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Preparation and Structural Characterization of *ansa*-Mono(cyclopentadienyl)dimethylsilylamido Group 4 Metal Butadiene Complexes. Observation of a Tetranuclear Structure for $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)$ Featuring Bridging Butadiene Ligands

Joachim W. Strauch[1] and Jeffrey L. Petersen*

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

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The metathetical reactions of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]MCl_2$, M = Ti, Zr, with $[Mg(C_4H_6)(THF)_2]_n$ afford the respective group 4 metal butadiene complexes, $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]M(C_4H_6)$. The solution NMR and X-ray crystallographic data for $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti(C_4H_6)$ indicate that the butadiene moiety adopts a symmetrical prone structure consistent with a Ti(II) π-diene bonding representation. Alternatively, the solution and solid-state structures for its Zr analogue are markedly different. Whereas the observed chemical shift dispersion for the anti and meso butadiene protons of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)$ supports a zirconacyclopentene structure in solution, the solid-state structure of this compound is actually tetranuclear. The four $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr$ units of $\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)\}_4$ are related by a crystallographically imposed S_4 rotation axis and are linked by four unsymmetrically bridging butadiene groups via an unusual $((1,2,3\text{-}\eta^3)\text{-}Zr-(4\text{-}\mu_2)\text{-}Zr)$ bonding interaction. The five-coordinate trigonal-bipyramidal geometry about the doubly bridging carbon is characterized by a nearly linear $Zr-(\mu_2\text{-}C)-Zr$ bond angle of 173.2(2)° and two rather long Zr−C bond distances of 2.636(5) and 2.530(5) Å.

Introduction

Early-transition-metal butadiene complexes represent a highly versatile class of electrophilic organometallic compounds that provide access to homogeneous Ziegler−Natta olefin polymerization catalysts. Erker and co-workers[2] demonstrated that treatment of the metallocene butadiene complexes, $(C_5H_5)_2M(C_4H_6)$, M = Zr, Hf, with $B(C_6F_5)_3$ affords the soluble zwitterionic betaine complexes $(C_5H_5)_2M^+[\eta^3\text{-}C_3H_4CH_2B^-(C_6F_5)_3]$, which are capable of catalyzing the polymerization of ethylene and propylene without the need for further activation. Researchers[3] at Dow in collaboration with Marks and co-workers prepared a series of electrophilic titanium diene complexes, $[(C_5Me_4)SiMe_2(NR_1)]Ti(R_2CH{=}CHCH{=}CHR_3)$, where R_1 = t-Bu, C_6H_5, R_2 = H, Me, and R_3 = H, Me by the reduction of $[(C_5Me_4)SiMe_2(NR_1)]TiCl_2$ with 2 equiv of *n*-BuLi in the presence of the appropriate diene. These Ti butadiene complexes may adopt either the “prone” Ti(II) π-diene structure, in which the open end of the diene cup is directed away from the C_5Me_4 ring, or the alternative “supine” Ti(IV) σ^2,π-metallacyclopentene structure, in which the opening of the diene cup is disposed toward the C_5Me_4 ring. Upon activation with MAO, $(HNMe_2Ph)[B(C_6F_5)_4]$, or $B(C_6F_5)_3$, these Ti diene compounds are transformed into active copolymerization catalysts. An X-ray structural analysis[4] of the zwitterionic Ti−betaine complex $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti^+(\eta^3\text{-}CH(Me)CHCHCH_2B^-(C_6F_5)_3]$ revealed that the B atom is bound to the CH_2 terminus of the pentadiene fragment. The formation of the dative CH_2-B bond leads to a highly distorted five-coordinate geometry at this C with both of its H atoms displaced toward the electrophilic Ti center.

Erker and co-workers[5] recently reported that the metathetical reaction of $[Mg(C_4H_6)(THF)_2]_n$ with $[(C_5Me_4)SiMe_2(NR)]MCl_2$ (M = Ti, R = t-Bu; M = Zr, R = t-Bu, $CHMe(1\text{-}C_{10}H_7)$) affords the corresponding butadiene derivatives in good yield. Whereas the $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]M(C_4H_6)$ compounds exist as a mixture of supine and prone stereoisomers for Ti (5:95) and Zr (85:15) in solution, $[(C_5Me_4)SiMe_2(NCHMe(1\text{-}C_{10}H_7))]Zr(C_4H_6)$ is obtained as a single stereoisomer. The corresponding zwitterionic Zr−betaine species generated from the reaction of $B(C_6F_5)_3$ with $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)$ showed markedly lower activity toward ethylene polymerization.

In view of the catalytic potential of “constrained geometry” group 4 metal butadiene complexes, a re-

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[1] Institut für Organische Chemie, University of Münster, visiting student.

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search effort was initiated in our laboratories to investigate the stereoelectronic effect that replacement of the C_5Me_4 ring by the C_5H_4 ring has on the molecular structure and reactivity of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]M(C_4H_6)$. These compounds are readily prepared by treatment of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$[6] and $\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl(\mu\text{-}Cl)\}_2$[7] with magnesium butadiene. The results of an X-ray structural analysis demonstrate that the lower π-donating capacity and smaller steric size of the C_5H_4 ring have a dramatic influence on the solid-state structure exhibited by $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)$. Specific details regarding the synthesis and structural characterization of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]M(C_4H_6)$ (M = Ti, Zr) are reported herein.

Experimental Section

Reagents. Standard methods[8] were used to purify the hydrocarbon and ethereal solvents. Toluene and pentane were refluxed over Na/K under a nitrogen flush and then transferred to separate storage flasks containing $[(C_5H_5)_2Ti(\mu\text{-}Cl)_2]_2Zn$[9] or $(C_5H_5)_2ZrMe_2$. Hexamethyldisiloxane was dried over $LiAlH_4$. C_6D_6 (Cambridge Isotopes, 99.5%), $CDCl_3$ (Aldrich 99.8%), $t\text{-}BuNH_2$ (Aldrich), $SiMe_2Cl_2$ (Aldrich), and $SiMe_3Cl$ (Aldrich) were dried over activated 4A molecular sieves. Modified literature procedures were used for the preparation of $MCl_4(THF)_2$ (M = Ti, Zr),[10] $[Mg(C_4H_6)(THF)_2]_n$,[11] NaC_5H_5,[12] $Ti(NMe_2)_4$,[13] and $Zr(NMe_2)_4$.[14] $TiCl_4$ (Aldrich), $ZrCl_4$ (Alfa), *n*-BuLi (Aldrich, 1.6 M in hexane), C_4H_6 (Matheson), $LiNMe_2$ (Aldrich), and 2,4-dimethyl-1,3-butadiene (Aldrich) were used as received. The triply sublimed Mg (Alfa) used for the preparation of $[Mg(C_4H_6)(THF)_2]_n$ was activated[15] by stirring the Mg chips in a dry toluene solution containing 2,4-dimethyl-1,3-butadiene and iodine at 70 °C for 30 h. $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti(NMe_2)_2$ and $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(NMe_2)_2$ were prepared via the thermally induced amine elimination reactions of $Ti(NMe_2)_4$ and $Zr(NMe_2)_4$ with $(C_5H_5)SiMe_2(N(H)\text{-}t\text{-}Bu)$, respectively, and then purified by sublimation. Treatment of these dimethylamido compounds with excess $SiMe_3Cl$ afforded $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$[6] and $\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl(\mu\text{-}Cl)\}_2$.[7]

The instrumentation employed for the ^1H and ^{13}C NMR measurements was described previously.[16] The electronic spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer using a 1.00 cm quartz cell equipped with a Teflon stopcock. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Parsippany, NJ 07054.

General Considerations. To avoid any contact with air or moisture, all reactions were carried out on a double-manifold high-vacuum line or in a Vacuum Atmospheres glovebox equipped with an HE-493 Dri-Train. Unless otherwise noted, the reactions were performed in pressure-equalizing filter frit assemblies equipped with high-vacuum Teflon stopcocks and Solv-seal joints. Nitrogen was purified by passage over reduced BTS catalysts and activated 4A molecular sieves. Prior to use, all glassware was oven-dried and then flame-dried under vacuum. The NMR sample tubes were sealed under about 500 Torr of nitrogen.

Synthesis of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti(C_4H_6)$. A 100 mL pear-shaped flask was charged with 1.00 g (3.2 mmol) of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ and with 0.82 g (3.68 mmol; 15% excess) of $[Mg(C_4H_6)(THF)_2]_n$. Approximately 50 mL of toluene was added via vacuum distillation. When the solution was warmed slowly to room temperature, the color of the solution turned from orange to a deep purple. After the solution was stirred for 3 h, the toluene was removed in vacuo. The product was extracted with hexamethyldisiloxane. Rapid removal of the hexamethyldisiloxane yielded purple crystals suitable for an X-ray crystallographic analysis. The reaction is nearly quantitative, with an isolated yield of 0.804 g (85% yield). ^1H NMR (C_6D_6): δ 0.59 (s, 6H, $SiMe_2$), 1.12 (s, 9H, $NCMe_3$), 1.82 (m, 2H, anti CH_2), 3.28 (m, 2H, syn CH_2), 4.20 (m, 2H, meso CH), 5.01 (t, 2H, C_5H_4), 6.22 (t, 2H, C_5H_4). Gated nondecoupled ^{13}C NMR (C_6D_6): δ 3.0 (q, $SiMe_2$, 119), 35.1 (q, $NCMe_3$, 125), 58.1 (s, *C*$NCMe_3$), 62.8 (ddd, CH_2, 161, 138, 9), 102.4 (s, bridgehead C), 107.2 (ddd, CH, 157, 9, 7), 113.4 (dq, C_5H_4, 170, 7), 118.5 (dq, C_5H_4, 171, 7). 2D HETCOR NMR: δ 1.83, 3.28/62.8 (CH_2), 4.20/107.2 (=CH), 5.01/113.4 (C_5H_4), 6.22/118.5 (C_5H_4). λ_{max} = 630 nm (broad); $\epsilon_{max} = 2.08 \times 10^2$ L mol^{-1} cm^{-1}. Anal. Calcd for $C_{15}H_{25}NSiTi$: C, 61.00; H, 8.53, N, 4.74. Found: C, 60.48; H, 8.53; N, 4.69.

Synthesis of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)$. A 100 mL pear-shaped flask was charged with 0.250 g (0.35 mmol) of $\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl(\mu\text{-}Cl)\}_2$ and with 0.180 g (0.81 mmol; 15% excess) of $[Mg(C_4H_6)(THF)_2]_n$. Approximately 20 mL of toluene was added via vacuum distillation. When the solution was warmed slowly to room temperature, the solution turned orange after it was stirred for 3 h. Following filtration, the toluene was removed under vacuum and the product residue was washed with pentane. Recrystallization from pentane or toluene afforded bright yellowish orange crystals that were suitable for an X-ray crystallographic analysis. The isolated yield was 0.191 g (80% yield). ^1H NMR (C_6D_6): δ −0.64 (m, 2H, anti CH_2), 0.53 (s, 6H, $SiMe_2$), 0.80 (s, 9H, $NCMe_3$), 3.31 (m, 2H, syn CH_2), 5.56 (t, 2H, C_5H_4), 5.98 (m, 2H, meso CH), 6.84 (t, 2H, C_5H_4). Gated nondecoupled ^{13}C NMR (C_6D_6): δ 2.74 (q, $SiMe_2$, 119), 36.4 (q, $NCMe_3$, 124), 53.8 (ddd, CH_2, 157, 133, 9), 57.8 (s, *C*$NCMe_3$), 107.6 (s, bridgehead C), 112.4 (dq, C_5H_4, 171, 7), 114.0 (dq, C_5H_4, 170, 7), 122.0 (ddd, =CH, 157, 9, 8). 2D HETCOR NMR: δ −0.64, 3.31/53.8 (CH_2), δ 5.56/114.0 (C_5H_4), δ 5.98/122.0 (=CH), δ 6.84/112.4 (C_5H_4). λ_{max} = 510 nm (broad), ϵ_{max} = 24 L mol^{-1} cm^{-1}. Anal. Calcd for $C_{15}H_{25}NSiZr$: C, 53.20; H, 7.44; N, 4.14. Found: C, 53.47; H, 7.78; N, 4.06.

X-ray Structural Analyses of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti(C_4H_6)$ and $\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)\}_4$. The same general procedures were followed for the X-ray structural analyses of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti(C_4H_6)$ and $\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)\}_4$. A suitable crystal of each compound was sealed under nitrogen in a glass capillary tube and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The reflections that were used for the unit cell determination were located and indexed by the automatic peak search routine provided with XSCANS.[17] $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti(C_4H_6)$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5, No. 14), which is uniquely determined by the systematic absences $\{h0l\}$, $l = 2n + 1$, and $\{0k0\}$, $k = 2n + 1$. In contrast, $\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)\}_4$ adopts a tetragonal unit cell. In this case the observed systematic absences of $\{hk0\}$, $h + k = 2n + 1$, and of $\{00l\}$, $l = 2n + 1$, are compatible with the centrosymmetric

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Table 1. Crystallographic Data for the X-ray Structural Analyses of [$(C_5H_4)SiMe_2$(N-t-Bu)]$Ti(C_4H_6)$ and {[$(C_5H_4)SiMe_2$(N-t-Bu)]$Zr(C_4H_6)$}$_4$

	[$(C_5H_4)SiMe_2$(N-t-Bu)]$Ti(C_4H_6)$	{[$(C_5H_4)SiMe_2$(N-t-Bu)]$Zr(C_4H_6)$}$_4$
	A. Crystal Data	
empirical formula	$C_{15}H_{25}NSiTi$	$C_{15}H_{25}NSiZr$
color	deep purple	orange
cryst dimens, mm	0.24 × 0.40 × 0.50	0.20 × 0.24 × 0.32
cryst syst	monoclinic	tetragonal
space group	$P2_1/c$	$P4_2/n$
a, Å	9.068(5)	17.922(1)
b, Å	12.174(4)	17.922(1)
c, Å	14.934(6)	10.206(1)
β, deg	103.36(4)	
vol, Å^3	1604.1(12)	3278.1(6)
Z	4	8 (monomer units)
fw	295.35	338.67 (per monomer)
calcd density, g/cm^3	1.223	1.372
μ, cm^{-1}	5.93	7.29
F(000)	632	1408
temp, °C	22 ± 1	22 ± 1
	B. Data Collection and Structural Analyses	
scan type	ω, variable	ω, variable
scan rate, deg/min	6.0−20.0	2.0−10.0
2θ range, deg	4.36−50.0	4.54−45.0
2θ range, cent rflns, deg	10−25	10−25
rflns sampled	h (0−10) k (0−14) l (−17 to 17)	h (−1−19) k (−1−19) l (−1 to 10)
no. of rflns collected	2997	2964
no. of unique data	2810 (R_{int} = 0.0293)	2121 (R_{int} = 0.0276)
no. of data, $I > 2\sigma(I)$	1844	1481
a, b	0.0491	0.0271, 1.694
abs cor	none	none
R indices, $I > 2\sigma(I)$	R1 = 0.0496 wR2 = 0.0992	R1 = 0.0366 wR2 = 0.0681
R indices, all data	R1 = 0.0926 wR2 = 0.1173	R1 = 0.0680 wR2 = 0.0783
σ_1, GOF	1.045	1.038
no. of variables	186	180
max diff peak and hole, e/Å^3	0.284, −0.243	0.547, −0.217

tetragonal space group $P4_2/n$ (C_{4h}^4, No. 86). The final lattice parameters and orientation matrix were calculated from a nonlinear least-squares fit of the orientation angles of at least 35 reflections at 22 °C. The lattice parameters and other pertinent crystallographic information are summarized in Table 1 for [$(C_5H_4)SiMe_2$(N-t-Bu)]$Ti(C_4H_6)$ and {[$(C_5H_4)SiMe_2$(N-t-Bu)]$Zr(C_4H_6)$}$_4$.

Intensity data were measured with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and variable ω scans. Background counts were measured at the beginning and at the end of each scan with the crystal and counter kept stationary. The intensities of 3 standard reflections were measured after every 100 reflections. For [$(C_5H_4)SiMe_2$(N-t-Bu)]$Ti(C_4H_6)$ their combined intensities decreased by 8%, whereas for {[$(C_5H_4)SiMe_2$(N-t-Bu)]$Zr(C_4H_6)$}$_4$ there was no indication of crystal decomposition during the data collection period. The raw data were corrected for Lorentz−polarization effects.

Initial coordinates for the non-hydrogen atoms were determined by a combination of direct methods and difference Fourier calculations performed with the algorithms provided in SHELXTL-IRIS operating on a Silicon Graphics Iris Indigo workstation. The Ti compound exhibits a mononuclear structure with all of the non-hydrogen atoms lying on general positions. In contrast, the Zr compound exhibits a tetranuclear structure in the solid state. The atomic coordinates of the symmetry-related atoms within this structure are given by the following relationships: x, y, z; ${}^{3}/_{2} - y, x, {}^{1}/_{2} - z$; $y, {}^{3}/_{2} - x, {}^{1}/_{2} - z$; ${}^{3}/_{2} - x, {}^{3}/_{2} - y, z$ (where x, y, and z are the fractional coordinates for the unique atoms within the crystallographic asymmetric unit). The hydrogen atom positions within the *ansa*-mono(cyclopentadienyl)amido ligand were fixed, whereas those for the anti and syn hydrogen atoms of the butadiene ligand were varied. The isotropic temperature factors for all hydrogen atoms were set at 1.2 times that of the adjacent carbon. The positions of the methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. Full-matrix least-squares refinement with SHELXL-93,[18] based upon the minimization of $\sum w_i|F_o^2 - F_c^2|^2$ with weighting given by the expression $w_i^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$, converged to give the values of the final discrepancy indices[19] provided in Table 2.

Table 2. Interatomic Distances (Å) and Bond Angles (deg) for [$(C_5H_4)SiMe_2$(N-t-Bu)]$Ti(C_4H_6)$ and {[$(C_5H_4)SiMe_2$(N-t-Bu)]$Zr(C_4H_6)$}$_4$[a,b]

	M = Ti	M = Zr
	A. Interatomic Distances	
M−N	1.978(3)	2.107(4)
M−Cp(c)	2.031	2.202
M−C(12)	2.188(4)	2.367(5)
M−C(13)	2.296(4)	2.483(5)
M−C(14)	2.297(4)	2.492(5)
M−C(15)	2.180(4)	2.635(5)
Zr−C(15)′		2.530(5)
Si−C(1)	1.857(4)	1.850(6)
Si−N	1.741(3)	1.740(4)
N−C(8)	1.504(4)	1.481(7)
C(12)−C(13)	1.414(6)	1.424(7)
C(13)−C(14)	1.378(6)	1.373(7)
C(14)−C(15)	1.411(6)	1.462(7)
	B. Bond Angles	
N−M−Cp(c)	110.1	101.0
N−Si−C(1)	94.6(2)	95.3(2)
Si−N−M	100.32(13)	104.4(2)
Si−N−C(8)	122.3(2)	122.6(3)
M−N−C(8)	137.1(2)	132.9(3)
C(12)−C(13)−C(14)	126.1(4)	121.3(5)
C(13)−C(14)−C(15)	126.2(4)	122.4(5)
M−C(12)−C(13)	75.8(3)	77.4(3)
M−C(15)−C(14)	76.2(3)	68.1(3)
Zr″−C(15)−C(14)		110.7(3)
Zr−C(15)−Zr″		173.2(2)

[a] Cp(c) corresponds to the centroid of the five-membered cyclopentadienyl ring. [b] The symmetry transformations used to generate the equivalent primed (′) atoms and doubled primed (″) atoms in the Zr butadiene compound are $y, {}^{3}/_{2} - x, {}^{1}/_{2} - z$ and ${}^{3}/_{2} - y, x, {}^{1}/_{2} - z$, respectively.

Results and Discussion

Preparation and Structural Characterization of [$(C_5H_4)SiMe_2$(N-t-Bu)]$Ti(C_4H_6)$. The metathetical reaction of [$(C_5H_4)SiMe_2$(N-t-Bu)]$TiCl_2$ with a 15% molar excess of $[Mg(C_4H_6)(THF)_2]_n$ proceeds within several hours to afford [$(C_5H_4)SiMe_2$(N-t-Bu)]$Ti(C_4H_6)$ (eq 1). This deep purple Ti butadiene compound is highly soluble in toluene and shows modest solubility in pentane and hexamethyldisiloxane.

A series of related titanium diene complexes were prepared by researchers at The Dow Chemical Co. in

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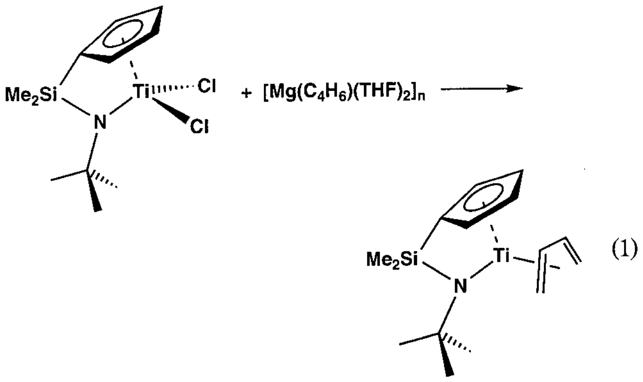
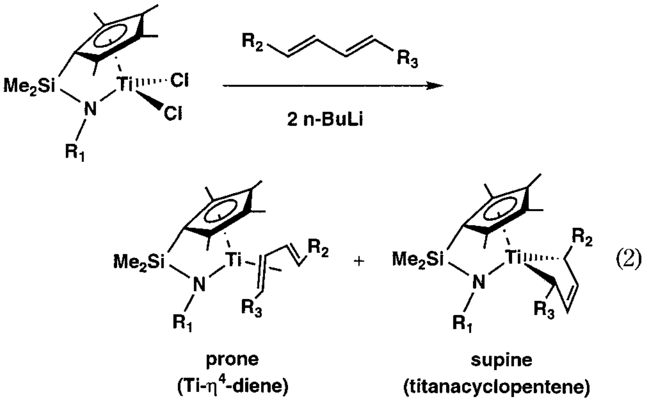
(18) SHELXL-93 is a FORTRAN-77 program (Prof. G. Sheldrick, Institut für Anorganische Chemie, University of Göttingen, D-37077 Göttingen, Germany) for single-crystal X-ray structural analyses.

(19) The discrepancy indices were calculated from the expressions R1 = $\sum||F_o| - |F_c||/\sum|F_o|$ and wR2 = $[\sum(w_i(F_o^2 - F_c^2)^2)/\sum(w_i(F_o^2)^2)]^{1/2}$, and the standard deviation of an observation of unit weight (GOF) is equal to $[\sum(w_i(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters varied during the last refinement cycle.



collaboration with Professor Marks and co-workers at Northwestern University by the reduction of [(C$_5$Me$_4$)SiMe$_2$(NR$_1$)]TiCl$_2$ (R$_1$ = t-Bu, Ph) with 2 equiv of *n*-BuLi in the presence of the diene (eq 2). Solution NMR measurements revealed that these Ti diene complexes may adopt two isomeric forms, with their relative amounts being dependent on the substituent R$_1$ at the amido N and the substituents R$_2$ and R$_3$ on the terminal butadiene carbons. The titanacyclopentene structure with the open end of the butadiene cup pointed toward the cyclopentadienyl ring corresponds to the "supine" structure. The alternative Ti$-\eta^4$-diene structure has the open end of the butadiene cup pointed in the opposite direction away from the cyclopentadienyl ring and is designated as the "prone" structure.[20] These two structures are differentiated in solution by the chemical shift difference $\Delta\delta_H$ ($\delta_m - \delta_a$) between the downfield proton resonance (δ_m) for the meso hydrogen atoms of the internal methine carbons and the upfield proton resonance (δ_a) for the anti hydrogen atoms of the terminal carbons of the coordinated diene fragment. The magnitude of $\Delta\delta_H$ is considerably larger for the supine metallacyclopentene structure than for the alternative prone metal π-diene structure.[3]



	prone:supine ratio
R$_1$ = t-Bu, R$_2$ = R$_3$ = Me	100:0
R$_1$ = t-Bu, R$_2$ = Me, R$_3$ = H	100:0
R$_1$ = Ph, R$_2$ = R$_3$ = Me	70:30
R$_1$ = Ph, R$_2$ = Me, R$_3$ = H	55:45

The solution ^{1}H and ^{13}C NMR data for [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti(C$_4$H$_6$) are consistent with the presence of mirror symmetry. The ^{1}H NMR spectrum exhibits the expected four proton resonances for the bifunctional *ansa*-mono(cyclopentadienyl)amido ligand and three distinct multiplets of equal intensity at δ 1.82, 3.28, and 4.20 for the anti, syn, and meso protons of the butadiene ligand, respectively. The multiplet at δ 1.82 is upfield relative to the multiplet at δ 2.10, assigned to the anti protons of the 2,4-hexadiene ligand in [(C$_5$Me$_4$)SiMe$_2$(N-t-Bu)]Ti(MeC*H*CHCHC*H*Me), whereas the multiplet at δ 4.20 is further downfield compared to the multiplet at δ 3.73 for the meso protons of [(C$_5$Me$_4$)SiMe$_2$(N-t-Bu)]Ti(MeCHC*H*C*H*CHMe).[3] The observed chemical shift difference $\Delta\delta$ of ca. 2.4 ppm for [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti(C$_4$H$_6$) indicates that this compound adopts the prone structure in solution.

The ^{13}C NMR spectra exhibit eight distinct carbon resonances. The two methyl carbons of the SiMe$_2$ bridge appear as a quartet at δ 3.0 ($^1J_{C-H}$ = 119 Hz), and the three methyl carbons of the *tert*-butyl substituent and the quaternary carbon bound to the amido N exhibit a quartet at δ 35.1 ($^1J_{C-H}$ = 125 Hz) and a singlet at δ 58.1, respectively. The cyclopentadienyl ring displays a singlet at δ 102.4 for the bridgehead carbon and a pair of doublet of quartets centered at δ 113.4 ($^1J_{C-H}$ = 170 Hz, $^{3,4}J_{C-H}$ = 7 Hz) and δ 118.5 ($^1J_{C-H}$ = 171 Hz, $^{3,4}J_{C-H}$ = 7 Hz) for the proximal and distal ring carbons. The two terminal and internal carbon resonances of the butadiene ligand each appear as a doublet of doublets of doublets. The resolved eight-line pattern located at δ 62.8 exhibits two different $^1J_{C-H}$ coupling constants of 161 and 138 Hz and a $^3J_{C-H}$ coupling constant of 9 Hz and therefore corresponds to the terminal CH$_2$ carbons of the butadiene ligand. The observation of two different $^1J_{C-H}$ coupling constants indicates that the chemical environments of the anti and syn protons of the terminal carbon remain inequivalent on the NMR time scale. The eight-line pattern centered at δ 107.2 displays one $^1J_{C-H}$ coupling constant at 157 Hz consistent with the presence of one H atom bound to this carbon and two smaller $^3J_{C-H}$ coupling constants of 9 and 7 Hz due to coupling with the two inequivalent CH$_2$ protons. Thus, this resonance is unambiguously assigned to the internal carbons of the butadiene ligand.

The molecular structure of [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti(C$_4$H$_6$) was determined by an X-ray structural analysis. Its solid structure is well-behaved with no indication of any crystallographic disorder. A perspective view of the molecular structure of this mononuclear compound is provided in Figure 1 with the appropriate atom-labeling scheme for the non-hydrogen atoms. The Ti coordination sphere consists of the π-bonded cyclopentadienyl ring and the amido N-donor atom of the *ansa*-mono(cyclopentadienyl)amido ligand and a symmetrically bound η^4-butadiene ligand. The nearly equal Ti$-$C(12) and Ti$-$C(15) distances of 2.188(4) and 2.180(4) Å for the two terminal butadiene carbons are ca. 0.11 Å shorter than the Ti$-$C(13) and Ti$-$C(14) distances of 2.296(4) and 2.297(4) Å for the two internal butadiene carbons. The analogous variation in these four Ti$-$C distances is observed for the π-bound 2,4-hexadiene ligand of [(C$_5$Me$_4$)SiMe$_2$(N-t-Bu)]Ti(MeCHCHCHCHMe), with Δd = Ti$-$C(terminal) $-$ Ti$-$C(internal) also being $-$0.11 Å.[3] The Ti$-$N distance of 1.978(3) Å in [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti(C$_4$H$_6$) is ca. 0.07 Å longer than the Ti$-$N distance

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[20] For the definitions of the "prone" and "supine" designations, see: Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410.

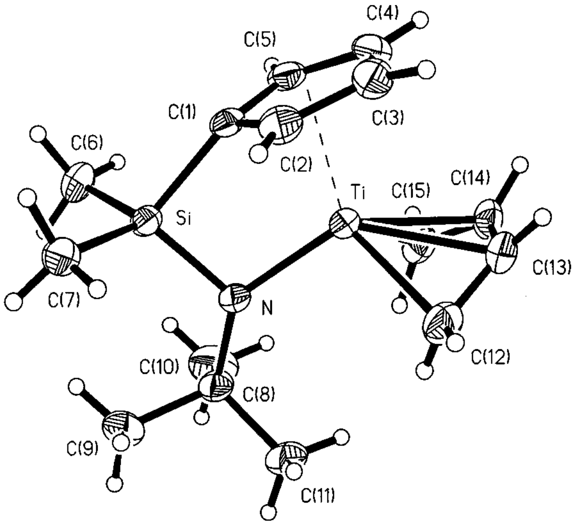


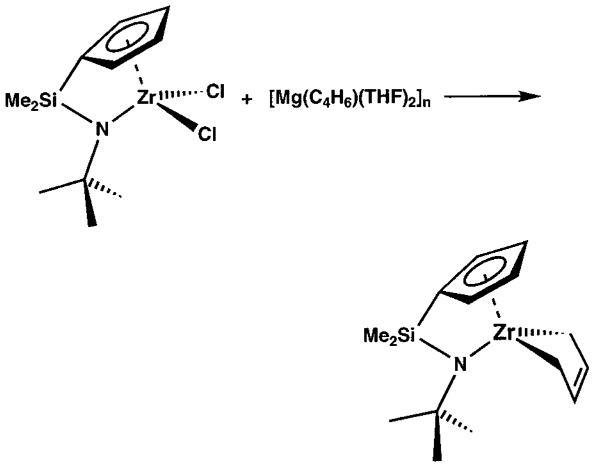
Figure 1. Perspective view of the molecular structure of [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti(C$_4$H$_6$) with the non-hydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

of 1.907(4) Å in [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]TiCl$_2$[6] but ca. 0.03 Å shorter than the corresponding Ti−N distance of 2.007(4) Å in [(C$_5$Me$_4$)SiMe$_2$(N-t-Bu)]Ti(MeCHCHCHCHMe).[3] The longer Ti−N distance in [(C$_5$Me$_4$)SiMe$_2$(N-t-Bu)]Ti(MeCHCHCHCHMe) reflects the greater π-donating ability of the permethylated cyclopentadienyl ring resulting in a concomitant reduction in the Lewis acidity of the Ti center. The Ti−N distances in [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti(C$_4$H$_6$) and [(C$_5$Me$_4$)SiMe$_2$(N-t-Bu)]Ti(MeCHCHCHCHMe) fall outside of the 1.86−1.96 Å range for Ti−N distances observed for formal Ti(IV) amido complexes[21−23] and are a consequence of the lower valent character and larger effective covalent radius of the Ti in these two diene complexes. The longer Ti−N bond is accompanied by a modest increase of ca. 3.1° in the Cp(c)−Ti−N angle of 107.0° in [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]TiCl$_2$[6] to 110.1° in [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti(C$_4$H$_6$). The corresponding Cp(c)−Ti−N angle of 107.6° in [(C$_5$Me$_4$)SiMe$_2$(N-t-Bu)]TiCl$_2$[6] increases to 109.8° in [(C$_5$Me$_4$)SiMe$_2$(N-t-Bu)]Ti(MeCHCHCHCHMe).[3] In contrast to the Ti−N distance, the Ti−Cp(c) distance is less sensitive to the replacement of the two chloride ligands by the η^4-diene. The Ti−Cp(c) distance of 2.031 Å in [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti(C$_4$H$_6$) is only 0.012 Å longer than the Ti−Cp(c) distance of 2.019 Å in its dichloride precursor.[6]

The most notable structural feature is the orientation of the butadiene moiety, which adopts the analogous prone structure observed for [(C$_5$Me$_4$)SiMe$_2$(N-t-Bu)]Ti(MeCHCHCHCHMe).[3] The three internal C−C bond distances of the butadiene ligand of [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti(C$_4$H$_6$) range from 1.378(6) to 1.414(6) Å and are comparable to those in [(C$_5$Me$_4$)SiMe$_2$(N-t-Bu)]Ti(MeCHCHCHCHMe). The four carbon atoms of the butadiene fragment are coplanar, with the acute dihedral angle between the Ti, C(12), C(13) and C(12), C(13), C(14), C(15) planes being 73.1°. The plane of the butadiene ligand is 15.0° from being parallel to the plane of the cyclopentadienyl ring. The two internal C−C−C bond angles, C(12)−C(13)−C(14) and C(13)−C(14)−C(15), are identical within experimental error.

Therefore, the results of our X-ray structural analysis of [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti(C$_4$H$_6$) are consistent with a Ti(II) π-diene bonding description. The solution ^{1}H and ^{13}C NMR data further indicate that the symmetrical prone structure is retained in solution.

Preparation and Structural Characterization of [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Zr(C$_4$H$_6$). The corresponding metathetical reaction of {[(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]ZrCl(μ-Cl)}$_2$ with a 15% excess of [Mg(C$_4$H$_6$)(THF)$_2$]$_n$ affords the Zr butadiene complex [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Zr(C$_4$H$_6$) (eq 3). The ambient solution ^{1}H and ^{13}C NMR data are consistent with a symmetrical disposition of the butadiene ligand. The ^{1}H NMR spectrum exhibits the expected four resonances for the dianionic *ansa*-mono(cyclopentadienyl)amido ligand and is highlighted by the presence of three distinct multiplets at δ −0.64, 3.31, and 5.98 for the anti, syn, and meso protons of the butadiene ligand, respectively. In this case, the chemical shift difference, $\Delta\delta_H$, between the downfield meso and upfield anti proton resonances is 6.62 ppm, which is 2.8 times larger than the value of 2.4 ppm observed for [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Ti(C$_4$H$_6$). It is comparable to the values of 6.11 and 6.16 ppm observed for [(C$_5$Me$_4$)SiMe$_2$(NCHMe(1-C$_{10}$H$_7$))]Zr(C$_4$H$_6$)[5] and [(C$_5$Me$_4$)SiMe$_2$(N-i-Pr)]Zr(C$_4$H$_6$),[24] respectively. X-ray structural analyses performed on these two Zr butadiene complexes revealed that both display the alternative "supine" structure characterized by a σ^2,π-type Zr−butadiene interaction. Therefore, the chemical shift dispersion observed for the anti and meso butadiene protons of [(C$_5$H$_4$)SiMe$_2$(N-t-Bu)]Zr(C$_4$H$_6$) supports a similar zirconacyclopentene structure in solution.



(3)

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(24) Christy, M.; Petersen, J. L. Unpublished results. Crystallographic data from a preliminary X-ray structural analysis of [(C$_5$Me$_4$)SiMe$_2$(N-i-Pr)]Zr(C$_4$H$_6$): orthorhombic, *Pnma*, a = 10.211(1) Å, b = 12.986(3) Å, c = 14.970(3) Å, V = 1985.0(5) Å^3, Z = 4, d_c = 1.274 g/cm^3, T = 295 K. Full-matrix refinement (on F_o^2) of 21 non-hydrogen atoms and 19 idealized hydrogen atoms converged with R1 = 0.0785 for 554 data with $I > 2\sigma(I)$ and GOF = 0.976. ^{1}H NMR data for [(C$_5$Me$_4$)SiMe$_2$(N-i-Pr)]Zr(C$_4$H$_6$) in C$_6$D$_6$: δ −0.31 (m, 2H, anti CH$_2$), 0.61 (s, 6H, SiMe$_2$), 0.78 (d, 6H, CH*Me*$_2$, 6.4), 1.61, 2.37 (s, 6H, C$_5$Me$_4$), 2.93 (m, 2H, syn CH$_2$), 3.54 (sept., 1H, C*H*Me$_2$, 6.4), 5.85 (m, 2H, meso CH). Gated nondecoupled ^{13}C NMR data (C$_6$D$_6$): δ 6.80 (q, SiMe$_2$, 117), 11.3, 15.1 (q, C$_5$*Me*$_4$, 126, 126), 29.7 (q, CH*Me*$_2$, 126), 51.7 (d, *C*HMe$_2$, 133), 55.1 (t, CH$_2$, 143), 123.1 (d, CH, 163), 123.7, 126.5 (s, C$_5$Me$_4$).

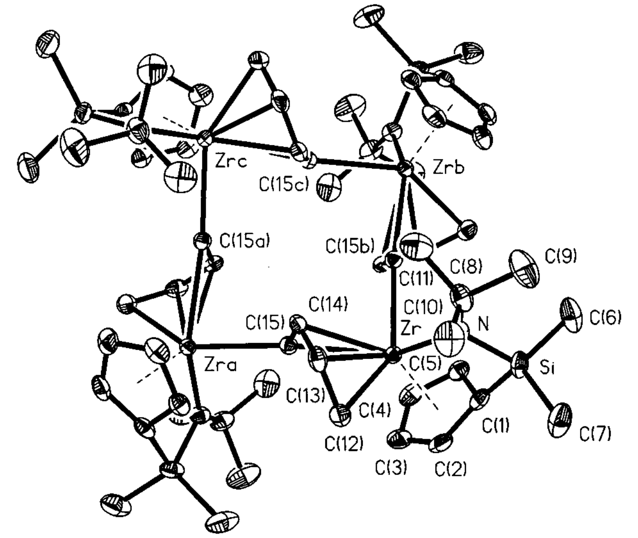

Figure 2. Perspective view of the tetranuclear structure of $\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)\}_4$ with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. The hydrogen atoms are not included for the purpose of clarity.

The ^{13}C NMR spectra for $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)$ display eight characteristic carbon resonances. The methyl carbons of the $SiMe_2$ bridge appear as a quartet at δ 2.74 ($^1J_{C-H} = 119$ Hz) and the three methyl carbons and the quaternary carbon of the *tert*-butyl substituent exhibit a quartet at δ 36.4 ($^1J_{C-H} = 124$ Hz) and a singlet at δ 57.8, respectively. The cyclopentadienyl ring exhibits a singlet at δ 107.6 for the bridgehead carbon and a pair of doublet of quartets centered at δ 112.4 ($^1J_{C-H} = 171$ Hz, $^{3,4}J_{C-H} = 7$ Hz) and δ 114.0 ($^1J_{C-H} = 170$ Hz, $^{3,4}J_{C-H} = 7$ Hz) for the proximal and distal ring carbons. The terminal and internal carbon resonances of the butadiene ligand each appear as a distinct doublet of doublets of doublets. The resolved eight-line pattern centered at δ 53.8 exhibits two different $^1J_{C-H}$ coupling constants of 157 and 133 Hz and a $^3J_{C-H}$ coupling constant of 9 Hz and therefore corresponds to the carbon termini of the butadiene ligand. The other eight-line pattern centered at δ 122.0 displays one $^1J_{C-H}$ coupling constant of 157 Hz consistent with the presence of one H atom bound to this carbon and two smaller $^3J_{C-H}$ coupling constants of 9 and 8 Hz due to coupling to the anti and syn protons. The chemical shift difference, $\Delta\delta_C$, for the terminal and internal butadiene carbon resonances in $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)$ of 68.2 ppm is effectively equal to the respective values of 68.1 (average) and 68.0 ppm for $[(C_5Me_4)SiMe_2(NCHMe(1\text{-}C_{10}H_7))]Zr(C_4H_6)$[5] and $[(C_5Me_4)SiMe_2(N\text{-}i\text{-}Pr)]Zr(C_4H_6)$.[24] A 2D HETCOR NMR spectrum confirmed that the anti and syn proton resonances at δ −0.64 and 3.31 correspond to the hydrogens on the terminal butadiene carbons and the downfield meso proton resonance at δ 5.98 belongs to the protons on the internal methine carbons.

An X-ray structural analysis of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)$ revealed that this compound exhibits a tetranuclear structure in the solid state rather than the expected mononuclear structure. As evident from the perspective view depicted in Figure 2, the four $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr$ units, which are related by a crystallographically imposed S_4 rotation axis, are linked by four unsymmetrically bridging butadiene groups. One of the two terminal carbons, C(12), and the two internal carbon atoms, C(13) and C(14), of the butadiene fragment are bound to only one Zr center, whereas the remaining terminal carbon atom, C(15), links two different Zr atoms. The Zr−C(12), Zr−C(13), and Zr−C(14) distances of 2.367(5), 2.483(5), and 2.492 (5) Å, respectively, are comparable to the Zr−C distances (range 2.405(4)−2.549(3) Å) for a η^3-π-allyl ligand in $(C_5H_5)Zr(C_3H_5)_3$[25] and to the Zr−C distances for the η^3-π-allyl (2.443(7) and 2.446(8) Å) and planar 1,3-butadiene (2.360(5) and 2.463(5) Å) ligands in $(C_5H_5)Zr(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4H_6)$[26] and show considerably less variation than the corresponding Zr−C distances (range 2.4−2.7 Å) observed for the π-allyl functionality in zirconoxycarbene complexes obtained from the reaction of zirconocene butadiene with an assortment of electron-rich metal carbonyls.[27] The two independent Zr−C(15) distances of 2.635(5) and 2.530(5) Å are rather long and reflect an unsymmetrical bridging interaction for C(15), which bonds more strongly to the other electrophilic Zr center than to the Zr atom bound to the remaining three carbons of the same butadiene fragment.

The Zr−butadiene bonding interaction resembles that reported for the bridging butadiene ligand in $(C_5Me_5)_2La(\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_4H_6)La(C_5Me_5)_2(THF)$.[28] In this dinuclear lanthanum complex, three of the four carbons of the cis-configured butadiene are bound to the $Cp_2{}^*La$ unit, forming a η^3-allyl unit, whereas the remaining terminal carbon, C_t, is σ-bonded to the $Cp_2{}^*La(THF)$ fragment with the resultant $La-C_t$ bond distance being 2.633(4) Å. The interatomic separation between C_t and the other La atom of 2.894(4) Å is substantially longer. The unsymmetrical disposition of C_t for the $\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_4H_6$ ligand, however, does not significantly perturb the skeletal structure of the nearly planar butadiene, as evidenced by the fact that the two independent C−C−C bond angles of 126.2(4) and 126.8(4)° remain essentially equal.

The butadiene bonding interaction in $\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)\}_4$ is distinctly different from that reported for the bridging butadiene fragment in the binuclear Zr/Al complex $(C_5H_5)_2Zr(\mu\text{-}C_4H_6)(\mu\text{-}Cl)AlCl_2$, prepared by the addition of 1 equiv of $AlCl_3$ to a s-cis/s-trans equilibrium mixture of zirconocene butadiene.[29] One terminal carbon of the bridging butadiene is bound to Zr with a Zr−C distance of 2.348(2) Å, whereas the other terminal carbon is bound only to the Al with a Al−C distance of 1.966(2) Å. Of the internal carbons of the bridging butadiene unit, the Zr−C(2) and Zr−C(3)

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distances of 2.525(3) and 3.04 Å indicate that only carbon C(2) is bound directly to the d^0 Zr center, thus ruling out the presence of a π-allyl bonding interaction in this compound. On the basis of their structural data, Erker and co-workers[29] concluded that this novel bonding mode displayed by the butadiene moiety in $(C_5H_5)_2$Zr(μ-C_4H_6)(μ-Cl)$AlCl_2$ is best represented as μ-((1,2-η^2)-Zr−(4-η^1)-Al). In contrast, carbons C(12), C(13), and C(14) of the bridging butadiene moiety of {[$(C_5H_4)SiMe_2$(N-t-Bu)]Zr(C_4H_6)}$_4$ coordinate as an unsymmetrical π-allyl functionality to one Zr center with the remaining carbon, C(15), coordinated to two Zr centers. The acute dihedral angle of 12.8° between the planes containing carbon atoms C(12), C(13), C(14) and C(13), C(14), C(15) reveals that the butadiene ligand is not strictly planar. The two meso hydrogen atoms of the bridging butadiene adopt a cis orientation rather the alternative trans disposition observed in $(C_5H_5)_2$Zr(μ-C_4H_6)(μ-Cl)$AlCl_2$.[29] The three carbon distances of C(12)−C(13), C(13)−C(14), C(14)−C(15) of 1.424(7), 1.373(7), and 1.462(7) Å further demonstrate that some π-delocalization is retained within the butadiene backbone. The two C(12)−C(13)−C(14) and C(13)−C(14)−C(15) bond angles of 121.3(5) and 122.4(5)° are consistent with sp^2 hybridization at the two internal carbons.

The bridging coordination mode exhibited by the 1,3-butadiene ligands of {[$(C_5H_4)SiMe_2$(N-t-Bu)]Zr(C_4H_6)}$_4$ is consistent with a ((1,2,3-η^3)-Zr−(4-μ_2)-Zr) representation. A similar ((1,2,3-η^3)-Ti−(4-μ_2)-B) arrangement is observed for the bridging 1,3-pentadiene ligand in the zwitterionic Ti−betaine complex [$(C_5Me_4)SiMe_2$(N-t-Bu)]-Ti^+(η^3-CH(Me)CHCHC$H_2B^-(C_6F_5)_3$], in which the terminal butadiene carbon is bound to both the cationic Ti and anionic B centers. However, in the latter case, the two H atoms of the doubly bridging CH_2 are displaced toward the electrophilic Ti center, consistent with the presence of a pair of agostic C−H···Ti interactions. In contrast, for {[$(C_5H_4)SiMe_2$(N-t-Bu)]Zr(C_4H_6)}$_4$, these H atoms are not preferentially directed toward either Zr center bridged by the butadiene ligand.

The five-coordinate geometry about C(15) is comprised of carbon atom C(14), two σ-bonded hydrogen atoms, and two Zr atoms. This arrangement is characterized by a nearly linear Zr−C(15)−Zr″ bond angle of 173.2(2)°, a distorted-trigonal arrangement of carbon atom C(14) and the two hydrogen atoms of C(15), and two distinctly different C(14)−C(15)−Zr and C(14)−C(15)−Zr″ angles of 68.1(3) and 110.7(3)°, respectively. This structural feature resembles the trigonal-bipyramidal arrangement reported by Marks and co-workers for the bridging methyl ligand in {[(1,2-$C_5H_3Me_2)_2$ZrMe]$_2$(μ-Me)}[MePBB].[30a] Within the dinuclear cation, the nearly equal Zr−C distances of 2.439(8) and 2.409(8) Å for the μ-Me bridge indicate that the methyl carbon symmetrically bridges the two d^0 Zr(IV) centers. This five-coordinate geometry is characterized by a nearly linear Zr−C(μ-Me)−Zr bond angle of 170.9(4)° and a trigonal-planar arrangement of its three methyl protons. By using the three in-plane sp^2 hybridized carbon orbitals to construct the three C−H σ-bonds, the remaining filled p orbital of the μ-Me ligand is properly oriented to share its lone pair with the two electron-deficient Zr centers.[31,32] The three-center, two-electron bond in this binuclear cation affords two bridging Zr−C(methyl) bonds which are substantially longer than the two normal terminal Zr−C(methyl) bonds of 2.235(8) and 2.247(9) Å.[30b] A similar bonding description accounts for the five-coordinate geometry about C(15) in {[(C_5H_4)-$SiMe_2$(N-t-Bu)]Zr(C_4H_6)}$_4$. The observed distortions from an idealized structure are a consequence of the η^3-π-allyl Zr bonding interaction, which prevents C(15) from adopting a symmetric disposition between the two Zr centers.

The bridging mode of coordination for the butadiene ligands in {[$(C_5H_4)SiMe_2$(N-t-Bu)]Zr(C_4H_6)}$_4$ is in stark contrast to the symmetrical zirconacyclopentene structures observed in the solid state for [$(C_5Me_4)SiMe_2$-(NCHMe(1-$C_{10}H_7$))]Zr(C_4H_6),[5] [$(C_5Me_4)SiMe_2$(N-i-Pr)]-Zr(C_4H_6),[24] and the s-cis isomer of $(C_5H_5)_2$Zr(C_4H_6).[33] This structural variation arises from a combination of steric and electronic effects. For *ansa*-mono(cyclopentadienyl)amido Zr complexes, the replacement of the more strongly π-donating C_5Me_4 ring with C_5H_4 simultaneously reduces the steric congestion and enhances the electrophilicity of the Zr and has a pronounced influence on the crystal structures exhibited by the related 14-electron Zr dichloride complexes. Whereas [$(C_5Me_4)SiMe_2$(N-t-Bu)]ZrCl_2 is mononuclear, {[(C_5H_4)-$SiMe_2$(N-t-Bu)]ZrCl(μ-Cl)}$_2$ is a centrosymmetric dimer in the solid state.[6,34] The construction of this dinuclear structure utilizes three metal orbitals on each d^0 Zr(IV) center to form the terminal and two bridging Zr−Cl bonding interactions. However, the outer and internal bridging Zr−Cl distances of 2.618(1) and 2.657(1) Å are substantially longer than the terminal Zr−Cl distance of 2.453(1) Å.[34b] The fact this dinuclear structure is not retained in solution reflects the relative ease by which the bridging Zr−Cl bonding interactions are disrupted upon solvation. For [$(C_5H_4)SiMe_2$(N-t-Bu)]Zr-(C_4H_6), the lower steric demands and electron deficiency of the [$(C_5H_4)SiMe_2$(N-t-Bu)]Zr moiety lead to the unsymmetrical coordination of bridging butadiene units in the solid state. In view of the rather long bridging Zr−C(15) distances observed for {[$(C_5H_4)SiMe_2$(N-t-Bu)]-

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$Zr(C_4H_6)\}_4$, one expects this tetrameric structure to dissociate readily in solution. This statement is borne out by the ambient NMR data, showing that the symmetrical σ^2,π-zirconacyclopentene structure prevails in solution.

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Supporting Information Available: Complete tables of the results from the X-ray crystallographic analyses performed on $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti(C_4H_6)$ and $\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(C_4H_6)\}_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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