Inorg. Chem. **2003**, *42*, 6225–6229

Inorganic Chemistry
Article

Synthesis and Structural Investigation of *N,N′,N′′*-Trialkylguanidinato-Supported Zirconium(IV) Complexes

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Received April 28, 2003

The addition of 2 equiv of *N,N′,N′′*-triisopropylguanidine (guanH$_2$) to Zr(CH$_2$Ph)$_4$ produced the bis(guanidinato)-bis(benzyl)zirconium complex $\{(^i\mathrm{PrNH})\mathrm{C}(\mathrm{N}^i\mathrm{Pr})_2\}_2\mathrm{Zr}(\mathrm{CH}_2\mathrm{Ph})_2$ (**1**). The mono(guanidinato) complex $\{(^i\mathrm{PrN})_2\mathrm{C}(\mathrm{NH}^i\mathrm{Pr})\}\mathrm{ZrCl}_3$ (**2**) was accessible by the reaction of 2 equiv of guanH$_2$ with ZrCl$_4$. Guanidinium hydrochloride, $\{\mathrm{C}(\mathrm{NH}^i\mathrm{Pr})_3\}\mathrm{Cl}$, is a byproduct of this reaction. When crystallized from THF, complex **2** was isolated as the THF adduct $\{(^i\mathrm{PrNH})\mathrm{C}(\mathrm{N}^i\mathrm{Pr})_2\}\mathrm{ZrCl}_3(\mathrm{THF})$ (**2**-THF). The mixed cyclopentadienyl guanidinato complex $\{\eta^5\text{-}1,3\text{-}(\mathrm{Me}_3\mathrm{Si})_2\mathrm{C}_5\mathrm{H}_3\}\{(^i\mathrm{PrNH})\mathrm{C}(\mathrm{N}^i\mathrm{Pr})_2\}\mathrm{ZrCl}_2$ (**3**) was prepared by treatment of $\{1,3\text{-}(\mathrm{Me}_3\mathrm{Si})_2\mathrm{C}_5\mathrm{H}_3\}\mathrm{ZrCl}_3$ with the in situ generated lithium triisopropylguanidinate salt. The reaction of guanH$_2$ with $\{1,3\text{-}(\mathrm{Me}_3\mathrm{Si})_2\mathrm{C}_5\mathrm{H}_3\}\mathrm{ZrMe}_3$ affords the dimethyl derivative $\{\eta^5\text{-}1,3\text{-}(\mathrm{Me}_3\mathrm{Si})_2\mathrm{C}_5\mathrm{H}_3\}\{(^i\mathrm{PrNH})\mathrm{C}(\mathrm{N}^i\mathrm{Pr})_2\}\mathrm{ZrMe}_2$ (**4**). Definitive evidence for the molecular structures of these products is provided through single-crystal X-ray characterization of **1**, **2**-THF, and **3**, which are presented. The extent of π delocalization within the guanidinato ligand is discussed in the context of the metrical parameters obtained from these structural studies.

Introduction

Significant efforts to modify the reactivity of the metallocene framework have, over the past decade, led to the fruitful design of new nonmetallocene complexes that perform as single-site olefin polymerization catalysts.[1] Chelating amidinate anions, [RNC(R′)NR]$^-$, have received attention as ancillary ligands for such applications and a variety of cis-octahedral bis(amidinate) group 4 complexes have been prepared.[2,3] When activated with methylalumoxane (MAO), many of these compounds have been found to be active catalytic precursors for the polymerization of ethylene and propylene, the oligomerization of 1,5-hexadiene, and the isomerization of internal and terminal olefins.[4] Also well established in this regard are mono(cyclopentadienyl)-zirconium(IV) amidinate complexes, $[(\eta^5\text{-C}_5\mathrm{Me}_5)\{\mathrm{RNC(R')NR}\}\mathrm{ZrX}_2]$ (R = alkyl, R′ = Me; R = SiMe$_3$, R′ = aryl; X = halide, alkyl).[5]

N-substituted guanidinate anions, [RNC(NR′$_2$)NR′′]$^-$, have received increasing attention as ancillary ligands for both

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[1] For selected reviews, see: (a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283 and references therein. (b) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236 and references therein. (c) Ittel, S. D.; Johnson, L. K.; Brookhardt, M. *Chem. Rev.* **2000**, *100*, 1169 and references therein.

[2] Edelmann, F. T. *Top. Curr. Chem.* **1996**, *179*, 113 and references therein. Kilner, M.; Baker, J. *Coord. Chem. Rev.* **1994**, *133*, 219 and references therein. Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403 and references therein.

[3] (a) Hagadorn, J. R.; Arnold, J. *Organometallics* **1998**, *17*, 1355. (b) Hagadorn, J. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **1997**, 3087. (c) Hagadorn, J. R.; Arnold, J. *J. Am. Chem. Soc*. **1996**, *118*, 893. (f) Hagadorn, J. R.; Arnold, J. *Organometallics* **1994**, *13*, 4670.

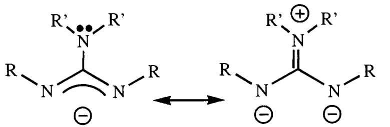
[4] (a) Volkis, V.; Nelkenbaum, E.; Lisovskii, A.; Hasson, G.; Semiat, R.; Kapon, M.; Botoshansky, M.; Eishen, Y.; Eisen, M. S. *J. Am. Chem. Soc.* **2003**, *125*, 2179. (b) Averbuj, C.; Tish, E.; Eisen, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 8640. (c) Richter, J.; Edelmann, F. T.; Noltemeyer, M.; Schmidt, H.-G.; Shmulinson, M.; Eisen, M. S. *J. Mol. Catal*. **1998**, *130*, 149. (d) Volkis, V.; Shmulinson, M.; Averbuj, C.; Lisovskii, A.; Edelmann, F. T.; Eisen, M. S. *Organometallics* **1998**, *17*, 3155. (e) Littke, A.; Sleiman, N.; Bensimon, C.; Richeson, D. S.; Yap, G. P. A.; Brown, S. *Organometallics* **1998**, 17, 446. (g) Walter, D.; Fischer, R.; Görls, H.; Koch, J.; Scheweder, B. J. *J. Organomet. Chem*. **1996**, *508*, 13. (h) Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279. (i) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1995**, *14*, 1827. (j) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1995**, *14*, 2106. (k) Herscovics-Korine, D.; Eisen, M. S. *J. Organomet. Chem*. **1995**, *503*, 307.

[5] (a) Keaton, R. J.; Sita, L. R. *J. Am. Chem. Soc.* **2002**, *124*, 9070. (b) Keaton, R. J.; Koterwas, L. A.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2002**, *124*, 5932. (c) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 10754. (d) Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 6197. (e) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958. (f) Gomez, R.; Green, M. L. H.; Haggitt, J. L. *J. Chem. Soc., Dalton Trans.* **1996**, 939. (g) Gomez, R.; Duchateau, R.; Chernega, A. N.; Teuben, J. N.; Edelmann, F. T.; Green, M. L. H. *J. Organomet. Chem*. **1995**, *491*, 153. (h) Gomez, R.; Duchateau, R.; Chernega, A. N.; Meetsma, A.; Edelmann, F. T.; Teuben, J. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1995**, 217. (i) Gomez, R.; Green, M. L. H.; Haggitt, J. L. *J. Chem. Soc., Chem. Commun.* **1994**, 2607.

10.1021/ic034445a CCC: $25.00

main-group and transition-metal complexes due to their flexible coordination behavior and their potentially tunable steric and electronic properties.[6−10] Guanidinate complexes are now beginning to emerge as interesting species in small-molecule activation.[7d,9a,b]

A characteristic feature of guanidinate ligands is the presence of the NR'_2 function that is capable of donating lone pair electron density to the central carbon of the ligand and stabilizing a zwitterionic resonance structure (**I**). This results in formal negative charges on both of the metal-bonded nitrogen atoms and might ultimately lead to increased electron donation to the metal.



I

To maximize this effect the NR'_2 center should be sp^2 hybridized with the lone electron pair residing in a p-orbital that is oriented to overlap with the conjugated NCN moiety. This second feature requires a small dihedral angle between the planes defined by the CNR'_2 groups and that defined by NCN chelate. It is worth noting that the attendant steric congestion caused by the two organic substituents should encourage a larger dihedral angle and disfavor the appropriate orientation for π conjugation. Our efforts to encourage resonance contribution **I** have, as one focus, the application of *N*,*N′*,*N″*-trialkylguanidinato ligands which possess a less sterically demanding exocyclic N(H)R′ group.

Herein we present the synthesis and characterization of zirconium(IV) complexes with triisopropylguanidinato- and mixed cyclopentadienyl/guanidinato-supporting ligation. The guanidinate anion was introduced into the coordination sphere of Zr(IV) through proton-transfer coupled with HCl or hydrocarbon elimination reactions and through salt metathesis reactions. Metrical parameters of the guanidinato ligands have been examined using X-ray crystallography and are discussed in relation to resonance structure **I**.

Experimental Section

General Considerations. All manipulations were carried out in either a nitrogen-filled drybox or under nitrogen using standard Schlenk techniques. $ZrCl_4$ and MeLi (1.4 M in diethyl ether) was used as received from Aldrich Chemical Co. Solvents were distilled from Na/K alloy under nitrogen. ^1H and ^{13}C NMR spectra were run on a Varian Gemini-200, a Bruker 300 MHz, or a Bruker 500 MHz spectrometer using the residual protons of the deuterated solvent for reference. $Zr(CH_2Ph)_4$ was prepared using literature procedures. $\{\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3\}ZrCl_3$ was prepared by the reaction of $1,1,3\text{-}(Me_3Si)_3C_5H_3$ with $ZrCl_4$. $\{\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3\}ZrMe_3$ was prepared by the reaction of MeLi with $\{\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3\}ZrCl_3$.

$\{(^iPrN)_2C(NH^iPr)\}_2Zr(CH_2Ph)_2$ (1). To an orange solution of $Zr(CH_2Ph)_4$ (0.173 g, 0.380 mmol) dissolved in 2 mL of dichloromethane was added a colorless 2 mL dichloromethane solution of triisopropylguanidine (0.146 g, 0.788 mmol). An immediate color change to clear yellow was observed. The mixture was allowed to sit at room temperature undisturbed for 72 h. The solvent was then removed to give a light yellow solid (0.214 g, 88% yield). Yellow crystals of **1** were obtained from diethyl ether at −35 °C.

^1H NMR (C_6D_6): δ 0.90 (m, 12H, CH_3), 1.13 (d, 24H, CH_3), 2.67 (s, 4H, CH_2), 3.48 (br, 4H, CH and NH), 3.64 (sept, 4H, CH), 6.92 (t, 1H, C_6H_5), 7.26 (t, 2H, C_6H_5), 7.45 (d, 2H, C_6H_5). ^{13}C NMR (C_6D_6): δ 24.6, 24.8 (CH_3), 46.3, 46.8 (*C*H), 70.9 (CH_2), 119.8, 127.4, 128.2, 150.7 (C_6H_5), 168.6 (CN_3).

Anal. Calcd for $ZrN_6C_{34}H_{58}$: C, 63.60; H, 9.11; N, 13.09. Found: C, 63.20; H, 8.96; N, 13.40.

$\{(^iPrN)_2C(NH^iPr)\}ZrCl_3$ (2). To a suspension of $ZrCl_4$ (0.626 g, 2.686 mmol) in 30 mL of toluene was added a toluene solution of triisopropylguanidine (0.996 g, 5.372 mmol). The mixture was allowed to stir for 16 h. Filtration and removal of solvent gave a fluffy white solid (0.612 g, 60% yield). The insoluble materials were identified as guanidinium hydrochloride ($(^iPrNH)_3CCl$) by comparison with spectroscopic parameters of an authentic sample.

^1H NMR (C_6D_6): δ 0.83 (d, 6H, CH_3), 1.45 (d, 12H, CH_3), 3.52 (broad, 4H, CH and NH). ^{13}C NMR (C_6D_6): δ 24.30 (CH_3), 24.64 (CH_3), 46.71 (*C*H), 47.40 (*C*H), 148.67 (CN_3).

Anal. Calcd for $ZrN_3C_{10}H_{22}Cl_3$: C, 31.45; H, 5.81; N, 11.00. Found: C, 31.25; H, 5.96; N, 10.70.

Recrystallization of **2** from THF at at −35 °C yielded crystals of the THF adduct of **2**, which were analyzed by single-crystal X-ray analysis.

$\{1,3\text{-}(Me_3Si)_2C_5H_3\}\{(^iPrN)_2C(NH^iPr)\}ZrCl_2$ (3). Dropwise addition of methyllithium (0.9 mL of 1.4 M, 1.26 mmol) to a solution of triisopropylguanidine (0.233 g, 1.26 mmol) dissolved in about 30 mL of ether produced a colorless reaction mixture that was stirred for 40 min. Solid $1,3\text{-}(Me_3Si)_2CpZrCl_3$ (0.52 g, 1.28 mmol) was added to this reaction mixture. The solution turned orange/red and eventually became a pale yellow followed by formation of a precipitate. The reaction was stirred overnight, and all volatiles were removed under vacuum. The product was extracted in 40 mL of hexane, which was filtered through a Celite pad, and the volatiles were removed to yield the product as a yellow solid (0.40 g, 58%). The product could then be further purified by recrystallization from diethyl ether at −25 °C.

^1H NMR (C_6D_6): δ 0.38 (s, 18H, $Si(CH_3)_3$), 0.74 (d, 6 H, $CH(CH_3)_2$), 1.27 (d, 12 H, $CH(CH_3)_2$), 3.38 (sept, 1H, $CHMe_2$), 3.59 (overlapping br, 1H, NH, and sept, 2H, $CHMe_2$), 6.98 (d, 2H, Cp H), 7.13 (t, 1H, Cp H). ^{13}C NMR (C_6D_6): δ 0.1 ($Si(CH_3)_3$), 23.4 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 45.8 ($CHMe_2$), 48.0 ($CHMe_2$), 125.4 (Cp H), 130.4 (Cp−Si), 131.1 (Cp H), 162.0 (CN_3).

We were unable to obtain satisfactory microanalysis for **3**. As alternative support of the purity of this compound, the ^1H and ^{13}C NMR spectra of **3** are included in the Supporting Information.

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(6) Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91 and references therein.

(7) (a) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2002**, *41*, 4149. (b) Ong, T.-G.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 2839. (c) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *Polyhedron* **2002**, *21*. 619. (d) Ong, T.-G.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 1. (e) Lu, Z.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2001**, *20*, 706. (f) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *J. Chem. Soc., Chem. Commun.* **2000**, 1515. (g) Thirupathi, N.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2000**, *19*, 2573. (h) Thirupathi, N.; Yap, G. P. A.; Richeson, D. S. *J. Chem. Soc., Chem. Commun.* **1999**, 2483. (i) Wood, D.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **1999**, *38*, 5788.

(8) Coles, M. P.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **2001**, 1169.

(9) (a) Mullins, S. M.; Duncan, A. P.; Bergman, R. G.; Arnold, J. *Inorg. Chem.* **2001**, *40*, 6952. (b) Duncan, A. P.; Mullins, S. M.; Arnold, J.; Bergman, R. G. *Organometallics* **2001**, *20*, 1808. (c) Giesbrecht, G. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2001** 923. (d) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *Organometallics* **2000**, *19*, 2809.

(10) Okamoto, S.; Livinghouse, T. *Organometallics* **2000**, *19*, 1449.

Table 1. Selected Crystal Data and Data Collection Parameters for $\{(^{i}PrN)_2C(NH^{i}Pr)\}_2Zr(CH_2Ph)_2$ (**1**), $\{(^{i}PrN)_2C(NH^{i}Pr)\}ZrCl_3(THF)$ (**2**-THF), and $\{1,3\text{-}(Me_3Si)_2C_5H_3\}\{(^{i}PrN)_2C(NH^{i}Pr)\}ZrCl_2$ (**3**)

empirical formula	$C_{34}H_{58}N_6Zr$ (**1**)	$C_{14}H_{30}Cl_3N_3OZr$ (**2**-THF)	$C_{21}H_{43}Cl_2N_3Si_2Zr$ (**3**)
fw	642.08	453.98	555.88
T (K)	203(2)	203(2)	203(2)
wavelength (Å)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
cryst system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	Cc	Pbca
a (Å)	10.4142(13)	9.424(2)	14.706(1)
b (Å)	15.2097(19)	15.105(4)	19.030(2)
c (Å)	22.600(3)	15.152(4)	20.916(2)
β (deg)	96.563(2)	104.70(2)	
V (Å^3)	3556.3(8)	2086(2)	5853(1)
Z	4	4	8
abs coeff (mm^{-1})	0.339	0.915	0.652
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.0325 wR2 = 0.0639	R1 = 0.0586 wR2 = 0.1665	R1 = 0.0507 wR2 = 0.1394

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. wR2 = $(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

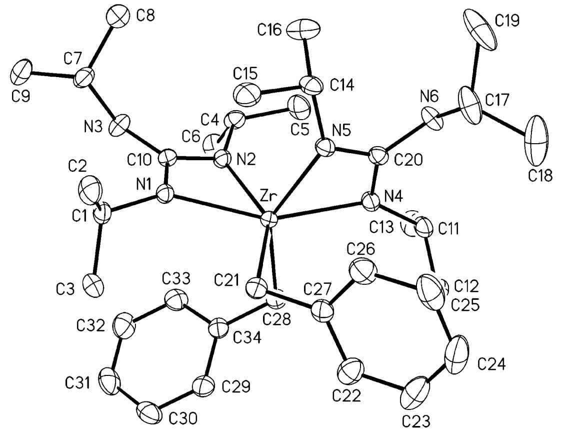


Figure 1. Molecular structure and atom numbering scheme for $\{(^{i}PrN)_2C(NH^{i}Pr)\}_2Zr(CH_2Ph)_2$ (**1**).

Table 2. Selected Bond Distances and Angles for $\{(^{i}PrN)_2C(NH^{i}Pr)\}_2Zr(CH_2Ph)_2$ (**1**)

Bond Distances (Å)			
Zr−N(1)	2.290(2)	Zr−N(2)	2.209(2)
Zr−N(4)	2.295(2)	Zr−N(5)	2.188(2)
Zr−C(28)	2.312(2)	Zr−C(21)	2.312(2)
N(1)−C(10)	1.327(2)	N(4)−C(20)	1.335(2)
N(2)−C(10)	1.348(2)	N(5)−C(20)	1.345(2)
N(3)−C(10)	1.378(2)	N(6)−C(20)	1.370(2)
Bond Angles (deg)			
N(4)−Zr−N(2)	101.96(6)	N(1)−C(10)−N(3)	125.3(2)
N(2)−Zr−N(1)	59.27(5)	N(2)−C(10)−N(3)	122.1(2)
N(4)−Zr−N(5)	59.40(6)	N(5)−C(20)−N(4)	112.1(2)
N(1)−Zr−N(5)	105.94(6)	N(5)−C(20)−N(6)	123.7(2)
C(28)−Zr−C(21)	93.02(7)	N(4)−C(20)−N(6)	124.7(2)
C(10)−N(3)−C(7)	122.6(2)	C(27)−C(21)−Zr	111.5(1)
C(20)−N(6)−C(17)	123.5(2)	C(34)−C(28)−Zr	112.7(1)
N(1)−C(10)−N(2)	112.6(2)		
N(1)−N(2)−C(10)/ C(9)−C(10)−N(3)^a	56.2	N(4)−N(5)−C(20)/ C(19)−C(20)−N(6)^a	52.2

^{a} The angle between the planes of the chelate (N−C−N) and the isopropylamino substituent.

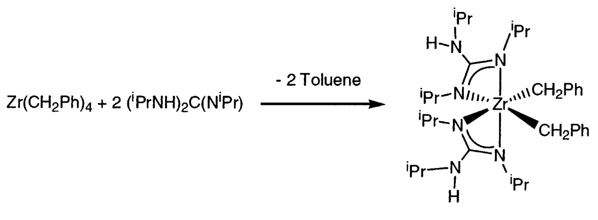
$\{1,3\text{-}(Me_3Si)_2C_5H_3\}\{(^{i}PrN)_2C(NH^{i}Pr)\}ZrMe_2$ (4). A toluene solution of triisopropylguanidine (0.185 g, 1 mmol) was added to $1,3\text{-}(Me_3Si)_2CpZrMe_3$ (0.345 g, 1 mmol) dissolved in about 20 mL of toluene. The reaction was allowed to stir at room-temperature overnight. All volatiles were removed under vacuum to leave a white solid that was identified as pure **4** (0.510 g, 99%).

^{1}H NMR (C_6D_6): δ 0.31 (s, 18H, $Si(CH_3)_3$), 0.44 (s, 6H, $ZrCH_3$) 0.88 (d, 6 H, $CH(CH_3)_2$), 1.18 (d, 12 H, $CH(CH_3)_2$), 3.48 (overlapping br, 1H, NH, and sept, 2H, $CHMe_2$), 3.58 (sept, 1H, $CHMe_2$), 6.72 (d, 2H, Cp H), 6.99 (t, 1H, Cp H). ^{13}C NMR (C_6D_6): δ 0.36 ($Si(CH_3)_3$), 24.1 ($CH(CH_3)_2$), 24.5 ($CH(\mathit{C}H_3)_2$), 40.7 (Zr−$\mathit{C}H_3$), 46.1 ($\mathit{C}HMe_2$), 47.1 ($\mathit{C}HMe_2$), 121.2 (Cp H), 124.9 (Cp−Si), 127.6 (Cp H), 167.3 ($\mathit{C}N_3$).

We were unable to obtain satisfactory microanalysis for **4**. As alternative support of the purity of this compound, the ^{1}H and ^{13}C NMR spectra of **4** are included in the Supporting Information.

Results and Discussion

The direct reaction of a 1:2 molar ratio of $Zr(CH_2Ph)_4$ and *N,N′,N″*-triisopropylguanidine, $(^{i}PrN){=}C(NH^{i}Pr)_2$, in toluene at room temperature proceeds via proton transfer and toluene elimination to yield a new species $[\{(^{i}PrNH)C(N^{i}\text{-}Pr)_2\}_2Zr(CH_2Ph)_2]$ (**1**) in 88% isolated yield (eq 1).^{7d} The ^{1}H and ^{13}C NMR spectra of 1 display two sets of ^{i}Pr signals in a 2:1 ratio and a single methylene resonance attributed to the benzyl ligands. Complex **1** is stable for at least 24 h at temperatures up to 100 °C even in the presence of excess *N,N′,N″*-triisopropylguanidine. To establish the molecular structure of **1** a single-crystal X-ray analysis was undertaken and the results are presented in Figure 1 and Tables 1 and 2. Complex **1** exhibits two guanidinato ligands that span axial/equatorial positions. The N(1)−Zr−N(4) angle of 155.96(5)° supports the assignment of N(1) and N(4) to the pseudoaxial positions of a distorted octahedral complex with approximate C_2 symmetry. The equatorial plane is defined by two guanidinato nitrogens (N(2) and N(5)) and the two benzyl groups. Structural analysis confirmed the lack of η^2 bonding for the benzyl groups.



(1)

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The spectroscopic equivalence for the ^{i}Pr groups (both CH and CH_3) bonded to N(1) and N(4) with those on N(2) and N(5) as well as the appearance of a singlet for the benzylic protons indicates that the guanidinato ligands in **1** are fluxional in solution. Furthermore, this exchange occurs only

Table 3. Selected Bond Distances and Angles for $\{({}^iPrN)_2C(NH^iPr)\}ZrCl_3(THF)$ (**2**-THF)

Bond Distances (Å)			
Zr−N(1)	2.13(2)	Zr−N(2)	2.15(2)
Zr−O(1)	2.27(2)	Zr−Cl(1)	2.450(9)
N(1)−C(10)	1.34(2)	Zr−Cl(2)	2.439(7)
N(2)−C(10)	1.34(3)	Zr−Cl(3)	2.412(7)
N(3)−C(10)	1.35(3)		

Bond Angles (deg)			
N(1)−Zr−N(2)	61.8(6)	C(10)−N(2)−C(4)	123.7(2)
O(1)−Zr−Cl(3)	174.5(5)	C(10)−N(2)−Zr	92.8(1)
N(2)−Zr−Cl(2)	154.9(5)	C(4)−N(2)−Zr	142.3(2)
N(1)−Zr−Cl(1)	159.0(5)	C(10)−N(3)−C(7)	129.8(2)
C(10)−N(1)−C(1)	123(2)	N(1)−C(10)−N(3)	127.8(2)
C(10)−N(1)−Zr	93.8(1)	N(1)−C(10)N(2)	111.1(2)
C(1)−N(1)−Zr	140.0(2)	N(3)C(10)−N(2)	121.1(2)
C(7)−N(3)−C(10)/ N(1)−C(10)−N(2)[a]	30.3		

[a] The angle between the planes of the chelate (N−C−N) and the isopropylamino substituent.

between the nitrogen centers bonded to Zr and does not involve the noncoordinated NH(^{i}Pr) groups of the guanidinato ligands. These observations are similar to those for the recently reported complex $[\{(Me_2N)C(N^iPr)_2\}_2Zr(CH_2Ph)_2]$ (**A**).[9b]

The bond distances around N(1), N(2), and C(10) and N(4), N(5), and C(20) average 1.34 Å indicating partial double-bonding character and a π-conjugated NCN chelate. The N(3)−C(10) and N(6)−C(20) bond distances of 1.378(2) and 1.370(2) Å are shorter than a typical C−N single bond of 1.42−1.45 Å and also shorter than the Me_2N−C distance in **A** of 1.394(4) and 1.385(4) Å.[9b] The only measurable angles about N(3) (122.33(15)°) and N(6) (123.25(16)°) are consistent with sp^2-hybridized nitrogen atoms. However, the dihedral angles between the N(H)^{i}Pr groups and the N−C−N chelate rings (average 54°) indicate little contribution from resonance structure **I**.

Guanidinato ligands can also be introduced into the Zr coordination sphere by the reaction shown in eq 2. This method employs 2 equiv of neutral guanidine in reaction with zirconium tetrachloride. We anticipated that 1 equiv of guanidine would be incorporated into a new complex, **2**, with the second 1 equiv facilitating the removal of HCl and forming guanidinium hydrochloride. When the reaction of *N*,*N′*,*N″*-tri(isopropyl)guanidine with $ZrCl_4$ was carried out in toluene the two products could be easily separated on the basis of differing solubility. The NMR spectra of **2** indicate the presence of the guanidinato ligand with a characteristic ratio of 2:1 isopropyl groups.

$$ZrCl_4 + 2({}^iPrNH)_2C(N^iPr) \rightarrow \underset{\mathbf{2}}{Cl_3Zr\{({}^iPrN)_2C(NH^iPr)\}} + ({}^iPrNH)_3CCl \quad (2)$$

Although we have been unable to obtain crystals of **2** that were satisfactory for single-crystal structural analysis, recrystallization from THF did yield single crystals (**2**-THF) that were subjected to X-ray diffraction analysis. The results of this study are summarized in Tables 1 and 3 and displayed in Figure 2. Complex **2**-THF possesses a distorted octahedral geometry with a single cis-chelating guanidinato ligand and three chlorides in support of the formulation of **2**. In addition, **2**-THF has one molecule of THF that completes the coordination sphere of the Zr(IV) center.

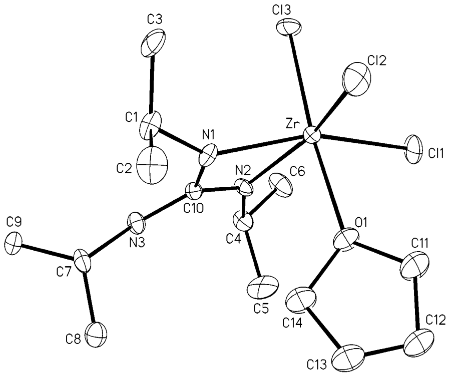


Figure 2. Molecular structure and atom numbering scheme for $\{({}^iPrN)_2C(NH^iPr)\}ZrCl_3(THF)$ (**2**-THF).

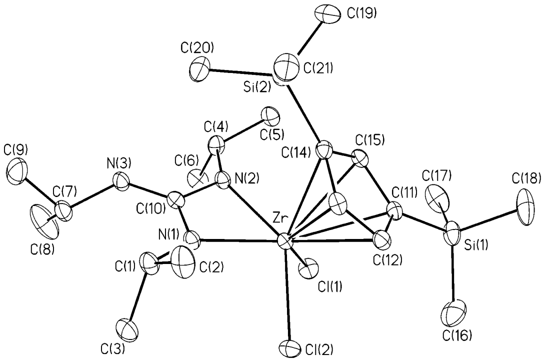


Figure 3. Molecular structure and atom numbering scheme for $\{1,3\text{-}(Me_3Si)_2C_5H_3\}\{({}^iPrN)_2C(NH^iPr)\}ZrCl_2$ (**3**).

The equivalent N(2)−C(10) and N(1)−C(10) bond distances (1.34(2) Å) are consistent with partial double-bond character and support π delocalization over an sp^2-hybridized core. The fact that the N(3)−C(10) bond distance is equivalent to those in the chelate ring (1.35(2) Å) and that the angle between the C(7)−N(3)−C(10) plane and the plane defined by N(1)−C(10)−N(2) is only 30.3° indicates that, in contrast to complex **1**, the zwitterionic resonance structure for the guanidato ligand is important in this complex. Further support for the contribution of **I** is given by the observation that the average Zr−N bonds in **2**-THF are 0.11 Å shorter than the average Zr−N distances of **1**. Although these effects are subtle, these data suggest that the electronic environment at the metal center has some bearing on the extent of π donation from the exocyclic ^{i}PrNH group and, hence, to the overall donor strength of the guanidinato ligand. The ligand appears to act as a more powerful electron donor toward the relatively electron poor metal center of complex **2**-THF compared to more electron-rich metal center of **1**.

Complexes with a combination of guanidinato- and cyclopentadienyl-supporting ligands are directly related to mono(cyclopentadienyl)zirconium(IV) amidinato.[5] We have explored two routes to such complexes that are summarized in eq 3. The reaction of the appropriate monocyclopentadienyl zirconium starting materials with lithium guanidinate or guanidine offer two methods for preparation of complexes with mixed supporting ligands. The lithium salt of *N*,*N′*,*N″*-

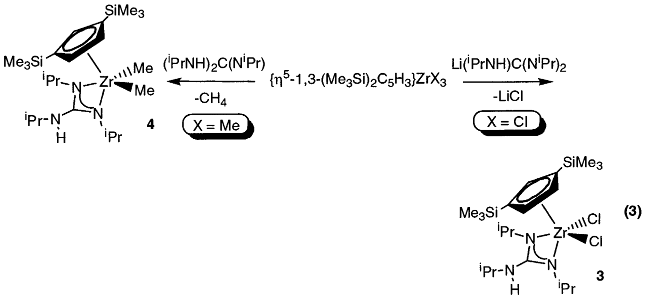
Table 4. Selected Bond Distances and Angles for $\{1,3\text{-}(Me_3Si)_2C_5H_3\}\{(^iPrN)_2C(NH^iPr)\}ZrCl_2$ (**3**)

Bond Distances (Å)			
Zr−Cl(1)	2.435(1)	Zr−Cl(2)	2.491(1)
Zr−N(1)	2.194(3)	Zr−N(2)	2.214(4)
N(1)−C(10)	1.355(6)	N(3)−C(1)	1.358(6)
N(2)−C(10)	1.347(5)	Zr−C(12)	2.550(4)
Zr−C(13)	2.533(4)	Zr−C(14)	2.560(4)
Zr−C(15)	2.530(4)	Zr−C(11)	2.567(4)

Bond Angles (deg)			
C(1)−Zr−Cl(2)	91.36(3)	N(1)−Zr−N(2)	60.43(9)
N(1)−C(1)−N(2)	111.1(3)	C(9)−N(3)−C(1)	121.0(3)
N(1)−C(10)−N(2)/ C(10)−N(3)−C(7)[a]	30.1		

[a] The angle between the planes of the chelate (N−C−N) and the isopropylamino substituent.

trisisopropylguanidinate was generated by in situ deprotonation of guanidine with MeLi. Reaction with $1,3\text{-}(Me_3Si)_2CpZrCl_3$ proceeds smoothly to generate **3** with elimination of LiCl. The mono(cyclopentadienyl)(guanidinato)zirconium dimethyl analogue can be prepared by the direct reaction of $1,3\text{-}(Me_3Si)_2CpZrMe_3$ and *N*,*N*′,*N*″-triisopropylguanidine. In this case the guanidinate is deprotonated by one of the zirconium methyl groups with elimination of methane to yield **4**.



The NMR spectra of complexes **3** and **4** are similar and clearly support the formulations of eq 3. To confirm the structural details for these species and to examine the metrical parameters for the guanidinato ligand the molecular structure of **3** was determined by single-crystal X-ray diffractometry. The results of this analysis are summarized in Table 1 and depicted in Figure 3. Selected bond lengths and angles are provided in Table 4.

The structural parameters for the guanidinato ligand in **3** are similar to those observed for **2**-THF. Specifically, the C(10)−N(3) bond length of the guanidinato ligand in **3** of 1.358(6) Å is equivalent to the C−N distances within the chelate ring (1.355(6), 1.347(5) Å) suggesting a significant degree of double-bond character between these atoms. This is likely the result lone pair π donation from the $N(H)^iPr$ group to the central carbon of the chelate ring and suggests that resonance structure **I** is significant for **3**. Consistent with this proposal are the small angle between the two planes defined by C7−N3−C10 and N1−C10−N2 of 30.3° and the Zr−N bond lengths that are between those of **1** and **2**. A comparison of these metrical parameters with the recently reported of tetrasubstituted guanidinate-bearing complex $CpZr((^iPrN)_2CNMe_2)Cl_2$ (**B**)[9b] suggests that replacing the exocyclic NMe_2 group with a less sterically demanding $N(^iPr)H$ favors resonance contribution **I**. Specifically, **B** displayed a larger dihedral angle (44.78°) between the Me_2N plane and the CNC plane of the chelate ring and a longer $C{-}NMe_2$ bond length (1.373(4) Å) than did **3**.

Conclusions

We have shown that neutral organozirconium complexes bearing guanidinato ancillary ligands can be synthesized and isolated by employing alkane, HCl, and LiCl elimination reactions. Structural investigations indicate that π donation from the isopropylamino moiety of the guanidinato ligand plays a role in some of these complexes. We are currently investigating the implications of this electronic effect on the reactivity of guanidinato-supported complexes. Along with this effort, our continuing investigations are oriented at further revealing the steric and electronic features that influence the reactivity of transition metal guanidinate compounds.

Acknowledgment. This work was supported by the NSERC of Canada. P.B. is the recipient of an NSERC Postgraduate Scholarship.

Supporting Information Available: Crystallographic data in CIF format and tables of crystal data and structure solution and refinement details, atomic coordinates, bond lengths and angles, and anisoptropic thermal parameters for compounds **1**, **2**-THF, and **3** and ^1H and ^{13}C NMR spectra of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034445A