Contents lists available at ScienceDirect

Polyhedron

Reactions of the metallocene dichlorides [M(Cp)$_2$Cl$_2$] (M = Zr, Hf) and [Ti(MeCp)$_2$Cl$_2$] with the pyridine-2,6-dicarboxylate($-$2) ligand: Synthesis, spectroscopic characterization and X-ray structures of the products

Theocharis C. Stamatatos [a], Spyros P. Perlepes [a], Catherine P. Raptopoulou [b], Vassilis Psycharis [b], Nikolaos Klouras [a,*]

[a] Department of Chemistry, University of Patras, 265 00 Patras, Greece
[b] Institute of Materials Science, NCSR "Demokritos", 153 10 Aghia Paraskevi Attikis, Greece

ARTICLE INFO

ABSTRACT

The reactivity pattern of the 16-electron species [M(Cp)$_2$Cl$_2$] (M = Zr, Hf; Cp$^-$ = η^5-C$_5$H$_5$$^-$) and [Ti(MeCp)$_2Cl_2$] (MeCp$^-$ = η^5-C$_5$H$_4$CH$_3$$^-$) towards the dipicolinate($-$2) (dipic^{2-}) ligand under mild (ambient temperature) and convenient (aerobic reactions, aqueous media) conditions have been investigated. The syntheses, molecular structures and spectroscopic (IR, ^{1}H NMR) characterization are reported for the 18-electron products [Zr(Cp)$_2$(dipic)] (**1**), [Hf(Cp)$_2$(dipic)] (**2**) and [Ti(MeCp)$_2$(dipic)] (**3**). The dipic^{2-} ion behaves as *N,O,O'*-chelating ligand in the three complexes, while the centroids of the Cp$^-$ (**1**, **2**) and MeCp$^-$ (**3**) rings formally occupy the fourth and fifth coordination sites about the central metal. The two identical/very similar bite angles of only ~70° make the dipic^{2-} ligand particularly suited to form stable metallocene derivatives with 5-coordinate geometry. IR and ^{1}H NMR data are discussed in terms of the known structures and the tridentate chelating mode of the dipic^{2-} ligand.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The systematic development of the coordination chemistry of pyridine-2,6-dicarboxylic acid (dipicolinic acid; dipicH$_2$) and its derivatives over many years has led to a remarkable variety of metal complexes [1]. Such species have been of interest from several viewpoints, including the versatile coordination modes of dipicH$^-$ and dipic^{2-} (Scheme 1) [2], their capacity to stabilize unusual oxidation states [3], and the relevance of metal dipicolinate complexes to the interdisciplinary fields of bioinorganic chemistry [4] and metallosupramolecular chemistry [5]. In contrast to other transition metals, the chemistry of Group 4 metal dipicolinate complexes has been much less investigated. It is remarkable that no Hf/dipicH$^-$ or dipic^{2-} compounds have been reported.

We have long been interested in the reactivity chemistry of η^5-C$_5$H$_5$$^-$ (Cp$^-$), η^5-C$_5$Me$^-$ (Cp^{*-}) or other substituted derivatives of Ti^{IV}, Zr^{IV} and Hf^{IV} (metallocenes) with either chelating or bridging polydentate organic ligands which results in structurally interesting complexes [6]. For example, we have recently reported that the reaction of [Ti(Cp)$_2$Cl$_2$] and 2,6-bis(3,5-dimethylpyrazolyl-1-

yl)pyridine (bdmpp) in Me$_2$CO proceeded with the complete substitution of the cyclopentadienyl ligands and afforded complex [Ti^{IV}Cl$_2$(O$_2$)(bdmpp)] containing the side-on (η^2) O$_2$$^{2-}$ group [6c].

As part of a broad research program aiming at investigating the reactivity of complexes [M^{IV}(η^5-C$_5$H$_4$R)$_2$X$_2$] (M = Ti, Zr, Hf; R = H, Me, SiMe$_3$,...; X = Cl, Br,...) with polydentate organic ligands, this report is an amalgamation of the two, above mentioned research areas. We describe the reactions between [M(Cp)$_2$Cl$_2$] (M = Zr, Hf) and [Ti(MeCp)$_2$Cl$_2$] (MeCp$^-$ is the methylcyclopentadienyl ligand) with dipic^{2-} under various conditions, and the full structural and spectroscopic characterization of the products. The starting materials have a formal 16-electron configuration and are quite labile towards halide substitution by other ligands that will satisfy the requirement for a stable 18-electron configuration [7]. The single-crystal, X-ray structure of [Ti(Cp)$_2$(dipic)] has been reported independently by two groups [8].
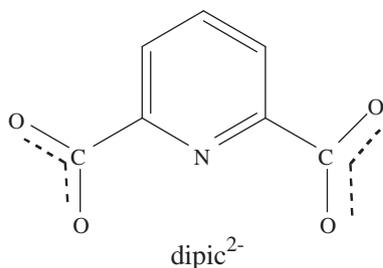
2. Experimental

2.1. General and spectroscopic measurements

All manipulations were performed under aerobic conditions using chemicals as received, unless otherwise stated. [Hf(Cp)$_2$Cl$_2$]

* Corresponding author. Tel./fax: +30 2610 997140.
  E-mail address: n.klouras@chemistry.upatras.gr (N. Klouras).

Scheme 1. The pyridine-2,6-dicarboxylate(−2) (dipicolinate; dipic^{2-}) ligand discussed in the text.

[9] and [Ti(MeCp)$_2$Cl$_2$] [10] were prepared as reported elsewhere. Where necessary, solvents were purified by standard methods and freshly distilled before use.

Microanalyses (C, H, N) were performed by the in-house facilities at the University of Patras using an EA 1108 Carlo Erba analyser. IR spectra (4000–450 cm^{-1}) were recorded on a Perkin–Elmer 16 PC FT-spectrometer using samples prepared as KBr pellets. ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer using DMSO-d_6 as solvent; chemical shifts (δ) are reported relative to Me$_4$Si.

2.2. Compound preparation

2.2.1. Bis(η^5-cyclopentadienyl)(dipicolinato)zirconium(IV), [Zr(Cp)$_2$(dipic)] (**1**)

Method A: Dipicolinic acid (dipicH$_2$; 0.167 g, 1.0 mmol) and anhydrous Na$_2$CO$_3$ (0.106 g, 1.0 mmol) were added to H$_2$O (3 mL). The solids soon dissolved with effervescence (evolution of CO$_2$) to form a homogeneous colorless solution. To this solution was added a solution of [Zr(Cp)$_2$Cl$_2$] (0.292 g, 1.0 mmol) in CHCl$_3$ (30 mL). The reaction mixture was stirred for 2 h to give a milky solution and a white precipitate. The solvent was evaporated to dryness in vacuo at 30–35 °C. H$_2$O (12 mL) was added in the flask and the remaining solid was collected by filtration, washed with Et$_2$O (2 × 5 mL) and dried in air. Recrystallization of the solid from CHCl$_3$ gave colorless, X-ray quality crystals of the product. Yield: 0.144 g (37%); T_{dec} > 300 °C. *Anal.* Calc. for C$_{17}$H$_{13}$ZrNO$_4$: C, 52.82; H, 3.39; N, 3.62. Found: C, 52.48; H, 3.18; N, 3.57%. Diagnostic IR bands (KBr, cm^{-1}): 1668vs, 1384vs, 824s. ^{1}H NMR data (400 MHz, DMSO-d_6): δ 6.26 (10H, s), 8.45–8.53 (3H, m).

Method B: An aqueous solution (30 mL) of Na$_2$dipic was prepared as described above from the reaction of 10.0 mmol of dipicH$_2$ and 10.0 mmol of Na$_2$CO$_3$. This solution was added to a colorless slurry of [Zr(Cp)$_2$Cl$_2$] (1.462 g, 5.0 mmol) in freshly distilled MeOH (90 mL). The resulting suspension was stirred for 2 h and filtered in vacuo (Büchner, filter SS589). The white flakes on the filter were washed with Et$_2$O (2 × 25 mL) and dried in air. The white solid was taken up with H$_2$O (25 mL) to dissolve the excess of Na$_2$dipic and the NaCl by-product. The remaining solid was collected by filtration (G4 glass filter) and dried under high vacuum to give a glistening product. Yield: 1.593 g (82% based on the available Zr^{IV}). The identity of the product was confirmed by elemental analyses, and IR and ^{1}H NMR spectroscopic comparison with authentic material from method A.

2.2.2. Bis(η^5-cyclopentadienyl)(dipicolinato)hafnium(IV), [Hf(Cp)$_2$(dipic)] (**2**)

Using [Hf(Cp)$_2$Cl$_2$] (0.127 g, 0.33 mmol) and in-situ prepared Na$_2$dipic (0.66 mmol), and following a completely analogous procedure with that described for the preparation of **1** (the volumes

of H$_2$O, MeOH and Et$_2$O were scaled down) by method B, a white microcrystalline powder of the product was isolated. Vapor diffusion of petroleum ether into a solution of **2** in CHCl$_3$ gave X-ray quality crystals after 24 h. Yield: 0.106 g (67% based on the available Hf^{IV}); T_{dec} > 225°C. *Anal.* Calc. for C$_{17}$H$_{13}$HfNO$_4$: C, 43.10; H, 2.77; N, 2.96. Found: C, 43.19; H, 3.08; N, 3.16%. Diagnostic IR bands (KBr, cm^{-1}): 1674vs, 1364vs, 832vs. ^{1}H NMR data (400 MHz, DMSO-d_6): δ 6.26 (10H, s), 8.46–8.51 (3H, m).

2.2.3. Bis(η^5-methylcyclopentadienyl)(dipicolinato)titanium(IV), [Ti(MeCp)$_2$(dipic)] (**3**)

Solids dipicH$_2$ (0.084 g, 0.5 mmol) and Na$_2$CO$_3$ (0.053 g, 0.5 mmol) were added to H$_2$O (3 mL). The solids soon dissolved with effervescence (evolution of CO$_2$) to form a colorless solution (solution A). A solution of [Ti(MeCp)$_2$Cl$_2$] (0.139 g, 0.5 mmol) in H$_2$O (12 mL) was prepared by dissolving the solid in the hot solvent (70–80 °C), filtration and cooling the orange-red filtrate to room temperature (solution B). Solution B was added rapidly to solution A under vigorous stirring. The resulting yellow solution was stirred for a further 2 h at ambient temperature, during which time no color change or precipitation were observed. The solvent was evaporated to dryness in vacuo at 40 °C and the residue extracted with CHCl$_3$ (30 mL), followed by filtration and complete removal of the solvent under vacuum. The obtained yellow powder, which is quite soluble in CHCl$_3$ and toluene, was analytically and spectroscopically pure. Vapor diffusion of petroleum ether into a solution of the yellow powder in CHCl$_3$ gave X-ray quality, yellow crystals of **3** after 12 days. Yield: 0.098 g (53%); T_{dec} > 230°C. *Anal.* Calc. for C$_{19}$H$_{17}$TiNO$_4$: C, 61.47; H, 4.62; N, 3.77. Found: C, 61.37; H, 4.72; N, 3.52%. Diagnostic IR bands (KBr, cm^{-1}): 1650vs, 1368vs, 832s. ^{1}H NMR data (400 MHz, DMSO-d_6): δ 1.62 (6H, s), 5.78 (4H, t), 6.33 (4H, t), 8.13 (2H, d), 8.46 (1H, t).

2.3. Single-crystal X-ray crystallography

Parallelepiped crystals of **1–3** were taken directly from the mother solution and immediately cooled to −113 °C. Diffraction measurements were made on a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite monochromated Cu Kα radiation. Data collection (ω-scans) and processing (cell refinement, data reduction and empirical absorption correction) were performed using the CRYSTALCLEAR program package [11]. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range 22 < 2θ < 54°. Important crystal data and parameters for data collection and refinement are listed in Table 1.

The three structures were solved by direct methods using SHEL-XS-97 [12a] and refined on F^2 with SHELXL-97 [12b]. All non-H atoms were refined anisotropically. In the structures of **1** and **2**, all H atoms were introduced at calculated positions as riding on their respective bonded atoms. In the structure of **3**, all H atoms were located by difference maps and refined isotropically.

3. Results and discussion

3.1. Synthetic comments

The previous use of dipicH$_2$ in [M^{IV}(Cp)$_2$Cl$_2$] (M = Ti, Zr, Hf) chemistry involved the preparation and single-crystal X-ray structure of [Ti(Cp)$_2$(dipic)] (**4**) [8], as well as the preparation of a powder with the empirical formula Zr(Cp)$_2$(dipic) [7]; a monomeric structure was assigned for the latter based mainly on FAB-MS data. The powder was isolated by two procedures outlined in Eqs. (1) and (2).

Table 1
Crystallographic data for complexes **1–3**.

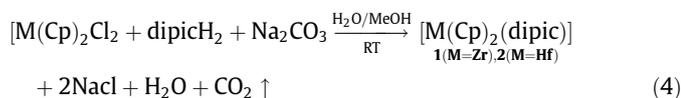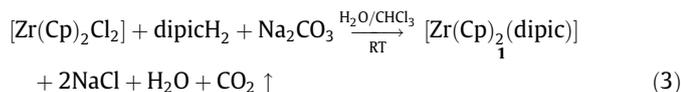| Parameter	**1**	**2**	**3**
Formula	$C_{17}H_{13}ZrNO_4$	$C_{17}H_{13}HfNO_4$	$C_{19}H_{17}TiNO_4$
Formula weight	386.50	473.77	371.24
Crystal system	tetragonal	tetragonal	monoclinic
Space group	$P4_32_12$	$P4_32_12$	$P2_1/n$
a (Å)	7.9863(1)	7.9593(1)	7.5672(1)
b (Å)	7.9863(1)	7.9593(1)	25.4142(1)
c (Å)	22.5101(4)	22.5458(4)	8.3911(4)
α (°)	90	90	90
β (°)	90	90	92.798(1)
γ (°)	90	90	90
V (Å^3)	1435.72(4)	1428.29(4)	1611.80(8)
Z	4	4	4
ρ_{calc} (g cm^{-3})	1.788	2.203	1.530
Radiation, λ (Å)	Cu Kα, 1.54178	Cu Kα, 1.54178	Cu Kα, 1.54178
Temperature (K)	160(2)	160(2)	160(2)
μ (mm^{-1})	6.471	13.702	4.717
Data collected/ unique (R_{int})	22473/1218 (0.0489)	9483/1214 (0.0767)	18154/2727 (0.0298)
Data with $I > 2\sigma(I)$	1209	1202	2585
R_1 $(I > 2\sigma(I))^a$	0.0181	0.0254	0.0294
wR_2 $(I > 2\sigma(I))^b$	0.0465	0.0637	0.0771

^a $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$.
^b $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

$$[Zr(Cp)_2(CH_3)_2] + dipicH_2 \xrightarrow[RT]{THF,Ar} \text{“}Zr(Cp)_2(dipic)\text{”} + 2CH_4 \uparrow \quad (1)$$

$$[Zr(Cp)_2Cl_2] + dipicH_2 + 2Et_3N \xrightarrow[70\,°C]{toluene,Ar} \text{“}Zr(Cp)_2(dipic)\text{”} + 2Et_3NHCl \quad (2)$$
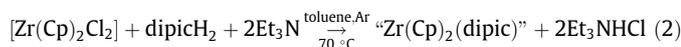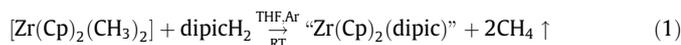
Our first goal in this work was to crystallize the powder and prove the suggested, 5-coordinate mononuclear structure by single-crystal X-ray crystallography. Simultaneously we were interested in developing convenient (*aerobic conditions*, *ambient temperature*, *aqueous media*) methods of its synthesis replacing the rather cumbersome procedures (anaerobic conditions, anhydrous solvents and use of [Zr(Cp)$_2$(Me)$_2$] as starting material) reported by Brintzinger and co-workers [7]. Both tasks were successful. We synthesized compound [Zr(Cp)$_2$(dipic)] (**1**) using either a two-phase procedure (Eq. (3)) or a H$_2$O/MeOH reaction solvent (Eq. (4), M = Zr) from the reaction between [Zr(Cp)$_2$Cl$_2$] and in situ formed dipic^{2-}. Recrystallization of the powder from CHCl$_3$ gave X-ray quality crystals of **1**, thus permitting the solution of its crystal structure (vide infra).

$$[Zr(Cp)_2Cl_2] + dipicH_2 + Na_2CO_3 \xrightarrow[RT]{H_2O/CHCl_3} [Zr(Cp)_2(dipic)]_{\mathbf{1}}$$
$$+ 2NaCl + H_2O + CO_2 \uparrow \quad (3)$$

$$[M(Cp)_2Cl_2 + dipicH_2 + Na_2CO_3 \xrightarrow[RT]{H_2O/MeOH} [M(Cp)_2(dipic)]_{\mathbf{1(M=Zr),2(M=Hf)}}$$
$$+ 2Nacl + H_2O + CO_2 \uparrow \quad (4)$$

In a next step we wondered if the Hf^{IV} analog of **1** could be prepared by the experimentally convenient procedure of Eq. (4), and thus pursued its synthesis and crystallization. There are two reasons to prepare such a complex: (i) to determine if it would be isostructural with **1**; and (ii) if it is isostructural to assess any influence of the Zr versus Hf difference on the reactivity chemistry of [M(Cp)$_2$(dipic)] towards nucleophiles (such studies will be reported in a forthcoming paper; preliminary studies show that both complexes are quite inert towards hydrolysis). Complex **2** was easily prepared, see Experimental and Eq. (4), and crystallized (in a form suitable for single-crystal X-ray crystallography) by vapor diffusion of petroleum ether into a solution of the powder in CHCl$_3$. Note that an 100% excess of dipicH$_2$ in the procedures represented by Eq. (4) is beneficial to the yields of the reactions; the yields were 82% and 67% for the preparations of **1** and **2**, respectively.

In a final step of the work reported here we wondered if analogs of **4**, whose structure has been published [8], could be prepared using substituted cyclopentadienyl ligands. We were also interested in investigating whether such reactions could have been carried out in completely aqueous solution. Note that **4** had been prepared under a variety of conditions, namely by the reaction of [Ti(Cp)$_2$(CH$_3$)$_2$] and dipicH$_2$ in dry toluene [8a], from [Ti(Cp)$_2$Cl$_2$] and dipicH$_2$ in MeOH/H$_2$O [8b], and by the reaction between [Ti(Cp)$_2$Cl$_2$], dipicH$_2$ and Na$_2$CO$_3$ in H$_2$O [14], all at room temperature. Since [Ti(MeCp)$_2$Cl$_2$] (MeCp$^-$ is the η^5-C$_5$H$_4$CH$_3^-$ ligand, sometimes abbreviated as Cp′ [13]) was available at our hands [10b], we used this complex as starting material. The 1:1:1 [Ti(MeCp)$_2$Cl$_2$]/dipicH$_2$/Na$_2$CO$_3$ reaction mixture in H$_2$O at ambient temperature gave the desired complex [Ti(MeCp)$_2$(dipic)] (**3**), in yields higher than 50%. Its formation is summarized in Eq. (5). The product is soluble in CHCl$_3$ from which it could be crystallized by vapor diffusion with petroleum ether.

$$[Ti(MeCp)_2Cl_2] + dipicH_2 + Na_2CO_3$$
$$\xrightarrow[RT]{H_2O} [Ti(MeCp)_2(dipic)_{\mathbf{3}} + 2NaCl + H_2O + CO_2 \uparrow \quad (5)$$
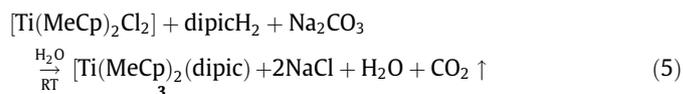
Compounds **1–3** are stable solids at room temperature and are non-sensitive toward air and moisture.

3.2. IR spectra

The IR bands at 1650–1674 and 1364–1384 cm^{-1} in the spectra of **1–3** are assigned to the $v_{as}(CO_2)$ and $v_s(CO_2)$ modes, respectively, of the dipic^{2-} ligand [1d, 1g, 4a]. The parameter Δ, where $\Delta = v_{as}(CO_2) - v_s(CO_2)$, is very large (>280 cm^{-1}), as expected for the monodentate mode of the carboxylate ligation [15]. The in-plane deformation band of the pyridine ring of free dipicH$_2$ at 646 cm^{-1} shifts upwards ($\sim$675 cm^{-1}) in **1–3**, confirming the involvement of the heterocyclic N-atom in coordination [1d,16]. The spectra of the three complexes are quite similar in the regions of the coordinated cyclopentadienyl ligands, except that the methyl substituent of the cyclopentadienyl ring in **3** introduces extra vibrational "structure" due to the C–H stretch, C–C stretch, asymmetric CH$_3$ deformation and CH$_3$ wag which are located at $\sim$2920, 1625, 1500 and 1250 cm^{-1}, respectively [17]. The cyclopentadienyl bands in **1–3** appear at $\sim$3100, (v(CH)), 1420 (v(CC)), 1020 (δ(CH)), 830 (π(CH)) and $\sim$480 (ring tilt) cm^{-1} [17,18].

3.3. ^1H NMR spectra

^{1}H NMR data for **1–3** (DMSO-d_6, 400 MHz) are presented in Table 2. Assignments have been given by using literature reports [7,8a,14,17,19,20], and in comparison with the spectra of the starting materials dipicH$_2$ and [Ti(MeCp)$_2$Cl$_2$] (recorded by us) which are also listed in Table 2.

As expected from the very similar solid-state structures of **1** and **2** (vide infra), their ^{1}H NMR spectra are almost identical. The spectra exhibit resonances at δ 6.26(s) and 8.49(m) and these are attributed [8a,20] to the Cp$^-$ groups and the aromatic protons of the dipic^{2-} ligand, respectively. The ratio of the integrals is consistent with their structures (Scheme 2). In the region of the dipic^{2-} ligand, the spectrum of **3** contains a triplet centered on δ 8.46, corresponding to H(4), and a doublet at δ 8.13, corresponding to H(3) and H(5), with $J = 7.8$ Hz, a typical value for aromatic systems of this nature. The δ values and the ratio of the integrals both are typical for a symmetric tridentate coordination of dipic^{2-} (Scheme 2) [19]. The aromatic H resonances of **1–3** are shifted downfield compared with those of dipicH$_2$, indicating a deshielding of these protons upon coordination. The ^{1}H NMR spectrum of the 18-electron complex **3** contains two groups of peaks in the ratio 6:8 due to the two types of protons on the Me groups of the MeCp$^-$ ligands

Table 2
^{1}H NMR data[a,b,c] for the starting materials dipicH$_2$, [Ti(MeCp)$_2$Cl$_2$] and complexes **1**–**3**.

Compound	Chemical shifts and their assignments		
	dipicH$_2$/dipic^{2-} ring	Cyclopentadienyl ring	CH$_3$
dipicH$_2$	8.18–8.25 (m)		
1	8.45–8.53 (3H, m)[d]	6.26 (10H, s)	
2	8.46–8.51 (3H, m)[d]	6.26 (10H, s)	
[Ti(MeCp)$_2$Cl$_2$]		6.32 (4H, pt, *J* = 2.60 Hz)	2.18 (6H, s)
		6.62 (4H, pt, *J* = 2.60 Hz)	
3	8.13 (2H, d, *J* = 7.77 Hz)[e]	6.33 (4H, pt, *J* = 2.47 Hz)	1.62 (6H, s)
	8.46 (1H, t, *J* = 7.77 Hz)[f]	5.78 (4H, pt, *J* = 2.39 Hz)	

Abbreviations: d = doublet, m = multiplet, pt = pseudotriplet, s = singlet, t = triplet.
[a] In DMSO-d_6 at 400 MHz.
[b] Chemical shifts (δ values) are given in ppm relative to Me$_4$Si.
[c] This table is better read in relation to Scheme 2.
[d] H(3), H(4), H(5).
[e] H(3), H(5).
[f] H(4).
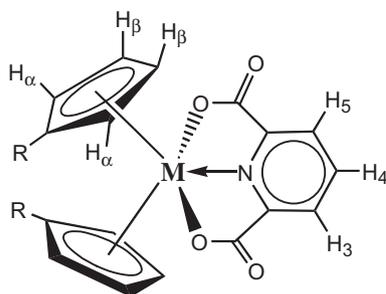
Scheme 2. The general structural formula of a metallocene/dipicolinate(−2) complex with the numbering scheme of the pyridine ring H atoms (R = H for M = Zr and Hf in **1** and **2**; R = CH$_3$ for M = Ti in **3**). The α and β designation for the H atoms in the cyclopentadienyl ring is valid only for complex **3**.

and the ring protons of the same ligands [17]. The Me protons show up as one singlet at δ 1.62. For the remaining eight protons of the two rings, the H$_\alpha$ and H$_\beta$ (Scheme 2) signals appear as pseudotriplets at δ 6.33 and 5.78, respectively [7]. These pseudotriplets arise from the coupling between the α- and β-protons [17]. The analogous signals in the spectrum of the 16-electron starting material [Ti(MeCp)$_2$Cl$_2$] appear at δ 2.18(s), 6.32(pt) and 6.62 (pt), respectively. The upfield of the Me and H$_\beta$ signals in **3** is attributed to dipic^{2-} coordination which leads to a small shielding of the MeCp$^-$ protons. The above *tentative* assignments for the H$_\alpha$ and H$_\beta$ protons of the MeCp$^-$ ligands in **3** and [Ti(MeCp)$_2$Cl$_2$] (since these assignments are tentative, they do not appear in Table 2) are in accordance with studies from Brintzinger's group [7,21]; these researchers have observed that 16-electron complexes, such as the [Ti(MeCp)$_2$Cl$_2$] starting material, have their α-H signals at higher fields than their β-H signals, whereas these signals appear in reversed order for 18-electron complexes, such as **3**; thus, the relative positions of α- and β-H signals provide a useful diagnostic criterion for the presence of 5-coordinate, 18-electron metallocene complexes in solution [7].

3.4. Description of structures

The molecular structures of complexes **1**, **2** and **3** are depicted in Figs. 1–3, respectively. Selected interatomic distances and angles are listed in Tables 3–5.

A structural comparison of **1** and **2** demonstrates that the substitution of Zr^{IV} by Hf^{IV} (both metal ions have almost identical radii

[13]) does not have an effect on the basic molecular configuration in that the corresponding bond distances and angles differ negligibly. The Zr^{IV} or Hf^{IV} atom and the pyridine N(1) and C(9) atoms are located on a crystallographic C_2 axis. The dipic^{2-} group is bound to the metal center by its pyridine nitrogen atom and two oxygen atoms (O(1), O(1')) from different carboxylate groups; it thus behaves as a tridentate *N,O,O'*-chelating ligand (Scheme 2). The centroids (Cp, Cp') of the two Cp$^-$ rings formally occupy the fourth and fifth coordination sites about the central metal ion. The Cp$^-$ centroids are at distances of 2.224 (**1**) and 2.211 (**2**) Å from the metal center and span angles of 133.5° and 133.3° at the Zr^{IV} and Hf^{IV} atoms, respectively, the two cyclopentadienyl planes intersecting at an angle of 47.6° for **1** and 48.1° for **2**. This (Cp)$_2$M (M = Zr, Hf) unit is almost indistinguishable from that in [Ti(Cp)$_2$(dipic)] (**4**) [8]. The Zr^{IV} or Hf^{IV} center and its nitrogen and oxygen atoms donors are coplanar by symmetry. The MO(1)N(1)O(1') plane is perpendicular to the ring centroid–metal–centroid plane, the two planes intersecting at angles of 89.54(3)° (**1**) and 89.67(7)° (**2**). Interestingly, the plane of the pyridine ring is not quite coplanar with the MO(1)N(1)O(1') plane in the two structures. A slight rotational deviation of these two planes by 4.06° (**1**) and 4.11° (**2**) is
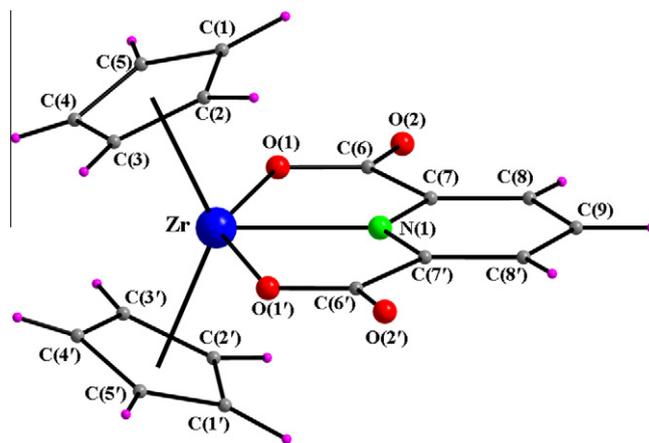
Fig. 1. Labeled PovRay representation of complex **1** with the atom numbering scheme. Primes are used for symmetry-related atoms. Color scheme: Zr^{IV}, blue; O, red; N, green; C, gray; H, purple. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
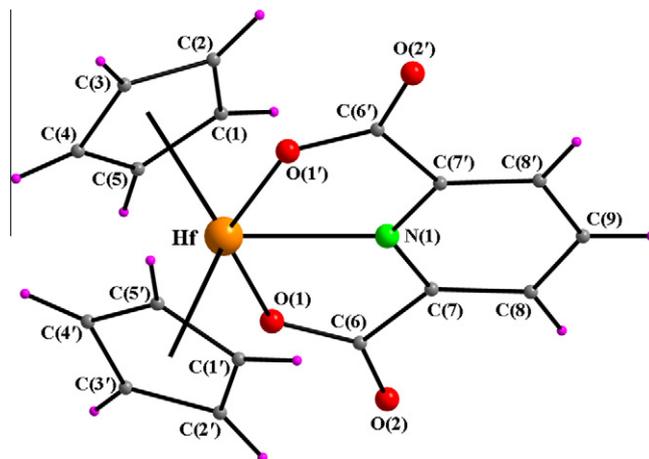
Fig. 2. Labeled PovRay representation of complex **2** with the atom numbering scheme. Primes are used for symmetry-related atoms. Color scheme: Hf^{IV}, orange; O, red; N, green; C, gray; H, purple. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Labeled PovRay representation of complex **3** with the atom numbering scheme. Color scheme: Ti[IV], yellow; O, red; N, green; C, gray; H, purple. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
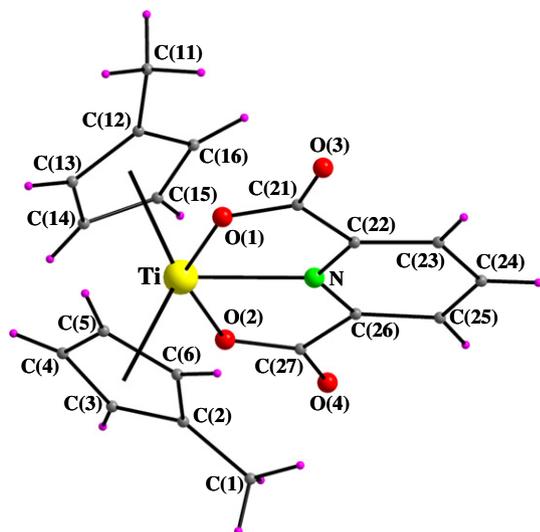
Table 3
Selected interatomic distances (Å) and angles (°) for complex **1**.[a,b]

Zr–O(1)	2.186(2)	Zr–C(3)	2.508(2)
Zr–N(1)	2.289(2)	Zr–C(4)	2.521(2)
Zr–C(1)	2.535(2)	Zr–C(5)	2.524(2)
Zr–C(2)	2.538(3)	Zr–Cp	2.224
C(1)–C(2)	1.411(4)	C(4)–C(5)	1.394(4)
C(2)–C(3)	1.407(4)	C(5)–C(1)	1.410(4)
C(3)–C(4)	1.404(4)	mean C–C	1.405(4)
O(1)–Zr–N(1)	68.78(4)	O(1)–Zr–Cp	98.61
O(1)–Zr–O(1')	137.56(8)	O(1)–Zr–Cp'	97.82
Cp–Zr–Cp'	133.49	N(1)–Zr–Cp	113.26
C(1)–C(2)–C(3)	108.1(3)	C(4)–C(5)–C(1)	108.5(3)
C(2)–C(3)–C(4)	107.9(3)	C(5)–C(1)–C(2)	107.4(2)
C(3)–C(4)–C(5)	108.2(2)	Aver. C–C–C	108.0(3)

[a] Primed atoms are related to the unprimed ones by the symmetry operation 1 − x, 1 − y, 1/2 − z.
[b] Cp and Cp' are the cyclopentadienyl centroids.

Table 4
Selected interatomic distances (Å) and angles (°) for complex **2**.[a,b]

Hf–O(1)	2.176(3)	Hf–C(3)	2.500(6)
Hf–N(1)	2.264(6)	Hf–C(4)	2.503(6)
Hf–C(1)	2.522(7)	Hf–C(5)	2.504(6)
Hf–C(2)	2.530(7)	Hf–Cp	2.211
C(1)–C(2)	1.415(9)	C(4)–C(5)	1.389(8)
C(2)–C(3)	1.415(9)	C(5)–C(1)	1.390(10)
C(3)–C(4)	1.401(8)	mean C–C	1.402(10)
O(1)–Hf–N(1)	69.1(1)	O(1)–Hf–Cp	97.86
O(1)–Hf–O(1')	138.1(2)	O(1)–Hf–Cp'	98.43
Cp–Hf–Cp'	133.28	N(1)–Hf–Cp	113.36
C(1)–C(2)–C(3)	107.5(6)	C(4)–C(5)–C(1)	108.5(6)
C(2)–C(3)–C(4)	107.3(6)	C(5)–C(1)–C(2)	107.9(6)
C(3)–C(4)–C(5)	108.7(4)	Aver. C–C–C	108.0(6)

[a] Primed atoms are related to the unprimed ones by the symmetry operation 1 − x, 1 − y, 1/2 − z.
[b] Cp and Cp' are the cyclopentadienyl centroids.

Table 5
Selected interatomic distances (Å) and angles (°) for complex **3**.[a]

Ti–O(1)	2.122(1)	C(1)–C(2)	1.494(3)
Ti–O(2)	2.132(1)	C(2)–C(3)	1.415(3)
Ti–N	2.199(2)	C(3)–C(4)	1.394(3)
Ti–C(2)	2.463(2)	C(4)–C(5)	1.405(3)
Ti–C(3)	2.417(2)	C(5)–C(6)	1.410(3)
Ti–C(4)	2.388(2)	C(6)–C(2)	1.400(3)
Ti–C(5)	2.349(2)	C(11)–C(12)	1.486(3)
Ti–C(6)	2.403(2)	C(12)–C(13)	1.391(3)
Ti–C(12)	2.508(2)	C(13)–C(14)	1.419(3)
Ti–C(13)	2.394(2)	C(14)–C(15)	1.388(3)
Ti–C(14)	2.340(2)	C(15)–C(16)	1.394(3)
Ti–C(15)	2.415(2)	C(16)–C(12)	1.410(3)
Ti–C(16)	2.443(2)	mean C–C[b]	1.405(3)
Ti–{Cp(Me)}A	2.087	mean C–C[c]	1.400(3)
Ti–{Cp(Me)}B	2.107		
O(1)–Ti–N	70.78(5)	O(2)–Ti–{Cp(Me)}A	96.71
O(2)–Ti–N	70.31(5)	O(2)–Ti–{Cp(Me)}B	98.94
O(1)–Ti–O(2)	141.07(5)	{Cp(Me)}A–Ti–{Cp(Me)}B	131.42
O(1)–Ti–{Cp(Me)}A	98.05	N–Ti–{Cp(Me)}A	114.26
O(1)–Ti–{Cp(Me)}B	97.80	N–Ti–{Cp(Me)}B	114.32
C(2)–C(3)–C(4)	108.7(2)	C(12)–C(13)–C(14)	108.4(2)
C(3)–C(4)–C(5)	108.3(2)	C(13)–C(14)–C(15)	107.6(2)
C(4)–C(5)–C(6)	107.1(2)	C(14)–C(15)–C(16)	108.1(2)
C(5)–C(6)–C(2)	109.2(2)	C(15)–C(16)–C(12)	108.6(2)
C(6)–C(2)–C(3)	106.7(2)	C(16)–C(12)–C(13)	107.0(2)
Aver. C–C–C[b]	108.0	Aver. C–C–C[c]	107.9

[a] {Cp(Me)}A and {Cp(Me)}B are the centroids for the cyclopentadienyl rings C(2)C(3)C(4)C(5)C(6) and C(12)C(13)C(14)C(15)C(16), respectively.
[b] For the C(2)C(3)C(4)C(5)C(6) ring.
[c] For the C(12)C(13)C(14)C(15)C(16) ring.

The Zr–O(1) bond distance is 2.186(2) Å, and is significantly shorter than the Zr–N(1) bond length, 2.289(2) Å. The Zr–O and Zr–N distances in **1** are comparable to values of 2.16–2.22 Å for Zr–O [7,22] and of 2.30–2.40 Å for Zr–N [7,22b,22c,23], reported for other 5-coordinate zirconocene complexes. The bite angle for the chelate is 68.8° and 69.1° for **1** and **2**, respectively. These values compare well with those seen in [Zr{rac-C$_2$H$_4$(4,5,6,7-tetrahydro-indenyl)$_2$(dipic)] (68.0° and 68.2°) [7]. The coordination geometry about Zr[IV] or Hf[IV] is extremely distorted and can be described either as distorted square pyramidal (quasi square pyramidal) or as distorted trigonal bipyramidal (quasi trigonal bipyramidal); adopting the former view the apical site is occupied by N(1), while in the latter description atoms O(1) and O(1') define the axial sites.

Complex **3** lacks any symmetry elements. The dipic^{2-} group behaves as N,O,O'-chelating ligand, with the centroids of the cyclo-pentadienyl rings of the MeCp$^-$ ligands occupying formally the fourth and fifth coordination sites about Ti[IV]. The coordination geometry is extremely distorted and can be described either as trigonal bipyramidal (with atoms O(1) and O(2) occupying the axial sites, O(1)–Ti–O(2) = 141.1°) or as square pyramidal (with the N atom occupying the apical site, the trans "basal" coordination angles are 141.1° and 131.4°). The ring centroids are at distances of 2.122 and 2.132 Å from the metal center and span an angle of 131.4° at Ti[IV], the two rings intersecting at an angle of 53.0°. The (MeCp)$_2$Ti geometry of the 5-coordinate **3** is very similar to that in the 4-coordinate [Ti(CpMe)$_2$Cl$_2$] precursor [17]. However, the average Ti-centroid distance in the former (2.097 Å) is slightly larger than in the latter (2.067 Å), as expected from the larger coordination "number" of Ti[IV] in **3**. The rather long Ti–O distances (2.122, 2.132 Å) points to a low level of O→Ti donation into the metal center; it seems likely that the geometry around the carboxylate oxygen atoms is forced to allow coordination of the pyridine nitrogen atom to Ti[IV] [20]. The Ti–N bond length (2.199 Å) falls into the expected range for such bonds in 5-coordinate Ti[IV] complexes [8,20]. The C(ring)–CH$_3$ bond lengths (average 1.490 Å) is in the expected range for a C(sp^3)–C(sp^2) bond distance [17]. The general

connected with a rotation of both carboxylate –CO$_2$ groups by 5.27° (**1**) and 5.22° (**2**) out of the plane of the pyridine ring, and by 7.71° (**1**) and 6.67° (**2**) out of the MO(1)N(1)O(1') plane.

features of the molecular structure of **3** in terms of distances and angles between the metal and the dipic^{2-} ligand, as well as the coordination parameters of the cyclopentadienyl ring to the Ti^{IV} center, are similar to those of complex [Ti(Cp)$_2$(dipic)] (**4**) [8]. This indicates that the mode of bonding of the rings to the metal is essentially invariant to the substitution of one Me group on each of the rings. A comparison of the molecular structure of **3** with that of the Zr^{IV} analog [Zr(MeCp)$_2$(dipic)] (**5**) [7] demonstrates that the metal substitution has a small effect on the basic features. A prominent difference is in the M–N, M–O and M–ring centroid distances which are 0.11, 0.05 and 0.13 Å shorter in **3**; this can be readily attributed to the smaller covalent radium of Ti (viz. 1.36 Å) compared to that of Zr (viz. 1.45 Å) [13]. The ring centroid–metal–ring centroid (131.4° in **3** versus 130.6° in **5**), O–metal–O (141.1° in **3** versus 136.6° in **5**) and average N–metal–O (70.6° in **3** versus 68.4° in **5**) angles are slightly larger in the Ti^{IV} compound than in its Zr^{IV} analog, while the angles between the rings are almost the same (53.0° in **3** versus 53.4° in **5**).

Complex **2** is the first structurally characterized Hf^{IV} complex of any form (dipicH$_2$, dipicH$^-$, dipic^{2-}) of dipicolinic acid as ligand. Complexes **3** and **1** join small families of Ti^{IV}/dipic^{2-} [8,20,24,25] and Zr^{IV}/dipic^{2-} [7,16c,19,26] complexes; only a handful of these complexes contain simultaneously organometallic-type ligands [7,8,20].

4. Concluding comments and perspectives

The present work extends the body of results that emphasize the reactivity chemistry of the complexes [M^{IV}(η^5-C$_5$H$_4$R)$_2$X$_2$], where M = Ti, Zr, Hf, R = H, Me, SiMe$_3$,... and X = Cl, Br,..., with polydentate, non-organometallic ligands. The main aspects of our work are: (i) We have obtained the Zr^{IV} complex **1** (which was previously reported as powder [7]) in a form suitable for single-crystal X-ray crystallography and have determined its structure, that was proven to be similar with that of [Ti(Cp)$_2$(dipic)] (**4**) [8]. (ii) We have prepared and fully characterized complex [Hf(Cp)$_2$(dipic)] (**2**) whose structure is almost identical with that of its Zr^{IV} analog **1**; compound **2** is the first structurally characterized Hf^{IV} dipicolinate complex and it thus covers a gap in the literature. (iii) We have proven that the reactivity of [Ti(MeCp)$_2$Cl$_2$] towards dipicH$_2$, is similar to that of [Ti(Cp)$_2$Cl$_2$], in that they both give 1:1 complexes, i.e., the new complex **3** and the known compound [Ti(Cp)$_2$(dipic)] (**4**) [8], respectively; and (iv) From the synthetic inorganic chemistry viewpoint, we have further developed [14] the use of convenient (ambient temperature, aqueous media, aerobic reactions) synthetic conditions for the preparation of Group 4 metal complexes with mixed cyclopentadienyl/carboxylate ligation. This opens the door for reactions of the [M^{IV}(η^5-C$_5$H$_4$R)$_2$X$_2$] complexes with a great variety of polydentate organic ligands.

We have no reason to believe that this research area is exhausted of new results. Indeed, ongoing experiments are producing additional products, and our belief is that we have seen only the tip-of-the-iceberg in the reactivity chemistry of the bis(cyclopentadienyl)metal reagents. As far as future perspectives are concerned, we currently try to synthetically "activate" the bridging capabilities of dipic^{2-} [1a,1f,4a,5b] in this chemistry, e.g., by using monocyclopentadienyl derivatives of Ti^{IV}, Zr^{IV} and Hf^{IV}. We are extending our investigations to the use of organic ligands with better bridging capabilities, e.g., the *gem*-diolate(−1,−2) and hemiketalate(−1) derivatives of di-2-pyridyl ketone, various anionic pyridyl alcohols, a variety of 2-pyridyloximate(−1) and 2,6-pyridyldioximate(−2) ligands etc., in our attempts to link {M^{IV}(η^5-C$_5$H$_4$R)$_2$}$^{2+}$ fragments and to prepare organometallic/coordination clusters and polymers. Finally, we are performing reactions between mono- and bis(cyclopentadienyl) Group 4 metal derivatives (the "metals") and mononuclear 3d-metal/2-pyridyl oxime complexes containing free O

sites (the "ligands") for the synthesis of M/3d clusters (M = Ti, Zr, Hf) using the "metal complexes as metals and metal complexes as ligands" approach.

Appendix A. Supplementary material

CCDC 796112, 796113 and 796114 contain the supplementary crystallographic data for **1**, **2** and **3**, respectively. 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)1223-336033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] (a) For example, see K. Hákanson, M. Lindahl, G. Svensson, J. Albertsson, Acta Chem. Scand. 47 (1993) 449;
(b) K. Browning, K.A. Abboud, G.J. Palenik, J. Chem. Crystallogr. 25 (1995) 851;
(c) E.E. Sileo, M.A. Blesa, G. Rigotti, B.E. Rivero, E.E. Castellano, Polyhedron 15 (1996) 4531;
(d) M. Koman, M. Melník, Ján Moncol, Inorg. Chem. Commun. 3 (2000) 262;
(e) M. Devereux, M. McCann, V. Leon, V. McKee, R.J. Ball, Polyhedron 21 (2002) 1063;
(f) C. Ma, C. Chen, Q. Liu, D. Liao, L. Li, Eur. J. Inorg. Chem. (2003) 1227;
(g) A.C. González-Baró, R. Pis-Diez, O.E. Piro, B.S. Barajón-Costa, Polyhedron 27 (2008) 502.
[2] (a) S.K. Sengupta, S.K. Shani, R.N. Kapoor, Polyhedron 2 (1983) 317;
(b) G. Chessa, G. Marangoni, B. Pitteri, V. Bertasi, V. Ferreti, Inorg. Chim. Acta 185 (1991) 201.
[3] D.L. Hoof, D.G. Tisley, R.A. Walton, J. Chem. Soc., Dalton Trans. (1973) 200.
[4] (a) L. Yang, D.C. Crans, S.M. Miller, A. la Cour, O.P. Anderson, P.M. Kaszynski, M.E. Godzala III, L.D. Austin, G.R. Willsky, Inorg. Chem. 41 (2002) 4859;
(b) P. Buglyo, D.C. Crans, E.M. Nagy, R.L. Lindo, L. Yang, J.J. Smee, W. Jin, L.–H. Chi, M.E. Godzala III, G.R. Willsky, Inorg. Chem. 44 (2005) 5146;
(c) J.J. Smee, L.A. Epps, K. Ooms, S.E. Bolte, T. Polenova, B. Baruah, L. Yang, W. Ding, M. Li, G.R. Willsky, A. La Cour, O.P. Anderson, D.C. Crans, J. Inorg. Biochem. 103 (2009) 575.
[5] (a) L. Mao, Y. Wang, Y. Qi, M. Cao, C. Hu, J. Mol. Struct. 688 (2004) 197;
(b) L. Wang, L. Duan, E. Wang, D. Xiao, Y. Li, Y. Lan, L. Xu, C. Hu, Transition Met. Chem. 29 (2004) 212;
(c) I. Ucar, A. Bulut, A. Karadağ, C. Kazak, J. Mol. Struct. 837 (2007) 38.
[6] (a) For example, see I. Demakopoulos, N. Klouras, C.P. Raptopoulou, A. Terzis, Z. Anorg. Allg. Chem. 621 (1995) 1761;
(b) N. Klouras, N. Tzavellas, C.P. Raptolpoulou, Monatsh. Chem. 128 (1997) 1201;
(c) A. Sofetis, F. Fotopoulou, C.P. Raptopoulou, Th.F. Zafiropoulos, S.P. Perlepes, N. Klouras, Polyhedron 28 (2009) 3356.
[7] U. Niemann, J. Diebold, C. Troll, U. Rief, H.–H. Brintzinger, J. Organomet. Chem. 456 (1993) 195.
[8] (a) R. Leik, L. Zsolnai, G. Huttner, E.W. Neuse, H.H. Brintzinger, J. Organomet. Chem. 312 (1986) 177;
(b) P.D. Kheirollahi, H. Aghabozorg, A. Moghimi, Anal. Sci. 21 (2005) x153.
[9] P. Druce, B. Kingston, M. Lappert, T. Spalding, R. Srivastava, J. Chem. Soc. A (1969) 2106.
[10] (a) L.T. Raynolds, G. Wilkinson, J. Inorg. Nucl. Chem. 9 (1959) 86;
(b) H. Köpf, N. Klouras, Chem. Scripta 19 (1982) 122.
[11] CrystalClear, Rigaku/MSC Inc., The Woodlands, Texas, USA, 2005.
[12] (a) G.M. Sheldrick, SHELXS-97, Structure Solving Program, University of Göttingen, Germany, 1997;
(b) G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1997.
[13] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, sixth ed., Wiley, New York, 1999. pp. xi, 695, 878.
[14] M.G. Meirim, E.W. Neuse, M. Rhemtula, S. Schmitt, H.H. Brintzinger, Transition Met. Chem. 13 (1988) 272.
[15] (a) G.B. Deacon, R.J. Phillips, Coord. Chem. Rev 33 (1980) 227;
(b) D. Martínez, M. Motevallli, M. Watkinson, Dalton Trans 39 (2010) 446.
[16] (a) A.B.P. Lever, A. Mantovani, Inorg. Chem. 10 (1971) 817;
(b) S.C. Dixit, R. Sharan, R.N. Kapoor, Inorg. Chim. Acta 158 (1989) 109;
(c) H. Aghabozorg, A. Moghimi, F. Manteghi, M. Ranjbar, Z. Anorg. Allg. Chem. 631 (2005) 909.
[17] J.L. Petersen, L.F. Dahl, J. Am. Chem. Soc. 97 (1975) 6422.

[18] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic and Bioinorganic Chemistry, fifth ed., Wiley, New York, 1997. pp. 285–291.

[19] G.R. Willey, T.J. Woodman, M. Fisher, M.G.B. Drew, Transition Met. Chem. 23 (1998) 476.

[20] R. Fandos, B. Gallego, A. Otero, A. Rondríguez, M.J. Ruiz, P. Terreros, C. Pastor, Dalton Trans. (2006) 2683.

[21] S. Gutmann, P. Burger, M.–H. Prosenc, H.H. Brintzinger, J. Organomet. Chem. 397 (1990) 21.

[22] (a) U. Thewalt, T. Güthner, J. Organomet. Chem 379 (1989) 59;
    (b) T. Güthner, U. Thewalt, J. Organomet. Chem 371 (1989) 43;

(c) Z.–Q. Wang, S.–W. Lu, H.-F. Guo, N.–H. Hu, Y.–S. Liu, Polyhedron 10 (1991) 2341;
    (d) S. Klima, U. Thewalt, J. Organomet. Chem. 354 (1988) 77.

[23] S.I. Bailey, D. Golgan, L.M. Engelhardt, W.P. Leung, R.I. Papasergio, C.L. Raston, A.H. White, J. Chem. Soc., Dalton Trans. (1986) 603.

[24] M. Shavit, E.Y. Tshuva, Eur. J. Inorg. Chem. (2008) 1467.

[25] (a) D. Schwarzenbach, Helv. Chim. Acta 55 (1972) 2990;
    (b) H. Manohar, D. Schwarzenbach, Helv. Chim. Acta 57 (1974) 1086;
    (c) D. Schwarzenbach, Inorg. Chem. 9 (1970) 2391.

[26] S. Daneshvar, H. Aghabozorg, F. Manteghi, Acta Crystallogr. E 64 (2008) m1308.