

A Homoleptic Zirconium Complex with Four Bulky η^2 -Pyrazolato Ligands

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Dedicated to Prof. Dr. Walter Siebert on the occasion of his 65th birthday

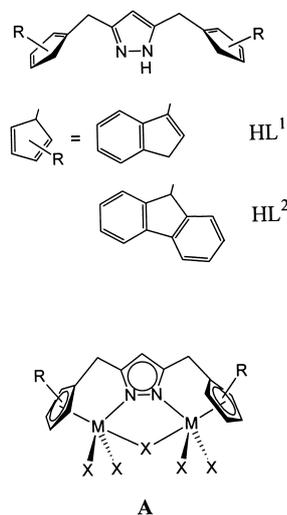
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Pyrazolates, Zirconium, N-Ligands

Two new tetrakis(η^2 -pyrazolato) zirconium complexes are prepared from the reaction of $Zr(CH_2Ph)_4$ with bulky pyrazolate ligands bearing indenylmethyl (HL^1) or fluorenylmethyl (HL^2) substituents, respectively. $Zr(L^2)_4$ has been analyzed by X-ray crystallography, which represents the first structural characterisation of a homoleptic η^2 -pyrazolato zirconium compound.

Introduction

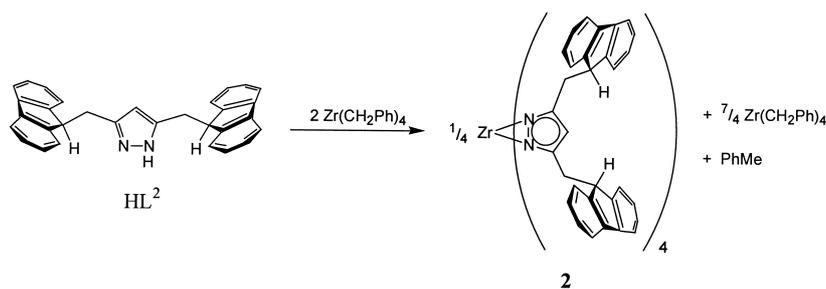
Pyrazolate coordination chemistry has received considerable attention in recent years, which in great part is stimulated by the discovery of a variety of new binding modes of this versatile ligand [1, 2]. Among other developments, η^2 (N,N'-bonded) pyrazolate ligation that for a long time was restricted to f-block elements has meanwhile been found common also for early d-block and main group metals [3 - 7]. This progress offers new perspectives with respect to the use of η^2 pyrazolates as ancillary ligand sets, *e. g.* in metal-catalyzed reactions, and η^2 pyrazolates have already been proposed as substitutes for the ubiquitous cyclopentadienyl ligands [6, 7]. Most of the systems with pyrazolate η^2 coordination reported to date are d^0 metal compounds, in particular Ti^{IV} and Zr^{IV} complexes, since empty d orbitals are considered favorable for this binding mode. However, while tetrakis(η^2 -pyrazolato)titanium(IV) species were among the first d-metal compounds featuring such η^2 coordination and at that time even represented the first homoleptic monomeric η^2 -pyrazolato complexes of any metal [3], to the best of our knowledge no homoleptic tetrakis(η^2 -pyrazolato)zirconium complex has hitherto been structurally characterized. Here we report the preparation and X-ray crystallographic characterization of a zirconium complex



of that type, bearing bulky substituents in the 3- and 5-positions of the pyrazole heterocycle. This compound was obtained serendipitously when we scouted a synthetic route to bimetallic type **A** complexes.

Results and Discussion

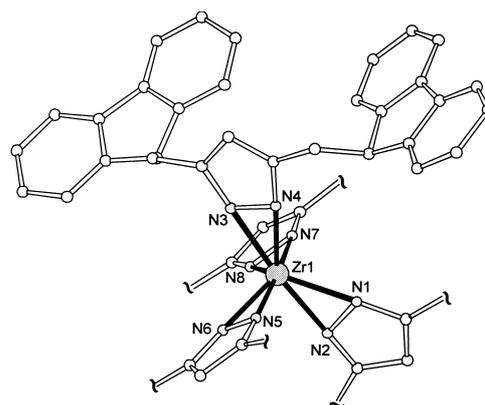
Pyrazolate-based ligands HL^1 and HL^2 have recently been considered as starting materials for bimetallic type **A** compounds [8], which can be described as coupled versions of the heavily stud-

Scheme 1. Reaction of HL² with Zr(CH₂Ph)₄ to give **2**.Table 1. Selected interatomic distances [Å] and bond angles [°] for **2**.

Zr1-N1	2.210(3)	N1-Zr-N2	36.9(1)
Zr1-N2	2.158(3)	N3-Zr-N4	36.6(1)
Zr1-N3	2.196(3)	N5-Zr-N6	37.4(1)
Zr1-N4	2.193(3)	N7-Zr-N8	36.8(1)
Zr1-N5	2.186(3)	(N1N2)-Zr-(N3N4) ^a	141.0
Zr1-N6	2.171(3)	(N1N2)-Zr-(N5N6) ^a	97.0
Zr1-N7	2.206(3)	(N1N2)-Zr-(N7N8) ^a	95.2
Zr1-N8	2.173(7)	(N3N4)-Zr-(N5N6) ^a	98.7
N1-N2	1.382(4)	(N3N4)-Zr-(N7N8) ^a	97.3
N3-N4	1.377(5)	(N5N6)-Zr-(N7N8) ^a	136.6
N5-N6	1.397(4)		
N7-N8	1.380(4)		

^a (N_xN_y) denotes the midpoint of the N_x-N_y bond.

ied mononuclear cyclopentadienyl complexes with tethered N-donor ligands. In this context we aimed at introducing two early 3d metal ions by a procedure well established for the mononuclear analogues, *i. e.* by using reactive ZrR₄ or Zr(NR₂)₄ precursors [9]. The reactions of HL¹ and HL², respectively, with Zr(CH₂Ph)₄ were conducted in flame-sealed NMR tubes in C₆D₆, D₈-toluene or CD₂Cl₂ solution and investigated by NMR spectroscopy. At first, two equivalents of Zr(CH₂Ph)₄ were employed according to the anticipated stoichiometry that should lead to type **A** compounds. However, only one eighth of the expected amount of toluene was observed, while 1.75 equivalents of the Zr(CH₂Ph)₄ starting material remained unchanged. In addition, a shift of all ligand NMR resonances indicated complex formation, but the characteristic signals of the indenyl and fluorenyl moieties showed that CH deprotonation had not occurred. Heating of the reaction mixtures did not lead to any further reaction, but gradual decomposition of Zr(CH₂Ph)₄ took place. The use of Zr(NR₂)₄ basically gave similar results, although reactions proceeded more sluggishly. Almost quantitative product formation (as

Fig. 1. Molecular structure of **2**. For the sake of clarity, fluorenyl substituents have been omitted for three of the four pyrazolato ligands.

judged by NMR spectroscopy) was achieved when Zr(CH₂Ph)₄ and the respective ligand were mixed in the appropriate 1:4 ratio.

In view of the recent discovery of η^2 bonding of pyrazolato ligands in group IV metal chemistry, we considered that contrary to our initial expectation the formation of homoleptic Zr(κ^2 N,N'-L¹)₄ (**1**) and Zr(κ^2 N,N'-L²)₄ (**2**) might indeed be the favored reaction path. This was confirmed by the crystallographic analysis of single crystals of **2** obtained from C₆D₆ solution in an NMR tube. The molecular structure of **2** is depicted in Fig. 1, and selected interatomic distances and bond angles are listed in Table 1.

The coordination geometry around the Zr atom can be described as distorted dodecahedral and thus is very similar to the coordination observed for a homoleptic η^2 -pyrazolato titanium complex reported previously [3]. Considering the midpoints (NN) of the N-N bonds of all pyrazolato ligand, there are two wide angles (NN)_i-Zr-(NN)_j at 136.6° / 141.0°

and four small angles in the range 95.2° - 98.7° (Table 1), indicating that the (NN) arrangement around the Zr is severely distorted from tetrahedral towards square planar. This distortion can be quantified by evaluating the parameter β which is defined as a half of the mean value of the two largest ligand-metal-ligand angles (*i. e.* the *trans* ligand-metal-ligand angles in a square-planar complex) [10]. β Equals 90° for a purely square-planar complex and 54.7° for a tetrahedral one, and it is 69.4° for the midpoints (NN) in **2**, thus indicating a moderate degree of distortion. Two of the pyrazolate ligands show significant differences in their individual Zr-N bond lengths [$d(\text{Zr1-N1}) = 2.210(3)$ versus $d(\text{Zr1-N2}) = 2.158(3)$ Å and $d(\text{Zr1-N7}) = 2.206(3)$ versus $d(\text{Zr1-N8}) = 2.173(3)$ Å], while for each of the other two pyrazolates the N atoms are almost equidistant from Zr. The dangling fluorenyl groups of the ligand side arms constitute a compact hydrophobic shell with the Zr well buried in its interior, in accordance with the good solubility of **2** in non-polar solvents. Several edge-to-face (T-shaped) C-H $\cdots\pi$ interactions as well as slipped (offset) stacking motifs can be detected between the aromatic rings of the outer fluorenyl groups.

In conclusion, we have demonstrated that η^2 -pyrazolato complexes of early transition metals do not only form with simple pyrazoles bearing methyl, *tert.*-butyl or phenyl substituents in the 3- and 5-positions of the heterocycle, but also with more complex pyrazole ligands like HL¹ and HL². The crystal structure of **2** represents the first for a homoleptic zirconium compound of that type.

Experimental Section

General procedures and methods: Reactions were carried out in NMR tubes which were loaded under an atmosphere of dry argon in a glove box. Solvents were vacuum transferred into the NMR tubes and the tubes were flame-sealed. Solvents were dried according to established procedures. $\text{Zr}(\text{CH}_2\text{Ph})_4$ [11] as well as HL¹ and HL² [8] were synthesized according to the reported methods, all other chemicals were used as purchased. Microanalyses: Mikroanalytische Laboratorien des Organisch-Chemischen Instituts der Universität Heidelberg. – NMR spectra: Bruker AC 200 at 200.13 (¹H) and 50.32 (¹³C) MHz, or Bruker DRX 300 at 300.13 MHz (¹H) and 75.47 (¹³C) MHz, or Bruker DRX 500 at 500.13 MHz (¹H) and 125.77 (¹³C) MHz; assignments are based on a series of 2D experiments.

Synthetic procedure for $\text{Zr}(\text{L}^1)_4$ (1**) and $\text{Zr}(\text{L}^2)_4$ (**2**):** An NMR tube was filled with HL¹ (16.2 mg, 0.05 mmol) or HL² (21.2 mg, 0.05 mmol) and $\text{Zr}(\text{CH}_2\text{Ph})_4$ (5.7 mg, 0.0125 mmol) and 0.5 ml of the solvent (C_6D_6 , D_8 -toluene, or CD_2Cl_2) was condensed into the tube, which was then flame-sealed under vacuum. The reaction mixture was analyzed by NMR spectroscopy, and product formation was found to be essentially quantitative. In the case of $\text{Zr}(\text{L}^2)_4$ (**2**), colorless crystals suitable for X-ray crystallography were obtained from C_6D_6 solution. These were isolated by breaking the NMR tube in a glove box.

1: ¹H NMR (300.13 MHz, D_8 -toluene): $\delta = 2.85$ (s, 16H, $\text{CH}_2^{\text{in},1}$), 3.82 (s, 16H, CH_2), 5.89 (s, 8H, $\text{CH}^{\text{in},2}$), 6.29 (s, 4H, $\text{CH}^{\text{pz},4}$), 7.01-7.20 (32H, $\text{CH}^{\text{in},4/5/6/7}$). – ¹³C{¹H} NMR (75.47 MHz, D_8 -toluene): $\delta = 26.3$ (CH_2), 37.2 ($\text{CH}_2^{\text{in},2}$), 113.2 ($\text{CH}^{\text{pz},4}$), 118.8, 123.3, 124.8, 125.8 ($\text{CH}^{\text{in},4/5/6/7}$), 129.9 ($\text{CH}^{\text{in},2}$), 142.0 ($\text{C}^{\text{in},3}$), 144.1, 144.7 ($\text{C}^{\text{in},3a/7a}$), 147.1 ($\text{C}^{\text{pz},3/5}$).

2: ¹H NMR (200.13 MHz, CD_2Cl_2): $\delta = 2.87$ (d, ³J = 7.2 Hz, 16H, CH_2), 4.19 (t, ³J = 7.2 Hz, 8H, $\text{CH}^{\text{fl},9}$), 5.83 (s, 4H, $\text{CH}^{\text{pz},4}$), 6.75 (d, ³J = 7.5 Hz, 16H, $\text{CH}^{\text{fl},1/8}$), 6.98 (*pseudo-t*, ³J = 7.2 Hz, 16H, $\text{CH}^{\text{fl},2/7}$), 7.22 (*pseudo-t*, ³J = 7.5 Hz, 16H, $\text{CH}^{\text{fl},3/6}$), 7.73 (d, ³J = 7.5 Hz, 16H, $\text{CH}^{\text{fl},4/5}$). – ¹³C{¹H} NMR (50.32 MHz, CD_2Cl_2): $\delta = 31.8$ (CH_2), 47.1 ($\text{CH}^{\text{fl},9}$), 113.7 ($\text{CH}^{\text{pz},4}$), 119.9 ($\text{CH}^{\text{fl},4/5}$), 124.7 ($\text{CH}^{\text{fl},1/8}$), 127.2, 127.4 ($\text{CH}^{\text{fl},2/3/6/7}$), 141.0 ($\text{C}^{\text{fl},4a/4b}$), 147.1 ($\text{C}^{\text{fl},8a/9a}$), 148.6 ($\text{C}^{\text{pz},3/5}$). – $\text{C}_{124}\text{H}_{92}\text{N}_8\text{Zr}$ (1785.4): calcd. C 83.42, H 5.19, N 6.27; found C 82.67, H 5.45, N 6.10.

X-ray crystallography. Data collection for **2** was carried out on a Bruker AXS CCD diffractometer at 173 K using graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å). Structures were solved by direct methods (SHELXS-97) and refined by full matrix least squares techniques based on F^2 (SHELXL-97) [12]. Atomic coordinates and thermal parameters of the non-hydrogen atoms were refined in fully anisotropic models. Hydrogen atoms were placed at calculated positions and allowed to ride on the atoms they are attached to. – $\text{C}_{124}\text{H}_{92}\text{N}_8\text{Zr}\cdot\text{C}_6\text{H}_6$, $M = 1863.4$: triclinic, space group $P\bar{1}$, $a = 16.9225(4)$, $b = 17.5172(4)$, $c = 18.6695(4)$ Å, $\alpha = 111.821(2)^\circ$, $\beta = 103.077(2)^\circ$, $\gamma = 98.821(2)^\circ$; $V = 4828.9(2)$ Å³, $Z = 2$, $\rho_{\text{calcd.}} = 1.282$ g cm⁻³, $\mu(\text{Mo-}K_\alpha) = 0.173$ mm⁻¹, $2.5^\circ < 2\theta < 50.0^\circ$, 52689 measured reflections, 17009 unique ($R_{\text{int}} = 0.077$), 10664 observed [$I > 2\sigma(I)$], 1288 parameters, final $R[I > 2\sigma(I)] = 0.056$, $wR2 = 0.163$, goodness of fit on $F^2 = 1.027$, largest diff. peak $+1.02/-0.67$ eÅ⁻³. – CCDC 181456 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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