$  and  $2190 \pm 20 \text{ cm}^{-1}$  were observed. In Raman spectra, only band of the symmetric C≡N stretching vibration (2230  $cm^{-1}$  for 1 and 2236  $cm^{-1}$  for 2) was found.

The <sup>1</sup>H NMR spectrum of compound **1** shows two singlet signals at 6.27 ppm (Cp protons) and 5.32 ppm (CH<sub>2</sub>Cl<sub>2</sub>) in an integral ratio of 10:1. <sup>13</sup>C NMR spectrum of **1** contains single resonance of Cp ring carbons at 116.8 ppm and low intensity signal of dca ligand carbons at 134.2 ppm. The presence of one resonance for both carbons of dca group suggests fluxionality of dicyanamide ligand in solution during NMR experiment. Singlet signal at 53.4 ppm was assigned to carbon resonance of dichloromethane, which is present in crystal lattice (see Fig. 1).

The EPR spectrum of acetone solution of **2** measured at room temperature shows the expected eight lines due



Fig. 1. ORTEP drawing of the molecular structure of  $[Cp_2Ti(dca)]_2O$ .  $CH_2Cl_2$  (1) with atom numbering scheme. (ellipsoids: 30% probability).

Table	1
	-

Isotropic hyperfine coupling constant  $(10^{-4} \text{ cm}^{-1})$  and *g*-tensor for *N*-bonded pseudohalide complexes (Cp<sub>2</sub>VX<sub>2</sub>)

Х	$ A_{\rm iso} ^{\rm a}$	$g_{ m iso}$	Ref.
dca	70.2	1.984	this work
NNN	66.7	1.985	[3]
NCO	70.5	1.985	[3]
NCS	67.9	1.991	[3]
NCSe	68.4	1.990	[3]

<sup>a</sup> Data from [3] were converted from the units of G to the  $10^{-4}$  cm<sup>-1</sup> through division by the factor 1.0698 (g<sub>e</sub>/g), where g<sub>e</sub> = 2.0023.

to the interaction of the unpaired electron with <sup>51</sup>V (I = 7/2; 99.8%) nucleus. Both isotropic hyperfine coupling constant ( $|A_{iso}| = 70.2 \times 10^{-4} \text{ cm}^{-1}$ ) and isotropic *g*-factor ( $g_{iso} = 1.984$ ) are in the range characteristic for other *N*-bonded pseudohalide vanadocene complexes (see Table 1) [3].

Fig. 1 depicts the molecular structure of the complexes 1, important bond lengths and angles are summarized in Table 2. The compound **1** is dinuclear complex with two titanocene units connected via oxygen bridge and the whole molecule has approximately  $C_2$  symmetry. Similar to the other oxo-bridged dinuclear complexes, the Ti-O-Ti moiety is nearly linear (Ti-O-Ti angle is 172.9°). The coordination at each titanium center approaches the tetrahedral geometry (Cp-Ti- $Cp = 131.2^{\circ}, 131.3^{\circ}, N-Ti-O = 93.5^{\circ}, 94.6^{\circ}$ ). The comparison of structural parameters with the other titanocene dinuclear complexes shows that the structural parameters of (Cp<sub>2</sub>Ti)<sub>2</sub>O moiety are not significantly affected by the pseudohalide ligand exchange (see Table 4). Both dca groups act as univalent ligands coordinated through the terminal nitrogen atom. The Ti-N bond lengths (2.10 Å) are comparable with dinuclear complexes  $[(Cp)_2Ti(N_3)]_2O$  (2.09 Å) [15] or  $[(CH_3-$ 

Table 2

Selected bond dist	ances (A) and an	ngles (°) for complex 1	1
Coordination about	t the titanium ato	oms	
Til-Cg1 <sup>a</sup>	2.0671(13)	Ti1–N1	2.097(2)
Til-Cg2 <sup>a</sup>	2.0643(11)	Ti2–N4	2.097(2)
Ti2–Cg3 <sup>a</sup>	2.0743(11)	Ti1–O1	1.8432(14)
Ti2-Cg4 <sup>a</sup>	2.0668(11)	Ti2–O1	1.8314(14)
Cg1-Til-Cg2a	131.28(5)	Ti1-O1-Ti2	172.89(9)
Cg <sub>3</sub> -Ti2-Cg <sub>4</sub> <sup>a</sup>	131.21(5)	Til-Nl-Cl	163.34(18)
N1-Ti1-O1	93.48(7)	Ti2-N4-C3	168.77(19)
N4-Ti2-O1	94.63(7)		
Dicyanamide group	25		
C(1)–N(1)	1.147(3)	C(3)–N(4)	1.145(3)
N(2)–C(1)	1.291(3)	N(5)–C(3)	1.298(3)
N(2)–C(2)	1.301(3)	N(5)–C(4)	1.316(4)
C(2)–N(3)	1.161(3)	C(4)–N(6)	1.155(4)
N(1)-C(1)-N(2)	171.9(3)	N(4)-C(3)-N(5)	175.3(3)
C(1)-N(2)-C(2)	122.9(2)	C(3)-N(5)-C(4)	118.9(2)
N(2)-C(2)-N(3)	173.0(3)	N(5)-C(4)-N(6)	174.3(3)

<sup>a</sup> Cg – the centroid of cyclopentadienyl ring.

Table 3	
Selected bond distances (Å) and angles (°) for complex	x 2

Coordination about	t the vanadium	atom	
V1-Cg1 <sup>a</sup>	1.9597(9)	V1-N1	2.0524(17)
V1-Cg2 <sup>a</sup>	1.9633(6)	V1-N6	2.0515(15)
Cg <sub>1</sub> -V1-Cg <sub>2</sub> <sup>a</sup>	133.67(4)	V1-N1-C2	174.42(18)
N1-V1-N6	85.04(7)	V1-N6-C7	175.91(17)
Dicyanamide group	<i>PS</i>		
C(2)–N(1)	1.154(3)	C(7)–N(6)	1.152(3)
N(3)–C(2)	1.290(3)	N(8)–C(7)	1.301(3)
N(3)–C(4)	1.308(3)	N(8)–C(9)	1.322(3)
C(4)–N(5)	1.146(3)	C(9)–N(10)	1.153(3)
N(1)–C(2)–N(3)	174.0(2)	N(6)-C(7)-N(8)	173.5(2)
C(2)–N(3)–C(4)	121.4(2)	C(7)-N(8)-C(9)	119.35(18)
N(3)-C(4)-N(5)	174.3(2)	N(8)-C(9)-N(10)	173.2(2)

<sup>a</sup> Cg – the centroid of cyclopentadienyl ring.

 $C_5H_4)_2Ti(NCSe)]_2O(2.09 Å)$  [8] and slightly longer than those in mononuclear compounds  $Cp_2Ti(NCO)_2$  [5],  $Cp_2Ti(NCS)_2$  [6],  $(t-BuC_5H_4)_2Ti(NCS)_2$  [7],  $(CH_3C_5-H_4)_2Ti(NCSe)_2$  [8] or  $Cp_2Ti(N_3)_2$  (2.01–2.04 Å) [9]. The compound 1 crystallizes with one molecule of  $CH_2Cl_2$ , which connects terminal nitrogen atoms of dicyanamide group by intermolecular hydrogen interactions N3···H5B–C5 and N6···H5A–C5 (N···C 3.295(4) Å, N···H–C 163° and 3.295 Å, 163°, respectively).

Fig. 2 presents molecular structure of the complex 2; Table 3 lists the important structural parameters. The molecule of **2** has typical bent metallocene structure in which two  $\eta^5$ -bonded Cp rings and two nitrogen atoms of dca ligands occupy the pseudotetrahedral coordination sites around the vanadium(IV) center. V-ring centroid distance (1.96 Å) and ring centroid–V–ring centroid angle (133.7°) are comparable with the other vanadocene(IV) complexes [11,16–19]. As well as in **1**, the dicyanamide ligands are monodentate bonded via the terminal nitrogen atom and V–N–C bond angles (174.4°, 175.9°) are almost linear. The vanadium–nitrogen bond lengths (2.05 Å) are slightly shorter than in

Table 4 Comparison of structural parameters for the oxygen-bridged titanocene complexes [Cp<sub>2</sub>TiX]<sub>2</sub>O

······ ·······························						
Х	Ti–Cg <sup>a</sup>	Ti–O	Cg–Ti–Cg <sup>a</sup>	O–Ti-X	Ti-O-Ti	Ref.
dca	2.068	1.837	131.2	94.1	172.9	this work
N <sub>3</sub>	2.088	1.831	131.4	95.5	172.0	[15]
SeCN <sup>b</sup>	2.090	1.838	131.8	94.2	173.4	[8]
CN	2.075	1.836	132.9	94.0	174.1	[21]
Cl	2.084	1.837	129.6	95.9	173.1	[22]
OOCCF <sub>3</sub>	2.083	1.836	131.6	93.7	173.3	[23]
NO <sub>3</sub>	2.076	1.835	131.4	88.4	171.8	[24]
C <sub>9</sub> H <sub>7</sub> N <sup>c</sup>	2.068	1.835	131.8	92.7	174.6	[25]
CH <sub>3</sub> CN <sup>d</sup>	2.068	1.835	132.0	93.9	176.1	[26]

<sup>a</sup> Cg – the centroid of the cyclopentadienyl ring.

<sup>b</sup>  $[(CH_3C_5H_4)_2Ti(NCSe)]_2O.$ 

<sup>c</sup> [(Cp<sub>2</sub>Ti(NCCH<sub>2</sub>CH<sub>2</sub>Ph))<sub>2</sub>O][FeCl<sub>4</sub>]<sub>2</sub>.

<sup>d</sup>  $[(Cp_2Ti(NCCH_3))_2O][BPh_4]_2.$ 



Fig. 2. ORTEP drawing of the molecular structure of  $Cp_2V(dca)_2$  (2) with atom numbering scheme. (ellipsoids: 30% probability).

complex 1 (2.10 Å) and close to corresponding vanadocene compounds  $(CH_3C_5H_4)_2V(NCO)_2$  (2.03 Å) [10] or  $Cp_2V(N_3)_2$  (2.08 Å) [11].

The geometrical parameters of dicyanamide moiety in titanocene compound **1** as well as in vanadocene compound **2** (C $\equiv$ N = 1.145–1.16 Å, N–C = 1.29–1.32 Å, N– C–N = 171.9–175.3°, C–N–C = 118.9–122.9°) are comparable with the values founded for ionic salt Na(dca) [20].

#### 3. Conclusions

Sodium dicyanamide reacts with vanadocene and titanocene dichlorides in aqueous solution forming new pseudohalide complexes. Two types of complexes were evidenced by X-ray structure analysis: dinuclear oxo-bridged titanocene complex 1 and monomeric vanadocene complex 2. Both complexes were characterized by spectroscopic measurements and mass spectrometry. It was shown that in both studied compounds the dicyanamide ligand is monodentate bonded via terminal nitrogen. Formation of these different complexes reflects diverse reactivity of vanadocene dichloride and titanocene dichloride in water solution.

# 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 purified by standard methods, distilled and saturated with argon. Metallocene dichlorides Cp<sub>2</sub>TiCl<sub>2</sub> and Cp<sub>2</sub>VCl<sub>2</sub> were prepared according to published procedures [27]. Sodium dicyanamide was prepared by reaction of Ag(dca) with Na<sub>2</sub>S in aqueous solution, and crude Na(dca) was crystallized from hot methanol.

# 4.2. Measurements

Positive- and negative-ion electrospray ionization (ESI) mass spectra were measured on an Esquire 3000 ion trap analyzer (Bruker Daltonics, Bremen, Germany) in the range m/z = 50-1000. The samples were dissolved in acetonitrile (Merck, Darmstadt, Germany) and analyzed by direct infusion at a flow rate of 1 µl/min. The selected precursor ions were further analyzed by MS/MS analyses under the following conditions: the isolation width m/z = 4, the collision amplitude 0.8 V, the ion source temperature 300EC, the flow rate and the pressure of nitrogen 4 l/min and 10 psi, respectively.

IR spectra were recorded in 4000–350 cm<sup>-1</sup> region on a Perkin-Elmer 684 in KBr pellets. Raman spectra in the region 50–3500  $\text{cm}^{-1}$  were recorded in quartz capillaries on a Bruker IFS 55 with FRA 106 extension.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured at 300 K (CDCl<sub>3</sub> solution) on a Bruker Avance 500 and the chemical shifts were referenced to external neat  $(CH_3)_4Si.$ 

The EPR spectrum was recorded on an ERS 221 (ZWG Berlin) spectrometer at X-band as acetone solution at ambient temperature.

Electronic absorption spectra were run on a Hewlett-Packard 8453 spectrometer (solvent CH<sub>2</sub>Cl<sub>2</sub>;  $10^{-2}$ – $10^{-3}$ M solutions in 2-cm cuvette).

# 4.3. Synthesis of $[(\eta^5 - C_5 H_5)_2 Ti(dca)]_2 O \cdot CH_2 Cl_2 (1)$

0.5 g (2.0 mmol) of  $(\eta^5-C_5H_5)_2$ TiCl<sub>2</sub> was dissolved in 30 ml of boiling water. To this solution, 0.4 g (4.5 mmol) of sodium dicyanamide was added and the mixture was rapidly cooled to room temperature. Bright orange precipitate was filtered, washed with water and vacuum dried. Crude product was extracted with boiling dichloromethane on a frit and red extract was concentrated in vacuum. The orange powder precipitated after cooling dichloromethane solution at dry ice temperature (yield: 0.48 g, 81%). The crystals of 1 suitable for X-ray analysis were obtained by careful layering of CH<sub>2</sub>Cl<sub>2</sub> solution with double volume of hexane.

The crystals are stable for several days in air, low soluble in acetone, CHCl<sub>3</sub> and CH<sub>3</sub>CN, and almost insoluble in *n*-hexane. Heating causes cracking of crystals at about 60 °C (desolvating) and the resulting yellow fragments decompose above 180 °C without melting.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 6.27 (s, 20H); 5.32 (s, 2H).

Table 5

Crystal data for complex	es 1 and 3, measurement	and refinement details <sup>a</sup>
--------------------------	-------------------------	-------------------------------------

Compound	1	2
Empirical formula	C24H20N6OTi2.CH2Cl2	$C_{14}H_{10}N_{6}V$
Molecular weight	589.19	313.22
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)
a (Å)	11.0270(3)	9.6380(4)
b (Å)	14.6820(3)	9.6310(4)
<i>c</i> (Å)	16.0680(3)	14.8460(5)
β (°)	97.1690(14)	106.458(3)
Ζ	4	4
$V(Å^3)$	2581.05(10)	1321.60(9)
$D_{\text{calc}} (\text{g cm}^{-3})$	1.516	1.574
Crystal size (mm)	$0.4 \times 0.25 \times 0.1$	$0.25 \times 0.125 \times 0.075$
Crystal shape	orange plate	green prism
$\mu (\mathrm{mm}^{-1})$	0.857	0.752
<i>F</i> (000)	1200	636
h k l Range	-14, 14; -19, 19; -20, 20	-12, 12; -12, 12; -19, 19
$\theta$ Range (°)	1–27.5	1–27.5
Number of reflections measured	36075	19508
Number of independent reflections $(R_{int})^a$	5910 (0.0520)	3025 (0.042)
Number of observed reflections $[I > 2\sigma(I)]$	4412	2436
Number of parameters refined	325	190
Maximum/minimum $\Delta \rho$ (e Å <sup>-3</sup> )	0.409/-0.627	0.458/-0.435
Goodness-of-fit (GoF) <sup>b</sup>	1.025	0.928
$R^{\rm c}, wR^{\rm c}$	0.040, 0.1023	0.036, 0.1226

<sup>a</sup>  $R_{\text{int}} = \sum |F_{o}^2 - F_{o,\text{mean}}^2| / \sum F_{o}^2$ . <sup>b</sup>  $\text{GoF} = [\sum (w(F_{o}^2 - F_{c}^2)^2) / (N_{\text{diffrs}} - N_{\text{params}})]^{1/2}$  for all data. <sup>c</sup>  $R(F) = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|$  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.

<sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 116.8 (s, Cp); 134.2 (broad s, dca); 53.4 (s, CH<sub>2</sub>Cl<sub>2</sub>).

Positive-ion MS m/z: 543  $[M + K]^+$ ; 527  $[M + Na]^+$ (100%); 505  $[M + H]^+$ ; 438  $[M - dca]^+$ .

MS/MS of 527 m/z 462 [M + Na–Cp]<sup>+</sup> (100%); 438 [M – dca]<sup>+</sup>; 397 [M + Na–2Cp]<sup>+</sup>; 267 [Cp<sub>2</sub>Ti(dca) + - Na]<sup>+</sup>; 178 [Cp<sub>2</sub>Ti]<sup>+</sup>.

Negative-ion MS m/z (%): 570 [M + dca]<sup>-</sup>; 505 [M + dca-Cp]<sup>-</sup>; 261 (100%) [Cp<sub>2</sub>Ti(dca)O]<sup>-</sup>.

IR (KBr-pellet, cm<sup>-1</sup>): 3112(m), 2984(w), 2291(vs), 2231(vs), 2171(vs), 1378(s), 1262(m), 1015(s), 820(s), 736(vs), 597(m), 415(m).

Raman (quartz capillary, cm<sup>-1</sup>): 3123(m), 3114(m), 2985(w), 2230(vs), 1365(m), 1133(vs), 420(m), 387(m), 273(vs), 129(m).

UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>, nm): maxima at 334 and 417.

4.4. Synthesis of  $(\eta^5 - C_5 H_5)_2 V(dca)_2$  (2)

0.5 g (2.0 mmol) of  $(\eta^5-C_5H_5)_2VCl_2$  was dissolved in 30 ml of water and 0.4 g of sodium dicyanamide (4.5 mmol) was added to this solution. The resulting mixture was stirred for 20 min when the dark green precipitate appeared. Crystals of prepared complex were filtered, washed with water and vacuum dried (yield: 0.54 g, 86%). Single crystals of **2** suitable for X-ray diffraction were obtained after cooling of saturated acetone solution to -15 °C.

The green crystals are stable for several days in air, soluble in acetone and CH<sub>3</sub>CN, low soluble in CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub> and practically insoluble in methanol and *n*-hexane. EPR (acetone solution):  $|A_{iso}| = 75.78$  G,  $g_{iso} = 1.9844$ .

Positive-ion MS m/z: 649 [2M + Na]<sup>+</sup>; 352 [M + K]<sup>+</sup>; 336 [M + Na]<sup>+</sup> (100%); 247 [M - (NCNCN)]<sup>+</sup>. MS/MS of 336: m/z 271 [M + Na–Cp]<sup>+</sup> (100%); 247 [M – dca]<sup>+</sup>.

Negative-ion MS m/z: 691 [2M-H + dca]<sup>-</sup>; 379 [M + dca]<sup>-</sup> (100%); 314 [M + dca-Cp]<sup>-</sup>.

IR (KBr-pellet, cm<sup>-1</sup>): 3105(s), 3083(m), 2299(vs), 2256(vs), 2210(vs), 1413(s), 1320(m), 1092(s), 1071m, 922(s), 903(vs), 721(m), 564(m).

Raman (quartz capillary, cm<sup>-1</sup>): 3113(m), 2236(vs), 1131(vs), 662(m), 423(m), 303(m), 286(vs), 142(m).

UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>, nm): maximum at 694 (d–d transitions).

#### 4.5. Structure determinations

The X-ray data for **1** and **2** 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  $\varphi$  and  $\omega$  scan mode. Data reductions were performed with DENZO-SMN [28]. The absorption was neglected. Structures were solved by direct methods

(Sir92) [29] and refined by full-matrix least-square based on  $F^2$  (SHELXL-97) [30].

Crystal data are summarized in Table 5. Hydrogen atoms were treated in both structures similarly; they were calculated into ideal positions, riding during refinement on the respective pivot atom. The isotropic displacement parameters of hydrogen atoms were set to 1.2  $U_{eq}$  of the attached atom.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 235476 and 235477 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

### Acknowledgements

This work was supported by grants from the Ministry of Education of the Czech Republic (No. CZ 253100001) and Grant Agency of the Czech Republic (No. 203/02/0436). Michal Holčapek (mass spectrometry) acknowledges the support of the Grant Project No. 203/03/1071 sponsored by the Grant Agency of the Czech Republic.

# Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version at doi:10.1016/ j.ica.2004.09.030.

### References

- J.L. Burmeister, E.A. Deardorff, A. Jensen, V.H. Christiansen, Inorg. Chem. 9 (1970) 58.
- [2] M. Morán, V. Fernández, J. Organomet. Chem. 165 (1979) 215.
- [3] G. Doyle, S. Tobias, Inorg. Chem. 7 (1968) 2479.
- [4] J.L. Burmeister, E.A. Deardorff, C.E. Van Dyke, Inorg. Chem. 8 (1969) 170.
- [5] S.J. Anderson, D.S. Brown, A.H. Norbury, J. Chem. Soc., Chem. Commun. (1974) 996.
- [6] A.C. Villa, A.G. Manfredotti, C. Guastini, Acta Crystallogr., Sect. B 32 (1976) 909.
- [7] I. Jibril, S.T. Abuorabi, S.A. Klaib, L. Zsolnai, G. Huttner, J. Organomet. Chem. 467 (1994) 189.
- [8] C.P. Raptopoulou, N. Tzavellas, N. Klouras, Z. Anorg. Allg. Chem. 622 (1996) 1387.
- [9] E.R. de Gil, M. de Burguera, A.V. Rivera, Acta Crystallogr., Sect. B 33 (1977) 578.
- [10] J. Honzíček, M. Erben, I. Císařová, J. Vinklárek, Appl. Organomet. Chem. (2004) in press.
- [11] J. Honzíček, M. Erben, I. Císařová, J. Vinklárek, Appl. Organomet. Chem. (2004) in press.

- [12] Cambridge Structural Database F.H. Allen, Acta Crystallogr., Sect. B 58 (2002) 380.
- [13] E. Diana, R. Rossetti, P.L. Stanghellini, S.F.A. Kettle, Inorg. Chem. 36 (1997) 382.
- [14] E. Samuel, Bull. Soc. Chim. France (1966) 3548.
- [15] J. Honziček, J. Vinklárek, M. Erben, I. Císařová, Acta Crystallogr., Sect. E 60 (2004) m1090.
- [16] P. Ghosh, A.T. Kotchevar, D.D. DuMez, S. Ghosh, J. Peiterson, F.M. Uckun, Inorg. Chem. 38 (1999) 3730.
- [17] P. Ghosh, S. Ghosh, C. Navara, R.K. Narla, A. Benyumov, F.M. Uckun, J. Inorg. Biochem. 84 (2001) 241.
- [18] P. Ghosh, S. Ghosh, O.J. D'Cruz, F.M. Uckun, J. Inorg. Biochem. 72 (1998) 89.
- [19] J. Honzíček, P. Nachtigall, I. Císařová, J. Vinklárek, J. Organomet. Chem. 689 (2004) 1180.
- [20] B. Jürgens, E. Irran, J. Schneider, W. Schnick, Inorg. Chem. 39 (2000) 665.

- [21] N. Klouras, V. Nastopoulos, N. Tzavellas, I. Leban, Z. Anorg. Allg. Chem. 621 (1995) 1767.
- [22] Y. Le Page, J.D. McCowan, B.K. Hunter, R.D. Heyding, J. Organomet. Chem. 193 (1980) 201.
- [23] G.S. Herrmann, H.G. Alt, U. Thewalt, J. Organomet. Chem. 399 (1990) 83.
- [24] U. Thewalt, H.P. Klein, Z. Anorg. Allg. Chem. 479 (1981) 113.
- [25] K. Berhalter, U. Thewalt, J. Organomet. Chem. 332 (1987) 123.
- [26] H. Aslan, S.H. Eggers, R.D. Fischer, Inorg. Chim. Acta 159 (1989) 55.
- [27] G. Wilkinson, J.M. Birmingham, J. Am. Chem. Soc. 76 (1954) 4281.
- [28] Z. Otwinowski, W. Minor, Methods Enzymol. A 276 (1997) 307.
- [29] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.
- [30] G.M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, 1997.