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Zirconium Complexes of Two Different Iminopyrrolyl Ligands – Syntheses and Structures

Ravi K. Kottalanka,^[a] Kishor Naktode,^[a] and Tarun K. Panda*^[a]

Dedicated to Professor Anil J. Elias on the Occasion of His 53rd Birthday

Keywords: Iminopyrrole; Zirconium; Metallacycles; Chelating ligands; Steric crowding

Abstract. The reaction involving N-aryliminopyrrolyl ligand, 2-((*p*-Me-C₆H₃N=CMe)-C₄H₃NH) (**1a**) (Imp^{Me}-H), and Zr(OrBu)₄ in a 2:1 molar ratio in toluene at 90 °C afforded the corresponding bis(iminopyrrolyl) complex of zirconium, [(Imp^{Me})₂Zr(OrBu)₂] (**2a**) having two bidentate iminopyrrole groups in the coordination sphere. In contrast, the bulkier 2-((2,6-*i*Pr₂C₆H₃N=CH)-C₄H₃NH) (**1b**) (Imp^{Dipp}-H) and Zr(OrBu)₄ in a 1:1 molar ratio under the same condition yielded

the corresponding mono(iminopyrrolyl) complex of zirconium, [(Imp^{Dipp})Zr(OrBu)₃(THF)] (**2b**), which contains only one bidentate iminopyrrole moiety in the coordination sphere. Both complexes were characterized by single-crystal X-ray diffraction analysis. The solid-state structures reveal that the bulky iminopyrrole ligands cause a steric crowding around the zirconium ion along with three *tert*-butoxide ligands attached to the central metal atom.

Introduction

In the post metallocene era, chelating nitrogen ligands with bulky substituent have been explored as alternatives to η⁵-cyclopentadienyl ligands for the design of olefin polymerization catalysts based on early and late transition metal complexes.^[1] It is well established that nitrogen-based multi-dentate ligands such as phenoxyimine,^[2–5] 2,6-bis(*N*-aryliminomethyl)pyridine,^[6] and α-diimine derivatives^[7] have already proven intense research interests due to their handiness in feasibility and flexibility in design to introduce sterically and electronically demanding features on the ligand as desired for polymerization catalysts.^[8] In addition, another class of ligands is the bidentate and tridentate iminopyrrole ligand systems. The recent exploration of the nitrogen-based ligand modification has promoted the synthetic application of the iminopyrrolyl ligands for preparing many kinds of transition metal complexes. Recently *Mashima* et al. reviewed the synthetic and structural features of transition metal and the lanthanide complexes with the multi-dentate iminopyrrolyl ligands and their catalytic activity, especially polymerization of α-olefins.^[9] In this field of research, a number of working groups have synthesized a wide variety of transition-metal complexes with bidentate as well as tridentate iminopyrrolyl ligands.^[10] Very recently *Roesky* et al. also reported the heavier alkaline earth metal complexes of tridentate 2,5 bis(*N*-2,6-(diisopropylphenyl)iminomethyl)-pyrrol ligands as hydroamination catalysts.^[11]

Recently, *Mashima* group reported the synthesis and characterization of the group 2 metal complexes supported by bidentate iminopyrrolyl ligands and their application for catalytic ring-opening polymerization of ε-caprolactone with respect to the effects of the ionic radii of these central metal atoms.^[12] They also studied zirconium mono(iminopyrrolyl) complexes, which are used as catalysts for ethylene polymerization under atmospheric pressure of ethylene in the presence of excess amounts of MMAO.^[13] Inspired by these results we were interested to prepare mono(iminopyrrolyl) zirconium complexes having alkoxides as the auxiliary ligands instead of benzyl groups. These can give a comparative stability of the central zirconium atom as we can anticipate a sluggish reactivity at the central metal atom due to presence of alkoxide ligands.

Herein we report the synthesis and solid-state structures of two zirconium complexes having less bulky 2-((*p*-Me-C₆H₃N=CMe)-C₄H₃NH) to more bulky 2-((2,6-*i*Pr₂C₆H₃N=CH)-C₄H₃NH) iminopyrrole ligands.

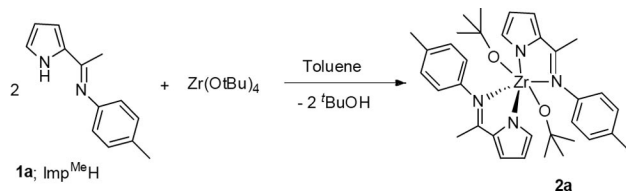
Results and Discussion

The title compound [(Imp^{Me})₂Zr(OrBu)₂] (**2a**) is obtained by elimination of *tert*-butanol. The compound 2-((*p*-Me-C₆H₃N=CMe)-C₄H₃NH) (**1a**) was treated with anhydrous zirconium(IV) *tert*-butoxide [Zr(OrBu)₄] in a 2:1 molar ratio in toluene at 90 °C and subsequent evaporation followed by crystallization from THF/pentane (1:2) in high yield (Scheme 1). However, if the same reaction is done by in 1:1 molar ratio, only compound **2a** is obtained in lower yield. In contrast, the bulkier iminopyrrole 2-((2,6-*i*Pr₂C₆H₃N=CH)-C₄H₃NH) (**1b**) was reacted with Zr(OrBu)₄ in a 1:1 molar ratio, title compound [(Imp^{Dipp})Zr(OrBu)₃(THF)] (**2b**) was iso-

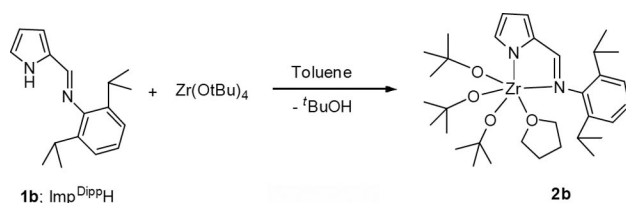
* Dr. T. K. Panda
Fax: + 91-40-23016032
E-Mail: tpanda@iith.ac.in

[a] Department of Chemistry
Indian Institute of Technology Hyderabad
Ordnance Factory Estate
Yeddumailaram 502205, Andhra Pradesh, India

lated after crystallization from THF/pentane (1:2) in high yield (Scheme 2). Both compounds **2a** and **2b** were characterized by standard combustion analysis as well as by spectroscopic techniques. The solid-state structures of both the compounds were established by single-crystal X-ray diffraction analysis.



Scheme 1.



Scheme 2.

The ^1H NMR spectrum of the diamagnetic compound **2a** shows three sharp singlets ($\delta = 2.10$, 1.74, and 1.23 ppm) in a 6:6:18 ratio assigned to one methyl groups at the imine carbon, one methyl group at the *p*-position of the aryl ring of each iminopyrrolyl ligand, and the six methyl groups from the two *tert*-butoxide ligands indicating the attachment of two iminopyrrolyl ligands into the central zirconium atom. The resonance of the protons at pyrrole moiety appeared at $\delta = 6.52$ and 6.40 ppm as the broad signals. It is noteworthy that the monoiminopyrrolyl zirconium complex of composition $(\text{Imp}^{\text{Me}})\text{Zr}(\text{OrBu})_3$ was not detected in the ^1H NMR spectrum as a side product, presumably due to the increased basicity of a *tert*-butoxide group bound to the central zirconium atom when one iminopyrrolyl ligand was introduced.

In the ^1H NMR spectrum of compound **2b**, a sharp singlet at $\delta = 1.26$ ppm corresponds to the methyl groups of the *tert*-butoxide groups and two doublets at $\delta = 1.16$ and 1.08 ppm with a coupling constant of 6.0 Hz each clearly representing the isopropyl methyl groups of iminopyrrolyl ligand. The signals of the protons at pyrrole moiety appear as multiplets in the similar position like compound **2a** ($\delta = 6.76$ – 6.75 and 6.50 – 6.48 ppm).

The solid-state structures of **2a** and **2b** were confirmed by single-crystal X-ray diffraction analysis. Data collection parameters are given in Table 1. Compound **2a** crystallizes in the orthorhombic space group *Pbca* having eight molecules in the unit cell, whereas compound **2b** crystallizes in the monoclinic space group *C2/c* having eight molecules in the unit cell. The solid-state structures of compounds **2a** and **2b** are shown in Figure 1 and Figure 2, respectively. In each complex, the central metal zirconium is six fold coordinated. In complex **2a**, the central metal zirconium is coordinated by two chelating bidentate iminopyrrolyl ligands and two monodentate *tert*-butoxide groups, adopting distorted octahedral arrangement. Two

five membered metallacycle Zr1-N1-C4-C5-N2 and Zr1-N3-C17-C18-N4 have been formed by the chelation of two bidentate iminopyrrolyl ligands to the zirconium atoms. The bond lengths of Zr-N^{Pyr} [Zr-N1 , 2.228(3) Å; Zr-N3 , 2.304(3) Å] are slightly shorter than those of $\text{Zr-N}^{\text{imine}}$ [Zr-N2 , 2.389(3) Å; Zr-N4 , 2.327(3) Å], which can be explained by considering the Zr-N^{Pyr} covalent and $\text{Zr-N}^{\text{imine}}$ coordination bonds. Zr-N distances are in the similar range [$\text{Zr-N}^{\text{Pyr}} = 2.203(4)$ and $\text{Zr-N}^{\text{imine}} = 2.361(4)$ Å] known for $[(\text{Imp}^{\text{Dipp}})\text{Zr}(\text{CH}_2\text{Ph})_2][\eta^6\text{-PhCH}_2\text{Al}(\text{C}_6\text{F}_5)_3]$ reported in the literature.^[14] The Zr-O bonds [1.916(2) and 1.928(2) Å] are in the range reported (1.900 Å) for the zirconium tri-*tert*-butoxide compound $[(\text{tritox})_2\text{ZrCl}_3\cdot\text{Li}(\text{OEt})_3]$.^[15] The dihedral angle between the two planes containing N1-Zr-N2 and N3-Zr-N4 is 76.56° , which is clear deviation from the octahedral arrangement.

Table 1. Crystallographic details of $[(\text{Imp}^{\text{Me}})_2\text{Zr}(\text{OrBu})_2]$ (**2a**) and $[(\text{Imp}^{\text{Dipp}})\text{Zr}(\text{OrBu})_3(\text{THF})]$ (**2b**).

	2a	2b
Formula	$\text{C}_{34}\text{H}_{44}\text{N}_4\text{O}_2\text{Zr}$	$\text{C}_{33}\text{H}_{56}\text{N}_2\text{O}_4\text{Zr}$
Formula weight	631.95	636.02
Crystal system	orthorhombic	monoclinic
Space group	<i>Pbca</i>	<i>C2/c</i>
<i>a</i> / Å	17.068(5)	30.067(5)
<i>b</i> / Å	18.700(5)	15.552(5)
<i>c</i> / Å	20.407(5)	18.399(5)
α / °	90	90
β / °	90	125.272(5)
γ / °	90	90
<i>V</i> / Å ³	6513(3)	7024(2)
<i>Z</i>	8	8
Density / $\text{mg}\cdot\text{m}^{-3}$	1.289	1.203
<i>T</i> / K	120(2)	120(2)
Radiation	$\text{Mo-K}\alpha$ ($\lambda = 0.71073$ Å)	$\text{Mo-K}\alpha$ ($\lambda = 0.71073$ Å)
μ / mm^{-1}	0.369	0.348
<i>F</i> (000)	2303	2720
Absorption correction	Empirical	Empirical
Reflections collected	109411	70632
Unique reflections	9850 [$R_{\text{int}} = 0.0149$]	10953 [$R_{\text{int}} = 0.0738$]
Completeness to θ	99.8 %	99.4 %
GOF	1.085	0.844
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
R_1 ; wR_2	0.1195; 0.1665	0.0668; 0.1665

In complex **2b**, the central metal zirconium is coordinated by one chelating bidentate iminopyrrolyl ligands and three monodentate *tert*-butoxide molecules along with one tetrahydrofuran molecule, adopting a distorted octahedral arrangement. A five membered metallacycle Zr1-N1-C1-C5-N2 was formed by the chelation of one bidentate iminopyrrolyl ligands to the zirconium metal. The Zr-N^{Pyr} bond length [Zr-N1 , 2.288(3) Å] is considerable shorter than that of $\text{Zr-N}^{\text{imine}}$ [Zr-N2 , 2.459(3) Å]. However, the elongation of all the zirconium–nitrogen distances compared with that of **2a** complex can be accounted due to higher steric crowding around the central zirconium atom due to the presence of two isopropyl groups at the ligand backbone in addition with three *tert*-butoxide groups attached to the central metal atom. Among

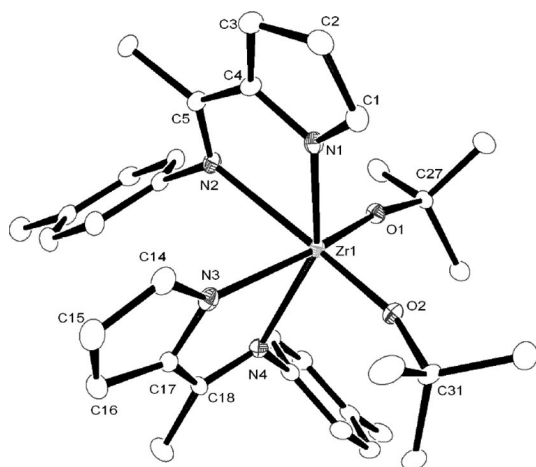


Figure 1. Solid-state structure of **2a** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths /Å and bond angles /°: Zr–O1 1.928(2), Zr–O2 1.916(2), Zr–N1 2.228(3), Zr–N2 2.389(3), Zr–N3 2.304(3), Zr–N4 2.327(2); O1–Zr–O2 103(11), O1–Zr–N1 106.20(11), O2–Zr–N1 95.29(11), O2–Zr–N3 90.90(11), O1–Zr–N3 160.70(11), N1–Zr–N3 84.58(11), O2–Zr–N4 97.61(11), O1–Zr–N4 94.82(11), N1–Zr–N4 151.93(11), N3–Zr–N4 70.43(11), O2–Zr–N4 70.43(11), O2–Zr–N2 161.61(11), O1–Zr–N2 91.88(11), N1–Zr–N2 70.63(11), N3–Zr–N2 91.88(11), N4–Zr–N2 90.66(11).

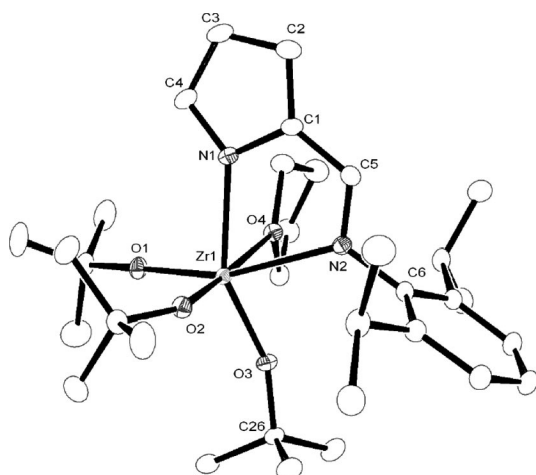


Figure 2. Solid-state structure of **2b** showing the atom labeling scheme, omitting hydrogen atoms. Selected distances /Å and angles /°: Zr–O1 1.940(2), Zr–O2 1.9407(19), Zr–O3 1.9566(19), Zr–N1 2.288(2), Zr–O4 2.391(2), Zr–N2 2.459(2); O1–Zr–O2 98.14(8), O2–Zr–O3 101.07(8), O1–Zr–O3 105.84(9), O2–Zr–N1 96.71(8), O1–Zr–N1 93.60(9), O3–Zr–N1 151.31(8), O2–Zr–O4 174.75(8), O3–Zr–O4 82.67(8), N1–Zr–O4 78.43(7), O2–Zr–N2 93.58(8), O1–Zr–N2 160.96(8), O3–Zr–N2 86.43(8), N1–Zr–N2 70.06(8), O4–Zr–N2 82.91(7).

Zr–O bond lengths, the Zr–O3 bond lengths [1.957(19) Å versus Zr–O1 1.940(2) and Zr–O2 1.9407(19) Å] is elongated due to the *trans* effect of the Zr–N^{pyr} bond.

Conclusions

New heteroleptic iminopyrrolyl complexes of zirconium by the reaction two different iminopyrrole ligands and zirconium

(IV) *tert*-butoxide were prepared and their molecular structures were elucidated by X-ray diffraction. The bulkier iminopyrrole ligand gave only one iminopyrrole attachment to the central metal atom, whereas less bulky iminopyrrole ligand gave two iminopyrrole moieties attached to the central zirconium. Both complexes adopt distorted octahedral arrangement and steric crowding was observed around the central zirconium atom in the complex with bulkier iminopyrrole ligand.

Experimental Section

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out in an argon atmosphere using the standard Schlenk technique or an argon-filled glove box. Hydrocarbon solvents (*n*-pentane) were distilled in a nitrogen atmosphere from LiAlH₄ and stored in a glove box. THF was dried and deoxygenated by distillation over sodium benzophenone ketyl in argon, distilled, and dried with CaH₂ prior to store in the glove box. [D₆]Benzene was dried with Na/K alloy and stored in glove box. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were measured with a BRUKER AVANCE III-400 spectrometer. Elemental analyses were performed with a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. Iminopyrrolyl ligands (**1a** and **1b**),^[16] were prepared according to the literature procedures and Zr(OrBu)₄ was purchased from Sigma Aldrich.

[(Imp^{Me})₂Zr(OrBu)₂] (2a): Ligand **1a** (200 mg, 1.01 mmol) and anhydrous [Zr(OrBu)₄] (191.5 mg, 0.5 mmol) were mixed and toluene (5 mL) was added. The whole reaction mixture was stirred for 20 h at 90 °C. The reaction mixture was cooled and after evaporation, a solid residue was obtained. The compound was crystallized from THF/pentane at –35 °C as colorless crystal after 1 d. Yield 300 mg (95%). ¹H NMR (400 MHz, C₆D₆, 35 °C): δ = 6.90–6.88 (m, 4 H, Ph), 6.79 (br., 4 H, Ph), 6.52 (br., 4 H, py), 6.40 (br., 2 H, Py), 2.10 (s, 6 H, CH₃), 1.74 (s, 6 H, CH₃), 1.23 (s, 18 H, CH₃). ¹³C{¹H} NMR (100 MHz, C₆D₆, 35 °C): δ = 148.5 (C=N), 140.1 (ipso C), 134.2 (*p*-C, Ph), 129.2 (*o*-C, Ph), 124.0 (py), 117.4 (py), 111.7 (py), 32.6 (CH₃) 20.6 (CH₃), 16.8 (CH₃). C₃₄H₄₄N₄O₂Zr (631.96): calcd. C 64.62, H 7.02, N 8.87%; found C 64.21, H 6.91, N 8.69%.

[(Imp^{Dipp})Zr(OrBu)₃(THF)] (2b): Synthesized by following a similar procedure as described above. Colorless crystals were obtained in 89% yield. ¹H NMR (400 MHz, C₆D₆, 35 °C): δ = 7.75 (br., 2 H, N = CH), 7.0–7.69 (m, 2 H, *p*-Ph), 7.60–7.59 (m, 4 H, *m*-Ph), 6.76–6.75 (m, 2 H, py), 6.50–6.48 (br., 4 H, py), 3.65–3.61 (m, 12 H, THF), 3.55–3.52 (m, 4 H, CH(CH₃)₂), 1.34–1.33 (br., 12 H, THF), 1.26 (s, 27 H, CH₃), 1.16 (d, 12 H, CH₃), 1.08 (d, 12 H, CH₃). ¹³C{¹H} NMR (100 MHz, C₆D₆, 35 °C): δ = 162.0 (C=N), 149.9 (ipso C), 140.7, 137.9, 137.4 (*p*-C, Ph), 124.9 (Ph), 123.7 (py), 122.3 (py), 112.4 (py), 68.3 (THF), 28.6 (CH₃), 25.7 (THF), 23.3 (CH₃). C₃₃H₅₆N₂O₄Zr (636.02): calcd. C 62.32, H 8.87, N 4.40%; found, C 62.17, H 8.65, N 4.22%.

X-ray Crystallographic Studies: Single crystals of **2a** and **2b** were grown from a solution of THF/pentane (1:2) in an argon atmosphere at a temperature of –35 °C. In each case a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 120(2) K. All measurements were made with a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo-K_α (0.71073 Å) radiation. Crystal data and structure refinement parameters are summarized in Table 1. The structure was solved by direct methods (SIR2004)^[17] and refined on *F*² by full-matrix least-squares methods using SHELXL-97.^[18] Non-hydrogen atoms were anisotropically re-

finied. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$ with $\sigma^2(F_o^2)$ from counting statistics. The function R_1 and wR_2 were $(\Sigma ||F_o| - |F_c||)/\Sigma |F_o|$ and $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma (wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-951863 (**2a**) and CCDC-951862 (**2b**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

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