

# The coordination chemistry of 2,4-di(*tert*-butyl)pentadienyl revisited



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## ABSTRACT

The coordination chemistry of the previously neglected 2,4-di(*tert*-butyl)pentadienyl (Pdl') ligand with transition metals is explored. Several open metallocenes  $[(\eta^5\text{-Pdl}')_2\text{M}]$  (M = Ti (**3**), V (**4**) and Cr (**5**)) were prepared and characterized by various spectroscopic techniques and X-ray diffraction. Attempts to prepare the open ferrocene  $[(\eta^5\text{-Pdl}')_2\text{Fe}]$  were hampered by its high thermal instability, which leads to the formation of iron metal and 2,4,7,9-tetra-*tert*-butyl-1,3,7,9-decatetraene (**2**). Nevertheless, the half-open ferrocene  $[(\eta^5\text{-Pdl}')\text{Fe}(\eta^5\text{-Cp}'')]$  (Cp'' = 1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>3</sub>, **6**) and mono(pentadienyl) iridium complex  $[(\eta^5\text{-Pdl}')\text{Ir}(\eta^4\text{-cod})]$  (**9**) were successfully synthesized. The electronic and molecular structures of the half-open ferrocene  $[(\eta^5\text{-Pdl}')\text{Fe}(\eta^5\text{-Cp}'')]$  (**6**) and its closed analogue  $[(\eta^5\text{-Cp}'')\text{Fe}(\eta^5\text{-Cp}'')]$  (**7**, Cp' = 1,3-(Me<sub>3</sub>C)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>) were compared. Complex **6** is significantly more encumbered than **7**, as shown by the short Pdl'<sub>cent</sub>-Fe distance. Clean oxidation of **6** and **7** can be accomplished electrochemically and chemically to give the half-open ferrocenium **6**<sup>+</sup> and closed ferrocenium **7**<sup>+</sup>, respectively, and in both cases steric strain is released upon oxidation. On heating of **6**<sup>+</sup> to 152 °C in the solid state H<sub>2</sub> and isobutene is eliminated to give  $[(\eta^5\text{-Cp}'')_2\text{Fe}]^+$  (**8**).

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## 1. Introduction

Since 1980 [1] pentadienyls have become well-established ligands in transition metal chemistry and adopt an intermediate position between the ubiquitous cyclopentadienyl and allyl systems [2–8]. Whereas cyclopentadienyls usually coordinate in pentahapto ( $\eta^5$ ) fashion, the allyl system is known to readily interconvert between  $\pi$ -( $\eta^3$ )-allyl and  $\sigma$ -( $\kappa\text{C}$ )-coordination. However, besides  $\eta^5$ -,  $\eta^3$ - and  $\kappa\text{C}$ -coordination, several additional coordination modes are available for pentadienyls, which allows them readily to accommodate the steric and electronic environment at the metal atom (Scheme 1).

Besides their structural flexibility, they also have other beneficial properties such as being better  $\pi$ -donors and  $\delta$ -acceptors than the cyclopentadienyl system. Furthermore, because of the open edge, the area enclosed by the five pentadienyl carbon atoms is significantly larger than that of the cyclopentadienyl ring, and so the metal has to move closer to the pentadienyl plane during M–C bond formation in order to maximize the metal-ligand orbital overlap. Although a large number of pentadienyl complexes have been prepared, these investigations have been mainly limited to the parent ligand, C<sub>5</sub>H<sub>7</sub>, or the alkyl- or trimethylsilyl-substituted derivatives such as 2,4-Me<sub>2</sub>C<sub>5</sub>H<sub>5</sub> or 1,5-(Me<sub>3</sub>Si)<sub>2</sub>C<sub>5</sub>H<sub>5</sub> [2–8]. Additionally, a number of so-called edge-bridged pentadienyl

ligands such as cyclooctadienyl [9] or 6,6-dimethylcyclohexadienyl (dmch) [10–15] have been reported.

We have for some time been interested in *t*Bu-substituted cyclopentadienyl [16–32], indenyl [24,33,34] and pyrrolyl ligands [35–38] for the synthesis and stabilization of unusual and/or reactive molecules. Hence, it was surprising to us that the sterically demanding 2,4-(Me<sub>3</sub>C)<sub>2</sub>C<sub>5</sub>H<sub>5</sub> (Pdl') system, which has long been known [39] and which is closely related to its cyclic congener 1,3-(Me<sub>3</sub>C)<sub>2</sub>C<sub>5</sub>H<sub>3</sub> (Cp'), has been more or less neglected in previous investigations (Scheme 2). At the beginning of our study the only known examples included  $[(\eta^5\text{-Pdl}')_2\text{M}]$  (M = Ti, Cr) [39],  $[(\eta^1\text{-Pdl}')_2\text{Zn}]$  [39],  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\eta^5\text{-Pdl}')]$  [40], and  $[(\eta^5\text{-Pdl}')_2\text{Ca}(\text{thf})]$  [41] and only two of these complexes were structurally characterized,  $[(\eta^1\text{-Pdl}')_2\text{Zn}]$  [39] and  $[(\eta^5\text{-Pdl}')_2\text{Ca}(\text{thf})]$  [41]. In the course of our investigations we have recently extended this series of Pdl'-containing complexes to the heavier group 2 homologues Sr and Ba, with our syntheses of  $[(\eta^5\text{-Pdl}')_2\text{Sr}(\text{thf})]$  and  $[(\eta^5\text{-Pdl}')_2\text{Ba}(\text{thf})_2]$  [42]; herein, we report on our investigations concerning the coordination chemistry of Pdl' with selected 3d-transition metals and iridium(I).

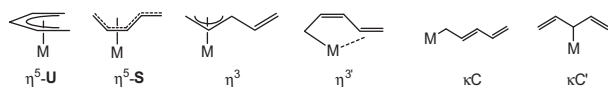
## 2. Experimental

### 2.1. General considerations

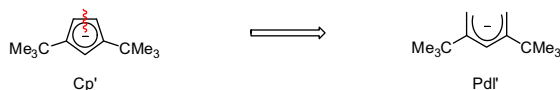
All experiments were carried out under an atmosphere of purified nitrogen, either in a Schlenk apparatus or in a glovebox. The

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**Scheme 1.** Coordination modes of the pentadienyl ligand.



**Scheme 2.** Relationship between the Cp' and PdI' ligand.

solvents were dried and deoxygenated by distillation under nitrogen atmosphere from sodium benzophenone ketyl (tetrahydrofuran) or CaH<sub>2</sub> (DMF) and by an MBraun GmbH solvent purification system (toluene, pentane, CH<sub>2</sub>Cl<sub>2</sub>). The following starting materials were prepared according to literature methods: KPdl' (**1**) [42], [TiCl<sub>3</sub>(thf)<sub>3</sub>] [43], [VCl<sub>3</sub>(thf)<sub>3</sub>] [44], [V<sub>2</sub>Cl<sub>3</sub>(thf)<sub>6</sub>]<sub>2</sub>[Zn<sub>2</sub>Cl<sub>6</sub>] [45], [VCl<sub>2</sub>(py)<sub>4</sub>] [46], [CrCl<sub>2</sub>(thf)<sub>2</sub>] [47], [(η<sup>5</sup>-Cp'')Fe]I<sub>2</sub> [23], and [Ir(cod)Cl]<sub>2</sub> [48]. NMR spectra were recorded on a Bruker DRX 400 spectrometer at 400 MHz (<sup>1</sup>H) or 101 MHz (<sup>13</sup>C) and a Bruker Avance II 300 at 300 MHz (<sup>1</sup>H) or 75 MHz (<sup>13</sup>C). All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents, which are internal standards, for proton and carbon chemical shifts. Elemental analyses were performed on a vario MICRO cube elemental analyzer. Cyclic voltammograms were recorded on a Metrohm μAutolab Type III potentiostat/galvanostat in a CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>] as supporting electrolyte. 99.9% platinum wires (φ 0.6 mm, Chempur) were used as working and counter electrodes, and the potentials were measured against a 99.9% silver wire (φ 0.6 mm, Chempur). Redox potentials were calculated using the formula  $\Delta E_{1/2} = \frac{1}{2} (E_p^{ox} + E_p^{red})$ , where  $E_p^{ox}$  and  $E_p^{red}$  are peak potentials. The couple [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe]<sup>+/</sup>/[(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe] displayed a reversible cyclic voltammetric trace with a redox potential  $\Delta E_{1/2} = +0.46$  V (in CH<sub>2</sub>Cl<sub>2</sub>) under these conditions [49]. The X-band EPR spectra were recorded on a Bruker EMX spectrometer with an OXFORD ESR900 continuous flow cryostat at temperatures  $T \approx 5$  K. The spectra were simulated with EasySpin 4.5.0 [50].

## 2.2. Complex synthesis

### 2.2.1. Preparation of [(η<sup>5</sup>-PdI')<sub>2</sub>Ti] (**3**)

A stirred solution of [TiCl<sub>3</sub>(thf)<sub>3</sub>] (0.113 g, 0.306 mmol) was dissolved in THF (30 mL) and cooled to −78 °C. To this solution KPdl' (**1**) (0.200 g, 0.916 mmol) suspended in THF (5 mL) was added, to form a deep green solution. The reaction mixture was allowed to warm to ambient temperature and stirred for 12 h. The solvent was removed under dynamic vacuum and the residue was extracted with pentane (20 mL). The extracts were filtered and the solvent evaporated. The 2,4,7,9-tetra-*tert*-butyl-1,3,7,9-decatetraene (**2**) was removed by sublimation (50 °C/1.0 × 10<sup>−3</sup> mbar). The residue was dissolved in a minimum amount of pentane and stored at −30 °C to give the product as deep green needles. Yield: 0.062 g (0.153 mmol, 50%). M.p. 141–143 °C (dec). *Anal.* Calc. for C<sub>26</sub>H<sub>46</sub>Ti (406.53 g/mol): C, 76.82; H, 11.41. Found: C, 76.10; H, 11.18%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ −1.18 (br.s, 2H, C(1)H<sub>2,endo</sub>), 1.02 (s, 18H, CMe<sub>3</sub>), 1.38 (s, 18H, CMe<sub>3</sub>), 1.85 (br.s, 2H, C(5)H<sub>2</sub>), 1.98 (br.s, 2H, C(5)H<sub>2</sub>), 3.81 (br.s, 2H, C(1)H<sub>2,exo</sub>), 7.84 (s, 2H, C(3)H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 32.5 (CH<sub>3</sub>) 33.0 (CH<sub>3</sub>), 40.4 (CMe<sub>3</sub>), 40.6 (CMe<sub>3</sub>), 65.9 (C1/C5), 70.9 (C5/C1), 108.7 (C3), 129.4 (C4/2), 138.7 (C2/4) ppm. The E.I. mass spectrum (70 eV) showed a molecular ion at  $m/z = 410$  amu with the following isotopic cluster distribution (in%): 400 (13),

401 (14), 402 (100), 403 (37), 404 (26), 405 (17), 406 (94), 407 (34), 408 (13), 409(2). Simulated distributions (in%) for: C<sub>26</sub>H<sub>46</sub>Ti: 404 (10), 405 (13), 406 (100), 407 (37), 408 (13), 409(3); C<sub>26</sub>H<sub>42</sub>Ti: 400 (10), 401 (12), 402 (100), 403 (36), 404 (13), 405 (3).

### 2.2.2. Preparation of [(η<sup>5</sup>-PdI')<sub>2</sub>V] (**4**)

*Method A:* A stirred solution of [VCl<sub>3</sub>(thf)<sub>3</sub>] (0.199 g, 0.53 mmol) in THF (25 mL) was cooled to −78 °C and a suspension of KPdl' (0.35 g, 1.60 mmol) in THF (5 mL) was added. The reaction mixture was allowed to warm to ambient temperature and a green-black solution and a colorless precipitate formed. The suspension was stirred for 12 h at room temperature and the solvent was removed under dynamic vacuum. After removal of the solvent the 2,4,7,9-tetra-*tert*-butyl-1,3,7,9-decatetraene (**2**) was removed by sublimation (50 °C/1.0 × 10<sup>−3</sup> mbar). The residue was extracted with pentane, and the extracts were filtered and concentrated and cooled to −30 °C. The product was isolated as deep green needles. Yield: 0.010 g (0.024 mmol, 5%). M.p. 133–135 °C (dec). *Anal.* Calc. for C<sub>26</sub>H<sub>46</sub>V (409.59 g/mol): C, 76.24; H, 11.32. Found: C, 76.80; H, 11.19%. The E.I. mass spectrum (70 eV) showed a molecular ion at  $m/z = 405$  amu with the following isotopic cluster distribution (in%): 405 (100), 406 (26), 407 (10), 409 (65), 410 (24), 411 (18). Simulated distributions (in%) for: C<sub>26</sub>H<sub>46</sub>V: 409 (100), 410 (29), 411 (4). C<sub>26</sub>H<sub>42</sub>V: 405 (100), 406 (30), 407 (4). *Method B:* A suspension of KPdl' (0.075 g, 0.34 mmol) in THF (5 mL) was added to a stirred solution of [VCl<sub>2</sub>(py)<sub>4</sub>] (0.075 g, 0.17 mmol, prepared from [V<sub>2</sub>Cl<sub>3</sub>(thf)<sub>6</sub>]<sub>2</sub>[Zn<sub>2</sub>Cl<sub>6</sub>] and pyridine and isolated as a crystalline solid) in THF (10 mL). The suspension was stirred for 30 min at ambient temperature. During this time the color changed from dark red to dark green and a precipitate was formed. The solvent was removed in dynamic vacuum and the residue was extracted with pentane (15 mL). After filtration and concentration the solution was stored at −30 °C to give green crystals after several days. Yield: 0.013 g (0.03 mmol, 18%). *Method C:* A stirred suspension of [V<sub>2</sub>Cl<sub>3</sub>(thf)<sub>6</sub>]<sub>2</sub>[Zn<sub>2</sub>Cl<sub>6</sub>] (0.093 g, 0.06 mmol) in THF (5 mL) was cooled to −78 °C and a suspension of KPdl' (0.100 g, 0.46 mmol) in THF (5 mL) was added and stirred for 1 h at this temperature. The reaction mixture was allowed to warm slowly to room temperature and the solvent was removed under dynamic vacuum. The dark residue was extracted with pentane (15 mL). The green extracts were filtered, concentrated and stored at −30 °C. After several days green crystals were isolated. Yield: 0.006 mg (0.015 mmol, 6%).

### 2.2.3. Preparation of [(η<sup>5</sup>-PdI')<sub>2</sub>Cr] (**5**)

A stirred solution of [CrCl<sub>2</sub>(thf)<sub>2</sub>] (0.061 g, 0.23 mmol) in THF (20 mL) was cooled to −78 °C and a suspension of KPdl' (0.10 g, 0.46 mmol) in THF (5 mL) was added. The reaction mixture was allowed to warm to ambient temperature and a green-black solution and a colorless precipitate formed. The suspension was stirred for 12 h at room temperature, the solvent was removed under dynamic vacuum, and the residue was extracted with pentane (10 mL). After filtration and solvent evaporation the residue was dissolved in a minimum amount of pentane and stored at −30 °C. The product was isolated as fine, dark green needles. Yield: 0.048 g (0.12 mmol, 51%). M.p. 178–180 °C (dec). *Anal.* Calc. for C<sub>26</sub>H<sub>46</sub>Cr (410.65 g/mol): C, 76.05; H, 11.29. Found: C, 76.46; H, 11.28%. The E.I. mass spectrum (70 eV) showed a molecular ion at  $m/z = 410$  amu with the following isotopic cluster distribution (in%): 406 (18), 407 (7), 408 (8), 409 (3), 410 (100), 411 (43), 412 (10), 413 (1). Simulated distributions (in%) for: C<sub>26</sub>H<sub>46</sub>Cr: 408 (5), 409 (2), 410 (100), 411 (40), 412 (18), 413 (16); C<sub>26</sub>H<sub>42</sub>Cr: 404 (5), 405 (2), 406 (100), 407 (41), 408 (11), 409(2).

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