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Amido Complexes of (Cyclopentadienyl)dichlorotitanium(IV): Ti–N Multiple-Bond Character

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Reaction of $(RC_5H_4)TiCl_3$ (**1a**, R = H; **1b**, R = CH_3) with Li{NH(*t*-Bu)} in THF affords $(RC_5H_4)TiCl_2$\{NH(*t*-Bu)\} (**2a**, R = H; **2b**, R = CH_3) in 80–90% isolated yields. The moisture-sensitive red-orange compounds can be crystallized from CH_2Cl_2/hexane mixtures. The X-ray structures for the two compounds were determined and found to be similar. Multiple-bond character in the Ti–N bond is suggested by short Ti–N distances, 1.879 (3) Å (**2a**) and 1.871 (5) Å (**2b**). Data were collected on an Enraf-Nonius CAD-4 diffractometer (λ(Mo Kα) = 0.710 73 Å) in the ω–2θ mode to a maximum 2θ of 52°. Crystal data for **2a**: $C_9H_{15}Cl_2NTi$, M_r = 256.03, monoclinic, $P2_1/m$, a = 6.149 (1) Å, b = 10.888 (3) Å, c = 9.004 (3) Å, β = 100.44 (2)°, V = 593 Å^3, D_{calcd} = 1.43 g cm^{-3}, Z = 2. A total of 1352 reflections were collected, of which 1239 were unique, and 836 reflections with $F_o^2 > 3.0\sigma(F_o)^2$ were used in the refinement, which gave R = 0.036 and R_w = 0.045. Crystal data for **2b**: $C_{10}H_{17}Cl_2NTi$, M_r = 270.06, monoclinic, $P2_1/c$, a = 6.198 (2) Å, b = 11.660 (2) Å, c = 17.748 (4) Å, β = 98.73 (2)°, V = 1268 Å^3, D_{calcd} = 1.41 g cm^{-3}, Z = 4. A total of 2865 reflections were collected, of which 2620 were unique, and 990 reflections with $F_o^2 > 3.0\sigma(F_o)^2$ were used in the refinement, which gave R = 0.048 and R_w = 0.051. A variable-temperature NMR study was conducted to further explore the π-character of the Ti–N bond.

Introduction

The electronic and steric properties of amido (NR_2) and imido (NR) ligands give rise to a rich chemistry in their transition metal complexes, both from a structural point of view and in their capacity as widely used reagents.[1,2] Additionally, metal–nitrogen bonding has been proposed as a key component in intermediates for the catalytic preparation of acrylonitrile, the hydrogenation of nitriles, and the fixation and reduction of molecular nitrogen.[3] Particularly for the early transition metals dπ–pπ interactions between metal and nitrogen can occur when available nitrogen lone pairs interact with empty d orbitals. Structural and spectroscopic studies have been undertaken to determine M–N multiple-bond character in amido complexes. An important aspect of structural studies is the ability to reveal the presence of M–N multiple bonding, as seen through short M–N distances and trigonal planar N atoms. Some caution is warranted in interpreting structural features because M–N distances can be sensitive to metal oxidation state[4] and the electronegativity difference between M and N may result in significant polar character in the M–N bond. Photoelectron spectroscopy of transition metal amides indicates some degree of N→M dπ–pπ-bonding, and the results have been found to agree with the structural data.[5] For several M–NR_2 complexes, variable-temperature NMR spectroscopy has been useful in disclosing the presence of rotational barriers about M–N bonds, which may be indicative of π-bonding. Chisholm and co-workers[6] have extensively investigated the 1,2-$M_2(X)_2(NMe_2)_4$ compounds, where M = Mo or W and X = alkyl, amido, aryl, halo, or phosphido, and found measurable activation barriers (11–24 kcal/mol) for rotation about the M–N bond. Electronic factors have been suggested as major contributors to these barriers because of the strong π-donor ability of dialkylamido ligands. Complexes containing the disilylamido ligand are known for most of the metals, but in contrast to the dialkylamido ligand, this ligand is considered to be a poor π-donor.[7,8] The M(X)\{N(SiMe$_3$)$_2$\}$_3$ compounds, where M = Ti, Zr, or Hf and X = Cl or Me[4,9] and where M = Nb and X = O,[10] have restricted rotation about the M–N bond, as observed in variable-temperature NMR studies. In the disilylamido complexes, steric congestion around the metal centers is considered to be a major contributor to the rotational barrier.

In this paper, we report the X-ray structure determination of the compounds $(RC_5H_4)TiCl_2$\{NH(*t*-Bu)\} (**2a**, R = H; **2b**, R = CH_3). Short Ti–N distances and planar nitrogen atoms indicate that the Ti–N bond contains π-bond character. A variable-temperature NMR study was conducted to further explore this possibility.

Experimental Section

Chemicals and Instrumentations. All reagents were newly purchased from commercial sources and used without further purification except where noted. *tert*-Butylamine, a 1.6 M solution of *n*-BuLi in hexane, cyclopentadiene dimer, methylcyclopentadiene dimer, sodium metal, and titanium tetrachloride were obtained from Aldrich. Hexane, THF, CH_2Cl_2, 12 N HCl, and $MgSO_4$ were procured from Fisher. $(C_5H_5)_2TiCl_2$ was purchased from Johnson Matthey Inc. $(CH_3C_5H_4)_2TiCl_2$,[11] $(C_5H_5)TiCl_3$, and $(CH_3C_5H_4)TiCl_3$[12] were prepared by literature methods. Hexane and THF were purified by distillation from NaK alloy, and CH_2Cl_2 was purified by distillation from P_2O_5. Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected. ^1H, ^{13}C, and $^{13}C\{^1H\}$ NMR spectra were obtained using a Varian VXR-400 FT-NMR spectrometer, and FT-IR spectra were recorded on a Nicolet

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(1) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, England, 1980.

(2) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 2, Chapter 13.4.

(3) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (b) Pandey, O. P.; Sengupta, S. K. *J. Sci. Ind. Res.* **1989**, *48*, 43.

(4) Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

(5) (a) Gibbins, S. G.; Lappert, M. F.; Pedley, J. B.; Sharp, G. J. *J. Chem. Soc., Dalton Trans.* **1975**, *72*. (b) Andersen, R. A.; Beach, D. B.; Jolly, W. L. *Inorg. Chem.* **1985**, *24*, 4741.

(6) (a) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356. (b) Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 905. (c) Chisholm, M. H. *Acc. Chem. Res.* **1990**, *23*, 419 and references therein.

(7) Green, J. C.; Payne, M.; Seddon, E. A.; Andersen, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 887.

(8) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273.

(9) Bradley, D. C.; Chudzynska, H.; Backer-Dirks, J. D. J.; Hursthouse, M. B.; Ibraham, A. A.; Motevalli, M.; Sullivan, A. C. *Polyhedron* **1990**, *9*, 1423 and references therein.

(10) Hubert-Pfalzgraf, L. G.; Tsunoda, M.; Le Borgne, G. *J. Chem. Soc., Dalton Trans.* **1988**, 533.

(11) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 4281.

(12) Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 4744.

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5 DX FT-IR spectrophotometer. CHN analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer.

Syntheses. The procedures used to prepare the compounds (RC_5H_4)-$TiCl_2\{NH(t\text{-Bu})]$ (**2a**, R = H; **2b**, R = CH_3) are similar in execution, isolation, and yield. A detailed description for only one is given.

Preparation of $(C_5H_5)TiCl_2\{NH(t\text{-Bu})\}$ (2a). Under an inert atmosphere 0.53 mL (5.0 mmol) of $NH_2(t\text{-Bu})$ was added dropwise to a solution of 3.2 mL of *n*-BuLi (1.6 M solution in hexane, 5.0 mmol) in THF (75 mL) at −80 °C. After 30 min the dry ice–acetone bath was removed and stirring continued at room temperature for 1 h. The resultant pale yellow solution was added to 360 mg (1.6 mmol) of $(C_5H_5)TiCl_3$ in 75 mL of THF at −80 °C. After 1 h the dry ice–acetone bath was removed and the resultant dark orange solution was stirred for 24 h at room temperature. Volatiles were evaporated under vacuum, the residue was extracted with a mixture of 20 mL of CH_2Cl_2 and 40 mL of hexanes, and the extract was filtered through a bed of Celite. The orange filtrate was concentrated to half-volume and stored at −30 °C for 72 h, which gave 260 mg of **2a** as orange-red crystals on filtration. Repeating this procedure, by further evaporating the filtrate to half-volume and cooling, gave an additional 100 mg of **2a**. The two crops of well-formed orange-red single crystals of **2a** were combined: 360 mg (1.4 mmol, 83%).

Data for 2a: mp 139–143 °C dec; CHN analysis; ^1H NMR ($CDCl_3$, 21 °C) δ 10.6 (br s, 1 H, NH), 6.67 (s 5 H, C_5H_5), 1.40 (s, 9 H, CH_3); ^1H NMR (CD_2Cl_2, −90 °C) δ 11.2 (br s, 1 H, NH), 6.69 (s, 5 H, C_5H_5), 1.32 (s, 9 H, CH_3); ^1H NMR (C_6D_6, 21 °C) δ 10.1 (br s, 1 H, NH), 5.94 (s, 5 H, C_5H_5), 1.31 (s, 9 H, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 21 °C) δ 117.7 (C_5H_5), 63.2 ($NC(CH_3)_3$), 31.4 ($NC(CH_3)_3$); IR (Nujol mull) 3293 cm^{-1} assigned to N–H stretch.

Data for $(CH_3C_5H_4)TiCl_2\{NH(t\text{-Bu})\}$ (2b): mp 123–124 °C; CHN analysis; ^1H NMR ($CDCl_3$, 21 °C) δ 10.6 (br s, 1 H, NH), 6.57 (dd, 2 H, $^3J_{C-H}$ = 2.7 Hz, C_5H_4), 6.40 (dd, 2 H, $^3J_{C-H}$ = 2.5 Hz, C_5H_4), 2.35 (s, 3 H, $C_5H_4CH_3$), 1.39 (s, 9 H, $NC(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 21 °C) δ 133.0 (s, $C_5H_4CH_3$), 118.7 (d, $^1J_{C-H}$ = 180 Hz, $C_5H_4CH_3$), 117.4 (d, $^1J_{C-H}$ = 170 Hz, $C_5H_4CH_3$), 63.6 (s, $NC(CH_3)_3$), 31.6 (q, $^1J_{C-H}$ = 130 Hz, $NC(CH_3)_3$), 16.7 (q, $^1J_{C-H}$ = 130 Hz, $C_5H_4CH_3$); IR (Nujol mull) 3297 cm^{-1} assigned to N–H stretch.

Collection and Reduction of X-ray Data. Single crystals selected for data collection were mounted with a trace of silicone grease in a glass capillary. X-ray diffraction data were collected with an Enraf-Nonius CAD-4 diffractometer (graphite monochromated, $\lambda(\mathrm{Mo}\ K\alpha) = 0.710\,73$ Å) in the ω–2θ mode. Data were collected to a maximum 2θ of 52°. The unit cell dimensions and their standard deviations were derived from a least-squares fit of the setting angles of 25 centered reflections in the ranges $9 < \theta < 16°$ (for **2a**) and $8 < \theta < 12°$ (for **2b**). The intensities of three standard reflections were measured every 50 min, indicating a total loss of intensity of 47.4% in **2a** and 6.7% in **2b**, respectively. Anisotropic decay corrections were applied with correction factors on I ranging from 0.988 to 1.771 (for **2a**) and 0.965 to 1.155 (for **2b**). The raw intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction (ψ-scan) was applied to the data set of **2b** (from 0.858 to 0.995 on I). Intensities of equivalent reflections were averaged; the agreement factors based on I are 1.8% (for **2a**) and 2.8% (for **2b**). For **2a**, a total of 1352 reflections (2865 for **2b**) were measured, of which 1239 were unique (2620 for **2b**), and 836 reflections with $F_o^2 > 3.0\sigma(F_o)^2$ (990 for **2b**) were used in the calculations.

Solution and Refinement of the Structures. All calculations were performed on a VAX11/750 computer using SDP.[13] In the case of **2a**, the observed systematic absences were consistent with the monoclinic space groups $P2_1$ and $P2_1/m$. The distribution of the normalized structure factors indicated the centrosymmetric space group. The successful structure solution and refinement confirmed this choice. In the case of **2b**, the space group could be unambiguously determined by systematic absences to be $P2_1/c$. Starting models for both structures were provided by direct methods. In the structure of **2a**, this starting model was further developed to a final structure model with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms by repeated least-squares refinements followed by difference Fourier syntheses. At this point, it seemed sensible to fix the hydrogen atom that is bonded to the nitrogen atom on its original position.[14] The positions of all other hydrogen atoms could be refined successfully. The remaining non-hydrogen atoms in the structure of **2b** were located from difference Fourier maps computed after least-squares refinements and anisotropically refined in the following calculations. The methyl hydrogen atoms of the methylcyclopentadienyl ring were calculated on idealized positions and included in the refinement as riding atoms with fixed isotropic thermal parameters, U(H), 1.3 times the equivalent isotropic U value of their bonding atom. All other hydrogen atoms could be located from difference Fourier maps. The hydrogen atom bonded to the nitrogen atom was fixed on its original position with U(H) equal to 1.3 times the equivalent isotropic U value of the nitrogen atom;[15] all other hydrogen parameters could be refined successfully. The final full-matrix least-squares refinement cycles included 98 (for **2a**) and 179 (for **2b**) variable parameters and converged with $R = \sum||F_o| - |F_c||/\sum|F_o| = 3.6\%$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 4.5\%$ for **2a** and $R = 4.8\%$ and $R_w = 5.1\%$ for **2b**. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o)^2$. Atomic scattering factors for spherical neutral free (non-H atoms) or bonded (H) atoms as well as anomalous scattering contributions were taken from standard literature.[16] Further details relevant to the data collection and structure refinements are collected in Table I, final positional parameters with standard deviations are provided in Table II, and selected distances and angles are reported in Table III.

Table I. Crystallographic Data for $(C_5H_5)TiCl_2\{NH(t\text{-Bu})\}$ and $(CH_3C_5H_4)TiCl_2\{NH(t\text{-Bu})\}$

	$(C_5H_5)TiCl_2\{NH(t\text{-Bu})\}$	$(CH_3C_5H_4)TiCl_2\{NH(t\text{-Bu})\}$
formula	$C_9H_{15}TiCl_2N$	$C_{10}H_{17}TiCl_2N$
M_r	256.03	270.06
a, Å	6.149 (1)	6.198 (2)
b, Å	10.888 (3)	11.660 (2)
c, Å	9.004 (3)	17.748 (4)
β, deg	100.44 (2)	98.73 (2)
V, Å^3	593	1268
Z	2	4
space group	$P2_1/m$	$P2_1/c$
T, K	294	294
$\lambda(\mathrm{Mo}\ K\alpha)$, Å	0.710 73	0.710 73
d_{calcd}, g cm^{-3}	1.43	1.41
μ, cm^{-1}	11.3	10.6
R, R_w	3.6, 4.5	4.8, 5.1

Results and Discussions

Synthesis and General Considerations. The compounds $(RC_5H_4)TiCl_3$ (**1a**, R = H; **1b**, R = CH_3) react with $Li\{NH(t\text{-Bu})\}$ in THF to afford $(RC_5H_4)TiCl_2\{NH(t\text{-Bu})\}$ (**2a**, R = H; **2b**, R = CH_3) in 80–90% isolated yields. Regardless of the presence of excess $Li\{NH(t\text{-Bu})\}$, only a single amido ligand replaces one of the three chloro ligands and small amounts (3–5%) of unreacted **1**, removable by either sublimation or recrystallization, still contaminate the reaction mixtures. The products can be characterized by FT-IR, ^1H NMR, and ^{13}C NMR spectroscopies and agree with Teuben's structural assignment for this class of compounds.[17] The new compound **2b** provides further information on the solution structure for this class of compounds because the NMR resonances for the $CH_3C_5H_4$ ligand reveal the presence of a plane of symmetry[18] bisecting the $(RC_5H_4)TiCl_2$ moiety.

Crystal Structures. Crystal structures of **2** consist of neutral monomeric complexes where the two compounds, **2a** and **2b**, are nearly isostructural; their structural features are not significantly different. Figure 1 shows the molecular structure of **2b** with its

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(13) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; p 64.

(14) The attempt to refine the positional parameters of H(N) resulted in a short N–H distance [0.75 (4) Å] probably due to the interpretation of N atom electron density to the H atom position.

(15) The attempt to refine the positional parameters of H(N) resulted in a short N–H distance [0.66 (6) Å] probably due to the interpretation of N atom electron density to the H atom position.

(16) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(17) Jekel-Vroegop, C. T.; Teuben, J. H. *J. Organomet. Chem.* **1985**, *286*, 309.

(18) Darkwa, J.; Giolando, D. M.; Jones, C. A.; Rauchfuss, T. B. *Inorg. Synth.* **1990**, *27*, 51.

Table II. Positional Parameters for $(CH_3C_5H_4)TiCl_2\{NH(t\text{-}Bu)\}$ and $(C_5H_5)TiCl_2\{NH(t\text{-}Bu)\}$[a]

atom	*x*	*y*	*z*	*B*, Å^2
		$(CH_3C_5H_4)TiCl_2\{NH(t\text{-}Bu)\}$		
Ti	0.3666 (2)	0.2336 (1)	0.79485 (7)	2.86 (2)
Cl(1)	0.1239 (3)	0.3791 (2)	0.7992 (1)	4.22 (4)
Cl(2)	0.1987 (3)	0.0916 (2)	0.8505 (1)	5.18 (5)
N	0.6173 (8)	0.2686 (5)	0.8638 (3)	3.0 (1)
C(1)	0.265 (1)	0.1803 (6)	0.6670 (4)	4.1 (2)
C(2)	0.418 (1)	0.1021 (6)	0.7002 (4)	4.5 (2)
C(3)	0.612 (1)	0.1589 (7)	0.7195 (4)	4.3 (2)
C(4)	0.580 (1)	0.2731 (6)	0.6989 (4)	3.5 (2)
C(5)	0.364 (1)	0.2876 (6)	0.6647 (4)	3.3 (2)
C(6)	0.267 (1)	0.3930 (7)	0.6286 (5)	6.1 (2)
C(7)	0.652 (1)	0.2864 (6)	0.9486 (4)	3.3 (2)
C(8)	0.440 (1)	0.3233 (7)	0.9748 (4)	4.4 (2)
C(9)	0.737 (1)	0.1752 (8)	0.9864 (5)	5.8 (2)
C(10)	0.816 (1)	0.3836 (8)	0.9668 (5)	5.3 (2)
H(N)[c]	0.793	0.250	0.852	3.9[b]
C*	0.448	0.2004	0.6901	
		$(C_5H_5)TiCl_2\{NH(t\text{-}Bu)\}$		
Ti	0.8402 (1)	0.25	0.10290 (8)	2.71 (1)
Cl	0.6371 (2)	0.08987 (9)	0.16453 (9)	4.83 (2)
N	1.1037 (6)	0.25	0.2460 (3)	3.23 (8)
C(1)	1.0587 (6)	0.3130 (3)	–0.0718 (3)	4.39 (8)
C(2)	0.8474 (7)	0.3531 (4)	–0.1257 (3)	5.26 (9)
C(3)	0.7171 (9)	0.25	–0.1564 (5)	6.3 (2)
C(4)	1.1478 (8)	0.25	0.4138 (4)	3.6 (1)
C(5)	0.9369 (9)	0.25	0.4780 (5)	5.8 (1)
C(6)	1.2813 (7)	0.3630 (5)	0.4657 (4)	6.4 (1)
H(N)[c]	1.250	0.25	0.193	6 (1)[d]
C*	0.9059	0.25	–0.1103	

[a] C* is the center of the cyclopentadienyl ring. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(8\pi^2/3)$ times trace of the orthogonalized U tensor. [b] Fixed isotropic thermal parameter (see text). [c] Atoms located in difference Fourier maps and included in the refinement with fixed positional parameters. [d] Isotropic thermal parameter.

Table III. Selected Distances (Å) and Angles (deg) for $(CH_3C_5H_4)TiCl_2\{NH(t\text{-}Bu)\}$ and $(C_5H_5)TiCl_2\{NH(t\text{-}Bu)\}$[a]

$(CH_3C_5H_5)TiCl_2\{NH(t\text{-}Bu)\}$		$(C_5H_5)TiCl_2\{NH(t\text{-}Bu)\}$	
	Distances		
Ti–Cl(1)	2.277 (2)	Ti–Cl	2.271 (1) (2×)
Ti–Cl(2)	2.261 (3)		
Ti–N	1.871 (5)	Ti–N	1.879 (3)
Ti–C*	2.036	Ti–C*	2.032
N–C(7)	1.502 (8)	N–C(4)	1.486 (5)
N–H(N)	1.16	N–H(N)	1.09
H(N)···Cl(1)″	2.81	H(N)···Cl″	3.00 (2×)
H(N)···Cl(2)″	3.12		
	Angles		
Cl(1)–Ti–Cl(2)	100.40 (9)	Cl–Ti–Cl′	100.28 (5)
Cl(1)–Ti–C*	115.4	Cl–Ti–C*	116.3 (2×)
Cl(2)–Ti–C*	117.0		
N–Ti–C*	110.0	N–Ti–C*	110.7
Cl(1)–Ti–N	107.6 (2)	Cl–Ti–N	106.06 (7) (2×)
Cl(2)–Ti–N	105.4 (2)		
Ti–N–C(7)	131.5 (4)	Ti–N–C(4)	132.3 (3)
Ti–N–H(N)	123	Ti–N–H(N)	112
C(7)–N–H(N)	103	C(4)–N–H(N)	115
N–H(N)···Cl(1)″	135.4	N–H(N)···Cl″	140.1 (2×)
N–H(N)···Cl(2)″	152.8		
Cl(1)–Ti–C(5)–C(6)	11.3 (6)		
Cl(2)–Ti–C(5)–C(6)	111.7 (6)		
C*–Ti–N–C(7)	–172.2	C*–Ti–N–C(4)	180

[a] C* is the center of the cyclopentadienyl ring. Symmetry positions: (′) *x*, 0.5 – *y*, *z*; (″) 1 + *x*, *y*, *z*.

atomic numbering scheme. The overall geometry of the molecules can be derived from the piano-stool arrangement of $(C_5H_5)TiCl_3$ and $(CH_3C_5H_4)TiCl_3$ by substitution of one chloro ligand with the amido ligand. To minimize steric interactions between RC_5H_4 and NH(*t*-Bu) ligands, an anti conformation is adopted with respect to the Ti–N bond. Space group $P2_1/m$ imposes a mirror plane on **2a** which bisects the molecule so that the torsional angle C*–Ti–N–C(4) (C* = Cp centroid) is 180°. In the case of **2b**, this plane is absent in space group $P2_1/c$ and C*–Ti–N–C(7) has a value of –172°. The distorted tetrahedral geometries about the titanium centers in **1**[19,20] and **2** are similar; however, substitution of a chloride with NH(*t*-Bu) results in a lengthening of Ti–L (L = C*, Cl) (Ti–C*: **1a**, 2.01 Å;[19a] **1b**, 2.004 Å; **2a**, 2.032 Å; **2b**, 2.036 Å. Ti–Cl_{av}: **1a**, 2.223 Å;[19a] **1b**, 2.225 Å; **2a**, 2.271 Å; **2b**, 2.269 Å) as well as a reduction in Cl–Ti–Cl_{av} angles (**1a**, 102.9°;[19a] **1b**, 102.9°; **2a** 100.3°; **2b**, 100.4°). We attribute this difference to the short Ti–N distance relative to the Ti–Cl distance and to the bulkiness of the *t*-Bu group, which together make the amido ligand much more sterically demanding.

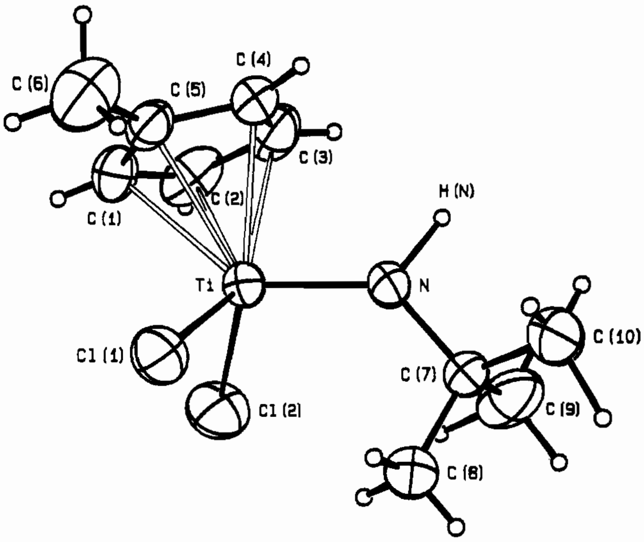

Figure 1. Structure and numbering scheme for $(C_5H_5)TiCl_2\{NH(t\text{-}Bu)\}$ with 50% probability ellipsoids.

Some degree of multiple bonding between Ti and N in **2** is suggested by the crystal structures of these two compounds. Possibilities for dπ–pπ interactions are evident from the planar environment about the sp^2-hybridized N atoms, as indicated by the sums of angles of 359° (**2a**) and 358° (**2b**). A more important indicator for multiplicity is the shortness of the Ti–N bond lengths, 1.879 (3) Å (**2a**) and 1.871 (5) Å (**2b**), as compared to estimated single-bond distances of 1.96–1.97 Å.[21] Recently, Feldman and Calabrese have reported the structures of two $(C_5Me_5)_2$Ti–amido complexes, for which π-bonding between Ti and N is most likely insignificant, with Ti–N distances of 2.054 (2) and 2.157 (5) Å,[22] Values of Ti–N distances in the range 1.800–1.897 Å have been suggested as indicative of dπ–pπ-bonding between four-coordinated Ti(IV) and amido ligands. For example: $(C_5H_5)TiCl_2\{N(SiMe_3)_2\}$, 1.882 Å;[23] $(NMe_2)_3Ti\text{–}Fe(CO)_2(C_5H_5)$, 1.884 [av] Å;[24] $(NMe_2)_3Ti\text{–}Ru(CO)_2(C_5H_5)$, 1.885 [av] Å;[25] $(NMe_2)(2,6\text{-}Me_2C_6H_3O)_2Ti\text{–}Ru(CO)_2(C_5H_5)$, 1.858 [6] Å;[26] $Ti(NMe_2)_2$-

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[19] Kirschbaum, K.; Giolando, D. M. *Acta Crystallogr.* **1991**, *C47*, 2216.

[20] (a) Engelhardt, L. M.; Papasergio, R. I.; Raston, C. L.; White, A. H. *Organometallics* **1984**, *3*, 18. (b) Ganis, P.; Allegra, G. *Atti Accad. Nazl. Lincei, Cl. Sci. Fis., Mat. Nat. Rend.* **1962**, *33*, 303.

[21] (a) Fayos, J.; Mootz, D. *Z. Anorg. Allg. Chem.* **1971**, *380*, 196. (b) Bürger, H.; Wiegel, K.; Thewalt, U.; Schomburg, D. *J. Organomet. Chem.* **1975**, *87*, 301. (c) Sheldrick, W. S. *J. Fluorine Chem.* **1974**, *4*, 415.

[22] Feldman, J.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1991**, 1042.

[23] Bradley, D. C.; Bennett, C.; Hursthouse, M. B.; Raithby, P. R. Unpublished results cited in: Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

[24] Sartain, W. J.; Selegue, J. P. *Organometallics* **1987**, *6*, 1812.

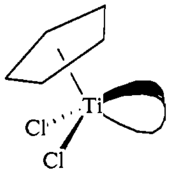
[25] Sartain, W. J.; Selegue, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 5818.

[26] Sartain, W. J.; Selegue, J. P. *Organometallics* **1989**, *8*, 2153.

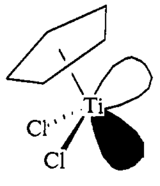
$(2,4,6\text{-}t\text{-Bu}_3C_6H_2O)_2$, 1.897 (5) and 1.864 (4) Å;[27] and $TiCl\{N(SnMe_3)_2\}(2,6\text{-}Ph_2C_6H_3O)_2$, 1.800 (1) Å).[28] Further discussion on the relationship between Ti–N distances and dπ–pπ-bonding has been presented for other classes of compounds.[29]

VT ^{1}H NMR Spectroscopy. Variable-temperature ^{1}H NMR studies are useful for examining rotational barriers about restricted bonds[30] because cooling decreases the available thermal energy needed to overcome the barrier for interconversion of rotomers and at sufficient low temperatures the rotomers become distinct. Compounds **2** are well suited for VT NMR studies to determine the rotational barrier about the Ti–N bond because their structures have only a single Ti–N bond, are monomeric, and are relatively unhindered about nitrogen. Furthermore, **2a** has the additional feature of an uncomplicated ^{1}H NMR spectrum. At 21 °C it consists of two sharp singlets assigned to the C_5H_5 and the $C(CH_3)_3$ groups and a broadened singlet assigned to the N*H* group, consistent with a rapidly exchanged spectrum on the NMR time scale. While cooling the sample to –90 °C by 10-deg increments, we expected Ti–N π-bonding to be manifested by splitting of the C_5H_5 and the $C(CH_3)_3$ resonances; however, the only observation is a slight broadening of the spectral features. To circumvent possible difficulties due to the presence of the sterically demanding *tert*-butylamido group, which may inhibit free rotation about the Ti–N vector, a VT NMR study on $(C_5H_5)TiCl_2(NMe_2)$ (**3**)[31] was also conducted. The ^{1}H NMR spectra of compound **3**, at 21 and –90 °C, each contain two sharp singlets assigned to the C_5H_5 and the $N(CH_3)_2$ groups. These results indicate that the rotational barriers about these Ti–N bonds are of very low energy ($\leq\sim 5$ kcal/mol),[32] indicating that there is free rotation about the Ti–N vector.

Concluding Remarks. The presence of Ti–N multiple bonding and free rotation about the Ti–N bond can be understood in terms of the appropriate frontier orbitals on the titanium fragment. Hoffmann et al. have examined the frontier orbitals involved in dπ–pπ interactions between $(C_5H_5)M(CO)_2$ fragments and a variety of π-ligands,[33] and Dilworth has utilized these results for the case involving $(C_5H_5)TiCl_2$ and $NRNR_2$ fragments.[34] The $(C_5H_5)TiCl_2$ moiety has two π-acceptor orbitals; one is orthogonal (a″) and the other aligned (a′) with the idealized plane of the fragment:



a″



a′

The amido ligands of **2** are planar sp^2-hybridized, sum of angles about N ca. 360°, placing the electron pair in a p orbital which can π-donate to either the a′ or the a″ orbital. The solid-state structures of **2** contain a C*–Ti–N–C(*t*-Bu) torsional angle of ca. 180°, which suggests that the ground state involves interaction of the nitrogen p orbital with the a″ orbital. Significant dπ–pπ contribution of this kind should lead to a Ti–N rotational barrier that is measurable on the NMR time scale. However, interaction of the nitrogen p orbital with the a′ orbital of the titanium fragment can provide a mechanism for free rotation while also maintaining dπ–pπ-bonding character, the overall effect being a reduction in the barrier for rotation about the Ti–N bond in compounds **2** and **3**.

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Supplementary Material Available: Tables of positional parameters, general displacement parameters, bond distances, bond angles, and torsional angles for **2a** and **2b** and a table of least-squares planes for **2b** (7 pages). Ordering information is given on any current masthead page.

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(27) Jones, R. A.; Hefner, J. G.; Wright, T. C. *Polyhedron* **1984**, *3*, 1121.

(28) Dilworth, J. R.; Hanich, J.; Krestel, M.; Beck, J.; Strahle, J. *J. Organomet. Chem.* **1986**, *315*, C9.

(29) (a) Bart, J. C. J.; Bassi, I. W.; Cerruti, G. F., Calcaterra, M. *Gazz. Chim. Ital.* **1980**, *110*, 423. (b) Hemmer, R.; Thewalt, U.; Hughes, D. L.; Leigh, G. J.; Walker, D. G. *J. Organomet. Chem.* **1987**, *323*, C29. (c) Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985.

(30) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

(31) Giolando, D. M.; Kirschbaum, K. Manuscript in preparation.

(32) (a) Binsch, G. *Top. Stereochem.* **1968**, *3*, 97. (b) Steigel, A. In *NMR Basic Principles and Progress: Dynamic NMR Spectroscopy*; Diehl, P., Fluck, E.; Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1978; Vol. 15.

(33) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(34) Dilworth, J. R.; Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Chem. Commun.* **1983**, 1368.