

Synthesis of tris(dicyclohexylamido) titanium and zirconium chloride and the structure of (c-Hex₂N)₃TiCl

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(Received 24 April 1996; accepted 26 June 1996)

Abstract—Reaction of MCl₄(THF)₂ (M = Ti and Zr) with excess LiNCy₂ in pentane affords crystalline (*c*-Hex₂N)₃MCl in greater than 70% yields. The products were characterized by ¹H, ¹³C, ¹H and ¹³C HETCOR NMR, and MS techniques. Crystalline (*c*-Hex₂N)₃TiCl was also characterized by a single-crystal X-ray structure. Trends in the structural dimensions of (R₂N)₃TiCl are noted. Copyright © 1996 Elsevier Science Ltd

Keywords: titanium; zirconium; amides; NMR.

Titanium and zirconium nitrides find uses as wearresistant coatings on machine tools [1], gold substitutes for decorative coatings [2], reflectance and hardness coatings for microelectronic devices [3], diffusion barriers in various semiconductor metallization schemes [4] and as ceramics with high thermal impact resistance [5]. Tris(dialkylamido) halides of these metals, $(R_2N)_3MX$, are of interest because of their potential as single-source MOCVD precursors to their corresponding nitride and carbonitride films, and also for their applications in important synthetic transformations. Thus, [(Me₃Si)₂N]₃TiF was recently studied for its ability to deposit TiN and TiCN films on silicon and steel substrates under N₂, H₂ and He [6]. Its analogue (Et₂N)₃TiCl is efficacious as a reagent in titanating allylmetal compounds [7,8], enolates [9], cyanomethyl lithium [10], benzylmagnesium bromide [10] and lithiated hydrazones [11] for use in chemoand stereoselective additions to carbonyl substrates [10]. Conversion of $(Et_2N)_3TiCl$ to $(Et_2N)_3TiMe$ allows the latter to be used for aminomethylation of aromatic aldehydes [10,12]. To our knowledge, however, no reports concerning the ring-substituted analogues $(c-\text{Hex}_2N)_3$ MCl (M = Ti and Zr) have been reported. In connection with our interest in tricyclic azatranes of group 4 [13] as precursors for MOCVD,

we report here the first synthesis and characterization of $(c-\text{Hex}_2N)_3\text{TiCl}(1)$ and $(c-\text{Hex}_2N)_3\text{ZrCl}(2)$, as well as the molecular and crystal structure of 1. Trends in the angles around titanium in $(R_2N)_3\text{TiCl}$ derivatives are observed and discussed.

EXPERIMENTAL

General procedures

All reactions were carried out under argon with strict exclusion of moisture using standard Schlenk or dry-box techniques [14]. Solvents were dried over, and distilled from, Na/benzophenone and stored prior to use over 4 Å molecules sieves under argon. Lithium dicyclohexylamide (97%) was purchased from Aldrich and was used as received. TiCl₄(THF)₂ and ZrCl₄(THF)₂ were synthesized according to literature procedures [15].

NMR spectra were recorded at 20°C on a Nicolet NT300 (¹H) or a Varian VXR300 spectrometer in C_6D_6 using the protio impurity of the solvent as an internal reference for ¹H spectra and the ¹³C resonance of C_6D_6 as a reference for the ¹³C NMR spectra. Twodimensional COSY 90 and HETCOR spectra were recorded on a Bruker DRX 400 spectrometer. Mass spectra were obtained on a Finnigan TSQ 700 instrument or a Kratos MS-50 spectrometer. Melting points (uncorrected) were determined with a Thomas–

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Hoover capillary apparatus. Elemental analyses were performed by Desert Analytics.

Tris(dicyclohexylamido)titanium chloride, 1

 $TiCl_4(THF)_2$ (1.10 g, 3.28 mmol) was added to a suspension of LiNCy₂ (2.95 g, 97%, 15.3 mmol) in pentane (90 cm³) at -78° C. The reaction mixture was warmed to room temperature, stirred for 17 h and then filtered through Celite. The residue was washed copiously with pentane. The filtrate and the washings were combined and concentrated to about 20 cm³. The solution was kept in a freezer to allow crystals to grow. The crystals were filtered off, washed with cold pentane $(4 \times 3 \text{ cm}^3)$ and dried in vacuo to give 1.47 g of product in 72% yield. M.p.: $> 148^{\circ}C$ (dec.). Found: C, 69.2; H, 10.7; N, 6.6. Calc. for C₃₆H₆₆ClN₃Ti: C, 69.3; H, 10.7; N, 6.7%. ¹H NMR (400 MHz): δ 4.06 [tt, 6 H, ${}^{3}JH_{a}H_{a} = 11.3$ Hz, ${}^{3}JH_{a}H_{e} = 2.9$ Hz, H(1_a)], 2.10 [apparent d, 12 H, ${}^{2}JH_{a}H_{e} + {}^{3}JH_{a}H_{e} + {}^{3}JH_{e}H_{e} = 11.7$ Hz, H(2_e)], 1.82 [apparent d, 12 H, ${}^{2}JH_{a}H_{e} + {}^{3}JH_{a}H_{e} + {}^{3}JH_{e}H_{e} = 12.7$ Hz, $H(3_{e})],$ 1.66 [apparent qd, 12 H. ${}^{2}JH_{a}H_{e} + {}^{3}JH(1_{a})H(2_{a}) + {}^{3}JH(2_{a})H(3_{a}) = 12.3$ Hz, ${}^{3}JH(2_{a})H(3_{e}) = 3.0$ Hz, $H(2_{a})$], 1.60 [apparent d, 6 H, ${}^{2}J_{a}H_{e} + {}^{3}JH_{a}H_{e} + {}^{3}JH_{e}H_{e} = 13.5$ Hz, H(4_e)], 1.38 [apparent qt, 12 H, ${}^{2}JH_{a}H_{e} + {}^{3}JH(2_{a})H(3_{a}) + 3JH(3_{a})$ $H(4_a) = 13.0 \text{ Hz}, {}^{3}JH(2_e)H(3_a) + {}^{3}JH(3_a)H(4_e) = 3.1$ Hz, $H(3_{a})],$ 1.15 [apparent H, qt, 6 $2JH_{a}H_{e} + {}^{3}JH(3_{a})H(4_{a}) = 13.0$ Hz, ${}^{3}JH(3_{e})H(4_{a}) =$ 3.8 Hz, H(4_a)]. ¹³C{¹H} NMR (75.43 MHz, C₆D₆): δ 62.28 (C(1)), 36.60 (C(2)), 27.46 (C(3)), 26.28 (C(4)). For proton and carbon subscript labels for 1 (and 2) see Fig. 1 in Results and Discussion. MS(EI) m/z [ion (M represents the most intense peak in a group of peaks due to the isotope distribution), relative intensity]: 623 (M⁺, 7.7), 586 (M-Cl-2H⁺, 98), 541 $(M - C_6 H_{10}^+, 4.2), 442 [M - HN(c-Hex)_2^+, 100], 357$ $[M - HN(c - Hex)_2 - HCy - H^+, 17.2], 181$ [HN(c-Hex)₂⁺, 11.7]. CIMS (NH₃) m/z (ion, relative intensity): 624 $(M + H^+, 3.2),$ 182 [HN(c- $Hex)_2 + H^+$, 100], 138 (35.9).

Tris(dicyclohexylamido)zirconium chloride, 2

The synthetic procedure for 2 was the same as that for 1 except that ZrCl₄(THF)₂ was used instead of TiCl₄(THF)₂. Yield: 73%. Found: C, 65.2; H, 10.4; N, 6.7. Calc. for C₃₆H₆₆ClN₃Zr: C, 64.8; H, 10.0; N, 6.3%. ¹H NMR (400 MHz): δ 3.32 [tt, 6 H, ${}^{3}JH_{a}H_{a} = 11.3$ Hz, ${}^{3}JH_{a}H_{e} = 3.2$ Hz, H(1_a)], 2.03 [apparent d, 12 H, ${}^{2}JH_{a}H_{e} + {}^{3}JH_{a}H_{e} + {}^{3}JH_{c}H_{e} = 11.7$ d, Hz, $H(2_{e})],$ 1.81 [apparent 12 H, ${}^{2}JH_{a}H_{e} + {}^{3}JH_{a}H_{e} + {}^{3}JH_{e}H_{e} = 13.0$ Hz, H(3_e)], 1.66 [apparent qd, 12 H, ${}^{2}JH_{a}H_{e} + {}^{3}JH(1_{a})H(2_{a}) +$ ${}^{3}JH(2_{a})H(3_{a}) = 12.3 \text{ Hz}, {}^{3}JH(2_{a})H(3_{e}) = 3.0 \text{ Hz}, H(2_{a})], 1.59 \text{ [apparent d, 6 H, } {}^{2}JH_{a}H_{e} + 1.59 \text{ [apparent d, 6 H, } {}^{2}JH$ ${}^{3}JH_{a}H_{e} + {}^{3}JH_{e}H_{e} = 13.5 \text{ Hz}, \text{ H}(4_{e}) \text{] } 1.38 \text{ [apparent qt,}$ 12 H, ${}^{2}JH_{a}H_{c} + {}^{3}JH(2_{a})H(3_{a}) + {}^{3}JH(3_{a})H(4_{a}) = 13.0$

Hz, ${}^{3}JH(2_{e})H(3_{a}) + {}^{3}JH(3_{a})H(4_{e}) = 3.1$ Hz, $H(3_{a})]$, 1.13 [apparent qt, 6 H, ${}^{2}JH_{a}H_{e} + {}^{3}JH_{a}H_{a} = 13.0$ Hz, ${}^{3}JH_{a}H_{e} = 3.8$ Hz, $H(4_{a})]$. ${}^{13}C{}^{1}H{}$ NMR (75.43 MHz, $C_{6}D_{6}$): δ 57.21 (C(1)), 37.42 (C(2)), 27.16 (C(3)), 26.06 (C(4)). MS (EI) m/z [ion (M represents the most intense peak in a group of peaks due to the isotope distribution), relative intensity]: 665 (M⁺, 7.5), 582 (M - C_{6}H_{11}^{+}, 12.0), 484 [M - HN(c-Hex)_{2}^{+}, 44.9], 401 [M - HN(c-Hex)_{2} - C_{6}H_{11}^{+}, 14.9], 317 [M - HN(c-Hex)_{2}, 16.2], 138 (51.0), 83 (C_{6}H_{11}^{+}, 100).

Crystal structure determination of 1

A yellow crystal of 1 with dimensions of $0.2 \times 0.1 \times 0.05 \text{ mm}^3$ was mounted on a Siemens P4RA diffractometer for data collection at $213(2) \pm 1$ K. The unit-cell constants were determined from reflections found from a rotation photograph. Twenty-five reflections in the θ range $15-25^\circ$ were used to determine precise cell constants. Lorentz and polarization corrections were applied to the data, as were non-linear corrections based on the decay in the standard reflections. A semi-empirical absorption correction based on azimuthal scans was applied.

The space group P1 was chosen based on systematic absences and intensity statistics. This assumption proved to be correct as determined by a successful directmethods solution [16] and subsequent refinement. All non-hydrogen atoms were placed directly from the E map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogens were treated as riding atoms with individual isotropic displacement parameters. Crystal data and refinement parameters are summarized in Table 1. Selected bond distances and angles are listed in Table 2. There was a significant amount of disorder in the final structure. Some of the atoms associated with the cyclohexyl rings exhibit a high degree of thermal motion. Atoms C(26) and C(29) were refined with a split occupancy of about 51-49% for each site. Refinement calculations were performed on a Digital Equipment Micro VAX 3100 computer using SHELXTL-Plus [16] and SHELXL-93 [17,18].

RESULTS AND DISCUSSION

The reaction of $MCl_4(THF)_2$ (M = Ti and Zr) with $LiNCy_2$ in pentane led to the formation of the title compounds in yields over 70%:

$$MCl_{4}(THF)_{2} + 3LiN(c-Hex)_{2} \xrightarrow{\text{pentane}} (c-Hex_{2}N)_{3}MCl + 3LiCl + 2THF.$$
(1)

Similar reactions were utilized to prepare $(R_2N)_3MCl$ (R = Me [19], Et [19], and SiMe₃ [20] using MCl₄ instead of MCl₄(THF)₂.

The molecular structure of $(c-\text{Hex}_2N)_3$ TiCl shown in Fig. 1 displays a distorted tetrahedral titanium Synthesis of tris(dicyclohexylamido) titanium and zirconium chloride

Table 1. Crystallographic data for 1

Formula	C36H66N3CITi
Formula weight	624.27
Colour	Yellow
Crystal size (mm)	$0.2 \times 0.1 \times 0.05$
Crystal system	Triclinic
Space group	<i>P</i> 1
a (Å)	9.606(5)
<i>b</i> (Å)	10.292(6)
c (Å)	20.258(11)
α()	98.76(5)
β()	90.27(4)
7 (°)	113.13(4)
$V(\text{\AA}^3)$	1815.7(17)
Z	2
d_{cate} (g cm ⁻³)	1.142
$\mu ({\rm mm^{-1}})$	2.857
$\hat{\lambda}$ (Cu- K_{α}) (Å)	1.54178
Weighting scheme, w^{-1}	$\sigma(F_0^2) + (0.0800P)^2$
	where $P = (F_0^2 + 2F_c^2)/3$
Final R indices $[I \ge 2\sigma(I)]$	$R_1^{\ a} = 0.0828, \ wR_2^{\ b} = 0.1949$
R indices (all data)	$R_1^{a} = 0.1666, w R_2^{b} = 0.2273$
GoF, observed and all	1.134, 0.831
data	

 ${}^{"}R_{1} = \Sigma ||F_{0}| - |F_{c}||\Sigma |F_{0}|.$ ${}^{h}wR_{2} = [\Sigma [w(F_{0}^{2} - F_{c}^{2})^{2}]/\Sigma [w(F_{0}^{2})^{2}]]^{0.5} \text{ where}$ $w = 1/[\sigma^{2}(F_{0}^{2}) + (aP)^{2} + bP + d + e\sin\theta].$ ${}^{*}\text{GoF} = [\Sigma [w(F_{0}^{2} - F_{c}^{2})^{2}]/(n-p)]^{0.5}.$

geometry with a propeller-like arrangement of the *c*-Hex₂N groups. There are two independent molecules in the unit cell. The geometries around each of the nitrogens is trigonal planar with average angle sums of $359.7(6)^{\circ}$. However, each of the angles around any given nitrogen is quite different (Table 2) implying a certain amount of flexibility which allows the rings to pack efficiently into the structure. Thus, the angles involving the carbon proximal to the chlorine are 107.5(4), 108.5(4) and $122.8(7)^{\circ}$ for C(1)N(1)Ti, C(13)N(2)Ti and C(25)N(3)Ti, respectively, while those containing the carbon distal to the chlorine are



Fig. 1. Drawing of 1 with the atom-labelling scheme. Ellipsoids are drawn at the 50% probability level.

123.5(5), 131.0(6) and 133.6(6)° for C(31)N(3)Ti, C(19)N(2)Ti and C(7)N(1)Ti, respectively. Interestingly, the C—C—C angle sums of the three Cy rings proximal to the chlorine (665–668°) and one of the distal Cy rings [C(31)—C(36) 665°] are not far from the value expected for an unstrained cyclohexane ring (654.0°). However, the other two distal C₆H₁₁ rings have angle sums (719°) close to that expected for a planar C₆ ring. Indeed the C(7)–C(12) and the C(19)–C(24) rings are each planar within 0.031 and 0.024 Å, respectively. This structural feature suggests that the distal rings experience substantial steric compression.

Although the overall geometries of $(R_2N)_3$ TiCl for R = Me [19], Et [19], *c*-Hex and SiMe₃ [20] are similar, there are significant differences in the dimensions. Table 3 summarizes some of the structural parameters for these complexes. For compound 1, the average CITiN and NTiN angles are almost the same. However, it can be seen that the average of the CITiN angles decreases in the order R = Me > Et > c-Hex > SiMe₃, with a concomitant increase of the average NTiN angles (Fig. 2). Since the bulk of the R

Ti—N(1)	1.879(6)	N(2)—C(13)	1.472(8)	
Ti—N(3)	1.878(6)	N(2)—C(19)	1.485(9)	
Ti-N(2)	1.890(6)	N(3)—C(25)	1.436(10)	
N(1) - C(7)	1.458(9)	N(3)C(31)	1.485(9)	
N(1) - C(1)	1.489(9)			
N(1)—Ti—N(3)	107.9(3)	C(1)-N(1)-Ti	107.5(4)	
N(1)— Ti — $N(2)$	110.1(3)	C(13) - N(2) - C(19)	120.0(7)	
N(3) - Ti - N(2)	110.1(3)	C(13)—N(2)—Ti	108.5(4)	
N(1)—Ti—Cl	110.0(2)	C(19)—N(2)—Ti	131.0(6)	
N(3)—Ti—Cl	110.9(2)	C(25) - N(3) - C(31)	113.5(8)	
N(2)—Ti—Cl	107.8(2)	C(25)—N(3)—Ti	122.8(7)	
C(7) - N(1) - C(1)	118.8(7)	C(31)—N(3)—Ti	123.5(5)	
C(7)—N(1)—Ti	133.6(6)			

Table 2. Selected bond lengths (Å) and angles (') for 1

R	ClTiN ^a (°)	NTiN ^a (°)	XNTi(proximal)	XNTi(distal)	Cl—Ti (Å)	Ti—N (Å)"	Ref.
Me	113.3(2)	105.4(2)	114.7(4) ^b	131.1(3) ^b	2.300(3)	1.866(4)	[19]
Et	111.4(1)	107.5(2)	$112.6(3)^{a,b}$	$132.7(4)^{a,b}$	2.300(2)	1.861(4)	[19]
c-Hex (1)	109.6(2)	109.4(2)	$112.9(5)^{a,b}$	129.4(6) ^{a,b}	2.309(3)	1.882(6)	This work
SiMe ₃	104.1(3)	114.3(3)	116.0(5) ^c	127.2(6) ^c	2.259(6)	1.940(10)	[20]

Table 3. Selected structural parameters for (R₂N)₃TiCl

"Average value.

 ${}^{b}\mathbf{X} = \mathbf{C}.$

 $^{c}X = Si.$

groups increases in the order Me < Et < c-Hex $< SiMe_3$, it is reasonable to assume that increasingly bulky R groups enlarge the NTiN angles and concomitantly shrink the CITiN angles. Thus, the trends displayed in Fig. 2 seem to be dominated by steric rather than electronic effects of the R groups.

The average C(or Si)NTi angles proximal to Cl are smaller than those distal to Cl (Table 3). Although steric compression among the distal SiMe₃ groups in $[(Me_3Si)_2N]_3$ TiCl would give rise to the largest average NTiN angles compared with the corresponding angles in the remaining $(R_2N)_3$ TiCl compounds, the distal SiNTi angle in $[(Me_3Si)_2N]_3$ TiCl is smaller than the distal CNTi angles for the $(R_2N)_3$ TiCl complexes. This suggests that by opening the NTiN angle sufficiently, the distal carbons (or silicon) move radially outwards to locations that permit the distal C (or Si)NTi angle to decrease. The Cl—Ti bond lengths are comparable for complexes with R = Me, Et and *c*-Hex and the same is true for Ti—N bond distances. However, the Cl—Ti bond length [2.259(6) Å] in [(Me₃Si)₂N]₃TiCl is smaller than those in the (R₂N)₃TiCl complexes, while the average TiN distance in the former is longer than in the latter species. Although the more sterically demanding SiMe₃ groups may be expected to favour a longer TiN bond, it is not clear on steric grounds why the Cl—Ti bond in [(Me₃Si)₂N]₃TiCl should be shorter, since the average ClTiN angle (which is the smallest among these complexes) is expected sterically to elongate the ClTi bond in [(Me₃Si)₂N]₃TiCl. If however, N \rightarrow Si π bonding is sufficiently strong, the Ti—N bonds are expected to lengthen and the Ti—Cl bond could be expected to shorten *via* a compensatory Cl \rightarrow Ti π interaction.

Compounds 1 and 2 exhibited a group of peaks at m/z 623 and 665, respectively, in their EI mass spectra, which exactly matched the theoretical isotopic pattern for the parent compound, confirming the volatility of this type of compound. Several groups of peaks corresponding to the removal of cyclohexyl, dicyclohexylamine and a combination of both cyclohexyl and dicyclohexylamine from the parent species were



Fig. 2. Plot of average NTiN angle against CITiN angle in $(R_2N)_3$ TiCl. The dots represent values based on the geometrical relationship for a trigonal pyramid $\cos \alpha = -0.500 \sin^2 \beta + \cos^2 \beta$ where α and β are the NTiN and CITiN angles, respectively. The squares in ascending order of average CITiN angle and descending average NTiN angle represent $R = SiMe_3$, c-Hex, Et, Me in $(R_2N)_3$ TiCl. The crosses on the squares are error bars.



Fig. 3. ¹H NMR spectrum of 2 in C₆D₆ and its ¹H¹H COSY 90 2D NMR spectrum. For labels see Results and Discussion.

also observed. From the NH₃/CI mass spectrum of the titanium complex, however, only a group of peaks at m/z 624 with low intensity for $(M + H^+)$ and a base peak at m/z 182 for $[HN(c-Hex)_2 + H^+]$ were found, probably owing to reactions of the complex with NH₃.

The ¹H NMR spectra of 1 and 2 displayed similar patterns, as did the ${}^{13}C{}^{1}H$ NMR spectra, indicating

the isostructural nature of these complexes. Although the ¹H NMR spectra in benzene- d_6 exhibited seven signals with different multiplicities (Fig. 3), the ¹³C{¹H} spectra showed only four singlets with relative intensities of approximately 1:2:2:1, indicative of the relative numbers of carbon atoms for each cyclohexyl ring. Since the single crystal structure of 1

	1	2		
$\delta(^{1}\text{H})$ (ppm), assgnt ^a	$\delta(^{13}C)$ (ppm), assgnt ^a	$\delta(^{1}\text{H})$ (ppm), assgnt ^a	$\delta(^{13}C)$ (ppm), assgnt ^a	
4.06, H(1 _a)	62.28, C(1)	$3.32, H(1_a)$	57.21, C(1)	
$2.10, H(2_e); 1.66, H(2_a)$	36.60, C(2)	$2.03, H(2_e); 1.66, H(2_a)$	37.42, C(2)	
$1.82, H(3_{e}); 1.38, H(3_{a})$	27.46, C(3)	$1.81, H(3_e); 1.38, H(3_a)$	27.16, C(3)	
$1.60, H(4_e); 1.15, H(4_a)$	26.28, C(4)	$1.59, H(4_e); 1.13, H(4_a)$	26.06, C(4)	

Table 4. Correlation of ¹H and ¹³C NMR chemical shifts for 1 and 2

"For atom-labelling scheme, see Fig. 1.

revealed a tetrahedral coordination environment about the metal centre, it is reasonable to suggest that both 1 and 2 have virtual C_{3r} symmetry in solution, as was the case for $(Me_2N)_3$ TiCl [19], $(Et_2N)_3$ TiCl [19] and [(Me₃Si)₂N)₃TiCl] [20]. This symmetry accounts for the four carbon resonances observed for 1 and 2 assuming rapid rotation on the NMR time-scale of the six-membered rings around the M-N and N-Cl bonds. The ¹³C chemical shifts obtained at lower field (75.4 MHz) for 1 and 2 are identical to those obtained at higher field (100.6 MHz). Similar phenomena were observed in their 'H NMR spectra, except that those obtained at lower field (300 MHz) exhibited much lower resolution than at high field (400 MHz). A depiction for the assignment of the ¹³C and ¹H NMR spectra is shown below with a indicating the axial protons and e representing the equatorial protons. The assignments of the signals in the ¹H and ¹³C{¹H}



NMR spectra of 1 and 2 are based on NMR integrations, couplings in the 'H NMR spectra and on ¹H⁻¹³C hetero correlated NMR spectra. The crosspeaks in the ¹H-¹³C HETCOR 2D NMR spectra of 1 and 2 give the connectivities between the proton and the carbon signals (Table 4). Each of the three carbon resonances at higher field corresponds to two (axial and equatorial) proton signals, while the one at lower field is seen to exhibit one proton resonance which can be assigned to the axial proton in the methine group. This assignment was further confirmed by its coupling pattern of a triplet of triplets, consistent with couplings to the neighbouring two axial and two equatorial methylene protons, respectively. Because axialaxial coupling constants are larger than the axialequatorial and the equatorial-equatorial couplings in general [21], the 11.3 Hz coupling was assigned to the $H(l_a)H(2_a)$ interaction while the 2.9 and 3.0 Hz

couplings were assigned to the $H(1_a)H(2_e)$ couplings for the Ti and Zr complex, respectively. From the ¹H-¹H 2D COSY 90 NMR spectrum (Fig. 3) it can be seen that the $H(1_{a})$ proton couples to only two proton signals, which are likely to be $H(2_a)$ and $H(2_e)$. Each of the $H(2_a)$ and $H(2_c)$ signals should be a doublet of doublets of doublets of doublets, owing to the geminal and neighbouring proton couplings. However, simpler coupling patterns with an apparent doublet and an apparent doublet of quartets for these protons were observed, probably owing to accidental overlap. Based on the above discussion, the peaks located at δ 1.66 were assigned to the $H(2_a)$ resonance, for which relatively large axial-axial couplings are expected, while those at δ 2.10 and 2.03 were assigned to the $H(2_e)$ peaks for 1 and 2, respectively. From the coupling relationship to $H(2_a)$ and $H(2_e)$ in the COSY 90 NMR spectrum (Fig. 3) the H(3) protons were easily recognized. For reasons analogous to the foregoing, the peaks at δ 1.38 were attributed to the H(3_a) resonances which exhibit an apparent doublet of quartets pattern, while those at δ 1.81 were assigned to the H(3_e) resonances, which display an apparent doublet. The signals for $H(4_a)$ and $H(4_e)$ were similarly assigned.

It is noteworthy that the chemical shifts in the titanium compound are more downfield in general than the zirconium derivative for both the ¹H and ¹³C NMR peaks, except for the $H(2_a)$, $H(3_a)$ and C(2) resonances (Table 4). This may be associated with the differences in metal electronegativities [22]. The same trend was observed for azametallatrane analogues containing these metals [13b].

Acknowledgement—The authors thank the National Science Foundation for grant support of this research.

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