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Dizirconium Complexes Supported by Preorganized Binucleating Bis(amidinates)

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Several new dizirconium complexes have been prepared using preorganized bis(amidinate) ligands featuring rigid 9,9-dimethylxanthene backbones. Reaction of the bis(amidine) $^{iPr}L_{Xan}H_2$ with 2 equiv of $Zr(NMe_2)_4$ forms the hexa(amido) derivative $^{iPr}L_{Xan}Zr_2(NMe_2)_6$ (**1**) in good yield. In a similar reaction, the unsymmetrical bis(amidine) $^{tBu,Et}L_{Xan}H_2$ reacts with $Zr(NMe_2)_4$ to form $^{tBu,Et}L_{Xan}Zr_2(NMe_2)_6$ (**2**) as a 9:1 mixture of C_2- and C_s-symmetrical rotational diastereomers. At elevated temperatures the two diastereomers interconvert, and the C_2-form is slightly preferred thermodynamically (ca. 0.3 kcal/mol). Metathesis reaction of $^{iPr}L_{Xan}Li_2$ with 2 equiv of $CpZrCl_3$ affords the mixed amidinate-cyclopentadienyl anion derivative $^{iPr}L_{Xan}Zr_2Cp_2Cl_4$ (**3**) in good yield. Solutions of **3** are readily converted to the σ-alkyl derivatives $^{iPr}L_{Xan}Zr_2Cp_2Me_4$ (**4**) and $^{iPr}L_{Xan}Zr_2Cp_2(CH_2SiMe_3)_4$ (**5**) by treatment with dialkylmagnesium and organolithium reagents. At slightly elevated temperatures, solutions of **5** react with H_2 to form yellow tetrahydride $^{iPr}L_{Xan}Zr_2Cp_2H_4$ (**6**). The solid-state structure of **6** reveals that three of the four hydrido ligands bridge the two metal centers, resulting in a short intermetal separation of 3.1050(6) Å. In solution, **6** undergoes a rapid fluxional process (observed by ^1H NMR spectroscopy) that exchanges the four hydrides. At low temperature, three distinct hydrides can be observed, which is consistent with either a dibridged structure or a tribridged species undergoing rapid exchange of the terminal hydride with only one of the three bridging hydrides.

Introduction

Dizirconium complexes supported by binucleating ligands are of interest as catalysts for a range of bond-forming processes, including olefin polymerization and organic carbonyl transformations. This interest originates largely from the notion that bimetallic systems can use cooperative reaction mechanisms that are unavailable to mononuclear systems.[1−12] To favor and ultimately control these cooperative processes, it is necessary to have access to a broad range of suitable binucleating ligands so that structural and electronic features can be tailored to the particular reaction. For the relatively large and Lewis-acidic early metals this need is far from being met. Indeed, the vast majority of reported dizirconium complexes have been supported by a relatively small set of related oligocyclopentadienyl ligands.[13,14] These complexes have largely been studied as olefin polymerization catalysts,[15−25] and some of them have demonstrated promising reactivity, including increased branching in ethene homopolymerization and increased comonomer incorporation in ethene/α-olefin copolymerization when compared to closely related mononuclear catalysts.[20] In addition to their use in polymerizations, dizirconium complexes have featured interesting structures and small-molecule reactivity. Notably, Petersen,[26−28] Cuenca,[29−31] and others[32−36]

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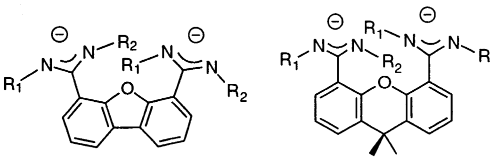
Scheme 1



	R_1	R_2
${}^{iPr}L_{DBF}$	${}^{i}Pr$	${}^{i}Pr$
${}^{tBu,Et}L_{DBF}$	${}^{t}Bu$	Et

	R_1	R_2
${}^{iPr}L_{Xan}$	${}^{i}Pr$	${}^{i}Pr$
${}^{tBu,Et}L_{Xan}$	${}^{t}Bu$	Et

have explored insertion and redox chemistry of fulvalene and bridged bis(cyclopentadienyl) systems.

One direction for the further development of binuclear early-metal chemistry involves the use of new binucleating ligands containing N- and O-donor atoms. Ligands with such donors have been widely used in mononuclear chemistry, oftentimes with dramatic effects on chemical reactivity.[37,38] However, this approach remains poorly developed in the context of early-metal binuclear systems. Recent examples include rigid bis(amido)[39,40] and phenolate donors[41] as well as amidinates.[42−45] To further develop this class of complexes, we[46,47] have been exploring several new preorganized binucleating bis(amidinate)[42,43,48−53] ligands (Scheme 1) built upon dibenzofuran and 9,9-dimethylxanthene backbones. These ligands have many desirable properties from a synthetic standpoint. First, they provide reasonable control over key structural features such as intermetal separation and sterics. Additionally, the amidinate donors are also known to bind effectively to a wide range of transition and main-group metals. In this report we describe several new dizirconium complexes including a structurally characterized polyhydride derivative that features fluxional behavior in solution.

Experimental Section

General Considerations. Standard Schlenk-line and glovebox techniques were used unless stated otherwise. ${}^{iPr}L_{Xan}H_2$,[46] ${}^{tBu,Et}L_{Xan}H_2$,[47] and Me_2Mg[54,55] were prepared following published methods. ${}^{iPr}L_{Xan}Li_2$ was prepared by reaction of 2 equiv of BuLi with ${}^{iPr}L_{Xan}H_2$ in hexanes. The essentially insouble product is isolated as a white solid in quantitative yield. $CpZrCl_3$, $Zr(NMe_2)_4$, and $LiCH_2SiMe_3$ were purchased from commercial sources and used as received. Hexanes, Et_2O, toluene, tetrahydrofuran (THF), and CH_2Cl_2 were passed through columns of activated alumina and sparged with N_2 prior to use. Hexamethyldisiloxane (HMDSO) was distilled from Na under N_2. C_6D_6 and D_8-toluene were vacuum transferred from Na-benzophenone ketyl. $CDCl_3$ was vacuum transferred from CaH_2. Chemical shifts (δ) for ^{1}H NMR spectra are given relative to residual protium in the deuterated solvent at 7.15, 7.24, and 2.10 ppm for C_6D_6, $CDCl_3$, and D_8-toluene, respectively. Infrared spectra were taken as mineral oil mulls between KBr plates unless stated otherwise. Elemental analyses were determined by Desert Analytics.

${}^{iPr}L_{Xan}Zr_2(NMe_2)_6$ (1). Toluene (35 mL) was added to a mixture of ${}^{iPr}L_{Xan}H_2$ (0.479 g, 1.04 mmol) and $Zr(NMe_2)_4$ (0.554 g, 2.07 mmol) to form a clear, colorless solution. After 9 h the volatiles were removed under reduced pressure, and the resulting residue was extracted with hexanes (40 mL). Cooling to 0 °C afforded the product as colorless crystals (0.57 g, 60%). ^{1}H NMR (C_6D_6): δ 7.10 (m, 4H), 6.90 (t, $J = 7.5$ Hz, 2H), 3.35 (sept, $J = 7.2$ Hz, 4H, $-NCMe_2\mathit{H}$), 3.27 (s, 36H, $-N\mathit{Me}_2$), 1.40 (s, 6H, $-C\mathit{Me}_2$), 1.28 (d, $J = 6.4$ Hz, 12H, $-NCHMe\mathit{CH}_3$), 1.06 (d, $J = 6.4$ Hz, 12H, $-NCHMe\mathit{CH}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 174.2, 147.3, 131.0, 128.5, 127.5, 123.7, 122.8, 50.1 ($-N\mathit{C}HMe_2$), 43.8 ($-N\mathit{Me}_2$), 34.7 ($-\mathit{C}Me_2$), 33.7 ($-C\mathit{Me}_2$), 26.7 ($-NCHMe\mathit{C}H_3$), 25.5 ($-NCHMe\mathit{C}H_3$). IR: 2918 (br), 2847 (br), 2809 (vs), 2757 (vs), 1463 (vs), 1423 (vs), 1376 (m), 1343 (s), 1245 (m), 1205 (m), 1149 (m), 942 (br), 881 (m), 799 (m), 751 (m), 540 (m) cm^{-1}. Anal. Calcd (found) for $C_{41}H_{76}N_{10}OZr_2$: C, 54.26 (54.39); H, 8.44 (8.37); N, 15.43 (15.39).

${}^{tBu,Et}L_{Xan}Zr_2(NMe_2)_6$ (2). A benzene solution (5 mL) of ${}^{tBu,Et}L_{Xan}H_2$ (0.326 g, 0.705 mmol) was added to a benzene (5 mL) solution of $Zr(NMe_2)_4$ (0.377 g, 1.41 mmol). The colorless solution was stirred for 9 h, after which the volatiles were removed under reduced pressure. The resulting residue was extracted with hexamethyldisiloxane (8 mL). Cooling to 0 °C afforded the product as colorless crystals (0.35 g, 55%). ^{1}H NMR spectroscopic analysis revealed the product to be a 9:1 mixture of C_2- and C_s-symmetrical diastereomers. **C_2-2:** ^{1}H NMR (C_6D_6): δ 7.10 (m, 4H), 6.86 (t, $J = 7.7$ Hz, 2H), 3.25 (s, 36H, $-N\mathit{Me}_2$), 3.25 (m, 2H, $-NC(H)\mathit{H}Me$), 2.88 (m, 2H, $-NC(H)\mathit{H}Me$), 1.38 (s, 6H, $-C\mathit{Me}_2$), 1.23 (s, 18H, $-NC(\mathit{CH}_3)_3$), 0.93 (t, $J = 7.0$ Hz, 6H, $-NCH_2\mathit{CH}_3$). ^{1}H NMR (D_8-toluene): δ 7.11 (m, 4H), 6.88 (t, $J = 7.7$ Hz, 2H), 3.24 (s, 36H, $-N\mathit{Me}_2$), 3.24 (m, 2H, $-NC(H)\mathit{H}Me$) 2.88 (m, 4H, $-NC(H)\mathit{H}Me$), 1.40 (s, 6H, $-C\mathit{Me}_2$), 1.22 (s, 18H, $-NC(\mathit{CH}_3)_3$), 0.93 (t, $J = 7.1$ Hz, 6H, $-NCH_2\mathit{CH}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 174.8($-N\mathit{C}N$), 146.8, 130.5, 129.5, 128.3, 127.6, 124.8, 123.1, 53.9 ($-N\mathit{C}HMe_2$), 43.5

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Table 1. Crystallographic Data and Collection Parameters for 1, 3, and 6

	1	**3**	**6**
formula	$C_{41}H_{76}N_{10}OZr_2$	$C_{39}H_{50}Cl_4N_4OZr_2$	$C_{39}H_{54}N_4OZr_2$
fw	907.56	915.07	777.30
space group	$P3_221$ (#154)	$Pna2_1$ (#33)	$Pna2_1$ (#33)
temp (°C)	−130	−136	−135
a (Å)	13.3607(3)	12.7785(4)	23.1814(6)
b (Å)	13.3607(3)	18.0385(5)	13.7921(4)
c (Å)	23.5264(8)	17.8506(5)	11.6429(3)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	120	90	90
Z	3	4	4
V (Å^3)	3637.0(2)	4144.7(2)	3722.5(2)
d_{calc} (g/cm^3)	1.243	1.477	1.387
θ range (deg)	1.76−31.52	2.26−31.51	2.29−25.02
μ (mm^{-1})	0.469	0.801	0.595
cryst size (mm)	0.5 × 0.45 × 0.4	0.3 × 0.2 × 0.2	0.18 × 0.13 × 0.05
no. of reflns collected	37 787	40 462	21 084
no. of unique reflns	8072	12 717	6531
no. of data/restraints/params	8072/0/254	12717/1/461	6531/1/441
R1 (for $F_o > 4\sigma F_o$)	0.0326	0.0377	0.0385
R1, wR2 (all data)	0.0366, 0.0873	0.0422, 0.1007	0.0520, 0.0846
GOF	1.024	1.021	0.974
largest peak, hole (e/Å^3)	0.57, −0.50	0.65, −0.75	0.305, −0.546

(−N*Me*$_2$), 34.5, 32.8, 32.7. ***C*$_s$-2** was identified in ^{1}H NMR spectra by the following distinct resonances (D$_8$-toluene): δ 1.49 (s, 3H, −C(Me)*Me*), 1.36 (s, 3H, −C(Me)*Me*), 1.21 (s, 18H, −NC(*CH*$_3$)$_3$), 0.92 (t, 7.1 Hz, 6H, −NCH$_2$*CH*$_3$).

$^{iPr}L_{Xan}Zr_2Cp_2Cl_4$ (3). Toluene (80 mL) was added to a mixture of $^{iPr}L_{Xan}Li_2$ (2.07 g, 4.36 mmol) and $CpZrCl_3$ (2.29 g, 8.72 mmol). The suspension was heated to 70 °C for 12 h. Filtration followed by the addition of hexanes (40 mL) and cooling to −40 °C afforded the product as yellow crystals (2.2 g, 55%). ^{1}H NMR (CDCl$_3$): δ 7.58 (dd, J = 7.6, 1.7 Hz, 2H), 7.25 (t, J = 7.6 Hz, 2H), 7.06 (dd, J = 7.6, 1.5 Hz, 2H), 6.77 (s, 10H, *Cp*), 3.29 (sept, J = 6.6 Hz, 4H, −NCMe$_2$*H*), 1.67 (s, 6H, −C*Me*$_2$), 1.20 (d, J = 6.4 Hz, 12H, −NCHMe*CH*$_3$), 1.05 (d, J = 6.4 Hz, 12H, −NCHMe*CH*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 172.0, 146.3, 131.0, 128.8, 128.0, 123.7, 118.9, 116.0 (Cp), 50.4, 34.3, 32.9, 25.2, 23.5. IR: 2953 (vs), 2855 (s), 1621 (s), 1445 (br, vs), 1421 (s), 1379 (m), 1364 (m), 1335 (m), 1241 (m), 1212 (s), 1198 (m), 1169 (m), 1117 (m), 834 (m), 817 (m), 801 (m) cm^{-1}. Anal. Calcd (found) for $C_{39}H_{50}Cl_4N_4OZr_2$: C, 51.19 (50.34); H, 5.51 (5.55); N, 6.12 (5.78).

$^{iPr}L_{Xan}Zr_2Cp_2Me_4$ (4). An Et$_2$O (20 mL) solution of Me$_2$Mg (0.046 g, 0.85 mmol) was added dropwise to an Et$_2$O (15 mL) solution of **3** (0.310 g, 0.338 mmol). The solution was stirred for 9 h, after which the volatiles were removed under reduced pressure. The resulting solid was extracted with toluene (20 mL) and filtered. Concentration to 4 mL followed by the addition of hexanes (15 mL) and cooling to −40 °C afforded the product as colorless crystals (0.22 g, 78%). ^{1}H NMR (C$_6$D$_6$): δ 7.05 (dd, J = 7.7, 1.5 Hz, 2H), 6.89 (dd, J = 7.3, 1.8 Hz, 2H), 6.84 (t, J = 7.6 Hz, 2H), 6.36 (s, 10H, *Cp*), 3.28 (sept, J = 6.6 Hz, 4H, −NCMe$_2$*H*), 1.34 (s, 6H, −C*Me*$_2$), 1.26 (d, J = 6.4 Hz, 12H, −NCHMe*CH*$_3$), 0.95 (d, J = 6.7 Hz, 12H, −NCHMe*CH*$_3$), 0.64 (s, 12H, Zr-*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 173.3, 146.6, 130.4, 129.0, 127.3, 123.5, 121.4, 112.1 (*Cp*), 50.1, 44.1 (Zr-*Me*), 34.2, 33.2, 26.4, 24.9. IR: 2923 (br, vs), 2853 (vs), 1461 (vs), 1421 (s), 1377 (s), 1243 (m), 1211 (m), 1169 (m), 799 (s), 751 (m), 722 (m), 641 (m) cm^{-1}. Anal. Calcd (found) for $C_{43}H_{62}N_4OZr_2$: C, 61.97 (61.52); H, 7.50 (7.40); N, 6.72 (6.41).

$^{iPr}L_{Xan}Zr_2Cp_2(CH_2SiMe_3)_4$ (5). A solution of LiCH$_2$SiMe$_3$ (0.158 g, 1.67 mmol) in toluene (20 mL) was added to a toluene solution (20 mL) of **3** (0.383 g, 0.419 mmol). The solution was stirred for 12 h, after which the volatiles were removed under reduced pressure. The resulting solid was extracted with warm Et$_2$O (60 mL) and filtered through a pad of diatomaceous earth on a glass frit. Concentration of the solution to 15 mL and cooling to −40 °C afforded the product as a colorless solid (0.23 g, 49%). ^{1}H NMR (C$_6$D$_6$): δ 7.14 (dd, J = 7.8, 1.6 Hz, 2H), 7.04 (dd, J = 7.8, 1.6 Hz, 2H), 6.83 (t, J = 7.7 Hz, 2H), 6.58 (s, 10H, *Cp*), 3.39 (sept, J = 6.7 Hz, 4H, −NCMe$_2$*H*), 1.31 (s, 6H, −C*Me*$_2$), 1.24 (d, J = 6.6 Hz, 12H, −NCHMe*CH*$_3$), 1.00 (d, J = 6.6 Hz, 12H, −NCHMe*CH*$_3$), 0.85 (d, ^2J = 11.2 Hz, 4H, Zr−C(H)*H*SiMe$_3$), 0.38 (d, ^2J = 11.2 Hz, 4H, Zr−C(H)*H*SiMe$_3$), 0.36 (s, 36H, −Si*Me*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 173.7, 146.7, 130.7, 128.5, 127.4, 123.5, 122.1, 111.8 (*Cp*), 59.9 (Zr−*C*H$_2$SiMe$_3$), 50.0, 34.2, 33.0, 26.4, 24.9, 3.6 (Si*Me*$_3$). IR: 2919 (br, vs), 2870 (br, vs), 1466 (vs), 1419 (s), 1377 (m), 1349 (m), 1241 (s), 917 (m), 908 (m), 852 (m), 819 (m), 798 (s), 748 (m), 725 (m) cm^{-1}. Anal. Calcd (found) for $C_{55}H_{94}N_4OSi_4Zr_2$: C, 58.87 (58.94); H, 8.44 (8.57); N, 4.99 (4.62).

$^{iPr}L_{Xan}Zr_2Cp_2H_4$ (6). Toluene (4 mL) was added to **5** (0.150 g, 0.134 mmol) in a Teflon-capped Schlenk tube to form a clear, colorless solution. Hexanes (5 mL) were added. The flask was evacuated briefly and then backfilled with H$_2$ (15 psig). The solution was heated to 35 °C for 30 h, yielding a yellow-orange solution. Cooling to 0 °C yielded the product as yellow-orange crystals (72 mg, 69%). ^{1}H NMR (C$_6$D$_6$): δ 7.08 (dd, J = 8.7, 1.5 Hz, 2H), 7.03 (dd, J = 7.5, 1.5 Hz, 2H), 6.82 (t, J = 7.7 Hz, 2H), 6.48 (s, 10H, *Cp*), 4.50 (br, 4H, Zr-*H*), 3.48 (sept, J = 6.2 Hz, 4H, −NCMe$_2$*H*), 1.37 (s, 6H, −C*Me*$_2$), 1.19 (d, 6.2 Hz, 12H, −NCHMe*CH*$_3$), 1.01 (d, 6.2 Hz, 12H, −NCHMe*CH*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 167.5, 147.2, 130.9, 129.6, 127.5, 123.0, 122.4, 109.6 (Cp), 49.0, 34.7, 33.7, 27.1, 26.2. We were unable to obtain vibrational and combustion analysis data for **6** due to its instability in the absence of H$_2$.

NMR Spectroscopic Studies of 6. ^{1}H NMR spectra were recorded on a Varian Inova-500 NMR spectrometer, operating at 500.37 MHz for proton observation. Low-temperature exchange experiments were carried out using a Varian ^{1}H/^{19}F probe capable of operating at temperatures from −125 to 100 °C. Sample temperatures were calibrated using 100% methanol in the same probe, operating under the identical temperature conditions. Two-dimensional exchange experiments were carried out using a standard NOESY/EXCHSY pulse sequence,[56] covering a range of mixing times from 2.4 to 60 ms. EXCHSY data were analyzed by fitting the ratio of cross-peak intensities to diagonal peak intensities (I_x/I_d) versus mixing time (t_m) according to the equation $I_x/I_d = [1 - \exp(-kt_m)]/[1 + \exp(-kt_m)]$.[57]

X-ray Crystallography. Table 1 lists a summary of crystal data and collection parameters for all crystallographically

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(56) For a more detailed description of the NOESY/EXCHSY pulse sequence, see: States, D. J.; Haberkorn, R. A.; Reuben, D. J. *J. Magn. Reson.* **1982**, *48*, 286.

Table 2. Selected Bond Distances and Angles for 1, 3, and 6

	(^{i}Pr$_4$Xan)Zr$_2$(NMe$_2$)$_6$ (**1**)		
Zr1−N1	2.232(2)	Zr1−N2	2.350(1)
Zr1−N3	2.041(2)	Zr1−N4	2.065(2)
Zr1−N5	2.065(2)	Zr1−Zr1A	7.1190(3)
N1−Zr1−N2	58.38(5)	N1−Zr1−N3	113.61(6)
N1−Zr1−N4	95.56(7)	N1−Zr1−N5	130.88(6)
N2−Zr1−N3	99.73(7)	N2−Zr1−N4	151.90(7)
N2−Zr1−N5	93.70(6)	N3−Zr1−N4	100.70(7)
N3−Zr1−N5	110.23(7)	N4−Zr1−N5	97.11(7)
	(^{i}Pr$_4$Xan)Zr$_2$Cp$_2$Cl$_4$ (**3**)		
Zr1−Cl1	2.4138(7)	Zr1−Cl2	2.4317(7)
Zr1−N1	2.231(2)	Zr1−N2	2.228(2)
Zr1−Cp$_{ave}$	2.50	Zr1−Zr2	6.5954(4)
Zr2−Cl3	2.4340(7)	Zr2−Cl4	2.4256(7)
Zr2−N3	2.229(2)	Zr2−N4	2.220(2)
Zr2−Cp$_{ave}$	2.49	N1−Zr1−N2	60.10(8)
Cl1−Zr1−Cl2	91.79(3)	N3−Zr2−N4	59.77(8)
Cl3−Zr2−Cl4	91.18(3)		
	(^{i}Pr$_4$Xan)Zr$_2$Cp$_2$H$_4$ (**6**)		
Zr1−N1	2.259(4)	Zr1−N2	2.216(4)
Zr1−Cp$_{ave}$	2.51	Zr1−H51	1.86(5)
Zr1−H52	1.88(4)	Zr1−H53	1.88(4)
Zr1−Zr2	3.1050(6)	Zr2−N3	2.293(4)
Zr2−N4	2.273(4)	Zr2−Cp$_{ave}$	2.53
Zr2−H51	1.94(4)	Zr2−H52	2.05(4)
Zr2−H53	1.87(4)	Zr2−H54	1.71(6)
N1−Zr1−N2	59.6(1)	H51−Zr1−H52	59(2)
H51−Zr1−H53	62(2)	H52−Zr1−H53	65(2)
H51−Zr2−H52	55(2)	H51−Zr2−H53	60(2)
H51−Zr2−H54	70(2)	H52−Zr2−H53	61(2)
H52−Zr2−H54	122(2)	H53−Zr2−H54	77(2)

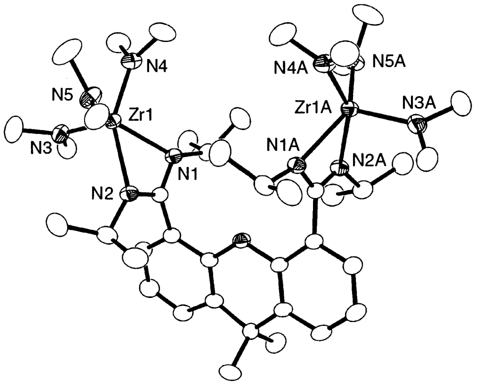

Figure 1. Molecular structure of (^{i}Pr$_4$Xan)Zr$_2$(NMe$_2$)$_6$ (**1**) drawn with 50% thermal ellipsoids.

characterized compounds. Single-crystal structure determinations were performed within the Department of Chemistry and Biochemistry at the University of Colorado. Full details are presented as Supporting Information.

General Procedure. A crystal of appropriate size was mounted on a glass fiber using Paratone-N oil, transferred to a Siemens SMART diffractometer/CCD area detector, centered in the beam (Mo Kα; $\lambda = 0.71073$ Å; graphite monochromator), and cooled by a nitrogen low-temperature apparatus. Preliminary orientation matrix and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. A minimum of a hemisphere of data was collected using 0.3° ϖ scans. The raw data were integrated and the unit cell parameters refined using SAINT. Data analysis was performed using XPREP. Absorption correction was applied using SADABS. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Structure solutions and refinements were performed (SHELXTL-Plus V5.0) on F^2.[58]

Structure of 1. Crystals suitable for X-ray diffraction studies were grown from Et$_2$O at −40 °C. Preliminary data indicated a primitive trigonal cell. Analysis of all data indicated systematic absences which suggested several space groups ($P3_1$, $P3_2$, $P3_121$, $P3_221$). This choice of $P3_221$ (#154) was confirmed by the successful solution and refinement of the structure. Solution in $P3_121$ gave significantly larger residuals. Refinement of the Flack parameter to 0.50 indicated a rotational twin. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Structure of 3. Crystals suitable for X-ray diffraction studies were grown from toluene−hexanes at ambient temperature. Preliminary data indicated a primitive orthorhombic cell. Analysis of all data indicated systematic absences which suggested space group *Pna*2(1) (#33). This choice was confirmed by the successful solution and refinement of the structure. The Flack parameter refined to −0.01(4), indicating that the correct absolute structure was chosen. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Structure of 6. Crystals suitable for X-ray diffraction studies were grown from toluene−hexanes at ambient temperature. Preliminary data indicated a primitive orthorhombic cell. Analysis of all data indicated systematic absences which suggested space group *Pna*2(1) (#33). This choice was confirmed by the successful solution and refinement of the structure. The Flack parameter refined to 0.00(4), indicating that the correct absolute structure was chosen. All non-H atoms were refined anisotropically. The four hydrido ligands were located in a difference Fourier map and were refined isotropically. Remaining hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Results and Discussion

The free-base forms of the binucleating ligands shown in Scheme 1 react with a range of Zr amidos and alkyls to form Zr-amidinate derivatives. For example, $^{iPr}L_{Xan}H_2$ reacted with 2 equiv of Zr(NMe$_2$)$_4$ to form colorless **1** in 60% isolated yield (Scheme 2). The 500 MHz ^{1}H NMR spectrum of **1** in C$_6$D$_6$ solution features a sharp singlet at δ 3.27 (36H) for all 12 methyls of the six amido ligands. Since any reasonable static structure would require at least two inequivalent amidos, these data indicate rapid fluxionality in solution similar to that observed for $^{iPr}L_{Xan}Zr_2Bn_6$ and $^{iPr}L_{DBF}Zr_2Bn_6$.[46] This result also suggests the absence of any bridging amidos. The solid-state structure of **1** was determined by single-crystal X-ray diffraction. **1** was found to lie on a 2-fold rotation axis which passes through the oxygen and the quaternary carbon of the 9,9-dimethylxanthene backbone (Figure 1). Each five-coordinate Zr features three bound amidos and an unsymmetrically coordinated amidinate. The two Zr−N$_{amidinate}$ distances (Zr1−N1, 2.232(1); Zr1−N2, 2.350(1) Å) differ by over 0.1 Å. The elongation of Zr1−N2 can be attributed to the trans influence of N4 (N2−Zr1−N4, 151.90(7)°). The six bulky NMe$_2$ ligands cause significant steric crowding between the two Zr centers. Notably, this forces each metal to bind unusually far (0.884(6) Å) out of the amidinate NCN plane to minimize these interactions. This binding

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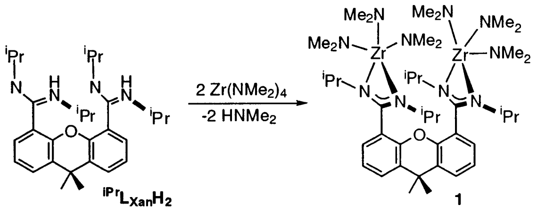
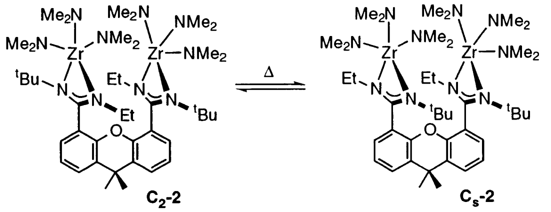
(57) *Modern Techniques in High-Resolution FT-NMR*; Springer-Verlag: New York, 1987; pp 193−197.

(58) Sheldrick, G. M. *SHELXTL*: A Program for Crystal Structure Determination, Version 5.03; Siemens Analytical X-ray Instruments: Madison, WI, 1995.

Scheme 2



Scheme 3



mode in turn yields a long intermetal distance of 7.1190(3) Å. As part of an attempt to further probe the solution dynamics of the bis(amidinate) complexes, the less symmetrical bis(amidine) $^{tBu,Et}L_{Xan}H_2$ was used to prepare compound **2**, which we thought might exist as a pair of interconvertable rotational diastereomers (Scheme 3). Upon the mixing of $^{tBu,Et}L_{Xan}H_2$ with 2 equiv of $Zr(NMe_2)_4$ in C_6D_6 solution, a 9:1 mixture of ***C_2*-2** to ***C_s*-2** was observed by ^1H NMR spectroscopy. The scaled-up reaction of $^{tBu,Et}L_{Xan}H_2$ with 2 equiv $Zr(NMe_2)_4$ in toluene gave similar results, and a 9:1 mixture of **2** was isolated as colorless crystals in 55% yield. Heating a D_8-toluene solution of the mixture to 67 °C overnight led to the formation of a 3:2 ratio of ***C_2*-2** to ***C_s*-2** along with ca. 10% decomposition to unknown product(s). Further heating did not significantly change the ratio and led to increased decomposition. Thus, the initial 9:1 ratio is attributed to kinetic factors, and the equilibrium shown in Scheme 3 is close to thermoneutral ($\Delta G° = 0.3$ kcal/mol).

Dizirconium complexes supported by mixed Cp-amidinate ligand sets are of interest because the related mononuclear complexes serve as precursors to living α-olefin polymerization catalysts.[59-62] Entry to this class of compounds was achieved by reaction of $^{iPr}L_{Xan}Li_2$ with 2 equiv of $CpZrCl_3$ in toluene solution at 70 °C. Following filtration and the addition of hexanes, yellow **3** was isolated as a crystalline solid in moderate yield (Scheme 4). Analysis by ^1H NMR spectroscopy is consistent with a C_{2v}-symmetrical environment on the time scale of the experiment. The solid-state structure (Figure 2) reveals a pair of crystallographically independent Zr centers; however, the coordination geometries of the two metals are virtually identical with each other. Metrical parameters are unremarkable, and related mononuclear Cp-amidinato[59,63] and Cp-guanidinato[64] derivatives feature similar structures. The reactive Zr−Cl bonds of **3** allow it to serve as a useful precursor to σ-organometallics by metathesis reactions with organolithium and dialkylmagnesium reagents. For example, **3** reacts readily with 2 equiv of Me_2Mg in Et_2O solution to afford the tetramethyl derivative **4** in high yield. Toluene solutions of **4** with 1 equiv of $B(C_6F_5)_3$ are inactive for the polymerization of ethene. However, the use of 2 equiv of the borane affords catalytically active solutions.[65] Reaction of **3** with 4 equiv of $LiCH_2SiMe_3$ afforded colorless **5** in moderate yield. Both **4** and **5** react readily with a range of small molecules (e.g., CO, CO_2, H_2). D_6-Benzene solutions of **5** reacted with H_2 (1 atm) at 35 °C to form yellow **6** and Me_4Si as the only observed products by ^1H NMR spectroscopy. Solutions of **6** under H_2 atmo-

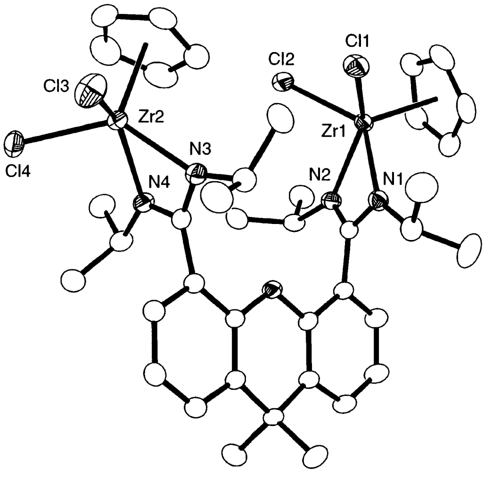
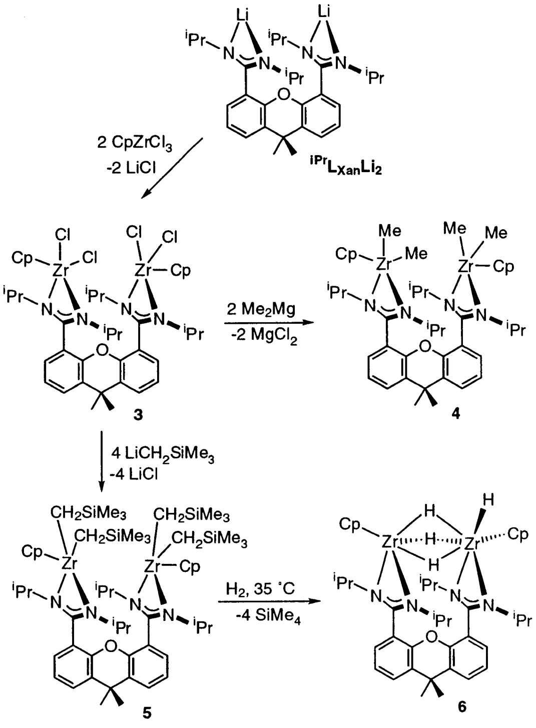


Figure 2. Molecular structure of ($^iPr_4Xan)Zr_2Cp_2Cl_4$ (**3**) drawn with 50% thermal ellipsoids.

Scheme 4



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(60) Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 6197−6198.

(61) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958−959.

(62) Sita, L. R.; Keaton, R. J.; Jayaratne, K. C.; Kissounko, D. A.; Zhang, Y. *Polym. Mater. Sci. Eng.* **2002**, *87*, 58.

(63) Gómez, R.; Duchateau, R.; Chernega, A. N.; Meetsma, A.; Edelmann, F. T.; Teuben, J. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1995**, 217−225.

(64) Duncan, A. P.; Mullins, S. M.; Arnold, J.; Bergman, R. G. *Organometallics* **2001**, *20*, 1808−1819.

(65) Results to be reported separately.

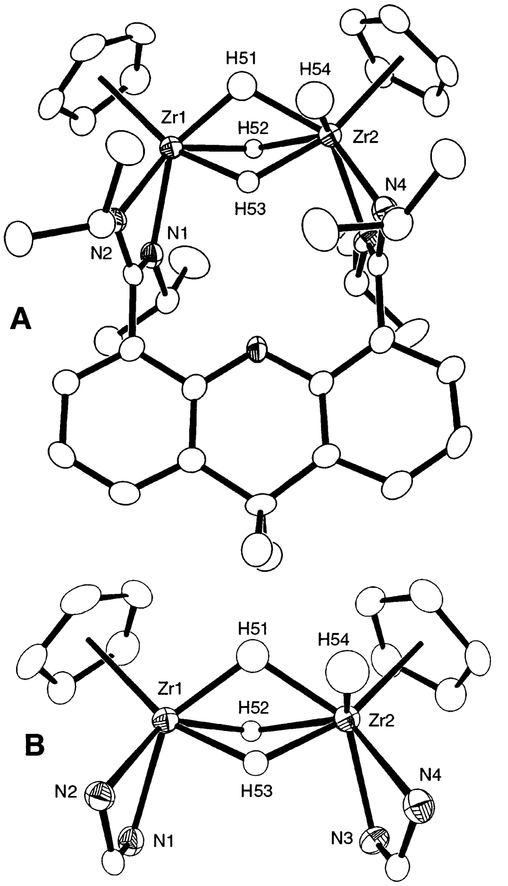


Figure 3. Views of the molecular structure of ($^{i}Pr_4Xan$)-Zr_2H_4 (**6**) drawn with 50% thermal ellipsoids. 9,9-Dimethylxanthene and ^{i}Pr groups omitted in **B** for clarity.

sphere are stable for days, but in the absence of H_2, degradation to unidentified products occurs. Crystals of **6** suitable for single-crystal X-ray diffraction studies were grown from toluene−hexanes mixtures under H_2. The solid-state structure is shown in Figure 3. The high quality of the data set allowed for the location and isotropic refinement of the four hydrido ligands. The dizirconium core features one terminal and three bridging hydrides. Due to the presence of three single-atom bridges, the Zr1−Zr2 distance (3.1050(6) Å) is much shorter than those of **1** and **3**. Related structurally characterized complexes featuring $[Zr_2(\mu\text{-}H)_3]^{5+}$ cores include $(C_5Me_5)_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)$[66] and $Zr_2(\mu\text{-}H)_3(BH_4)_5(PMe_3)_2$,[67] which have intermetal distances of 3.126(1) and 3.124(1) Å, respectively. The short intermetal separation in **6** causes the two metals to be pulled out of their respective NCN amidinate planes by an average of 0.78 Å. Only one of the bridging hydrides, H52, shows unsymmetrical coordination between the two Zr centers (Zr1−H52, 1.88(4); Zr2−H52, 2.05(4) Å). Interestingly, H52 is also roughly coplanar with the plane formed by the terminal hydride H54 and the two Zr centers. This is indicated by the Zr1−H52−Zr2−H54 torsion angle of only 19(3)°. These structural data may suggest a facile exchange pathway in solution (see later) by which these terminal (H54) and bridging (H52) hydrides exchange positions.

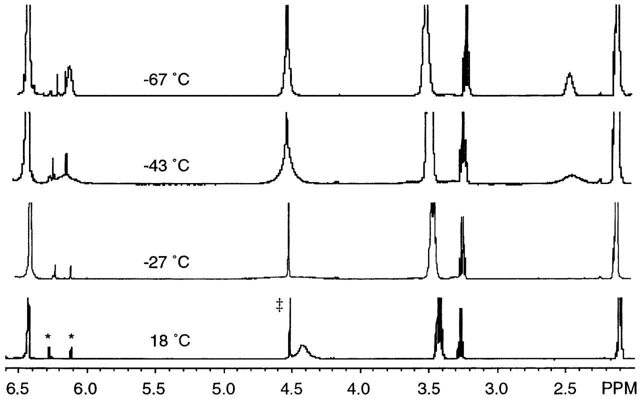
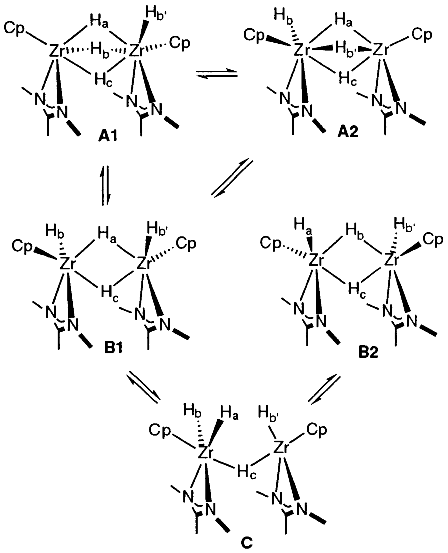


Figure 4. 500 MHz ^{1}H NMR spectra of **6** in D_8-toluene (asterisk denotes unidentified impurity, ‡ denotes dissolved H_2).

Scheme 5



The 500 MHz ^{1}H NMR spectrum of **6** (in D_8-toluene) indicates that the four hydride ligands are undergoing a rapid fluxional process that gives the molecule effective C_{2v} symmetry on the time scale of the experiment. Accordingly, a single broad resonance is observed at δ 4.45 ($\omega_{1/2}$ = 40 Hz) for the four hydrides despite their inequivalence in the solid state. Simultaneously, dissolved H_2 is observed as a sharp singlet at δ 4.50, indicating that exchange with H_2 is relatively slow. Upon cooling, the resonance at δ 4.45 broadens (T_c = −30.0 °C) and splits into three new resonances at δ 6.3, 4.5, and 2.4 with integrated intensities of one, two, and one hydrogen(s), respectively (Figure 4). Notably, only a single Cp resonance at δ 6.45 is observed even at low temperatures. Thus, the solution structure at low temperature is consistent with either a dibridged structure (**B1**) (Scheme 5) or a rapid fluxional process that interconverts tribridged **A1** and **A2**. This second process can be envisioned to occur through either a "roll-over" mechanism or a dissociative process involving **B1** as an intermediate.[68] For simplicity, further discussion will

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[66] van der Hende, J. R.; Hessen, B.; Meetsma, A.; Teuben, J. H. *Organometallics* **1990**, *9*, 537−539.

[67] Gozum, J. E.; Girolami, G. S. *J. Am. Chem. Soc.* **1991**, *113*, 3829−3837.

[68] A similar facile exchange process has been reported for $H_4Rh_2[P(O^{i}Pr)_3]_4$: Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878−4887.

be presented assuming **B** as the low-temperature structure. To further probe the dynamics of the exchange process, a 2D EXCHSY experiment was performed at −67 °C using the same sample. At mixing times from 2.4 to 60 ms, cross-peaks between all three hydrido resonances were observed. Analysis of the intensity of the cross-peaks relative to the mixing times afforded the rate constants $k_{a-b} = 61(8)\ s^{-1}$, $k_{b-c} = 28(8)\ s^{-1}$, and $k_{a-c} = 19(8)\ s^{-1}$ (assigning resonances a, b, c to δ 6.3, 4.5, 2.4, respectively). The significantly larger constant for the a−b exchange, relative to b−c, indicates that the two terminal hydrides (H_b and $H_{b'}$ of **B1**) exchange with one of the bridging hydrides (H_a) more easily than with the second (H_c). We speculate that the mechanism for the a−b exchange process may involve intermediate **C**, which features only a single bridging hydride. From **C**, only slight twisting and re-formation of the hydride bridge would be needed to give the a−b exchange product **B2**, with H_c remaining unexchanged. Thus a−b exchange may be faster than b−c exchange simply because dissociation of H_a to a terminal position yielding **C** occurs more readily than the analogous process involving dissociation of H_c.

Conclusions

We have demonstrated that preorganized bis(amidinates) are well suited to serve as supporting ligands for early-transition-metal bimetallics. A range of dizirconium complexes with reactive Zr−C and Zr−H bonds have been prepared and fully characterized. Additional reaction studies with these complexes are being performed to evaluate any cooperative mechanisms that may be favored with this system.

Acknowledgment. We acknowledge the University of Colorado and the Petroleum Research Fund, administered by the American Chemical Society, for financial support. NMR instrumentation used in this work was supported in part by the National Science Foundation CRIF program, award CHE-0131003.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, and metrical parameters are provided for **1**, **3**, and **6**. These data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034063C