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Synthesis and Structures of Zirconium−Pyrrolyl Complexes: Computational Analysis of the Factors That Influence the Coordination Modes of Pyrrolyl Ligands

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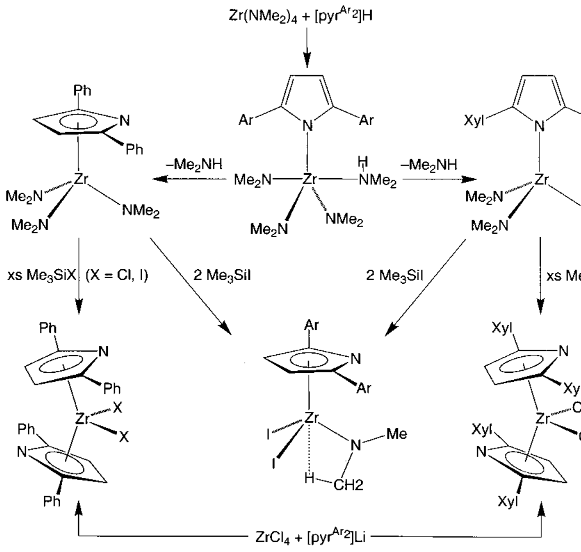
Summary: The first series of structurally characterized zirconium complexes that feature both η^1- and η^5-pyrrolyl coordination modes is reported. Specifically, 2,5-diaryl-pyrrolyl [pyr^{Ar_2}] ligands (Ar = Ph, 2,4-Xyl) have been used to prepare [pyr^{Ar_2}]Zr(NMe$_2$)$_3$(NMe$_2$H), [pyr^{Ar_2}]Zr(NMe$_2$)$_3$, [pyr^{Ar_2}]Zr(NMe$_2$)I$_2$, and [η^5-pyr^{Ar_2}]$_2$ZrCl$_2$. DFT calculations indicate that the relative stabilities of the various coordination modes are influenced by both steric factors and the Lewis acidity of the metal center.

The cyclopentadienyl ligand has, without doubt, played a critical role in the development of organo-transition-metal chemistry. By comparison to cyclopentadienyl, the related isoelectronic heterocyclic pyrrolyl ligand, [pyr^{R_n}],[1] has been little applied to transition-metal chemistry.[2] With respect to zirconium chemistry, of the few pyrrolyl complexes that have been structurally authenticated by X-ray diffraction, the pyrrolyl ligand is observed to bind only via the nitrogen atom in an η^1-mode,[3] rather than the η^5-mode common to cyclopentadienyl ligands. In this paper, we report the synthesis and structural characterization of the first series of mono- and bis(pyrrolyl)zirconium complexes that feature η^5-coordination of pyrrolyl ligands; furthermore, computational studies address the factors that influence the η^5-versus η^1-coordination mode of the pyrrolyl ligand in these derivatives.

Pyrrolyl ligands with aryl substituents in the 2- and 5-positions have not previously been employed in the chemistry of the early transition metals. Nevertheless, we considered that such substituents would provide stability that would facilitate the synthesis and isolation of zirconocene analogues of the type [η^5-pyr^{Ar_2}]$_2$ZrX$_2$. Indeed, [pyr^{Ar_2}]$_2$ZrCl$_2$ (Ar = Ph, 2,4-Xyl) may be obtained by reaction of ZrCl$_4$ with [pyr^{Ar_2}]Li[4] (Scheme 1), thereby providing pyrrolyl counterparts to the well-known bent-sandwich cyclopentadienyl complexes, (Cp^R)$_2$ZrCl$_2$. Likewise, facile access to half-sandwich zirconium−pyrrolyl complexes is provided by reaction of Zr(NMe$_2$)$_4$ with [pyr^{Ar_2}]H to yield [pyr^{Ar_2}]Zr(NMe$_2$)$_3$, via the dimethylamine adducts [pyr^{Ar_2}]Zr(NMe$_2$)$_3$(NMe$_2$H). [pyr^{Ar_2}]Zr(NMe$_2$)$_3$ is a precursor for other zirconium−pyrrolyl complexes. Thus, treatment of [pyr^{Ar_2}]Zr(NMe$_2$)$_3$ with 2 equiv of Me$_3$SiI yields the diiodide [pyr^{Ar_2}]Zr(NMe$_2$)I$_2$,[5] whereas 3 equiv results in ligand redistribution and the formation of [pyr^{Ar_2}]$_2$ZrI$_2$ (Ar = Ph). Likewise, the dichloride [pyr^{Ar_2}]$_2$ZrCl$_2$ may be obtained by reaction of [pyr^{Ar_2}]Zr(NMe$_2$)$_3$ with excess Me$_3$SiCl.

Scheme 1



Definitive identification of the pyrrolyl coordination mode in these complexes required analysis by X-ray diffraction (Figures 1−3).[6] Significantly, an η^5-pyrrolyl coordination mode was found for the phenyl-substituted pyrrolyl complexes [pyr^{Ph_2}]Zr(NMe$_2$)$_3$, [pyr^{Ph_2}]Zr(NMe$_2$)I$_2$, and [pyr^{Ph_2}]$_2$ZrX$_2$ (X = Cl, I) and the xylyl-substituted pyrrolyl complexes [pyr^{Xyl_2}]Zr(NMe$_2$)I$_2$ and [pyr^{Xyl_2}]$_2$ZrCl$_2$. The observation of η^5-coordination in this system is most noteworthy, in view of the fact that only η^1-coordination to zirconium has been previously authenticated by X-ray diffraction,[3] despite specific attempts to synthesize complexes that would feature η^5-coordination.[7] For example, the complexes Cp$_2$Zr[η^1-pyr^{Me_2}]$_2$ and [η^1-pyr^{Me_2}]$_4$Zr were synthesized with the

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[1] Pyrrolyl ligands (C$_5$R$_n$H$_{4-n}$N) are represented by the abbreviation [pyr^{R_n}], where the superscript indicates the number and type of substituents.

[2] (a) Kershner, D. L.; Basolo, F. *Coord. Chem. Rev.* **1987**, *79*, 279−292. (b) Nief, F. *Eur. J. Inorg. Chem.* **2001**, 891−904.

[3] (a) Bynum, R. V.; Hunter, W. E.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2368−2374. (b) Bynum, R. V.; Zhang, H. M.; Hunter, W. E.; Atwood, J. L. *Can. J. Chem.* **1986**, *64*, 1304−1307.

[4] [pyr^{Xyl_2}]H is obtained by a method similar to that used to prepare [pyr^{Ph_2}]H. See: Patterson, J. M.; Soedigdo, S. *J. Org. Chem.* **1968**, *33*, 2057−2061.

[5] [pyr^{Ph_2}]Zr(NMe$_2$)I$_2$ may also be obtained by reaction of [pyr^{Ph_2}]Zr(NMe$_2$)$_3$ with 4 equiv of MeI, in which case Me$_4$NI is the byproduct. Furthermore, the use of 2 equiv of MeI generates the monoiodide [pyr^{Ph_2}]Zr(NMe$_2$)$_2$I.

[6] See the Supporting Information for the crystallographic data.

[7] It is worth noting that η^5-coordination of the pyrrolyl fragment to zirconium has, nevertheless, been observed within porphyrinogen derivatives. See, for example: (a) Solari, G.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1997**, *16*, 508−510. (b) Jacoby, D.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1993**, *115*, 3595−3602.

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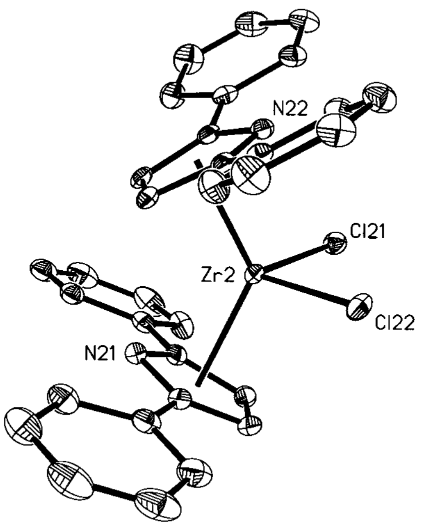

Figure 1. Molecular structure of $[\mathrm{pyr}^{\mathrm{Ph}_2}]_2\mathrm{ZrCl}_2$.

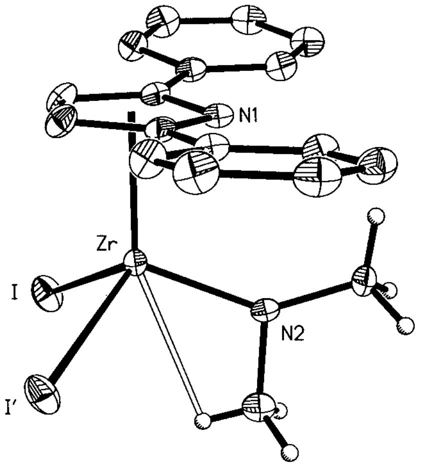

Figure 2. Molecular structure of $[\mathrm{pyr}^{\mathrm{Ph}_2}]_2\mathrm{Zr}(\mathrm{NMe}_2)\mathrm{I}_2$.

notion that the increased steric demands of the dimethylpyrrolyl ligand would favor η^5-coordination; however, η^1-coordination prevailed and the η^5-coordination mode remained elusive.[3b,8]

Notwithstanding the preference for η^5-coordination in the zirconium complexes reported here, $[\mathrm{pyr}^{\mathrm{Ar}_2}]\mathrm{Zr}(\mathrm{NMe}_2)_3(\mathrm{NMe}_2\mathrm{H})$ (Ar = Ph, Xyl) and $[\mathrm{pyr}^{\mathrm{Xyl}_2}]\mathrm{Zr}(\mathrm{NMe}_2)_3$ exhibit η^1-coordination. The observation of η^1-coordination for the dimethylamine adducts $[\mathrm{pyr}^{\mathrm{Ar}_2}]\mathrm{Zr}(\mathrm{NMe}_2)_3(\mathrm{NMe}_2\mathrm{H})$ is understandable in the sense that η^5-coordination is disfavored on steric grounds due to the increased coordination number. Not so easily rationalized, however, is the fact that the xylyl derivative $[\mathrm{pyr}^{\mathrm{Xyl}_2}]\mathrm{Zr}(\mathrm{NMe}_2)_3$ exhibits η^1-coordination of the pyrrolyl ligand, whereas the phenyl derivative exhibits η^5-coordination (Figure 3). This difference in coordination mode is counter to the notion that bulky substituents (e.g. Bu^t) in the 2- and 5-positions of the pyrrolyl ligand generally favor η^5-coordination over η^1-coordination.[2,9,10] Such a proposition is based on the fact that η^1-coordination would force the "cylindrical" substituents directly towards the metal center and thereby destabilize the interaction (Figure 4). The observation that the bulkier $[\mathrm{pyr}^{\mathrm{Xyl}_2}]$ ligand favors η^1-coordination to a greater extent than that of the $[\mathrm{pyr}^{\mathrm{Ph}_2}]$ ligand suggests that a different mechanism operates for aryl as compared to alkyl substituents, due to the aryl ligand being "flat". Specifically, an ortho substituent destabilizes a conformation in which the pyrrolyl and aryl rings are coplanar and thus shifts the preference from η^5-coordination towards that of η^1-coordination, as illustrated in Figure 4.

To address further this issue, we have performed a series of DFT calculations that evaluate the influence of the η^1- and η^5-pyrrolyl coordination modes on the stabilities of $[\mathrm{pyr}^{\mathrm{Ar}_2}]\mathrm{Zr}(\mathrm{NMe}_2)_3$ and $[\mathrm{pyr}^{\mathrm{Ar}_2}]\mathrm{Zr}(\mathrm{NMe}_2)\mathrm{I}_2$ (Ar = Ph, Xyl).[11] Examination of the data[12] indicate that η^5-coordination is favored to a greater degree for (i) the smaller $[\mathrm{pyr}^{\mathrm{Ph}_2}]$ ligand than for the $[\mathrm{pyr}^{\mathrm{Xyl}_2}]$ ligand by ca. 3 kcal mol^{-1} and (ii) the diiodide complex $[\mathrm{pyr}^{\mathrm{Ar}_2}]\mathrm{Zr}(\mathrm{NMe}_2)\mathrm{I}_2$ than for the tris(amide) $[\mathrm{pyr}^{\mathrm{Ar}_2}]\mathrm{Zr}(\mathrm{NMe}_2)_3$ by ca. 10 kcal mol^{-1}. The former trend may be rationalized by increased bulk in the ortho positions destabilizing η^5-coordination for the $[\mathrm{pyr}^{\mathrm{Xyl}_2}]$ ligand. Likewise, the latter trend may be rationalized by both the increased bulk and electron-donating ability of NMe_2 relative to I destabilizing η^5-coordination for the $[\mathrm{pyr}^{\mathrm{Ar}_2}]$ ligand in $[\mathrm{pyr}^{\mathrm{Ar}_2}]\mathrm{Zr}(\mathrm{NMe}_2)_3$ to a greater degree than that in $[\mathrm{pyr}^{\mathrm{Ar}_2}]\mathrm{Zr}(\mathrm{NMe}_2)\mathrm{I}_2$.

With respect to the η^5- versus η^1-coordination mode preference for $[\mathrm{pyr}^{\mathrm{Ph}_2}]\mathrm{Zr}(\mathrm{NMe}_2)_3$, it is noteworthy that the titanium analogue $[\mathrm{pyr}^{\mathrm{Ph}_2}]\mathrm{Ti}(\mathrm{NMe}_2)_3$ exhibits η^1-coordination of the pyrrolyl ligand. Furthermore, calculations indicate that the η^1-coordination mode is favored by 9.25 kcal mol^{-1} more than that in the zirconium counterpart, presumably due to exacerbated steric interactions resulting from the smaller size of titanium.

An interesting difference between the $[\mathrm{pyr}^{\mathrm{Ar}_2}]\mathrm{Zr}(\mathrm{NMe}_2)_3$ and $[\mathrm{pyr}^{\mathrm{Ar}_2}]\mathrm{Zr}(\mathrm{NMe}_2)\mathrm{I}_2$ derivatives is that the diiodide complexes exhibit β-agostic interactions between the methyl group of the NMe_2 ligand and the zirconium center. Evidence for this uncommon type of interaction for a NMe_2 ligand is provided by a marked distortion of the NMe_2 ligand from trigonal-planar geometry.[13] For example, the Zr−N−Me bond angles in $[\mathrm{pyr}^{\mathrm{Ph}_2}]\mathrm{Zr}(\mathrm{NMe}_2)\mathrm{I}_2$ are 108.9(8) and 141.3(6)°, substantially different from the mean value of 125.7° for structurally characterized zirconium−dimethylamido complexes listed in the Cambridge Structural Database.[14] The short $\mathrm{Zr}\cdots\mathrm{C}$ (2.84(1) Å) and $\mathrm{Zr}\cdots\mathrm{H}$ (2.61(8) Å) distances are also consistent with an agostic interac-

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(8) For zirconium pyrrolyl complexes that have not had their coordination mode verified by X-ray diffraction, see: (a) Kuhn, N.; Stubenrauch, S.; Boese, R.; Bläser, D. *J. Organomet. Chem.* **1992**, *440*, 289−296. (b) Dias, A. R.; Galvão, A. M.; Galvão, A. C. *J. Organomet. Chem.* **2001**, *632*, 157−163.

(9) Bynum, R. V.; Zhang, H. M.; Hunter, W. E.; Atwood, J. L. *Can. J. Chem.* **1986**, *64*, 1304−1307.

(10) (a) Dias, A. R.; Galvão, A. M.; Galvão, A. C.; Salema, M. S. *J. Chem. Soc., Dalton Trans.* **1997**, 1055−1061. (b) Dias, A. R.; Galvão, A. M.; Galvão, A. C. *Collect. Czech. Chem. Commun.* **1998**, *63*, 182−186.

(11) DFT geometry optimizations were performed at the B3LYP level using the LACVP** basis set. Single-point energies were calculated for the optimized structures at the B3LYP level using the triple-ζ basis set cc-pVTZ (-f) for all elements except for Ti, Zr, Cl, and I, for which the LACV3P** basis set was used (Jaguar 4.1, Schrodinger, Inc., Portland, OR, 2000).

(12) $\Delta E = E(\eta^5) - E(\eta^1)$ values (kcal mol^{-1}): $[\mathrm{pyr}^{\mathrm{Ph}_2}]\mathrm{Zr}(\mathrm{NMe}_2)_3$ (1.76), $[\mathrm{pyr}^{\mathrm{Xyl}_2}]\mathrm{Zr}(\mathrm{NMe}_2)_3$ (4.61), $[\mathrm{pyr}^{\mathrm{Ph}_2}]\mathrm{Zr}(\mathrm{NMe}_2)\mathrm{I}_2$ (−9.15), $[\mathrm{pyr}^{\mathrm{Xyl}_2}]\mathrm{Zr}(\mathrm{NMe}_2)\mathrm{I}_2$ (−5.73).

(13) Albeit uncommon, examination of the Cambridge Structural Database indicates that several other (dimethylamido)zirconium complexes exhibit such interactions. See, for example: (a) Chisholm, M. H.; Hammond, C. E.; Huffman, J. C. *Polyhedron* **1988**, *7*, 2515−2520. (b) Oberthür, M.; Hillebrand, G.; Arndt, P.; Kempe, R. *Chem. Ber./Recl.* **1997**, *130*, 789−794.

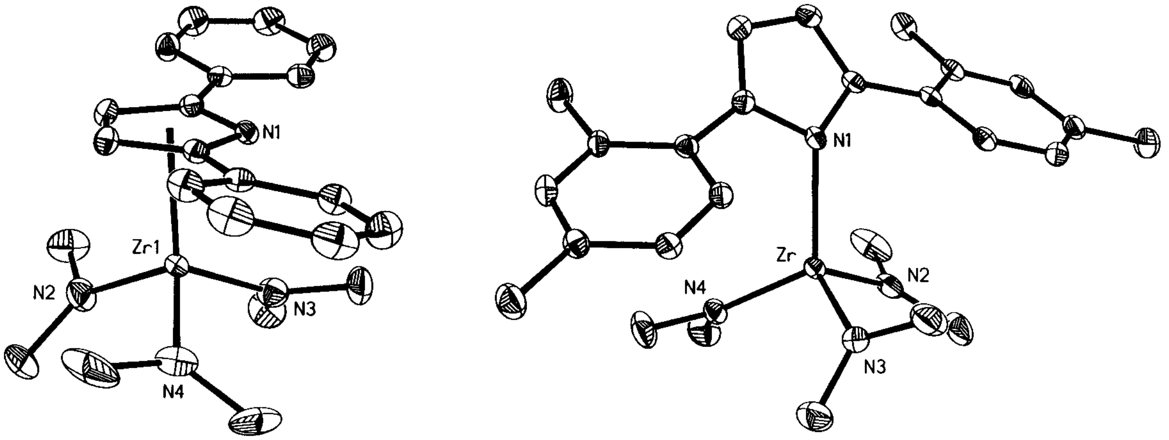

Figure 3. Molecular structure of $[pyr^{Ph_2}]_2Zr(NMe_2)_3$ (left) and $[pyr^{Xyl_2}]_2Zr(NMe_2)_3$ (right).

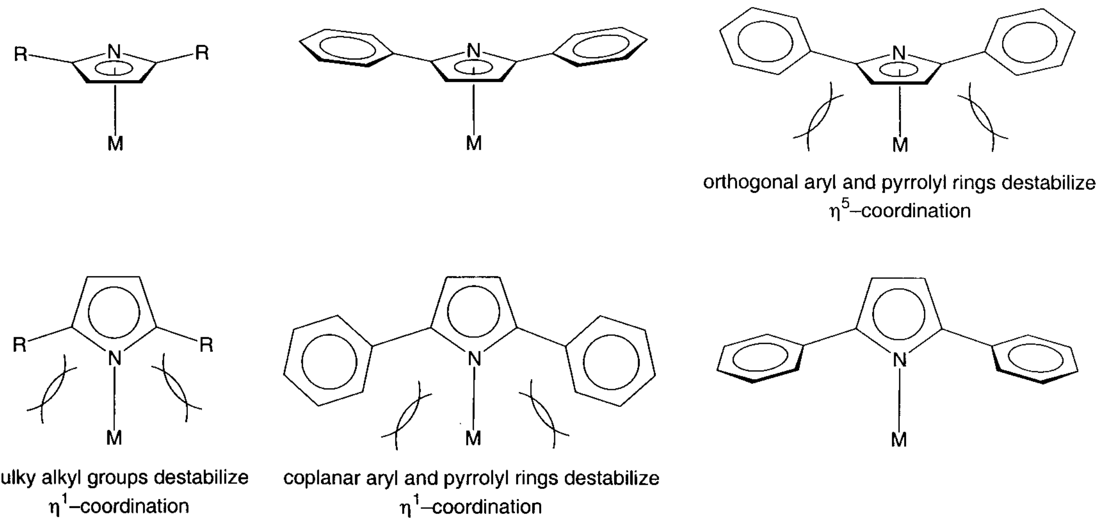

Figure 4. Steric influence of substituents of the coordination modes of pyrrolyl ligands. Bulky alkyl substituents promote η^5-coordination, while bulky aryl substituents promote η^1-coordination as a result of the substituents destabilizing coplanarity of the pyrrolyl and aryl rings.

tion. For example, the Zr···C distances in $[pyr^{Ph_2}]Zr(NMe_2)I_2$ are intermediate between the values in the cationic agostic ethyl complex $\{[Cp^{Me}]_2Zr(Et)(PMe_3)\}^+$ (2.63 Å)[15] and those with nonagostic ethyl ligands (3.17−3.42 Å).[14]

In view of the widespread use of zirconocene complexes as catalyst precursors for olefin polymerization, the catalytic activity of $[pyr^{Ph_2}]ZrCl_2$ in the presence of methylalumoxane (MAO) has been studied. The activity of $[pyr^{Ph_2}]ZrCl_2$/MAO towards ethylene polymerization is, however, substantially lower than that of Cp_2ZrCl_2/MAO by a factor of ca. 5×10^{-2}.

In summary, a series of zirconium complexes that feature both η^1- and η^5-pyrrolyl coordination modes of $[pyr^{Ar_2}]$ ligands has been obtained. DFT calculations indicate that the relative stabilities of the various coordination modes are influenced by both steric factors and the Lewis acidity of the metal center, such that bulky and π-donor ligands attached to the metal favor η^1-coordination. In addition to the influence of bulk on the metal center, ortho substitution of the aryl groups reduces the relative stability of η^5-coordination because it destabilizes a conformation in which the pyrrolyl and aryl rings are coplanar. As such, increasing the bulk of aryl groups may induce a structural effect opposite to that of alkyl substituents with respect to the preference for η^1- versus η^5-pyrrolyl coordination. The structures reported here indicate that substituted pyrrolyl ligands provide a versatile means for influencing the coordination geometry of zirconium complexes.

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Supporting Information Available: Text and tables giving experimental details, spectroscopic data, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Allen, F. H.; Kennard, O. CSD Version 5.21. 3D Search and Research Using the Cambridge Structural Database. *Chem. Design Automation News* **1993**, *8*(1), 1, 31−37.

(15) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289−1291.