

An Unprecedented Hybrid Scorpionate/Cyclopentadienyl Ligand

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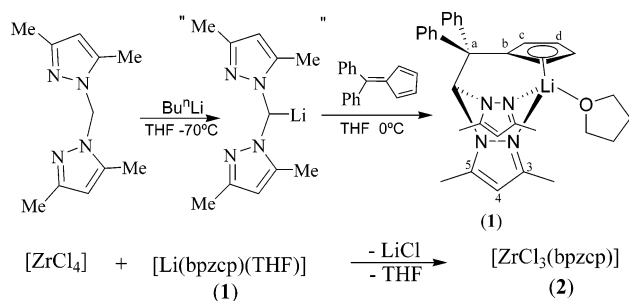
Metal complexes with donor-functionalized cyclopentadienyl ligands have been studied intensively in recent years because of their potential applications as catalysts in polymerization processes.¹ Replacement of cyclopentadienyl ring hydrogens by various substituents has been shown to result in significant changes in both steric and electronic effects on the metal centers.²

The most recent strategy in the design and modification of catalysts for olefin polymerization involved the development of noncyclopentadienyl-based complexes of group 4 metals, with particular attention focused on nitrogen- and/or oxygen-containing ligands.³ Given the impact of ligand design, we recently reported⁴ the preparation of new "heteroscorpionate" ligands.⁵ Our new ligands are related to the tris(pyrazol-1-yl)methane system,⁶ but in this case one of the pyrazole groups is replaced by a carboxylate, dithiocarboxylate, or ethoxy group to give a small degree of steric hindrance and considerable coordinative flexibility.

However, despite the development of donor-functionalized cyclopentadienyl ligands and the emerging importance of the "heteroscorpionate" ligands, hybrid scorpionate/cyclopentadienyl-lithium compound precursors for the introduction of these ligands into transition metal complexes are unknown. With the aim of addressing this situation, we have developed a simple and efficient synthetic route that allowed us to isolate the first hybrid scorpionate/cyclopentadienyllithium compound as a precursor for a new class of tridentate ligand.

Deprotonation at the methylene group of bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm)⁷ with BuⁿLi, followed by reaction with 6,6-diphenylfulvene yielded the lithium compound [Li(bpzcp)(THF)] **1** [bpzcp = 2,2-bis(3,5-dimethylpyrazol-1-yl)-1,1-diphenylethylcyclopentadienyl] (see Scheme 1).

Scheme 1. Summary of Reactions Leading to Compounds **1** and **2**



The ¹H and ¹³C{H} NMR spectra exhibit only one set of resonances, as would be expected for the presence of two equivalent pyrazolyl rings in the molecule. The mass spectrum (FAB) of **1**

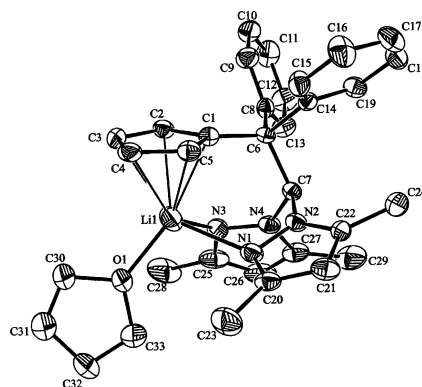


Figure 1. ORTEP diagram of **1** with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Li(1)–O(1), 1.96(1); Li(1)–N(1), 2.37(1); Li(1)–N(3), 2.13(1); O(1)–Li(1)–N(3), 105.4(5); N(1)–Li(1)–N(3), 83.4(4); O(1)–Li(1)–N(1), 103.5(5).

indicates a mononuclear formulation, which was corroborated by an X-ray crystal structure determination for **1** (see Figure 1).⁸ The geometry around the Li atom can be described as a distorted tetrahedron with a "heteroscorpionate" ligand that acts in a tridentate fashion (two coordinated pyrazole rings and a cyclopentadienyl ring) and one molecule of THF. Both Li–N distances [2.37(1) and 2.13(1) Å] are in good agreement with others determined for lithium scorpionate or poly(pyrazolyl)methane complexes.^{4a,d,9} The C₅H₄ ring is unsymmetrically bonded to the Li atom, with Li–C bond lengths ranging from 2.25(1) to 2.44(1) Å, and these distances are in agreement with other functionalized cyclopentadienyllithium complexes.¹⁰

This lithium compound is a new class of tridentate ligand and has been used for the synthesis of a new zirconium complex. Thus, lithium compound **1** reacted at -70 °C, in a 1:1 molar ratio (Scheme 1) with [ZrCl₄] in THF to give, after the appropriate workup, the complex [ZrCl₃(bpzcp)] (**2**), which was isolated as a red solid. The ¹H NMR spectrum of this complex exhibits one singlet for each of the H⁴, Me³, and Me⁵ pyrazole protons and two multiplets for the H^c and H^d cyclopentadienyl protons, indicating that the two pyrazolyl rings are equivalent and that a symmetry plane exists. These results are consistent with an octahedral structural disposition, and κ³-NNη⁵Cp coordination for the bpzcp ligand is proposed. The ¹³C{H} NMR spectrum of complex **2** confirms this disposition. This complex constitutes the first example of a group 4 metal complex bearing a hybrid scorpionate/cyclopentadienyl ligand.

To confirm the proposed structure for this complex, an X-ray crystal structure analysis was carried out (see Figure 2).⁸ The structure consists of a heteroscorpionate ligand bonded to the zirconium atom through the two nitrogen atoms and the cyclopentadienyl ring. In addition, the zirconium center is coordinated to three chlorine atoms. This center has a distorted octahedral

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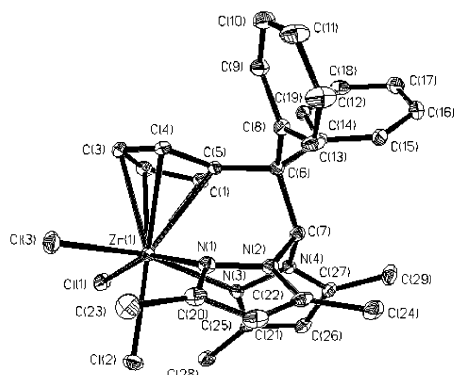


Figure 2. ORTEP diagram of **2** with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Zr(1)–N(3), 2.391(4); Zr(1)–N(1), 2.424(4); Zr(1)–Cl(1), 2.479(1); Zr(1)–Cl(3), 2.468(1); Zr(1)–Cl(2), 2.513(1); N(3)–Zr(1)–Cl(3), 160.66(9); N(1)–Zr(1)–Cl(1), 158.32(9); Cl(2)–Zr(1)–Cl(1), 148.6(1).

environment with a major distortion in the N(1)–Zr(1)–Cl(1) angle, which has a value of 158.32(9)°. The Zr(1)–Cl(1), Zr(1)–Cl(2), and Zr(1)–Cl(3) bond distances of 2.479(1), 2.513(1), and 2.468(1) Å, respectively, are as one would expect for a Zr pyrazolyl complex.¹¹ In this complex, in contrast to lithium complex **1**, the C₅H₄ ring is symmetrically bonded to the Zr atom with Zr–C bond distances of 2.523(4) to 2.572(4) Å.

In conclusion, we describe here a simple and efficient method for the preparation of the first hybrid scorpionate/cyclopentadienyllithium compound as a new class of tridentate ligand. This compound is an excellent reagent for the introduction of this ligand into transition metal complexes, a fact confirmed by reaction with a zirconium halide.

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Supporting Information Available: Spectroscopic data and details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) Crystallographic data for **1**: C₃₃H₃₇LiN₄O, monoclinic, P2₁/a, a = 16.576 (3), b = 11.509 (4), c = 17.059 (2) Å; β = 115.36(2)°; V = 2941 (1) Å³; Z = 4; D_{calcd} = 1.131 g/cm³; λ(Mo Kα) = 0.71073 Å; μ(Mo Kα) = 0.69 cm⁻¹; 250(2) K; NONIUS-MACH3 diffractometer, graphite monochromator; 5290 unique reflections; R = 0.0746; R_w = 0.1423. Crystallographic data for **2**: C₂₉H₂₉Cl₃N₄Zr·2THF, monoclinic, P2₁/n, a = 12.2220(11), b = 23.628 (2), c = 12.8891 (12) Å; β = 100.935(2)°; V = 3654.6 (6) Å³; Z = 4; D_{calcd} = 1.409 g/cm³; λ(Mo Kα) = 0.71073 Å; μ(Mo Kα) = 5.56 cm⁻¹; 173 (2) K; BRUKER SMART CCD diffractometer, graphite monochromator; 7472 unique reflections; R = 0.0538; R_w = 0.1530. Complete details of the data collection and refinement of **1** and **2** are included in Supporting Information.
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