Sterically Demanding Diamide Ligands: Synthesis and Structure of d⁰ Zirconium Alkyl Derivatives

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Received July 11, 1995[®]

Summary: The chelating diamide complexes (BDAP)Zr- $(NMe_2)_2$ (2), $(BDAP)ZrCl_2(py)_2$ (4), $(BDAP)ZrR_2$ (5a, R = CH_2Ph ; **5b**, R = Me), $(BDAP)Zr(\eta^5-Cp)Cl$ (**5c**), and $(BDAP)Zr(\eta^{2}(N,C)-NC_{5}H_{4})(CH_{2}CMe_{2}Ph) (5d) (BDAP =$ $ArNCH_2CH_2CH_2NAr$; $Ar = 2,6^{-i}Pr_2-C_6H_3$) have been prepared. An X-ray study of $(BDAP)Zr(\eta^2(N,C)-NC_5H_4)$ - (CH_2CMe_2Ph) (**5d**) revealed an η^2 -pyridyl moiety bound to zirconium. Proton and carbon NMR data suggest that the pyridyl moiety in 5d is rotating rapidly about the Zr-C bond on the NMR time scale.

Homogeneous "single site" olefin polymerization catalysts have developed rapidly in the last 15 years. Initial studies¹ on the polymerization activity of Cp₂ZrMe₂ (methylaluminoxane (MAO) cocatalyst) gave way to the ingeniously designed bridged-metallocene catalysts (e.g., $[rac-ethylenebis(\eta^5-tetrahydroindenyl)]$ ZrCl₂² and [isopropyl(η^5 -cyclopentadienyl)(η^5 -1-fluorenyl)]ZrCl₂³). Recent interest in constrained-geometry catalysts (e.g., $[(\eta^5 \cdot C_5 Me_4)SiMe_2(NCMe_3)]ML_n; M = Ti, Zr, Hf, Sc; L =$ halide, alkyl)⁴⁻⁶ that contain a linked cyclopentadienylamide ligand⁷⁻⁹ prompted us to investigate the chemistry of group 4 chelating diamide complexes. In fact, the bis(amide) complex [(Me₃Si)₂N]₂ZrCl₂¹⁰ is reported to polymerize propylene to 90% isotactic poly(propylene) when activated with MAO.¹¹ A number of chelating diamide complexes of group 4 have been prepared;¹²⁻¹⁶ however, most contain silyl substituents at nitrogen. We are particularly interested in the steric and electronic effects of diamide ancillaries that incorporate the voluminous 2,6-diisopropylphenyl moiety.¹⁷ We report here

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the synthesis of d^0 alkyl complexes of zirconium stabilized by a new bulky chelating diamide ligand.

The reaction of 2 equiv of LiNHAr (Ar = $2,6^{-i}Pr_2$ - C_6H_3) with 1,3-dibromopropane yields the diamine ligand (BDAP) H_2 (1),¹⁸ as a viscous oil (eq 1). The

$$2\text{LiNHAr} + \text{Br}(\text{CH}_2)_3\text{Br} \xrightarrow{\text{THF/tmeda/0-25 °C}}_{-2\text{LiBr}}$$
$$\text{ArHN}(\text{CH}_2)_3\text{NHAr} (1)$$
$$1$$

$$tmeda = Me_2NCH_2CH_2NMe_2$$

aminolysis reaction between (BDAP)H₂ and Zr(NMe₂)₄¹⁹ provides 2 equiv of HNMe₂ and the mixed-amide complex (BDAP)Zr(NMe₂)₂ (2), in high yield (eq 2).



Characteristic second-order patterns are observed for the methylene protons $(NCH_2 \text{ and } NCH_2CH_2)$ of the coordinated BDAP ligand in the proton NMR spectrum of complex 2.20 Additionally, the isopropyl methyl groups of the arene are diastereotopic, which we interpret as a consequence of restricted rotation about the N-C_{ipso} bond.^{17,21}

Chloride derivatives were desired as precursors to alkyl derivatives. Compound 2 reacts with 2 equiv of [Me₂NH₂]Cl to afford the octahedral dimethylamine adduct (BDAP) $ZrCl_2(NHMe_2)_2$ (3).¹⁸ We do not observe protonolysis of the BDAP ligand, although other amide donors are prone to this reaction.⁹ Compound 3 is unstable toward loss of dimethylamine, possibly due to steric congestion about the zirconium center. The bis-(pyridine) adduct proved to be more stable. Reaction of complex 2 with 2 equiv of [Me₂NH₂]Cl in the presence of excess pyridine affords a single bis(pyridine) geometrical isomer, (BDAP)ZrCl₂py₂ (4), in good yield.

0276-7333/95/2314-5478\$09.00/0

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^{(20) (}BDAP)Zr(NMe₂)₂ (2): ¹H NMR & 7.20 (m, 6H, Ar), 3.78 (sept, 4H, CHMe₂), 3.55 (m, 4H, NCH₂), 2.64 (s, 12H, NMe₂), 2.44 (m, 2H, NCH₂CH₂), 1.34 (d, 12H, CHMe₂), 1.32 (d, 12H, CHMe₂); ¹³C{¹H} NMR δ 146.4, 145.8, 125.2, 124.1, 59.1, 41.8, 32.3, 28.3, 26.2, 25.0. Anal. Calcd for C31H52N4Zr: C, 65.09; H, 9.16; N, 9.79. Found: C, 64.75; H,

^{9.19;} N, 9.65. (21) With the exception of **5b**, the proton NMR spectra of compounds $2\!-\!5$ display temperature-independent signals for diastereotopic isopropyl methyl groups.





^a Reagents and conditions: (i) 2 equiv of PhCH₂MgCl, Et₂O, -20 °C to room temperature, 18 h; (ii) 2 equiv of MeMgCl, Et₂O, -20 °C to room temperature, 18 h; (iii) 1 equiv of NaCp(DME), toluene, room temperature, 18 h; (iv) 2 equiv of PhMe₂CCH₂MgCl, THF, -20 °C to room temperature 18 h.

$$(BDAP)Zr(NMe_{2})_{2} + 2$$

$$2[Me_{2}NH_{2}]Cl \xrightarrow{py/CH_{2}Cl_{2}/-78 \text{ to } +25 \text{ °C}}{-4HNMe_{2}} (BDAP)ZrCl_{2}(py)_{2} (3)$$

$$4$$

The ¹H NMR spectrum of compound 4 displays a downfield shift for the ortho protons and an upfield shift for the meta and para protons of the coordinated pyridine.¹⁸ The C_{2v} symmetry of compound 4 necessitates a *cis,trans* arrangement (as opposed to *cis,cis*) of the chlorides and pyridines about zirconium; however, the specific arrangement is not possible to deduce from the available spectroscopic data.

With the aim of preparing zirconium alkyl derivatives, the reaction of compound 4 with various alkylating reagents has been investigated (Scheme 1). The addition of 2 equiv of PhCH₂MgCl to an ether suspension of compound 4 yields the formally 12-electron dibenzyl complex (BDAP)Zr(CH₂Ph)₂ (5a). The proton NMR $spectrum^{22}$ of complex **5a** displays a resonance at 1.95 ppm for the benzylic protons; however, more interestingly the ortho protons of the C_6H_5 ring appear as a high-field doublet at 6.65 ppm. In the carbon NMR spectrum, the $Zr-CH_2Ph$ resonance is observed at 64.2 ppm with ${}^{1}J_{C-H} = 124$ Hz. Although the coupling constant for the CH₂Ph group is low, these data are consistent²³ with some η^2 -benzyl character in the bonding with zirconium.^{8,24-28} Perhaps the steric bulk of the BDAP ligand prevents the close approach of the ipso carbon to zirconium, thus lowering the observed C-H coupling constant.

The white crystalline dimethyl derivative (BDAP)- $ZrMe_2$ (5b) was isolated from the reaction of compound

4 with 2 equiv of MeMgBr. The ¹H and ¹³C $\{^{1}H\}$ NMR spectra²⁹ of complex **5b** display a $Zr-CH_3$ resonance at 0.42 ppm and a Zr-CH₃ signal at 39.9 ppm. These data are comparable to those for the closely related complex $[(Me_3Si)_2N]_2ZrMe_2$ (Zr-CH₃, δ 0.94 ppm; Zr-CH₃, δ 48.8 ppm)¹⁰ and others.³⁰⁻³² Additionally, the proton NMR spectrum of the dimethyl derivative 5b is temperature-dependent. Above 35 °C the resonances attributed to the diastereotopic isopropyl methyl groups of the BDAP ligand sharpen to a single resonance, which we interpret as rapid rotation about the $N-C_{ipso}$ bond.

Compound 4 reacts with 1 equiv of NaCp(DME)³³ to yield the 16-valence-electron cyclopentadienyl complex $(BDAP)Zr(\eta^5-Cp)Cl$ (5c). The proton and carbon NMR spectra¹⁸ of compound **5c** are consistent with a pseudotetrahedral geometry and local C_s symmetry about zirconium. The remaining chloride in complex 5c can be metathesized with alkylating reagents such as MeMgBr, PhCH₂MgCl, and LiCH₂SiMe₃ to afford the alkyl derivatives (BDAP) $Zr(\eta^5$ -Cp)R (R = Me, CH₂Ph, CH_2SiMe_3).³⁴ The local C_s symmetry is retained in these compounds.

The reaction of the dichloride complex 4 with 2 equiv of PhMe₂CCH₂MgCl in THF did not give the anticipated dineophyl complex but rather the η^2 -pyridyl compound $(BDAP)Zr(\eta^2(N,C)-NC_5H_4)(CH_2CMe_2Ph)$ (5d). Spectroscopic data³⁵ suggest that compound **5d** has C_s symmetry, as evidenced by the AB pattern observed for the BDAP methylene protons (NC H_2 and NC H_2 C H_2). The ¹H NMR resonances for the η^2 -pyridyl moiety are comparable to those for other known complexes.^{36–38} We have observed nearly identical η^2 -pyridyl resonances (by ¹H NMR) in the reaction of compound 4 with 2 equiv of LiCH₂SiMe₃ but were unable to isolate pure product. We are exploring the use of other bases to stabilize the "(BDAP)ZrCl₂" fragment.

Colorless single crystals of 5d suitable for an X-ray analysis were grown from a saturated pentane solution at $-30 \,^{\circ}\text{C}^{.39}$ The molecular structure of complex 5d and selected bond distances and angles are shown in Figure 1. Overall the structure is best described as a capped tetrahedron with the pyridyl nitrogen occupying the

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(34) Scollard, J. D.; McConville, D. H. To be published. (35) (BDAP)Zr($\eta^2(N,C)$ -NC₅H₄)(CH₂CMe₂Ph) (**5d**): ¹H NMR δ 7.33– 7.10 (m, 10H, Ar, Ph, py), 6.88 (m, 1H, Ph), 6.78 (tt, 1H, py), 6.72 (m, 2H, Ph), 6.35 (ddd, 1H, py), 4.26 (sept, 2H, CHMe₂), 3.82 (m, 2H, NCH₂), 3.58 (m, 2H, NCH₂), 3.26 (sept, 2H, CHMe₂), 2.76 (m, 1H, NCH₂CH₂), 2.64 (m, 1H, NCH₂CH₂), 1.70 (s, 2H, CH₂CMe₂Ph), 1.59 (d, 6H, CHMe₂), 1.47 (d, 6H, CHMe₂), 1.18 (d, 6H, CHMe₂), 1.17 (s, 6H, CMe₂Ph), 0.64 (d, 6H, CHMe₂); ¹³C(¹H) NMR δ 153.9, 149.7, 145.5 144.6 134.6 134.8 129.3 128.1 125.3 125.1 125.1 124.7 124.0 123.8 144.6, 144.5, 134.8, 129.3, 128.1, 125.3, 125.1, 125.1, 124.7, 124.0, 123.8, 68.0, 59.6, 41.0, 35.5, 31.7, 28.3, 28.1, 27.0, 26.6, 25.2, 24.1. Anal. Calcd for C42H57N3Zr: C, 72.57; H, 8.26; N, 6.04. Found: C, 72.85; H, 8.61; N, 5.95

^{(22) (}BDAP)Zr(CH₂Ph)₂ (**5a**): ¹H NMR δ 7.19 (m, 6H, Ar), 7.01 (tt, 4H, Ph), 6.82 (tt, 4H, Ph), 6.65 (dd, 2H, Ph), 3.78 (sept, 4H, CHMe₂), 3.49 (m, 2H, NCH₂), 2.31 (m, 2H, NCH₂CH₂), 1.95 (s, 2H, CH₂Ph), 1.32 (d, 12H, CHMe₂), 1.27 (d, 12H, CHMe₂); ¹³C{H} NMR δ 145.9, 145.1, 145.0, 130.1, 126.6, 126.5, 124.7, 122.7, 64.2 (CH₂Ph, ¹J_{CH} = 124 Hz), 58.8, 29.1, 28.4, 26.6, 25.1. Anal. Calcd for C₄₁H₅₄N₂Zr: C, 73.93; H, 8.17; N, 4.21. Found: C, 73.54; H, 8.33; N, 4.27. (23) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. Organometallics **1985**, 4, 902. (24) Wolczanski, P. T.; Bercaw, J. E. Organometallics **1982**, 1, 793.

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^{(29) (}BDAP)ZrMe₂ (5b): ¹H NMR (20 °C) δ 7.17 (m, 6H, Ar), 3.75 (sept, 4H, CHMe₂), 3.47 (m, 2H, NCH₂), 2.25 (m, 2H, NCH₂CH₂), 1.36 (m, 12H, CHMe₂), 1.34 (m, 12H, CHMe₂), 1.34 (m, 12H, CHMe₂), 0.42 (s, 6H, ZrMe₂); $^{13}C{^{1}H}$ NMR (20 °C) δ 145.6, 143.2, 126.8, 124.5, 59.4, 39.9 (ZrMe₂), 29.9, 28.6, 25.8, Anal. Calcd for $C_{29}H_{46}N_2Zr$: C, 67.78; H, 9.02; N, 5.45. Found: (30) Anderson, R. A. Inorg. Chem. 1979, 18, 1724.
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Figure 1. (top) ORTEP drawing of 5d. (bottom) Chem 3D Plus representation of the core of 5d. Selected bond distances (Å) and angles (deg): Zr1-N1 = 2.050(9), Zr1-N2 = 2.031(9), Zr-C1 = 2.268(12), Zr1-C30 = 2.219(12), Zr1-N3 = 2.260(10); N1-Zr1-N2 = 95.4(4), C30-Zr1-C1 = 113.2(4), N1-Zr1-C1 = 103.9(4), N1-Zr1-C30 = 120.8(4).

capping position. The Zr1-N3-C30 ring is structurally similar to the Zr-N-C ring in the cationic complex [Cp₂-Zr(η^2 -picolyl)(PMe₃)](BPh₄).³⁸ Each amide donor in **5d** is sp²-hybridized, as evidenced by the sum of the angles about each nitrogen (N1, 360.0°; N2, 359.8°). The solidstate C₁ symmetry of compound **5d** coupled with the spectroscopically observed C_s symmetry in solution suggests that rapid rotation about the Zr1-C30 bond is occurring on the NMR time scale.

It is interesting that the pyridyl complex 5d is formed only with a large alkylating reagent. A preliminary investigation into the mechanism of formation of compound 5d is presented.⁴⁰ Two possible pathways for this Communications



reaction are depicted in Scheme 2. Substituting (BDAP)-ZrCl₂(d_5 -py)₂ for (BDAP)ZrCl₂(py)₂ readily discriminates between these two mechanisms. Path A outlines the formation of the pyridyl complex via an intermediate zirconium alkylidene⁴¹ complex. Transferring a deuterium from coordinated d_5 -pyridine to the alkylidene yields a d_1 -neophyl group. Alternatively (path B), the pyridyl complex could result from neophyl abstraction of deuterium from coordinated d_5 -pyridine.³⁸ In this case the retained neophyl group would show no deuterium incorporation. The reaction of (BDAP)ZrCl₂(d_5 py)₂ with 2 equiv of PhMe₂CCH₂MgCl yields a single pyridyl species, (BDAP)Zr($\eta^2(N,C)$ -NC₅D₄)(CH₂CMe₂Ph) (d_4 -5d) (as confirmed by NMR spectroscopy), suggesting that the mechanism in path B is operative.

The new chelating diamide ligand BDAP has been shown to stabilize d^0 dialkyl derivatives of zirconium. The rigid coordination of the ligand and enforced location of the aryl isopropyl groups creates a "pocket" opposite the ligand and necessarily protects the metal above and below the zirconium-diamide plane. We are currently exploring the catalytic olefin polymerization chemistry of putative cationic derivatives of compounds **5a,b** (e.g., [(BDAP)ZrR]⁺). In addition, we are preparing other chelating diamide complexes of groups 4 and 5 with different substitution on the arene ring.

Acknowledgment. This research was supported by the NSERC (Canada) and a University of Western Ontario Internal Research Grant (to D.H.M.).

Supporting Information Available: Text giving experimental details for compounds 1-5 and tables of crystal data, data collection details, final positional parameters, final thermal parameters, and all bond distances and angles (14 pages). Ordering information is given on any current masthead page.

OM950534M

⁽³⁹⁾ X-ray data for **5d**. Data were collected at 25 °C on a Siemens P4 diffractometer using graphite-monochromated Mo K α radiation. A total of 6209 reflections were collected in the θ range 2.0–23°, of which 5405 were independent ($R_{\rm int} = 0.0558$). The structure was solved by a combination of Patterson and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically except for two phenyl ring carbon atoms. In the final least-squares refinement cycle on F^2 , the model converged at R = 0.0951, $R_{\rm w} = 0.2287$, and GOF = 1.014 for 2999 reflections with $F_o \geq 4\sigma(F_o)$ and 289 parameters. Crystal data are a = 10.146(2) Å, b = 12.336(2) Å, c = 16.723(2) Å, $\alpha = 81.00(6)^\circ$, $\beta = 74.99(10)^\circ$, $\gamma = 76.24(9)^\circ$, V = 1953.6(6) Å³, space group P1, Z = 2, mol wt 695.13, and ρ (calcd) = 1.182 g/cm³.

⁽⁴⁰⁾ We are pursuing routes to base-stabilized alkylidenes of the form (BDAP)Zr(=CHR)(L), $(L = PR_3)$. We thank a reviewer for suggesting the deuterium labeling experiment.

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