

Mononuclear Titanium Complexes That Contain Aminopyridinato Ligands

Rhett Kempe* and Perdita Arndt

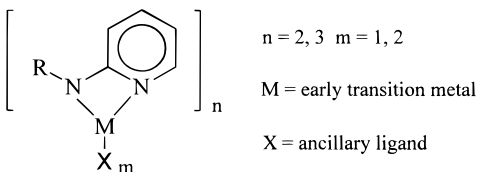
MPG AG "Komplekxkatalyse" an der Universität Rostock, Buchbinderstrasse 5–6,
18055 Rostock, Germany

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2-(Methylamino)pyridine (Me-APy-H), 2-anilino-pyridine (Ph-APy-H), and 4-methyl-2-((trimethylsilyl)amino)-pyridine (TMS-APy-H) were used to synthesize mononuclear monochloro complexes that contain two or three such aminopyridines as strained amido ligands. The reaction of 2 or 3 equiv of in situ generated lithium aminopyridinate with $\text{TiCl}_4(\text{THF})_2$ or TiCl_4 afforded just in the case of Me-APy-H a red crystalline product $(\text{Me-APy})_3\text{TiCl}$ (**1a**) but in unacceptably low yield. An alternative way to synthesize **1a** and $(\text{Ph-APy})_3\text{TiCl}$ (**1b**) is amine elimination, starting from mixed chlorodimethylamido complexes like $(\text{Me}_2\text{N})_3\text{TiCl}$ or $(\text{Me}_2\text{N})_2\text{TiCl}_2$. The reaction of $(\text{Me}_2\text{N})_3\text{TiCl}$ with 2 equiv of Me-APy-H, Ph-APy-H or TMS-APy-H afforded $(\text{Me-APy})_2\text{Ti}(\text{NMe}_2)\text{Cl}$ (**2a**), $(\text{Ph-APy})_2\text{Ti}(\text{NMe}_2)\text{Cl}$ (**2b**), or $(\text{TMS-APy})_2\text{Ti}(\text{NMe}_2)\text{Cl}$ (**2c**). These compounds represent novel unusual highly nitrogen-coordinated titanium complexes. X-ray diffraction studies of **1a** established its monomeric structure as having a disturbed pentagonal bipyramidal coordination geometry. X-ray crystal structure investigations of **2a–c** proved these compounds to be monomeric with a slightly distorted octahedral coordination geometry. The η^2 binding mode of the strained aminopyridinato ligands is discussed in comparison to the related amidinato ligand system by averaging bond distances and angles of the determined structures. The $\text{N}_{\text{py}}\text{—C—N}_{\text{amido}}$ angle of $108(1)^\circ$ instead of the desired 120° indicates the highly strained tweezers-like bonding mode. The Ti—N_{py} distances vary within the known range. The $\text{Ti—N}_{\text{amido}}$ distances are more than $0.1 \text{ \AA}$ longer than the expected values and indicate weak amido bonds. Variable-temperature NMR investigations of complex **2c** are indicative of exchange processes which proceed most likely via tetrahedral transition states. Crystallographic data (distances, $\text{\AA}$; angles, deg): **1a**, $\text{C}_{18}\text{H}_{21}\text{ClN}_6\text{Ti}$, $a = 9.313(1)$, $b = 10.277(1)$, $c = 11.302(1)$, $\alpha = 98.15(1)$, $\beta = 108.28(1)$, $\gamma = 102.98(1)$, triclinic, $P1$, $Z = 2$; **2a**, $\text{C}_{14}\text{H}_{20}\text{ClN}_5\text{Ti}$, $a = 8.725(1)$, $b = 9.258(1)$, $c = 10.778(1)$, $\alpha = 83.288(7)$, $\beta = 79.977(9)$, $\gamma = 78.766(8)$, triclinic, $P1$, $Z = 2$; **2b**, $\text{C}_{24}\text{H}_{24}\text{ClN}_5\text{Ti}$, $a = 17.652(3)$, $b = 7.959(1)$, $c = 18.017(3)$, $\beta = 111.37(1)$, monoclinic, $P2_1/a$, $Z = 4$; **2c**, $\text{C}_{20}\text{H}_{36}\text{ClN}_5\text{Si}_2\text{Ti}$, $a = 10.786(1)$, $b = 14.053(1)$, $c = 18.144(1)$, $\beta = 97.06(1)$, monoclinic, $P2_1/c$, $Z = 4$.

Introduction

Alternative amido-based ligands that stabilize early transition metal complexes in a Cp analogous fashion have been investigated intensively.^{1,18} Recently catalytic activity of such titanium complexes was reported in hydroboration² and olefin polymerization.³ With regard to possible catalytic applications, we are currently examining the chemistry of mononuclear early transition metal complexes that contain 2-aminopyridinato ligands.



Ligands of this type have been used to stabilize metal–metal multiple bonds,⁴ to synthesize polynuclear transition metal complexes⁵ and small clusters.⁶ Only a few examples of well characterized mononuclear transition metal complexes⁷ that contain a η^2 -bound aminopyridinato ligand are described. To our knowledge no group 3 (including lanthanides and actinides)

or group 4 metal complexes have been published so far. Such ligands are interesting because they combine a number of features which would make them attractive ligands for early transition metals in high oxidation states if they are bound in a η^2 fashion. Electronic requirements of highly Lewis acidic

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Table 1. Crystallographic Data for 1a and 2a–c

	1a	2a	2b	2c
empirical formula	C ₁₈ H ₂₁ ClN ₆ Ti	C ₁₄ H ₂₀ ClN ₅ Ti	C ₂₄ H ₂₄ ClN ₅ Ti	C ₂₀ H ₃₆ ClN ₅ Si ₂ Ti
fw	404.8	341.7	465.8	486.1
space group (No.)	P1 (2)	P1 (2)	P2 ₁ /a (14)	P2 ₁ /c (14)
temp, °C	20	20	20	20
ρ, g cm ⁻³	1.38	1.36	1.31	1.18
a, Å	9.313(1)	8.725(1)	17.652(3)	10.786(1)
b, Å	10.277(1)	9.258(1)	7.959(1)	14.053(1)
c, Å	11.302(1)	10.778(1)	18.017(3)	18.144(1)
α, deg	98.15(1)	83.288(7)		
β, deg	108.28(1)	79.977(9)	111.37(1)	97.06(1)
γ, deg	102.98(1)	78.766(8)		
V, Å ³	974.2(2)	837.8(2)	2357.2(6)	2729.3(4)
Z	2	2	4	4
μ mm ⁻¹	0.59	0.67	0.50	0.51
transm min %	90.6	88.0	94.0	77.2
transm max %	100.0	100.0	100.0	99.8
R1 ^a (I > 2σ(I))	0.036	0.035	0.055	0.048
wR2 ^b (all data)	0.112	0.107	0.171	0.146

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2 \}^{1/2}.$$

metal centers are fulfilled by the strong basicity of amide and pyridine ligands.⁸ Complex stability is supported by a chelating effect, and the strained η^2 binding mode causes an unusual reactivity. Substitution at the amide nitrogen and at the pyridine ring allows fine tuning of electronic properties, of bulkiness (stabilization of the metal complexes by steric shielding), and of solubility (including crystallization behavior). The offered set of electrons is similar to those of a Cp ligand, which suggests that the ligand could be considered as Cp analogous. The objectives of the present study were to develop syntheses of monomolecular monochloro titanium complexes that contain aminopyridinato ligands. Interest is also focused on structural aspects.

Experimental Section

Materials and Procedures. The complexes (Me₂N)₃TiCl₂¹² and (Me₂N)₂TiCl₂¹² were prepared according to a previously published procedure. 2-(Methylamino)pyridine was degassed and stored over 4 Å molecular sieves. All other reagents were obtained commercially and used as supplied. All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in (at 140 °C) dried Schlenk-type glassware on a dual-manifold Schlenk line, interfaced to a high-vacuum line, or in an argon-filled Vacuum Atmospheres glovebox (mBraun labmaster 130) with a high-capacity recirculator (<1.5 ppm of O₂). Solvents (Aldrich) and NMR solvents (Cambridge Isotope Laboratories, all 99 atom % D) were freshly distilled from sodium tetraethylaluminate.

Physical Measurements. The NMR spectra were recorded on a Bruker ARX 400 NMR spectrometer with a variable-temperature unit. Chemical shifts were referenced to signals of the solvents THF-*d*₈ (β-CH₂: δ_H = 1.73 ppm, δ_C = 25.2 ppm) and C₆D₆ (δ_H = 7.16 ppm, δ_C = 128.0 ppm). The spectra were assigned with the help of Dept and COSY experiments. Melting points were determined in sealed capillaries on a Büchi 535 apparatus. Elemental analyses were performed with a Leco CHNS-932. X-ray diffraction data were collected on a CAD4 MACH3 diffractometer using graphite-monochromated Mo Kα radiation. The crystals were sealed inside capillaries. Absorption corrections were carried out by Ψ-scans. The structures were solved

by direct methods (SHELXS-86)¹³ and refined by full-matrix least-squares techniques against F² (SHELXL-93).¹⁴ XP (SIEMENS Analytical X-ray Instruments, Inc.) and SCHAKAL-92 (E. Keller, University of Freiburg, Germany) were used for structure representations.

4-Methyl-2-(trimethylsilyl)amino)pyridine. To a solution of 2-amino-4-picoline (12.8 g, 0.12 mmol) in ether (120 mL) was added slowly via syringe 47.6 mL of *n*-BuLi in hexane (2.5 M, 0.118 mol) at 0 °C. The mixture was allowed to warm to room temperature over a period of 20 min and stirred for another 90 min. The mixture was cooled to 0 °C, and trimethylsilyl chloride (23.2 mL, 0.183 mol) was added slowly via syringe at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 12 h. The solution was filtered, and solvents were removed under vacuum. Distillation at 43 °C (0.03 mbar) afforded a colorless liquid. Yield: 18.0 g, 0.100 mol, 85%. ¹H NMR (303 K, C₆D₆): δ 8.04 (dd, 1H, Py H₆), 6.21 (dd, 1H, Py H₅), 5.87 (s, 1H, Py H₃), 3.80 (s, 1H, NH), 1.90 (s, 3H, Me), 0.33 (s, 9H, SiMe₃). ¹³C NMR (303 K, C₆D₆): δ 160.6 (Py C₂), 148.3 (Py C₆), 147.8 (Py C₄), 114.6, 110.6 (Py C₃/C₅), 20.8 (Me), 0.33 (SiMe₃).

(Me-APy)₃TiCl (1a). A solution of 600 mg (2.78 mmol) of (Me₂N)₃-TiCl in 15 mL of ether was added slowly via syringe to a solution of 8.95 mmol of 2-(methylamino)pyridine in 50 mL of ether. The color became immediately red. The mixture was stirred over a period of 30 min. The solution was filtered, and the volume was reduced under vacuum to approximately 20 mL. Cooling to -30 °C overnight afforded a red crystalline material. Yield: 721 mg, 1.78 mmol, 64%. ¹H NMR (303 K, C₆D₆): δ 7.56 (d, 1H, Py H₆), 6.95 (m, 1H, Py H₄), 6.02 (m, 1H, Py H₅), 5.77 (d, 1H, Py H₃), 3.20 (s, 3H, Me). ¹³C NMR (303 K, C₆D₆): δ 171.3 (Py C₂), 141.6 (Py C₆), 139.6 (Py C₄), 101.2, 101.0 (Py C₃/C₅), 38.1 (Me). Anal. Calcd for C₁₈H₂₁N₆TiCl: C, 53.42; H, 5.23; N, 20.76. Found: C, 52.22; H, 5.02; N, 20.08. Mp (uncorrected): 138 °C.

(Ph-APy)₃TiCl (1b). A solution of 432 mg (2.00 mmol) of (Me₂N)₃-TiCl in 20 mL of ether was added slowly via syringe to a solution of 1.056 g (6.20 mmol) of 2-anilinopyridine in 30 mL of ether. A red-purple color was seen. The mixture was stirred over a period of 30 min. The solution was filtered, and the volume was reduced under vacuum to approximately 20 mL. Cooling to -30 °C overnight afforded a purple crystalline material. Yield: 843 mg, 1.43 mmol, 71%. ¹H NMR (303 K, THF-*d*₈): 7.5 (br, 1H, Py H₆), 7.35 (t, 1H, Py H₄), 7.00 (t, 2H, m Ph), 6.86 (m, 1H, p Ph), 6.68 (d, 2H, o Ph), 6.45 (t, 1H, Py H₅), 6.10 (d, 1H, Py H₃). ¹³C NMR (303 K, THF-*d*₈): δ 149.5 (Py C₂), 142.9 (ipso-C Ph), 141.8 (Py C₆), 140.6 (Py C₄), 129.2 (m-C Ph), 125.0 (o-C Ph), 124.3 (p-C Ph), 112.5 (Py C₅), 104.3 (Py C₃). Anal. Calcd for C₃₃H₂₇N₆TiCl: C, 67.07; H, 4.61; N, 14.22. Found: C, 67.07; H, 4.91; N, 14.75. Mp (uncorrected): 140 °C.

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(15) QUESD3D and VISTA statistics from 18 Ti–N_{py} bond distances.

(16) QUESD3D and VISTA statistics from 117 Ti–N_{amido} bond distances.

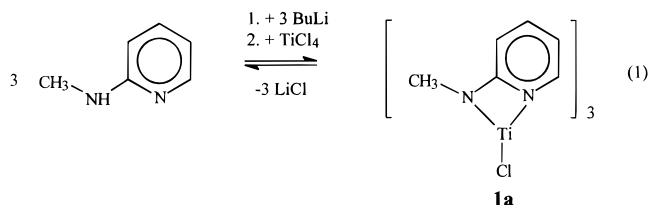
(Me-APy)₂Ti(NMe₂)Cl (2a). A solution of 307 mg (1.42 mmol) of (Me₂N)₃TiCl in 5 mL of ether was added slowly via syringe to a solution of 307 μ L (2.99 mmol) of 2-(methylamino)pyridine in 15 mL of ether. The color became immediately red. The mixture was stirred over a period of 10 min, during which a purple-red crystalline product precipitated. The product was isolated by filtration and washed with cold hexane. Yield: 192 mg, 0.56 mmol, 40%. ¹H NMR (303 K, THF-*d*₈): δ 7.61 (d, 2H, Py H₆), 7.44 (m, 2H, Py H₄), 6.36 (m, 2H, Py H₅), 6.16 (d, 2H, Py H₃), 3.68 (s, 6H, NMe₂), 3.15 (s, 6H, Py-NMe). ¹³C NMR (303 K, THF-*d*₈): δ 169.4 (Py C₂), 144.5 (Py C₆), 140.7 (Py C₄), 111.4 (Py C₅), 101.6 (Py C₃), 49.5 (NMe₂), 36.4 (Py-NMe). Anal. Calcd for C₁₄H₂₀N₅TiCl: C, 49.21; H, 5.90; N, 20.50. Found: C, 47.77; H, 5.33; N, 19.56. Mp (uncorrected): 140 °C.

(Ph-APy)₂Ti(NMe₂)Cl (2b). A solution of 343 mg (1.59 mmol) of (Me₂N)₃TiCl in 20 mL of ether was added slowly via syringe to a solution of 541 mg (3.18 mmol) of 2-anilinopyridine in 30 mL of ether. The color became immediately red-purple. The mixture was stirred over a period of 30 min. The solution was filtered, and the volume was reduced under vacuum to approximately 20 mL. Cooling to -30 °C overnight afforded a purple crystalline material. Yield: 563 mg, 1.21 mmol, 76%. ¹H NMR (303 K, THF-*d*₈): δ 7.8 (br, 2H, Py H₆), 7.4, 7.3, 7.0, 6.5 (m, 16H, Ph and Py), 3.55 (s, 6H, NMe₂). ¹³C NMR (303 K, THF-*d*₈): δ 166.9 (Py C₂), 148.9 (ipso-C Ph), 144.7 (Py C₆), 141.0 (Py C₄), 129.5, 124.3, 122.9 (o-, m-, p-C Ph), 112.9 (Py C₅), 104.9 (Py C₃), 49.7 (NMe₂). Anal. Calcd for C₂₄H₂₄N₅TiCl: C, 61.88; H, 5.19; N, 15.03. Found: C, 61.34; H, 5.32; N, 14.82. Mp (uncorrected): 175 °C.

(TMS-APy)₂Ti(NMe₂)Cl (2c). A solution of 315 mg (1.46 mmol) of (Me₂N)₃TiCl in 20 mL of ether was added slowly via syringe to a solution of 553 μ L (2.92 mmol) of 4-methyl-2-((trimethylsilyl)amino)pyridine in 20 mL of ether. The color became orange immediately. The mixture was stirred over a period of 30 min, after which the solution was filtered and the volume was reduced under vacuum to approximately 10 mL. Cooling to -30 °C afforded overnight an orange crystalline material. Yield: 647 mg, 1.33 mmol, 91%. ¹H NMR (303 K, C₆D₆): δ 7.8 (br, 2H, Py H₆), 6.20 (s, 2H, Py H₃), 5.91 (d, 2H, Py H₅), 3.70 (s, 6H, NMe₂), 1.73 (s, 6H, Py-Me), 0.36 (s, 18H, SiMe₃). ¹H NMR (230 K, THF-*d*₈): δ 8.15 (s, 1H, Py H₆), 7.01 (s, 1H, Py' H₆), 6.45 (d, 1H, Py H₅), 6.29 (s, 2H, Py H₃), 6.29 (d, 1H, Py' H₅), 3.62 (s, 6H, NMe₂), 2.24 (s, 3H, Py-Me), 2.20 (s, 3H, Py'-Me), 0.30 (s, 9H, SiMe₃), 0.03 (s, 9H, Si'Me₃). ¹³C NMR (303 K, C₆D₆): δ 167.2 (Py C₂), 150.8 (Py C₄), 143.1 (br, Py C₆), 113.2 (br, Py C₅), 110.7 (Py C₃), 51.7 (NMe₂), 21.5 (Py-Me), 1.2 (SiMe₃). Anal. Calcd for C₂₀H₃₆N₅TiCl: C, 49.47; H, 7.48; N, 14.43. Found: C, 49.51; H, 7.57; N, 14.27. Mp (uncorrected): 156 °C.

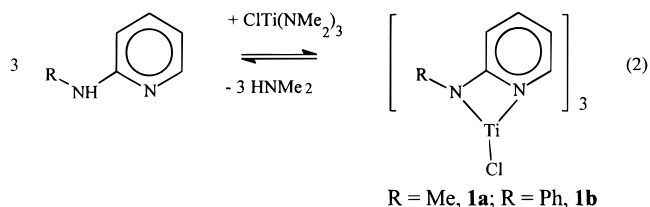
Results and Discussion

Synthesis of Complexes of the Types (R-APy)₃TiCl and (R-APy)₂Ti(NMe₂)Cl. 2-(Methylamino)pyridine (Me-APy-H) and 2-anilinopyridine (Ph-APy-H) are commercially available, and the synthesis of trimethylsilyl-substituted 2-aminopyridines was reported.⁹ 4-Methyl-2-((trimethylsilyl)amino)pyridine (TMS-APy-H) was prepared by method of Phillion.¹⁰ The reaction of 3 equiv of in situ generated lithium (methylamino)pyridinate (Me-APy-Li) with TiCl₄(THF)₂ or TiCl₄ affords a red crystalline product in only 10% yield.

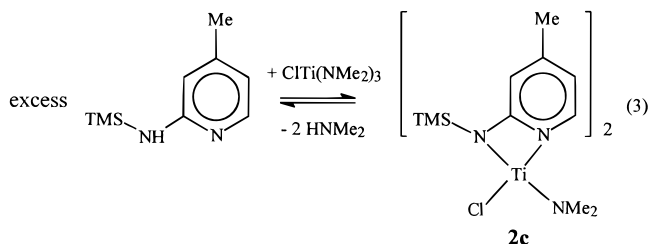


¹H and ¹³C NMR spectra indicate an overall 3-fold molecular symmetry showing the expected signals of one type of coordinated (methylamino)pyridinato ligand. Elemental analysis is consistent with the formula (Me-APy)₃TiCl (**1a**). Synthesis of the analogous phenyl- or trimethylsilyl-substituted aminopyridinato titanium complexes failed. An alternative way to

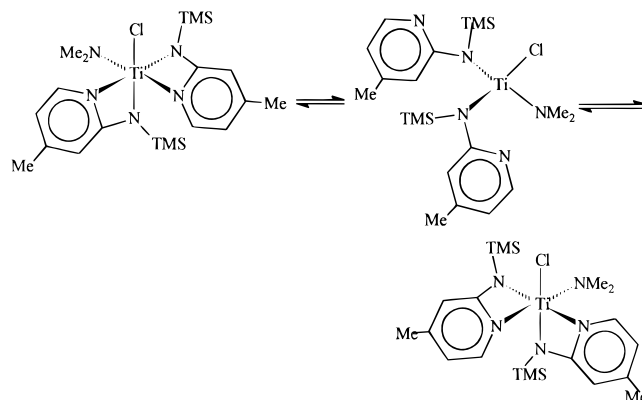
synthesize **1a** is amine elimination, starting from mixed chloro dimethylamido complexes like (Me₂N)₃TiCl or (Me₂N)₂TiCl₂, which are easily prepared via the comproportionation reactions between Ti(NMe₂)₄ and TiCl₄.¹² As anticipated, the reaction between (Me₂N)₃TiCl and 3 equiv of Me-APy-H proceeds without any significant side reaction (observed by ¹H NMR). The yield depends upon the solubility.



Unexpectedly, the reaction of only 2 equiv of Me-APy-H and (Me₂N)₂TiCl₂ affords the same product (**1a**). In situ generated dimethylamine acts as a base and deprotonates the aminopyridine. Me₂NH·HCl was observed as a byproduct. A smooth synthesis of (Ph-APy)₃TiCl (**1b**) proceeds via amine elimination according to eq 2. The reaction of (Me₂N)₃TiCl with 2 or 3 equiv of TMS-APy-H did not afford a complex of the type (R-APy)₃TiCl, presumably owing to steric repulsion. The ¹H and ¹³C NMR spectra of the product crystallized from hexane are indicative of two-coordinated aminopyridinato ligands and a "leftover" dimethylamide.



Elemental analysis is consistent with (TMS-APy)₃Ti(NMe₂)Cl (**2c**). Complexes of the type (R-APy)₂Ti(NMe₂)Cl were also synthesized from (Me₂N)₃TiCl and 2 equiv of Me-APy-H or Ph-APy-H to afford (Me-APy)₂Ti(NMe₂)Cl (**2a**) or (Ph-APy)₂Ti(NMe₂)Cl (**2b**) as a red crystalline compound, analogous to eq 3. All the aminopyridinato-containing complexes described herein are sensitive to air and moisture. The ¹H NMR spectrum of **2c** at room temperature shows broad or missing signals for the aminopyridinato ligand, indicating that exchange processes are occurring. The results from low-temperature NMR studies reveal that the aminopyridinato ligands are in two different environments, in accordance with the structure determined by X-ray diffraction studies. It is proposed that this exchange proceeds most likely via a tetrahedral transition state without pyridine coordination.



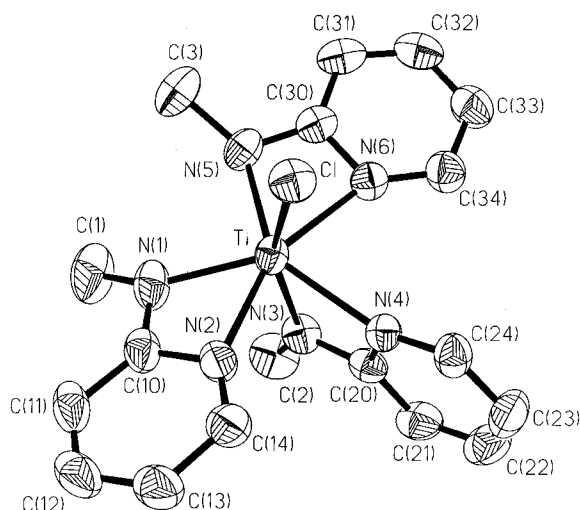


Figure 1. Structural representation of **1a**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 40% probability. Selected bond distances (Å) and angles (deg): N(1)–Ti 2.012(2), N(2)–Ti 2.183(2), N(3)–Ti 2.010(2), N(4)–Ti 2.191(2), N(5)–Ti 2.004(2), N(6)–Ti 2.204(2), Cl–Ti 2.3492(7), N(5)–Ti–N(3) 108.99(9), N(5)–Ti–N(1) 85.67(10), N(3)–Ti–N(1) 90.56(10), N(5)–Ti–N(2) 142.80(9), N(3)–Ti–N(2) 89.80(9), N(1)–Ti–N(2) 61.65(10), N(5)–Ti–N(4) 137.99(9), N(3)–Ti–N(4) 61.70(8), N(1)–Ti–N(4) 132.30(9), N(2)–Ti–N(4) 79.13(8), N(5)–Ti–N(6) 61.79(9), N(3)–Ti–N(6) 84.52(9), N(1)–Ti–N(6) 142.99(9), N(2)–Ti–N(6) 154.50(8), N(4)–Ti–N(6) 76.28(7), N(5)–Ti–Cl 90.73(7), N(3)–Ti–Cl 153.06(7), N(1)–Ti–Cl 109.58(7), N(2)–Ti–Cl 84.66(6), N(4)–Ti–Cl 91.36(5), N(6)–Ti–Cl 89.22(6).

Molecular modeling experiments suggest that no exchange mechanism in which the N_{amido} – and N_{py} –titanium bonds pass through an octahedral transition state is possible due to the cis arrangement of both the pyridines and the aminopyridinato amides. The temporary loss of the pyridines is supported by the highly strained binding mode. Furthermore it is proposed that **2a** and **2b** have similar dynamic behaviors which could not be slowed down to the NMR time scale at 230 K.

Solid State Structures of (Me-APy)₃TiCl (1a), (Me-APy)₂Ti(NMe₂)Cl (2a), (Ph-APy)₂Ti(NMe₂)Cl (2b), and (TMS-APy)₂Ti(NMe₂)Cl (2c). Large dark red crystals of **1a** suitable for X-ray analysis could be grown by layering a saturated ether solution with hexane. The single-crystal X-ray structure analysis of **1a** established its monomeric structure, as shown in Figure 1, including principal bond distances and angles. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Some important crystallographic features are shown in Table 1. The solid state structure shows a highly nitrogen-coordinated titanium complex. Coordination geometry is described best as pentagonal bipyramidal where the atoms N(1), N(2), N(4), N(5), and N(6) occupy the central plane and the Cl atom stands perpendicular to this plane. The “leftover” nitrogen cannot bind exactly opposite to the Cl atom because of the strained binding mode. Thus the coordination geometry is disturbed. The amide nitrogen atoms have an almost planar geometry, as has been found in virtually all structurally characterized transition metal amido complexes.⁸ As seen in Table 2, bond lengths and angles are almost identical for all three aminopyridinato ligands. The Ti–Cl bond distance of 2.3492(7) Å in **1a** is slightly longer than the average Ti–Cl bond distance (2.305 Å¹¹) and almost equivalent with the upper quartile (2.352 Å¹¹). Suitable crystals for X-ray diffraction studies of **2a**–**c** could be obtained by slowly cooling a saturated solution (**2a**, an ether solution to –30 °C; **2b**, an ether solution to 0 °C; **2c**, a hexane solution to –30 °C). Perspective ORTEP drawings of the molecular structures of **2a**–**c** are represented

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **1a**^a

	x	y	z	U(eq) ^a
C(1)	3867(4)	1919(4)	2625(4)	95(1)
C(2)	45(4)	1973(3)	–148(3)	79(1)
C(3)	1577(4)	–86(4)	3795(3)	79(1)
C(10)	3444(3)	4070(3)	3258(3)	58(1)
C(11)	4932(3)	4981(4)	3512(3)	75(1)
C(12)	5111(4)	6333(5)	3826(3)	86(1)
C(13)	3880(4)	6817(4)	3875(3)	77(1)
C(14)	2447(3)	5885(3)	3608(3)	62(1)
C(20)	–926(3)	3251(2)	811(2)	47(1)
C(21)	–1801(4)	3666(3)	–242(3)	67(1)
C(22)	–2727(4)	4442(3)	–55(4)	79(1)
C(23)	–2811(4)	4816(3)	1128(4)	73(1)
C(24)	–1920(3)	4387(3)	2131(3)	55(1)
C(30)	–1004(3)	30(3)	2592(2)	52(1)
C(31)	–1921(4)	–1259(3)	2560(3)	67(1)
C(32)	–3526(4)	–1525(3)	2022(3)	75(1)
C(33)	–4211(4)	–564(3)	1567(3)	72(1)
C(34)	–3233(3)	690(3)	1668(3)	61(1)
N(1)	2914(3)	2709(3)	2985(2)	64(1)
N(2)	2239(2)	4565(2)	3293(2)	52(1)
N(3)	85(3)	2507(2)	927(2)	53(1)
N(4)	–1010(2)	3627(2)	1975(2)	44(1)
N(5)	567(3)	578(2)	3001(2)	55(1)
N(6)	–1685(2)	970(2)	2161(2)	50(1)
Cl	476(1)	3103(1)	4818(1)	55(1)
Ti	645(1)	2495(1)	2793(1)	43(1)

^a U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

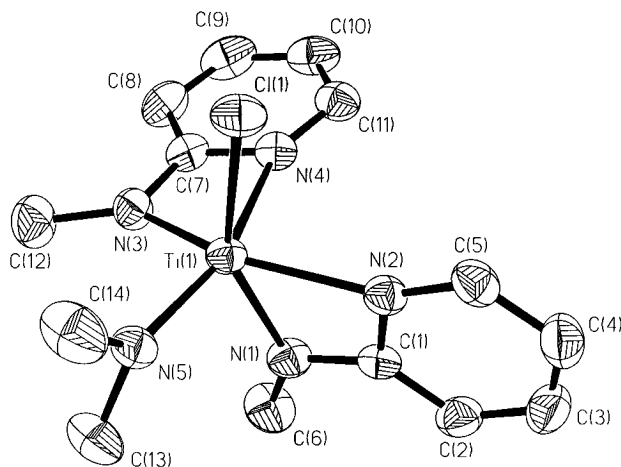


Figure 2. Structural representation of **2a**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 40% probability. Selected bond distances (Å) and angles (deg): N(1)–Ti(1) 2.016(2), N(2)–Ti(1) 2.185(2), N(3)–Ti(1) 1.968(2), N(4)–Ti(1) 2.299(2), N(5)–Ti(1) 1.899(2), Cl(1)–Ti(1) 2.3512(8), N(5)–Ti(1)–N(3) 96.73(10), N(5)–Ti(1)–N(1) 97.30(10), N(3)–Ti(1)–N(1) 98.65(10), N(5)–Ti(1)–N(2) 109.30(10), N(3)–Ti(1)–N(2) 149.25(10), N(1)–Ti(1)–N(2) 62.84(9), N(5)–Ti(1)–N(4) 158.48(10), N(3)–Ti(1)–N(4) 61.77(9), N(1)–Ti(1)–N(4) 85.72(9), N(2)–Ti(1)–N(4) 91.09(9), N(5)–Ti(1)–Cl(1) 97.99(8), N(3)–Ti(1)–Cl(1) 104.60(8), N(1)–Ti(1)–Cl(1) 150.34(8), N(2)–Ti(1)–Cl(1) 88.10(6), N(4)–Ti(1)–Cl(1) 89.24(6).

in Figure 2–4, including selected bond distances and angles. Crystallographic details are given in Table 1. Atomic coordinates, including equivalent isotropic displacement parameters, are listed in Table 3 for **2a**, in Table 4 for **2b**, and in Table 5 for **2c**. The coordination geometries of all three compounds are almost identical and described best as disturbed octahedral. The chloride atom stands perpendicular to the nitrogen plane. The pyridine nitrogen–titanium bond distances (N_{py} –Ti) of the aminopyridinato ligands in these planes are approximately 0.1 Å longer (average 2.26 Å) than the out-of-plane N_{py} –Ti bond (average 2.16 Å). The Ti– $N_{\text{dimethylamido}}$ and the Ti–Cl bond

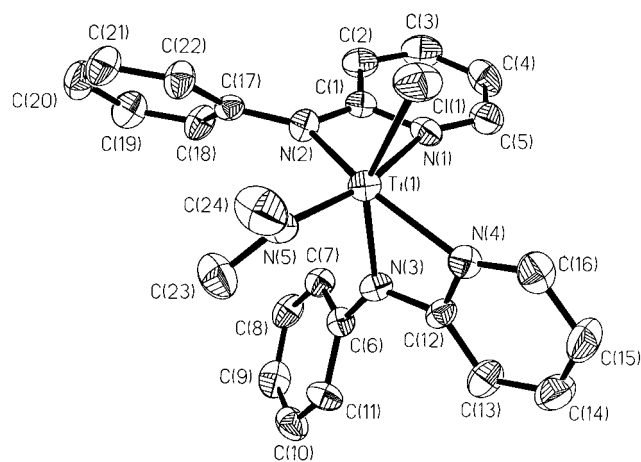


Figure 3. Structural representation of **2b**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 40% probability. Selected bond distances (Å) and angles (deg): N(1)–Ti(1) 2.257(5), N(2)–Ti(1) 2.007(4), N(3)–Ti(1) 2.101(4), N(4)–Ti(1) 2.144(4), N(5)–Ti(1) 1.890(5), Cl(1)–Ti(1) 2.310(2), N(5)–Ti(1)–N(2) 99.9(2), N(5)–Ti(1)–N(3) 94.4(2), N(2)–Ti(1)–N(3) 99.4(2), N(5)–Ti(1)–N(4) 103.5(2), N(2)–Ti(1)–N(4) 151.2(2), N(3)–Ti(1)–N(4) 62.4(2), N(5)–Ti(1)–N(1) 161.6(2), N(2)–Ti(1)–N(1) 62.2(2), N(3)–Ti(1)–N(1) 85.2(2), N(4)–Ti(1)–N(1) 92.7(2), N(5)–Ti(1)–Cl(1) 99.5(2), N(2)–Ti(1)–Cl(1) 102.12(14), N(3)–Ti(1)–Cl(1) 151.85(13), N(4)–Ti(1)–Cl(1) 90.50(13), N(1)–Ti(1)–Cl(1) 89.02(12).

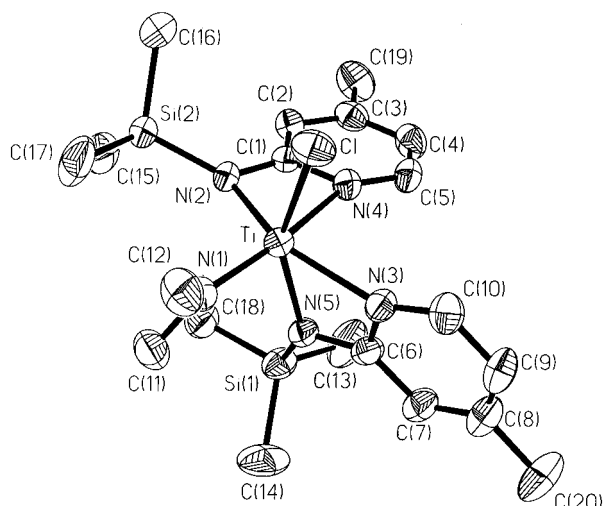


Figure 4. Structural representation of **2c**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 40% probability. Selected bond distances (Å) and angles (deg): N(1)–Ti 1.892(3), N(2)–Si(2) 1.747(3), N(2)–Ti 2.031(3), N(3)–Ti 2.141(3), N(4)–Ti 2.220(3), N(5)–Si(1) 1.729(3), N(5)–Ti 2.096(3), Cl–Ti 2.3241(13), N(1)–Ti–N(2) 106.92(13), N(1)–Ti–N(5) 95.93(13), N(2)–Ti–N(5) 100.96(12), N(1)–Ti–N(3) 102.32(13), N(2)–Ti–N(3) 148.29(13), N(5)–Ti–N(3) 63.58(12), N(1)–Ti–N(4) 169.38(13), N(2)–Ti–N(4) 63.51(12), N(5)–Ti–N(4) 82.07(12), N(3)–Ti–N(4) 86.19(12), N(1)–Ti–Cl 96.10(10), N(2)–Ti–Cl 100.01(10), N(5)–Ti–Cl 151.58(10), N(3)–Ti–Cl 88.70(9), N(4)–Ti–Cl 90.37(9).

distances are similar to known values. In order to express ligand steric properties, an angle φ similar to a cone angle¹⁷ was defined as the angle formed by the outermost H atom of the pyridine ring, the titanium atom, and the outermost H atom of the substituent (data were taken from the results of the X-ray diffraction studies). The TMS-substituted aminopyridinato ligand, which was expected to be the most sterically demanding ligand, has an angle $\varphi = 143^\circ$. The cone angles of the phenyl-substituted ($\varphi = 120^\circ$) and the methyl-substituted ligand ($\varphi = 119^\circ$) are similar. This fact explains that complexes of type **1**

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2a**

	x	y	z	$U(\text{eq})^a$
C(1)	4581(3)	2220(3)	818(3)	39(1)
C(2)	5783(4)	1870(4)	−198(3)	53(1)
C(3)	6970(4)	714(4)	−14(4)	63(1)
C(4)	7003(4)	−82(4)	1165(4)	58(1)
C(5)	5809(4)	315(3)	2127(3)	48(1)
C(6)	2972(6)	4358(5)	−142(4)	64(1)
C(7)	2259(4)	5449(3)	3325(3)	42(1)
C(8)	2118(5)	6887(4)	3662(3)	58(1)
C(9)	3458(6)	7343(4)	3832(4)	67(1)
C(10)	4897(5)	6424(4)	3666(3)	60(1)
C(11)	4960(4)	5014(4)	3351(3)	49(1)
C(12)	−507(5)	5466(5)	3211(5)	65(1)
C(13)	−113(5)	2404(5)	1339(4)	65(1)
C(14)	−181(6)	913(6)	3281(5)	75(1)
N(1)	3260(3)	3259(3)	909(2)	43(1)
N(2)	4616(3)	1425(2)	1966(2)	40(1)
N(3)	1132(3)	4723(3)	3106(2)	44(1)
N(4)	3678(3)	4534(3)	3178(2)	41(1)
N(5)	675(3)	1921(3)	2435(2)	42(1)
Cl(1)	2687(1)	1521(1)	4729(1)	49(1)
Ti(1)	2378(1)	2768(1)	2734(1)	35(1)

^a $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2b**

	x	y	z	$U(\text{eq})^a$
C(1)	6006(3)	3143(7)	7980(3)	36(1)
C(2)	6663(3)	3995(8)	8518(4)	48(2)
C(3)	6931(4)	5431(9)	8272(4)	59(2)
C(4)	6556(4)	6008(8)	7502(4)	57(2)
C(5)	5913(4)	5085(8)	6995(4)	51(2)
C(6)	3650(3)	3869(6)	7559(3)	33(1)
C(7)	4201(3)	4512(7)	8258(3)	39(1)
C(8)	3972(4)	5195(7)	8841(4)	49(2)
C(9)	3165(4)	5260(8)	8733(4)	55(2)
C(10)	2595(4)	4641(8)	8047(4)	56(2)
C(11)	2838(3)	3929(7)	7470(4)	44(2)
C(12)	3594(3)	3425(7)	6202(3)	36(1)
C(13)	2951(4)	4453(8)	5754(3)	50(2)
C(14)	2775(4)	4527(9)	4947(4)	62(2)
C(15)	3213(4)	3639(10)	4583(4)	65(2)
C(16)	3840(4)	2655(8)	5056(3)	54(2)
C(17)	5824(3)	800(7)	8777(3)	33(1)
C(18)	5864(3)	1550(7)	9482(3)	45(2)
C(19)	6018(4)	634(8)	10171(4)	54(2)
C(20)	6139(4)	−1085(8)	10171(4)	56(2)
C(21)	6065(4)	−1854(8)	9468(4)	54(2)
C(22)	5910(4)	−933(7)	8786(4)	47(2)
C(23)	3812(4)	−525(9)	7604(4)	67(2)
C(24)	4200(4)	−2087(9)	6665(5)	75(2)
N(1)	5650(3)	3700(6)	7223(3)	39(1)
N(2)	5624(3)	1670(5)	8053(2)	36(1)
N(3)	3927(2)	3145(5)	6998(2)	35(1)
N(4)	4015(3)	2537(6)	5842(3)	40(1)
N(5)	4242(3)	−477(6)	7055(3)	41(1)
Cl(1)	5588(1)	261(2)	6281(1)	64(1)
Ti(1)	4814(1)	1450(1)	6936(1)	36(1)

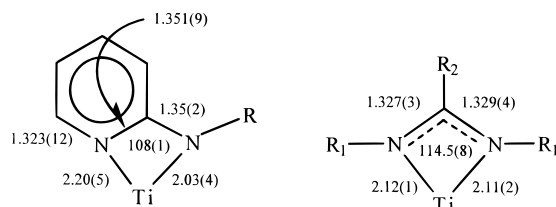
^a $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

could not be prepared using the sterically demanding TMS-APy ligand. The binding mode of the complexes described herein is illustrated in Chart 1 and compared with analogous bonding in titanium complexes that contain related amidinato ligands.¹⁸ The listed bond distances and angles are averaged by using all available structures. The standard deviation is the usual sample standard deviation resulting from the 9 observations (aminopyridinato ligands) or 12 observations (amidinato ligands). The C_n-N_{amido} (the carbon atom between the two

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2c**

	x	y	z	U(eq) ^a
C(1)	1293(3)	1990(3)	8562(2)	40(1)
C(2)	1527(4)	1690(3)	9305(2)	48(1)
C(3)	2430(4)	1008(3)	9504(2)	51(1)
C(4)	3100(4)	649(3)	8959(3)	58(1)
C(5)	2830(4)	973(3)	8242(2)	52(1)
C(6)	3312(3)	2830(3)	6912(2)	43(1)
C(7)	4544(4)	2845(3)	6711(2)	54(1)
C(8)	4829(4)	2284(4)	6136(2)	62(1)
C(9)	3930(4)	1696(4)	5775(2)	62(1)
C(10)	2749(4)	1686(3)	5987(2)	55(1)
C(11)	549(4)	4662(3)	6896(3)	65(1)
C(12)	2625(4)	4447(3)	8796(3)	65(1)
C(13)	4893(5)	3265(5)	8653(3)	90(2)
C(14)	4347(5)	5038(4)	7670(3)	96(2)
C(15)	-483(5)	3819(4)	9453(3)	79(2)
C(16)	-1751(4)	2012(3)	8870(3)	73(1)
C(17)	-1835(5)	3773(4)	7902(3)	91(2)
C(18)	-620(4)	3646(4)	6014(3)	68(1)
C(19)	2686(5)	648(4)	10288(3)	77(2)
C(20)	6139(4)	2310(5)	5904(3)	96(2)
N(1)	254(3)	3671(2)	6682(2)	44(1)
N(2)	481(3)	2671(2)	8248(2)	41(1)
N(3)	2455(3)	2241(2)	6542(2)	43(1)
N(4)	1958(3)	1612(2)	8046(2)	43(1)
N(5)	2804(3)	3321(2)	7445(2)	42(1)
Si(1)	3650(1)	4004(1)	8123(1)	54(1)
Si(2)	-851(1)	3066(1)	8616(1)	47(1)
Cl	-223(1)	1461(1)	6667(1)	61(1)
Ti	1063(1)	2650(1)	7225(1)	39(1)

^a U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Chart 1. Selected Averaged Bond Distances ($\text{\AA}$) and Bond Angles (deg) To Illustrate the Binding Mode of Aminopyridinato Ligands in Comparison with That of the Related Amidinato Ligand System

nitrogen atoms is called C_n) distance of the aminopyridinato ligand (1.35(2) $\text{\AA}$) is shorter as the expected value of the general $C_{\text{aromatic}}-\text{NH}_2$ bond length (1.375(25) $\text{\AA}$ ¹¹) but longer as the

$C_n-\text{N}_{\text{amidinato}}$ distance (1.329(4) $\text{\AA}$) and equivalent to the $C_n-\text{N}_{\text{py}}$ length. The $\text{Ti}-\text{N}_{\text{py}}$ distance is well in the range of such distances (2.247(7) $\text{\AA}$ ¹⁵). The $\text{Ti}-\text{N}_{\text{amido}}$ distance is more than 0.1 $\text{\AA}$ longer as the expected value of the averaged titanium-amido bond length (1.889(2) $\text{\AA}$ ¹⁶) and 0.1 $\text{\AA}$ shorter as the $\text{Ti}-\text{N}_{\text{amidinato}}$ distance. All these findings are indicative that a delocalization of titanium-nitrogen bonds as in case of the amidinato ligand system does not take place for aminopyridinato ligands. Instead, a typical $\text{Ti}-\text{N}_{\text{py}}$ and a weak $\text{Ti}-\text{N}_{\text{amido}}$ bond is observed. Nevertheless, the flexibility of both the amido and the pyridine nitrogen titanium distances may attest to a sensitivity of the binding situation depending on the substituents at the amido nitrogen and/or the pyridine ring. The $\text{N}_{\text{py}}-\text{C}_n-\text{N}_{\text{amido}}$ angle of 108(1)° instead of the desired 120° or the observed value for amidinato ligands (114.5(8)°) verifies the strained bonding mode.

Conclusion and Outlook

Several conclusions can be drawn from this study. First, the best way to prepare mononuclear titanium complexes that contain aminopyridinato ligands is via amine elimination starting from mixed chloro(dialkylamido)titanium complexes. The reactions are smooth and can be scaled up easily to a multigram scale. Second, despite the fact that aminopyridinato ligands can donate formally 6 electrons, they are not Cp analogous. They act because of their steric properties as an amide type ligand. For instance, complexes of the general type $(\text{R}_2\text{N})_3\text{TiCl}$ are described^{8,12,19} and are similar to complexes of the type $(\text{R}-\text{APy})_3\text{TiCl}$. Complexes **2a–c** represent the first examples of nonsymmetric group 4 tris(amido) complexes. Third, aminopyridinato ligands give rise to highly nitrogen-coordinated titanium complexes. Fourth, the strained binding mode and the flexibility in the $\text{Ti}-\text{N}_{\text{amido}}$ and/or $\text{Ti}-\text{N}_{\text{py}}$ bond may cause an unusual reactivity. The results may also provide the general conclusion that strained bound aminopyridinato ligands may act as the basis of a novel ligand system to stabilize mononuclear early transition metal complexes with unusual coordination geometries. The reactivity of the complexes presented in this paper is under investigation, and our interest is extended to other early transition metals and to other aminopyridinato ligands.

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Supporting Information Available: Tables of experimental details and crystal data, hydrogen positional parameters, full bond distances and angles, and thermal parameters (23 pages). Ordering information is given on any current masthead page.

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