

# Deprotonated diindolylmethanes as dianionic analogues of scorpionate bis(pyrazolyl)borate ligands: synthesis and structural characterization of representative titanocene and zirconocene complexes

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## Abstract

Deprotonation of di(3-methylindol-2-yl)phenylmethane ( $L_2H_2$ ) or 2-methoxyphenyldi(3-methylindol-2-yl)methane ( $L'_2H_2$ ) with two equivalents of  $tBuLi$ , followed by reactions with  $Cp_2TiCl_2$  or  $Cp_2ZrCl_2$  yielded complexes  $Cp_2TiL_2$  (**1**),  $Cp_2TiL'_2$  (**2**),  $Cp_2ZrL_2$  (**3**) and  $Cp_2ZrL'_2$  (**4**). Compounds **1–4** were characterized by NMR spectroscopy, and compounds **1**, **3**, and **4** were further analyzed by X-ray crystallography and elemental analysis. The molecular structures of **1**, **3**, and **4** illustrate that chelating di(3-methylindol-2-yl)methanes have a structural relationship to coordinated bis(pyrazolyl)borates.

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**Keywords:** Diindolylmethanes; Nitrogen-donor ligands; Titanium; Zirconium

## 1. Introduction

Anionic poly(pyrazolyl)borates are versatile ligands for fine-tuning coordination environments in inorganic and organometallic complexes [1]. Neutral poly(pyrazolyl)methanes have similarly been investigated to further extend the applications of this valuable family of ligands [2]. However, analogous and isoelectronic dianionic and trianionic ligands have not been heavily investigated. Considering that pyrazolyl and related heterocycles have advantages of reduced tendency for  $\pi$ -coordination and M–N–M bridging, and reduced proclivity for  $N \rightarrow M$   $\pi$ -donation [3–5], further exten-

sion of this class of ligands to include dianionic and trianionic analogues useful for metals in higher oxidation states are desirable [6]. Suitable dianionic and trianionic analogues of poly(pyrazolyl)borates can be envisioned via substitution of pyrrolyl [7] or bulkier indolyl moieties for pyrazolyl substituents in bis- and tris(pyrazolyl)methanes. In this regard, we recently demonstrated the utility of trianionic tri(pyrrol-2-yl)methane and tri(3-methylindol-2-yl)methane for the preparation of bulky, constrained  $\pi$ -acidic phosphines [8,9]. Here, we demonstrate that deprotonated di(3-methylindol-2-yl)phenylmethane ( $L_2H_2$ ) and 2-methoxyphenyldi(3-methylindol-2-yl)methane ( $L'_2H_2$ ) function as dianionic scorpionate chelates to transition metals. The synthesis and characterization of representative transition metal complexes  $Cp_2TiL_2$  (**1**),  $Cp_2TiL'_2$  (**2**),  $Cp_2ZrL_2$  (**3**) and  $Cp_2ZrL'_2$  (**4**) are reported.

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## 2. Experimental

### 2.1. General procedures

All reactions were performed under an atmosphere of purified nitrogen using standard inert atmosphere techniques. Hexanes and toluene were distilled from calcium hydride and sodium, respectively, prior to use. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl.  $\text{CDCl}_3$  was dried by storage over activated molecular sieves. Di(3-methylindol-2-yl)phenylmethane ( $\text{L}_2\text{H}_2$ ) [10,11] and 2-methoxyphenyldi(3-methylindol-2-yl)methane ( $\text{L}'_2\text{H}_2$ ) [11] were prepared by sulfuric acid-catalyzed reactions of 3-methylindole with benzaldehyde and 2-anisaldehyde, respectively, as previously reported. Dichlorobis( $\eta^5$ -cyclopentadienyl)titanium and dichlorobis( $\eta^5$ -cyclopentadienyl)zirconium were obtained from Strem Chemical and used as received. All other reagents were obtained from Aldrich Chemical Co. and used as received. Solution NMR spectra were recorded on a Varian Unity 400 spectrometer using  $\text{CDCl}_3$  as the solvent. Chemical shifts are reported relative to tetramethylsilane. Tentative  $^{13}\text{C}$  NMR assignments are based on previously reported NMR assignments for polyindolylmethanes [11,12] as well as on NMR assignments of indole derivatives reported by Park et al. [13]. In the reporting of NMR data, indole carbons are labeled C2–C7 with C3a and C7a indicating ring fusion positions. Phenyl carbons of the methine substituents are labeled Ph-C1–Ph-C6. All  $^{13}\text{C}\{^1\text{H}\}$  NMR resonances are singlets. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

### 2.2. Synthesis of bis( $\eta^5$ -cyclopentadienyl) {di(3-methylindol-2-yl)phenylmethane}titanium (1)

A solution of  $n\text{BuLi}$  (1.78 ml, 1.6 M in hexanes, 2.85 mmol) was added to a solution of di(3-methylindol-2-yl)phenylmethane (0.500 g, 1.43 mmol) in THF (10 ml) under nitrogen. After stirring at room temperature for 1 h, the dark red solution was added dropwise to a solution of dichlorobis( $\eta^5$ -cyclopentadienyl)titanium (0.355 g, 1.43 mmol) in toluene (10 ml). The resulting mixture was refluxed for 2 h, cooled to room temperature, and filtered through Celite<sup>®</sup>. Volatiles were removed from the filtrate in vacuo and the remaining solid was recrystallized from hot THF to afford black crystals. Yield: 0.548 g, 0.915 mmol, 64%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.58 (d, 2H, H7), 7.08 (m, 7H, phenyl and H4), 6.62 (d, 2H, H6), 6.59 (s, 5H, Cp), 6.36 (d, 2H, H5), 5.78 (s, 5H, Cp), 5.70 (s, 1H, CH), 3.75 (m, 4H,  $\text{CH}_2\text{O}$ , THF), 2.50 (s, 6H,  $\text{CH}_3$ ), 1.85 (m, 4H,  $\text{CH}_2$ , THF).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  145.42 (Ph-*ipso*), 143.69 (C7a), 143.42 (C2), 132.89 (C3a), 128.10 (Ph-*meta*), 127.16 (Ph-*ortho*), 125.94 (Ph-*para*),

120.88 (Cp), 119.84 (C5), 118.99 (Cp), 118.34 (C6), 118.14 (C4), 114.53 (C7), 113.63 (C3), 67.96 ( $\text{CH}_2\text{O}$ , THF), 40.23 (CH), 25.61 (THF), 9.65 ( $\text{CH}_3$ ). Anal. Calc. for  $\text{C}_{35}\text{H}_{30}\text{N}_2\text{Ti} \cdot \text{C}_4\text{H}_8\text{O}$ : C, 78.25; H, 6.40; N, 4.68. Found: C, 76.67; H, 5.90; N, 5.44%.

### 2.3. Synthesis of bis( $\eta^5$ -cyclopentadienyl) {2-methoxyphenyldi(3-methylindol-2-yl)methane}titanium (2)

A solution of  $n\text{BuLi}$  (1.1 ml, 1.6 M in hexanes, 1.8 mmol) was added to a solution of 2-methoxyphenyldi(3-methylindol-2-yl)methane (0.310 g, 0.815 mmol) in THF (15 ml) under nitrogen. After stirring at room temperature for 1 h, the dark green solution was added slowly via cannula to a solution of dichlorobis( $\eta^5$ -cyclopentadienyl)titanium (0.203 g, 0.815 mmol) in toluene (20 ml). The resulting mixture was refluxed for 1.5 h, cooled to room temperature, and the supernatant separated from precipitated LiCl by decantation. Volatiles were removed from the supernatant in vacuo. The resulting residue was dissolved in toluene (10 ml), the solution was filtered through Celite<sup>®</sup>, and volatiles were removed from the filtrate in vacuo. Dissolution of the remaining solid in hot chloroform followed by the addition of hexanes (20 ml) resulted in precipitation of the deep red product, which was isolated by filtration and dried under vacuum.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.44 (m, 2H, H7), 7.09 (s, 5H, Cp), 7.06–6.95 (m, 5H, aromatic), 6.84 (d, 1H, aryl), 6.74–6.66 (m, 4H, aromatic), 6.08 (s, 1H, CH), 5.53 (s, 5H, Cp), 3.69 (s, 3H,  $\text{OCH}_3$ ), 2.41 (s, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  156.53 (Ph-C2), 147.44 (C7a), 142.43 (C2), 133.53 (C3a), 132.80 (Ph-C1), 130.15 (Ph-C6), 127.13 (Ph-C4), 120.51 (Cp), 119.79 (Ph-C5), 119.69 (C5), 118.59 (Cp), 118.21 (C6), 117.87 (C4), 115.0 (C7), 113.88 (Ph-C3), 110.46 (C3), 55.17 ( $\text{OCH}_3$ ), 36.45 (CH), 9.95 ( $\text{CH}_3$ ).

### 2.4. Synthesis of bis( $\eta^5$ -cyclopentadienyl) {di(3-methylindol-2-yl)phenylmethane}zirconium (3)

A solution of  $n\text{BuLi}$  (1.80 ml, 2.88 mmol, 1.6 M) in hexane was added to a solution of di(3-methylindol-2-yl)phenylmethane (0.500 g, 1.43 mmol) in THF (10 ml) and the resulting dark red solution was stirred at room temperature for 1 h. This solution was added to a solution of dichlorobis( $\eta^5$ -cyclopentadienyl)zirconium (0.420 g, 1.44 mmol) in toluene (10 ml) and the resulting mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature and filtered through Celite<sup>®</sup> to remove lithium chloride. Volatiles were removed from the filtrate in vacuo to leave a black residue. Recrystallization from a minimum volume of hot THF afforded dark, red crystals of **3** that were isolated by filtration and dried in vacuo. Concentration of

the filtrate similarly yielded a second crop of crystalline product. Yield: 0.463 g, 0.721 mmol, 50%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.62 (d, 2H, H7), 7.14 (m, 5H, phenyl), 7.09 (d, 2H, H4), 6.82 (t, 2H, H6), 6.37 (s, 7H, Cp and H5), 5.84 (s, 1H, CH), 5.81 (s, 5H, Cp), 3.75 (m, 4H,  $\text{CH}_2\text{O}$ , THF), 2.50 (s, 6H,  $\text{CH}_3$ ), 1.86 (m, 4H, THF).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  144.33 (Ph-*ipso*), 144.13 (C7a), 143.35 (C2), 132.14 (C3a), 127.98 (Ph-*meta*), 127.38 (Ph-*ortho*), 126.06 (Ph-*para*), 120.14 (C5), 118.62 (C6), 118.57 (C4), 116.14 (Cp), 114.89 (Cp), 114.28 (C7), 113.83 (C3), 67.97 ( $\text{CH}_2\text{O}$ , THF), 40.17 (CH), 25.63 (THF), 9.62 ( $\text{CH}_3$ ). Anal. Calc. for  $\text{C}_{35}\text{H}_{30}\text{N}_2\text{Zr} \cdot \text{C}_4\text{H}_8\text{O}$ : C, 72.97; H, 5.97; N, 4.36. Found: C, 72.31; H, 5.94; N, 4.36%.

### 2.5. Synthesis of bis( $\eta^5$ -cyclopentadienyl){2-methoxyphenyldi(3-methylindol-2-yl)methane}zirconium (**4**)

Compound **4** was prepared from solutions of  $^n\text{BuLi}$  (1.20 ml, 1.92 mmol, 1.6 M) in hexane, 2-methoxyphenyldi(3-methylindol-2-yl)methane (0.310 g, 0.815 mmol) in THF (10 ml), and dichlorobis( $\eta^5$ -cyclopentadienyl)zirconium (0.238 g, 0.815 mmol) in toluene (10 ml) using a procedure analogous to that described for the synthesis of **3**. Recrystallization of the resulting black residue from a minimum volume of hot THF afforded dark, red crystals of **4** that were isolated by filtration and dried in vacuo. Concentration of the filtrate similarly yielded a second crop of crystalline product. In some cases a few crystals of unreacted ligand  $\text{L}'_2\text{H}_2$  were also isolated along with **4**.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.50 (m, 2H, H7), 7.07 (m, 5H, aromatic), 6.91 (s, 5H, Cp), 6.88 (m, 3H, aromatic), 6.73 (m, 2H, aromatic), 6.19 (s, 1H, CH), 5.47 (s, 5H, Cp), 3.66 (s, 3H,  $\text{OCH}_3$ ), 2.43 (s, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  156.49 (Ph-C2), 145.70 (C7a), 142.65 (C2), 132.88 (Ph-C1), 132.76 (C3a), 129.71 (Ph-C6), 127.12 (Ph-C4), 119.84 (C5), 119.66 (Ph-C5), 118.58 (C6), 118.29 (C4), 116.03 (Cp), 114.40 (Cp), 114.32 (C7), 113.96 (Ph-C3), 110.40 (C3), 55.23 ( $\text{OCH}_3$ ), 36.28 (CH), 9.84 ( $\text{CH}_3$ ). Anal. Calc. for  $\text{C}_{36}\text{H}_{32}\text{N}_2\text{OZr}$ : C, 72.08; H, 5.38; N, 4.67. Found: C, 71.59; H, 5.62; N, 4.39%.

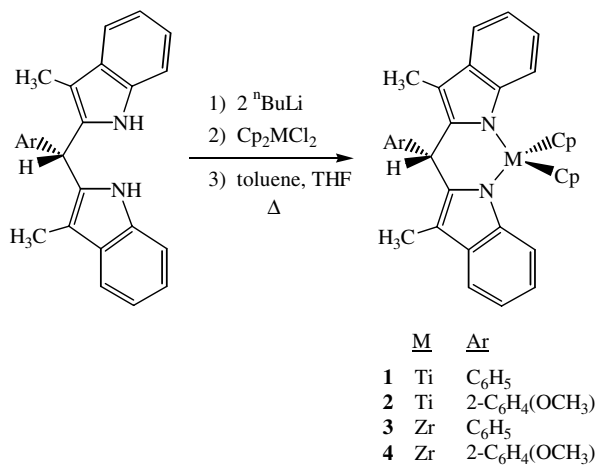
### 2.6. X-ray crystallography

Crystals of  $\mathbf{1} \cdot \text{C}_4\text{H}_8\text{O}$ ,  $\mathbf{3} \cdot \text{C}_4\text{H}_8\text{O}$ , and  $\mathbf{4} \cdot 0.5\text{C}_4\text{H}_8\text{O}$  were grown from THF solutions at  $-20^\circ\text{C}$ . X-ray diffraction data were collected on a Siemens CCD diffractometer using Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), general procedures for which have been previously reported [11]. Data were corrected for decay, Lorentz and polarization effects, and absorption. The structures were solved by direct methods ( $\mathbf{1} \cdot \text{C}_4\text{H}_8\text{O}$ ,  $\mathbf{3} \cdot \text{C}_4\text{H}_8\text{O}$ ) or the Patterson method ( $\mathbf{4} \cdot 0.5\text{C}_4\text{H}_8\text{O}$ ) using SHELXS-86 [14] and refined by least-squares methods on  $F^2$  using

SHELXL-93 [15]. All non-hydrogen atoms were refined anisotropically, except for the carbon and oxygen atoms of the THF solvate molecule of  $\mathbf{4} \cdot 0.5\text{C}_4\text{H}_8\text{O}$ , which were refined with isotropic displacement parameters. Hydrogen atoms in  $\mathbf{1} \cdot \text{C}_4\text{H}_8\text{O}$  and  $\mathbf{3} \cdot \text{C}_4\text{H}_8\text{O}$  were located and refined with isotropic displacement parameters, except for some of the hydrogen atoms bonded to the disordered THF molecules, which were placed in calculated positions and included in the refinement as riding atoms (2 H atoms in  $\mathbf{1} \cdot \text{C}_4\text{H}_8\text{O}$ ; all in  $\mathbf{3} \cdot \text{C}_4\text{H}_8\text{O}$ ). The hydrogen atoms in the room-temperature measurement of  $\mathbf{4} \cdot 0.5\text{C}_4\text{H}_8\text{O}$  were placed in calculated positions and included in the refinement as riding models. No hydrogen atoms were added for the disordered THF molecule. The THF solvent molecules exhibit a similar disorder in all three structures. One atom in the five-member ring assumes two different positions in the lattice. The two positions were refined with equal occupancies for  $\mathbf{1} \cdot \text{C}_4\text{H}_8\text{O}$  and  $\mathbf{4} \cdot 0.5\text{C}_4\text{H}_8\text{O}$ , and with occupancies of 70% and 30% for  $\mathbf{3} \cdot \text{C}_4\text{H}_8\text{O}$ . Details of data collection and refinement are provided in Table 1.

## 3. Results and discussion

Deprotonation of di(3-methylindol-2-yl)phenylmethane ( $\text{L}_2\text{H}_2$ ) or 2-methoxyphenyldi(3-methylindol-2-yl)methane ( $\text{L}'_2\text{H}_2$ ) with  $^n\text{BuLi}$ , followed by reactions with  $\text{Cp}_2\text{TiCl}_2$  yielded  $\text{Cp}_2\text{TiL}_2$  (**1**) and  $\text{Cp}_2\text{TiL}'_2$  (**2**) as brown-black and deep red crystals, respectively (Eq. (1)). NH resonances for the free di(3-methylindol-2-yl)methane ligands ( $\text{L}_2\text{H}_2$ : 7.56 ppm;  $\text{L}'_2\text{H}_2$ : 7.68 ppm) [11] are absent in the  $^1\text{H}$  NMR spectra for **1** and **2**, verifying that deprotonation was successful and that the di(3-methylindol-2-yl)methanes coordinate as dianions.



(1)

NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ ) of **1** and **2** exhibit the expected resonances for the di(3-methylindol-2-yl)methane ligands in each complex. The indolyl moieties are

Table 1  
Summary of X-ray crystallographic data

	1 · C <sub>4</sub> H <sub>8</sub> O	3 · C <sub>4</sub> H <sub>8</sub> O	4 · 0.5C <sub>4</sub> H <sub>8</sub> O
Formula	C <sub>39</sub> H <sub>38</sub> N <sub>2</sub> O <sub>2</sub> Ti	C <sub>39</sub> H <sub>38</sub> N <sub>2</sub> O <sub>2</sub> Zr	C <sub>38</sub> H <sub>36</sub> N <sub>2</sub> O <sub>1.5</sub> Zr
Formula weight	598.61	641.93	635.91
Color	Brown-black	Dark red	Red
Habit	Block	Chunk	Chunk
Crystal size (mm)	0.40 × 0.40 × 0.30	0.35 × 0.30 × 0.15	0.22 × 0.20 × 0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)	P2(1)	P2(1)/n
Unit cell dimensions			
<i>a</i> (Å)	9.504 (2)	9.5686 (3)	10.778 (1)
<i>b</i> (Å)	14.166 (3)	14.2549 (4)	13.275 (2)
<i>c</i> (Å)	11.620 (3)	11.5870 (4)	22.476 (3)
$\beta$ (°)	103.596 (1)	103.544 (1)	101.307 (2)
<i>V</i> (Å <sup>3</sup> )	1520.6 (6)	1536.51 (8)	3153.2 (7)
<i>Z</i>	2	2	4
<i>T</i> (°C)	−123	−123	20
$\mu$ (Mo K $\alpha$ ) (cm <sup>−1</sup> )	3.16	3.92	3.83
$\lambda$ (Å)	0.710 73	0.710 73	0.710 73
Transmission constants	0.992–0.792	0.992–0.920	0.840–0.674
2 $\theta$ limits (°)	5–59	5–59	4–57
Total number of data	17 170	11 031	18 748
Number of unique data	7518	6928	7255
Number of observed data <sup>a</sup>	7167	6689	5153
Number of parameters	545	517	385
<i>R</i> <sub>1</sub> <sup>a,b</sup>	0.0308	0.0214	0.0490
<i>wR</i> <sub>2</sub> <sup>a,c</sup>	0.0741	0.0538	0.1134
max, min peaks (e/Å <sup>3</sup> )	0.226, −0.233	0.261, −0.198	0.504, −0.349

<sup>a</sup>  $I > 2\sigma(I)$ .

<sup>b</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>c</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

chemically equivalent, and integration of the <sup>1</sup>H NMR spectra confirms the presence of two  $\eta^5$ -cyclopentadienyl ligands per diindolylmethane. The <sup>1</sup>H NMR spectra exhibit two singlets for the chemically inequivalent cyclopentadienyl ligands at 6.59 and 5.78 ppm for **1**, and at 7.09 and 5.53 ppm for **2**. The <sup>13</sup>C NMR spectra confirm that the two cyclopentadienyl ligands in each complex are not chemically equivalent. This chemical inequivalence of the cyclopentadienyl groups is due to the methine in the backbone of the diindolylmethane ligands that situates the aryl towards one of the cyclopentadienyl rings on titanium, whereas the other cyclopentadienyl ring is in the vicinity of the methine hydrogen. The <sup>1</sup>H and <sup>13</sup>C NMR resonances for the methoxy group of **2** were observed at 3.69 and 55.17 ppm, respectively, comparable with the chemical shifts of the methoxy resonances for the free ligand (3.73 and 55.87 ppm) [11]. Thus, the methoxy substituent of 2-methoxyphenyldi(3-methylindol-2-yl)methane is not coordinated to the titanium atom in **2**.

The molecular structure of **1** was further confirmed by X-ray crystallography (Fig. 1). The structure consists of a pseudo-tetrahedral titanium atom ligated by two inequivalent cyclopentadienyl ligands and a chelating, bidentate diindolylmethane. Both cyclopentadienyl rings adopt an  $\eta^5$  coordination mode with Ti–C distances ranging from 2.377(2) to 2.465(2) Å, typical of bis( $\eta^5$ -

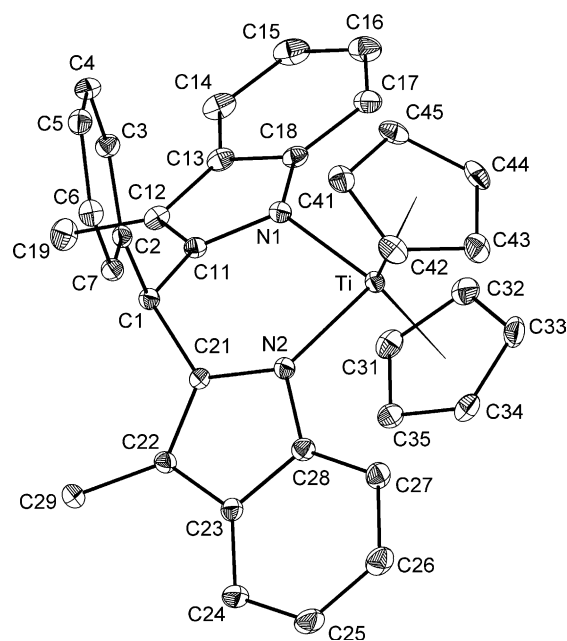


Fig. 1. ORTEP drawing of Cp<sub>2</sub>TiL<sub>2</sub> (**1**). Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ti(1)–N(1) 2.090(1), Ti(1)–N(2) 2.084(1), Ti(1)–C(31) 2.425(2), Ti(1)–C(32) 2.415(2), Ti(1)–C(33) 2.427(2), Ti(1)–C(34) 2.406(2), Ti(1)–C(35) 2.422(2), Ti(1)–C(41) 2.465(2), Ti(1)–C(42) 2.439(2), Ti(1)–C(43) 2.377(2), Ti(1)–C(44) 2.377(2), Ti(1)–C(45) 2.442(2), N(1)–Ti(1)–N(2) 95.15(5).

cyclopentadienyl)titanium(IV) complexes [16]. The di(3-methylindol-2-yl)phenylmethane ligand is coordinated to titanium via the two  $\eta^1$ -indolyl nitrogen atoms to form a six-member chelate ring. The chelate ring adopts a slight chair conformation and an N–Ti–N angle of  $95.15(5)^\circ$ . The Ti–N distances of 2.090(1) and 2.084(1) Å are comparable with the distances of 2.100(4) and 2.070(5) Å reported for  $\text{Cp}_2\text{Ti}(\text{pyrrolyl})_2$  [16]. The Ti–N distances in **1** are longer than those for strong  $\pi$ -donating dimethylamido groups in  $\text{Cp}^*\text{Ti}(\text{NMe}_2)_3$  (1.912(9) Å, 1.923(14) Å) [17], consistent with the reduced tendency for  $\pi$ -donation by  $\eta^1$ -*N*-indolyl ligands. We were unable to obtain X-ray quality crystals of compound **2**.

Deprotonation of  $\text{L}_2\text{H}_2$  or  $\text{L}'_2\text{H}_2$  with  $n\text{BuLi}$ , followed by reactions with  $\text{Cp}_2\text{ZrCl}_2$ , yielded dark red crystals of  $\text{Cp}_2\text{ZrL}_2$  (**3**) and  $\text{Cp}_2\text{ZrL}'_2$  (**4**), respectively (Eq. (1)). Yields of **4** were somewhat variable and the purity of **4** was often plagued by 1–2% of free diindolylmethane,  $\text{L}'_2\text{H}_2$ , based on integration of methyl resonances in the  $^1\text{H}$  NMR spectrum. This impurity could be removed by multiple recrystallizations from toluene.

Spectral data for **3** and **4** are similar to those obtained for titanium analogues **1** and **2**. Integration of the  $^1\text{H}$  NMR resonances for each compound confirms the presence of two  $\eta^5$ -cyclopentadienyl ligands per diindolylmethane. Singlet resonances for the chemically inequivalent cyclopentadienyl ligands are observed in the  $^1\text{H}$  NMR spectra at 6.37 and 5.81 ppm for **3** and 6.91 and 5.47 ppm for **4**. Corresponding cyclopentadienyl resonances are observed in the  $^{13}\text{C}$  NMR spectra at 116.14 and 114.89 ppm for **3** and 116.03 and 114.40 ppm for **4**. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR resonances for the methoxy group of **4** are observed at 3.66 and 55.23 ppm, respectively, and confirm that the methoxy substituent of the diindolylmethane ligand does not coordinate to the zirconium atom.

The molecular structures of **3** and **4** were confirmed by X-ray crystallography (Figs. 2 and 3). Each structure consists of a pseudo-tetrahedral zirconium atom ligated by two inequivalent cyclopentadienyl ligands and a chelating, bidentate diindolylmethane. Each cyclopentadienyl ring coordinates  $\eta^5$  with Zr–C distances ranging from 2.497(2) to 2.556(2) Å, comparable with distances of 2.49(2)–2.59(2) Å observed in  $\text{Cp}_2\text{Zr}(\text{pyrrolyl})_2$  and  $\text{Cp}_2\text{Zr}(2,5\text{-Me}_2\text{pyrrolyl})_2$  [16,18]. The diindolylmethane ligands each coordinate to zirconium via two  $\eta^1$ -*N*-indolyl moieties to form a six-member chelate ring. The chelate rings adopt a slight chair conformation and N–Zr–N angles of  $93.54(5)$  and  $91.86(9)^\circ$  for **3** and **4**, respectively. The Zr–N distances in **3** (2.155(1), 2.167(1) Å) and **4** (2.175(3), 2.186(2) Å) are in the range observed for representative  $\eta^1$ -*N*-pyrrolyl [3b,7c,16,18–20] and  $\eta^1$ -*N*-carbazolyl [5] complexes of zirconium (2.07–2.33 Å). The Zr–N distances in **3** and **4** are longer than those observed for strong  $\pi$ -donating dimethyl-

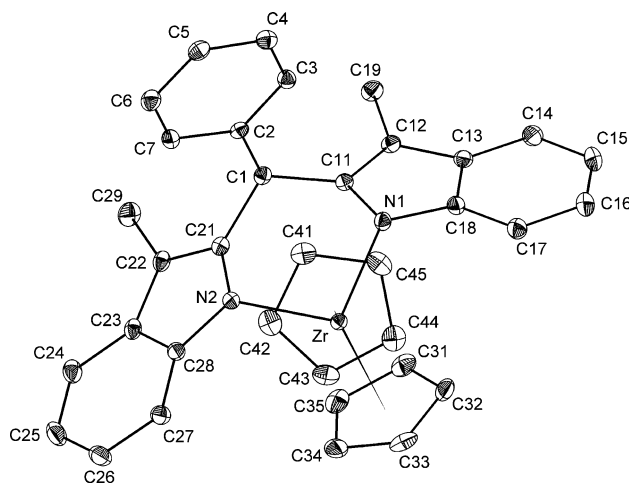


Fig. 2. ORTEP drawing of  $\text{Cp}_2\text{ZrL}_2$  (**3**). Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles ( $^\circ$ ): Zr(1)–N(1) 2.155(1), Zr(1)–N(2) 2.167(1), Zr(1)–C(31) 2.535(2), Zr(1)–C(32) 2.517(2), Zr(1)–C(33) 2.527(2), Zr(1)–C(34) 2.523(2), Zr(1)–C(35) 2.540(2), Zr(1)–C(41) 2.556(2), Zr(1)–C(42) 2.545(2), Zr(1)–C(43) 2.497(2), Zr(1)–C(44) 2.498(2), Zr(1)–C(45) 2.541(2), N(1)–Zr(1)–N(2)  $93.54(5)$ .

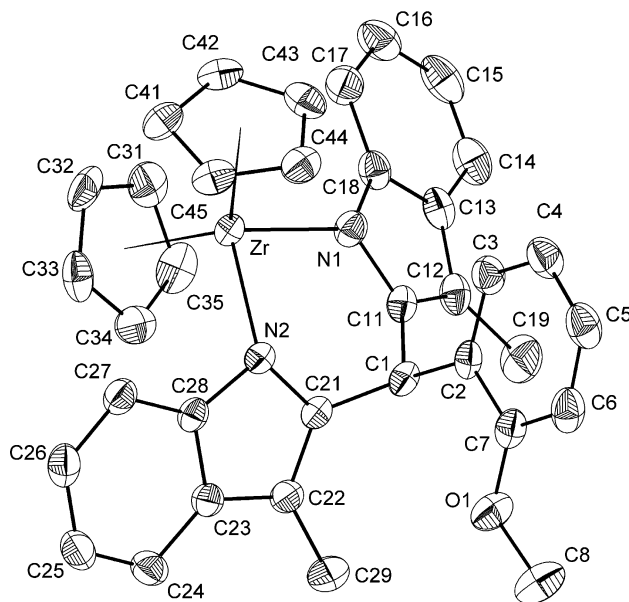


Fig. 3. ORTEP drawing of  $\text{Cp}_2\text{ZrL}'_2$  (**4**). Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles ( $^\circ$ ): Zr(1)–N(1) 2.175(3), Zr(1)–N(2) 2.186(2), Zr(1)–C(31) 2.509(4), Zr(1)–C(32) 2.519(3), Zr(1)–C(33) 2.507(4), Zr(1)–C(34) 2.512(4), Zr(1)–C(35) 2.514(4), Zr(1)–C(41) 2.517(3), Zr(1)–C(42) 2.499(3), Zr(1)–C(43) 2.524(4), Zr(1)–C(44) 2.543(3), Zr(1)–C(45) 2.539(3), N(1)–Zr(1)–N(2)  $91.86(9)$ .

amido groups in zirconium complexes such as  $\text{Zr}(\text{pyrrolyl})(\text{NMe}_2)_3(\text{HNMe}_2)$  (2.019(3), 2.053(3), 2.079(3) Å) [20],  $\text{Zr}(2,5\text{-Ph}_2\text{pyrrolyl})(\text{NMe}_2)_3$  (2.023(4), 2.025(4), 2.050(4) Å) [20], and  $\text{Zr}(\text{carbazolyl})_2(\text{NMe}_2)_2(\text{HNMe}_2)$  (2.022(4), 2.034(4) Å) [5]. The longer Zr–N<sub>indolyl</sub> distances are consistent with the reduced tendency for

$\pi$ -donation by  $\eta^1$ -*N*-indolyl ligands compared with that for dialkylamido ligands.

Another interesting feature in the molecular structures of **1**, **3**, and **4** is the orientation of the di(3-methylindol-2-yl)methane aryl group. This orientation is reminiscent of the scorpionate bis(pyrazolyl)borates [1] in that the aryl group is poised for coordination to the metal in the event that additional ligation were required. For example, 2-methoxyphenyldi(3-methylindol-2-yl)methane ( $L_2H_2$ ) is a potentially tridentate ligand, although its methoxy substituent does not coordinate to titanium or zirconium in **2** or **4**, respectively.

In summary, we have demonstrated that di(3-methylindol-2-yl)methanes function as dianionic, bidentate ligands to transition metals. The different anionic charge of deprotonated diindolylmethanes (−2) relative to bis(pyrazolyl)borates (−1) and bis(pyrazolyl)methanes (0) makes diindolylmethanes, and their potentially tridentate derivatives, an excellent complement to scorpionate bis(pyrazolyl)borates as ligands for inorganic and organometallic chemistry. As part of our continuing effort to explore this new class of ligands [6], the synthesis, characterization, and ethylene polymerization activity of amido complexes of titanium and zirconium ligated by di(3-methylindol-2-yl)methanes will be reported elsewhere [4a].

#### 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC 245763 for compound **1** · C<sub>4</sub>H<sub>8</sub>O, CCDC 245764 for compound **3** · C<sub>4</sub>H<sub>8</sub>O, and CCDC 245765 for compound **4** · 0.5 C<sub>4</sub>H<sub>8</sub>O. Copies of available materials can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).

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