## **Constrained-Geometry Titanium(II)** Diene Complexes. Structural Diversity and Olefin Polymerization Activity

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Summary: Reduction of  $(\eta^5:\eta^1 \cdot C_5 Me_4 Si Me_2 NR) Ti Cl_2$ with "BuLi in the presence of various 1,3-dienes yields  $(\eta^5:\eta^1-C_5Me_4SiMe_2NR)Ti(diene)$  complexes. The diene coordination mode ( $\pi$ , formally Ti(II), or metallacyclic, formally Ti(IV) and the activity for olefin polymerization (which can be very high) are highly sensitive to the identity of R.

The recent development of "constrained geometry" catalysts has had a major impact on homogeneous olefin polymerization technologies<sup>1</sup> and necessitates a better understanding of basic organo-group 4 metal chemistry with  $\eta^5: \eta^1-C_5Me_4SiMe_2NR$  ancillary ligation.<sup>2,3</sup> Multihapto ligands such as 1,3-dienes, which engage in a variety of bonding modes, offer a direct probe of  $(C_5$ -Me<sub>4</sub>SiMe<sub>2</sub>NR)M steric and electronic requirements which can then be compared to and contrasted with those of more conventional group 4 Cp<sub>2</sub>M and CpM metal-diene ligand arrays.<sup>4,5</sup> We communicate here the synthesis and unusual structural characteristics and diversities, as well as high olefin polymerization activities, of the first series of (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>NR)Ti(diene) complexes.

(C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>NR)Ti(diene) complexes are readily synthesized by reduction of the  $(C_5Me_4SiMe_2NR)TiCl_2$ precursors (1) with 2 equiv of <sup>n</sup>BuLi in the presence of dienes in refluxing hexane (eq 1).<sup>6,7</sup> Isolated yields of the dark purple complexes range from 20 to 97% after optional recrystallization from hexane.<sup>7</sup> As indicated

by NMR spectroscopy and X-ray diffraction (vide infra), minor changes in the ancillary ligation ( $R_1 = {}^tBu \rightarrow R_1$ )

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<sup>(6)</sup> The dienes (Aldrich) were used as mixtures of isomers. 2,4-Hexadiene was a 62:35.7% mixture of the *cis,trans* and *trans,trans* isomers. 1,3-Pentadiene was a 57.3:31.6% mixture of the trans and cis isomers.

<sup>(7) (</sup>a) Generalized procedure (using 2b as example): In an inertatmosphere glovebox, 0.500 g (1.36 mmol) of (C5Me4SiMe2N4Bu)TiCl2 was dissolved into approximately 50 mL of dry, degassed hexane. To this yellow solution was added 2.70 mL of technical grade piperylene (27.1 mmol) followed by 1.09 mL of "BuLi (2.72 mmol, 2.5 M in hexanes). Addition of the latter resulted in an immediate color change to dark red. The reaction mixture was heated to reflux for 45-60 min, after which time it was cooled to room temperature. The solution was filtered through Celite, using 10 mL of additional hexane to wash the insoluble byproducts. The combined hexane filtrate was taken to dryness under reduced pressure, yielding the product, (C5Me4SiMe2Nt Bu)Ti(prone-trans-1,3-pentadiene), as a red-purple solid in 97% yield Bu)<sup>11</sup>(prone-*trans*-1,3-pentadiene), as a red-purple solid in 97% yield (0.97 g). Analytical and spectroscopic data for complex **2b** are as follows. <sup>1</sup>H NMR ( $C_{6}D_{6}$ , ppm):  $\delta$  4.01 (m, CHH=CHCH=CHCH3, 1H); 3.84 (m, CHH=CHCH=CHCH3, 1H); 2.97 (m, CHH=CHCH=CHCH3, 1H); 2.13 (s, C<sub>5</sub>Me<sub>4</sub>, 3H); 2.1 (multiplet, partly overlapped by two singlets, CHH=CHCH=CHCH3, 1H); 2.05 (s, C<sub>5</sub>Me<sub>4</sub>, 3H); 1.88 (d, CHH=CHCH=CHCH3, 3H, J<sub>HH</sub> = 5.5 Hz); 1.75 (dd, CHH=CHCH=CHCH3, 1H, J<sub>HH</sub> = 13.3, 7.3 Hz); 1.23, 1.21 (s each, C<sub>5</sub>Me<sub>4</sub>, 3H each); 1.16 (s, <sup>1</sup>Bu, 9H); 0.76, 0.73 (s each, SiMe<sub>2</sub>, 3H each); <sup>1</sup>3Cl<sup>1</sup>H) NMR (C<sub>5</sub>D<sub>6</sub> pnm):  $\delta$  8.12, 8.88 14 37, 16.08 (C<sub>5</sub>Me<sub>4</sub>, 3H) each); 11.60  $^{13}C{^{1}H}$  NMR (C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  8.12, 8.88, 14.37, 16.08 (C<sub>5</sub>Me<sub>4</sub>); 11.60 (SiMe<sub>2</sub>); 19.14 (CH<sub>2</sub>=CHCH=CHCH<sub>3</sub>); 35.27, 57.22 (<sup>1</sup>Bu); 61.75 (CH<sub>2</sub>=CHCH=CHCH<sub>3</sub>); 76.76 (CH<sub>2</sub>=CHCH=CHCH<sub>3</sub>); 103.73 (C<sub>5</sub> carbon attached to Si); 107.67, 114.99 (CH2=CHCH=CHCH3); 123.17, 123.44, 130.51 ( $C_5$  ring, remaining resonance under  $C_6D_6$ ). Anal. Calcd for  $C_{20}H_{35}NSiTi$ : C, 65.73; H, 9.65; N, 3.83. Found: C, 66.36; H, 9.73; N, 3.59. (b) Complex 2a was prepared similarly to 2b in 20% yield. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  8.51, 11.74 (C<sub>5</sub>Me<sub>4</sub>); 14.50 (SiMe<sub>2</sub>); 19.00 (CH-(CH<sub>3</sub>)CHCHCH(CH<sub>3</sub>)); 35.32, 56.85 (Bu); 76.60 (CH(CH<sub>3</sub>)CHCHCH-(CH<sub>3</sub>)); 103.9 (C<sub>5</sub> carbon attached to Si); 110.39 (CH(CH<sub>3</sub>)CHCHCH-(CH<sub>3</sub>)); 122.83 (C<sub>5</sub>, remaining resonance under C<sub>6</sub>D<sub>6</sub>). Anal. Calcd for C21H37NSiTi: C, 66.46; H, 9.83; N, 3.69. Found: C, 66.85; H, 9.48; N, 3.51. (c) The mixture 2c/3c was prepared similarly to 2b in 36% yield. B.5.1.(c) The infection 2C are as follows. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  7.5–7.0 (m, Ph, 3H); 6.69 (d, Ph, 2H,  $J_{\rm HH} = 7.4$  Hz); 3.78 (m, CH-(CH<sub>3</sub>)CHCHCH(CH<sub>3</sub>), 2H); 2.19 (s, C<sub>5</sub>Me<sub>4</sub>, 6H); 1.90 (m, partially overlapped by a CH<sub>3</sub> doublet, CH(CH<sub>3</sub>)CHCHCH(CH<sub>3</sub>), 2H); 1.85 (d, CHCHCH(CH<sub>3</sub>), 2H); 1.85 (d, CHCHCH(CH<sub>3</sub>); 1.85 (d, CHCHCH(CH<sub>3</sub>); 1.85 (d, CHCHCH(CH<sub>3</sub>); 1.85 (d, CHCH  $CH(CH_3)CHCHCH(CH_3), 6H, J_{HH} = 4.6 Hz), 1.24 (s, C_8Me_4, 6H); 0.55 (s, SiMe_2, 6H). Assignments for$ **3c**are as follows. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,(s, SiMe<sub>2</sub>, 6H). Assignments for **3c** are as follows. <sup>1</sup>H NMR ( $C_6D_6$ , ppm):  $\delta$  7.5-7.0 (m, Ph, 3H); 6.1 (d, Ph, 2H); 5.26 (m, CH-(CH<sub>3</sub>)CHCHCH(CH<sub>3</sub>), 2H); 2.36 (s,  $C_5Me_4$ , 6H); 1.78 (d, CH(CH<sub>3</sub>)-CHCHCH(CH<sub>3</sub>), 6H,  $J_{HH} = 6.0$  H<sub>2</sub>); 1.46 (s,  $C_5Me_4$ , 6H); 0.47 (s, SiMe<sub>2</sub>, 6H); 0.3 (m, CH(CH<sub>3</sub>)CHCHCH(CH<sub>3</sub>), 2H). Anal. Calcd for  $C_{23}H_{33}$ -NSiTi: C, 69.15; H, 8.33; N, 3.51. Found: C, 69.68; H, 8.08; N, 3.32. (d) The mixture **2d/3d** was prepared similarly to **2b** in 49% yield. Assignments for **2d** are as follows. <sup>1</sup>H NMR ( $C_6D_6$ , ppm):  $\delta$  7.1 (m, Ph, 2H, partially overlapped by solvent); 6.85 (m, Ph, 1H); 6.70 (d, Ph, 2H, J<sub>HH</sub> = 8.4 H<sub>2</sub>); 4.05 (m, CHH=CHCH=CHCH<sub>3</sub>, 1H); 2.22 (s,  $C_5Me_4$ , 3H); 1.18 (m, partly overlapped, CHH=CHCH=CHCH<sub>3</sub>, 1H); 2.23 (s,  $C_5Me_4$ , 3H); 1.82 (d, CHH=CHCH=CHCH<sub>3</sub>, 3H, J<sub>HH</sub> = 2.0 H<sub>2</sub>); 1.8 (m, partly overlapped, CHH=CHCH=CHCH<sub>3</sub>, 3H) 3H, J<sub>HH</sub> = 2.0 Hz); 1.8 (m, partly overlapped, CHH-CHCH=CHCH3, 1H); 1.45 (m, partly overlapped, CHH-CHCH-CHCH3, 1H); 1.23 (s, 1H); 1.45 (m, party overlapped, CH7=CHCH=CHCH3, 1H); 1.23 (s, C<sub>5</sub>Me<sub>4</sub>, 6H); 0.56 (d, 0.55 (s each, SiMe<sub>2</sub>, 3H each). Assignments for **3d** are as follows. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm):  $\partial$  7.01 (m, Ph, 2H); 6.8 (m, Ph, 1H); 6.10 (d, Ph, 2H, J<sub>HH</sub> = 8.3 Hz); 5.4 (m, CHH=CHCH=CHCH3, 2H); 3.05 (m, CHH=CHCH=CHCH3, 1H); 2.34, 2.33 (s each, C<sub>5</sub>Me<sub>4</sub>, 3H each); 1.70 (d, CHH=CHCH=CHCH3, 3H), J<sub>HH</sub> = 5.9 Hz); 1.50 (s, C<sub>5</sub>Me<sub>4</sub>, 6H); 0.49, 0.48 (s each, SiMe<sub>2</sub>, 3H each); 0.4 (m, CHH=CHCH=CHCH3, 2H). Anal. Calcd for C<sub>22</sub>H<sub>31</sub>NSiTi: C, 68.55; U, each C<sub>5</sub>Me<sub>4</sub>, 0.49, 0.48 (S each, C<sub>3</sub>Me<sub>4</sub>, 0.49, 0.48 (s), 0.49 (m, CHH=CHCH=CHCH3, 0.4); 0.4 (m, 0.4); H, 8.11; N, 3.63. Found: C, 69.01; H, 8.13; N, 3.44.



= Ph) effect significant perturbations in the diene bonding pattern as well as polymerization activity.

For  $R_1 = {}^tBu$ , NMR indicates that eq 1 affords, at all stages, a single type of isomeric diene structure (2a,b). Thus, structurally diagnostic<sup>4,5</sup>  $\delta(H_a)$  and  $\delta(H_m)$  occur at 2.10 and 3.73 ppm in 2a and at 2.13, 1.75, 3.84, and 4.01 ppm in 2b



in good agreement with data for the structurally characterized complexes Cp\*TiCl(1,3-butadiene)<sup>5a</sup> and Cp<sub>2</sub>-Zr(s-trans-1,3-butadiene), which are predominantly  $\pi$ -diene in character.<sup>5e</sup>  $\delta(H_a) - \delta(H_m)$  exhibits a far greater dispersion in complexes such as Cp<sub>2</sub>Zr(s-cis-1,3-butadiene)<sup>4a,5f</sup> and Cp\*TiCl(supine-isoprene), which are predominantly  $\sigma$ -bound (metallacyclopentene) in character.<sup>5a,8</sup>  ${}^{1}J_{CH}$  data are less structurally definitive for group 4 diene complexes. Thus,  ${}^{1}J_{CH_{a}} = 134$  Hz in 2a and  ${}^{1}J_{CH_a}$  137.8 (CH<sub>a</sub>H<sub>s</sub>), 134 (CH<sub>a</sub>CH<sub>3</sub>) Hz in 2b would at first appear rather small in magnitude for "sp<sup>2</sup>" hybridization; however, the diffraction results for 2a (vide infra) show the H<sub>a</sub>'s to be severely displaced from the diene plane. In contrast to these results,  ${}^{1}J_{CH_{s}} =$ 159.4 Hz in 2b is more consistent with sp<sup>2</sup> hybridization and is identical with the larger of the two geminal  ${}^{1}J_{CH}$ values (159, 149 Hz) in  $\pi$ -bound Cp<sub>2</sub>Zr(s-trans-1.3butadiene).<sup>5e</sup> However, note that  ${}^{1}J_{CH_{a}}$  and  ${}^{1}J_{CH_{s}}$  values of 129 and 152 Hz, respectively, are observed in the static (-75 °C) spectrum of the fluxional, formally metallacyclic Cp<sub>2</sub>Zr(CH<sub>2</sub>CMeCMeCH<sub>2</sub>)<sup>5c</sup> and that thorium metallacyclopentene parameters are similar.<sup>9</sup> The <sup>13</sup>C CPMAS spectrum of 2a is consistent with the solution-phase spectrum, arguing that the solid-state structure persists in solution.

X-ray structural analysis of 2a<sup>10</sup> (Figure 1) shows the 2.4-hexadiene ligand to be coordinated in a "prone"  $\pi$ -fashion.<sup>4,11</sup> The two Ti-C(terminal) diene distances (Ti-C17 = 2.187(6) and Ti-C20 = 2.176(7) Å) differ from



Figure 1. Crystal structure of (C5Me4SiMe2NtBu)Ti(prone-2,4-hexadiene) (2a). Selected bond distances (Å) and angles (deg) are as follows: Ti-C17 = 2.187(6), Ti-C18 = 2.298-(6), Ti-C19 = 2.288(6), Ti-C20 = 2.176(7), C17-C18 =1.402(9), C18-C19 = 1.404(9), C19-C20 = 1.391(9), Ti-N1 = 2.007(4), Si1 - N1 = 1.733(5), Si1 - C1 = 1.869(6), Ti - C1 = 1.869(6) $\begin{array}{l} C1=2.228(5),\ Ti-C2=2.304(6),\ Ti-C3=2.481(6),\ Ti-C4=2.483(6),\ Ti-C5=2.331(6);\ Cp(Cg)-Ti-N=109.8, \end{array}$ Cp(Cg)-C1-Si1 = 153.2, C17-Ti-C20 = 90.0(3), N1-Si1-C1 = 94.5(2). Thermal ellipsoids are drawn at the 35% probability level.

the two Ti-C(internal) diene distances (Ti-C18 =2.298(6) and Ti-C19 = 2.288(6) Å) by only 0.112 Å. This difference<sup>12</sup> ( $\Delta d = -0.11$  Å) is similar to that reported for the  $Zr(II) \pi$ -butadiene complex  $CpZr(\eta^3$ -allyl)(supinebutadiene) ( $\Delta d = -0.103$  Å). The C–C distances in the 2,4-hexadiene ligand of 2a (C17-C18 = 1.402(9), C18-C19 = 1.404(9), C19-C20 = 1.391(9) Å) also support the assignment of a predominantly  $\pi$ -bound diene ligand. This C-C bonding sequence is similar to that observed in typical  $M(CO)_3(\eta^4$ -diene) (M = Fe, Ru) structures<sup>9,13</sup> and is in sharp contrast to patterns observed in typical metallacyclopentenes, such as Cp2-Zr(CH<sub>2</sub>CMeCMeCH<sub>2</sub>).<sup>5c</sup> Another important 2,4-hexadiene feature in 2a concerns the coplanarity of atoms C17-C20. The two methyl substituents (C16 and C21) are displaced from the diene plane by only 0.032 (toward Ti) and -0.007 (away from Ti) Å, respectively. However, H34 and H37, which are the anti (H<sub>a</sub>) protons of C17 and C20, respectively, are grossly displaced from the C17-C20 plane, away from Ti, by  $\sim$ 0.41 and  $\sim$ 0.44 Å, respectively. This distortion likely affects the magnitude of  ${}^{1}J_{CH_{a}}$  (vide supra). The structural features of the constrained-geometry ligand also support a formal divalent Ti oxidation state assignment and reveal the

<sup>(8)</sup> The chemical shifts for Ha and Hm in Cp2Zr(s-cis-1,3-butadiene)4a.d and Cp\*TiCl(supine-isoprene)<sup>5a</sup> occur at  $\delta$  -0.70 and 4.85 ppm and  $\delta$ 1.23, 1.10, and 5.68 ppm, respectively.

<sup>(9)</sup> Smith, G. M.; Suzuki, H.; Sonnenberger, D. C.; Day, V. W.; Marks, T. J. Organometallics 1986, 5, 549.  ${}^{1}J_{CH}$  values for Cp'<sub>2</sub>Th( $\eta^{4}$ -C<sub>4</sub>H<sub>6</sub>), at low temperature: 131, 153 Hz.

<sup>(10)</sup> Crystal data for C21H37NSiTi: triclinic system with cell dimensions at -120 °C of a = 8.786(6) Å, b = 9.760(6) Å, c = 14.285(8) Å,  $\alpha$ solution  $A^{(1)}_{\alpha}$  = 88.46(5)°,  $\gamma = 66.18(5)°$ , and V = 1072(1)Å<sup>3</sup>. The space group is P1 (No. 2) with Z = 2 and  $D_{calcd} = 1.175$  g/cm<sup>3</sup>. The structure was solved by direct methods and refined by full-matrix least-squares techniques using 3604 reflections having  $I > 3.00\sigma(I)$  and resulting in R = 0.073 and  $\breve{R}_{\rm w} = 0.085$ .

<sup>(11)</sup> A "prone" diene is coordinated with the "cup" of the diene oriented away from the Cp ligand. A "supine" diene is coordinated with the "cup" of the diene oriented toward the Cp ligand.<sup>4</sup> (12)  $\Delta d = [(Ti-C17) + (Ti-C20)]/2 - [(Ti-C18) + (Ti-C18)]/2$ 

<sup>-</sup>C19)/2.

<sup>13)</sup> Cotton, F. A.; Day, V. W.; Frenz, B. A.; Hardcastle, K. I.; Troup, J. M. J. Am. Chem. Soc. 1973, 95, 4522 and references therein.

effects of linking the amide substituent to the cyclopentadienyl ring via the silane bridge. The Ti-N distance in **2a** is 2.007(4) Å, which is significantly longer than in typical Ti(IV) amide complexes.<sup>14ab</sup> In Ti(IV) constrained-geometry complexes, typical Ti-N distances of 1.895-1.957 Å are observed.<sup>14c-e</sup> The present Ti-N distance is more consistent with those in lower valent ( $\leq$ II) Ti amide complexes (Ti-N = 2.023-2.066 Å).<sup>15</sup> The N-Ti-Cp(Cg) bond angle contraction to 109.8° in **2a** is doubtless due to the silane bridge. The effect of constraining the amide substituent is also seen in the displacement of the Si from the plane of the cyclopentadienyl ring (Cp(Cg)-C1-Si = 153.2°) as well as a slight slipping of the ring toward the silane bridge, as evidenced by the dispersion in the Ti-C(ring) distances.

Simple replacement of  $R_1 = {}^tBu$  by Ph drastically alters the products of eq 1. Thus, 2,4-hexadiene yields a 70/30 mixture of 2c and 3c, while 1,3-pentadiene yields 55/45 2d and 3d. It was not possible to separate these mixtures by fractional crystallization. <sup>1</sup>H NMR data<sup>7c,d</sup> supplemented by 2-D NOESY experiments indicate that 2c and 2d have prone, predominantly  $\pi$ -diene character similar to **2a** and **2b**, while the parameters for minor isomers 3c and 3d<sup>7c,d</sup> are characteristic of structures with predominant metallacyclopentene character having the diene fragment in the supine orientation. Thus, in 2d, NOESY data reveal a close proximity of H<sub>m</sub> to the Cp methyl groups farthest from the Si bridge and H<sub>a</sub> to the Ph ortho protons; exactly the opposite relationship is observed in 3d. All attempts to observe  $2c \Rightarrow 3c$  and  $2d \Rightarrow 3d$  equilibration by variable-temperature DNMR/2-D EXSY or prolonged heating (displacement of the equilibrium) experiments have been unsuccessful, arguing that the 2c/3c, 2d/3d pairs are kinetic products of eq 1 related by a large kinetic barrier.<sup>16</sup> This relationship stands in marked contrast to more typical group 4 diene complexes, where structural interconversions are frequently facile.<sup>4,5</sup>

When activated with cocatalysts such as  $B(C_6F_5)_3$ , (HNMe<sub>2</sub>Ph)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], or MAO, complexes **2a** and **2b** are highly active olefin polymerization catalysts. Under typical conditions<sup>17</sup> with  $B(C_6F_5)_3$  as a cocatalyst, **2a** and **2b** effect the random copolymerization of 1-octeneethylene with activities of  $7.7 \times 10^6$  <sup>18a</sup> and  $6.8 \times 10^6$ g/(mol·h·atm),<sup>18b</sup> respectively. In contrast, **2d/3d** exhibits an activity of only  $0.3 \times 10^6$  g/(mol·h·atm)<sup>18c</sup> under the same conditions.

These results demonstrate that constrained-geometry ancillary ligands can stabilize Ti-diene coordination in both predominantly  $\pi$ -diene (formally Ti(II)) and predominantly metallacyclopentene (formally Ti(IV)) bonding geometries and that such complexes exhibit a variety of interesting structural and catalytic characteristics. Further exploratory studies of constrainedgeometry group 4 chemistry are in progress.

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**Supporting Information Available:** Text giving details of the X-ray study, tables of crystal data and refinement details, positional and thermal parameters, and bond distances and angles, and a fully labeled structure diagram for compound **2a** (15 pages). Ordering information is given on any current masthead page.

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<sup>(16)</sup> In contrast,  $R_1 = {}^{t}Bu$  complexes with internally substituted dienes (isoprene, 2,3-dimethylbutadiene) undergo rapid 2 - 3 interconversion, presumably via inversion<sup>5c</sup> of the diene/metallacyclic structures. (Devore, D. D.; Timmers, F. J. Unpublished observations). (17) In a typical polymerization, a 2 L Parr reactor was charged with 740 g of Isopar E solvent and 118 g of 1-octene. Hydrogen was added for molecular weight control by differential pressure expansion from a 75 L addition tank at 25 psi. The reactor was heated to 140 °C and saturated with ethylene at 500 psig. Then 2.0 µmol each of catalyst and cocatalyst (0.005 M in toluene) were premixed in the drybox; the solution was transferred to a catalyst addition tank and injected into the reactor. Polymerization conditions were maintained for 15 min with ethylene on demand. The resulting polymer solutions were removed from the reactor, and a phenol antioxidant (Irganox 1010) was added.

Polymers were recovered by removal of solvent in vacuo at 120 °C for 20 h. Yields of polymer were 131 g (2a), 116 g (2b), and 5.3 g (2d/3d). (18) (a)  $M_w/M_n = 2.19$ ;  $M_w = 77\ 000$ . (b)  $M_w/M_n = 2.40$ ;  $M_w = 89\ 000$ . (c)  $M_w/M_n = 4.90$ ;  $M_w = 116\ 000$ .