Notes

Titanium and Niobium Complexes Stabilized by Tris(aminopyridinato) Ligands: Evidence of Variable Denticity in Trianionic Polydentate Ligands

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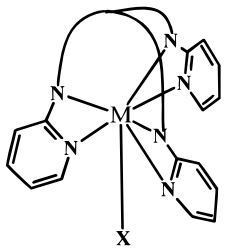
Summary: The reactions of 3 equiv of 4-methyl-2-aminopyridine and 4,6-dimethyl-2-aminopyridine with tris(bromodimethylsilyl)methane in the presence of 3 equiv of triethylamine gave respectively the two tris(aminopyridine) species $HC(SiMe_2NHC_5NH_3\text{-}4\text{-}Me)_3$ *((trisAP-4)*H_3*,* ***1a****) and* $HC(SiMe_2NHC_5NH_2\text{-}4,6\text{-}Me_2)_3$ *((trisAP-4,6)*H_3*,* ***1b****). Compound* ***1a*** *reacted with* $(Me_2N)_3TiCl$ *via amine elimination to give (trisAP-4)TiCl (****2****), a mononuclear titanium complex that is coordinated by six nitrogen atoms according to an X-ray analysis. The reaction of* $NbCl_3(DME)(\eta^2\text{-}PhC{\equiv}CSiMe_3)$ *with trilithiated* ***1b*** *(in situ) formed (trisAP-4,6)Nb(*η^2*-PhC*≡*CSiMe*$_3$*) (****3****). The tris(aminopyridinato) ligand trisAP-4,6 in* ***3*** *acts as a pentadentate ligand, in contrast to the hexadentate coordination of trisAP-4 in* ***2*** *and* ***3****. NMR investigations of the reaction of* ***3*** *with acetylene revealed neither alkyne exchange nor benzene formation.*

Introduction

Trianionic, chelating amido type ligands that stabilize early transition metals in medium or high oxidation states are of interest because they establish an unusual frontier orbital set to bind additional ligands in a well-defined reactive pocket. The orbital arrangement is in sharp contrast to what is provided by bent metallocenes[1] and, hence, makes the systems useful to broaden early-transition-metal chemistry. The triamidoamine ligands $[(RNCH_2CH_2)_3N]^{3-}$, first developed by Verkade et al.[2] and subsequently by Schrock et al.,[3] as well as the tridentate triamido ligands that enforce a tetrahedral coordination geometry introduced by Gade et al.[4,8,12] are two popular examples of such ligand systems. Gade and co-workers also presented tripod ligands containing an *active* ligand periphery by using weak donor functions (fluorine atoms) in the *ortho* position of phenyl-substituted tris(aminosilyl)methanes.[5] Our interest is focused on transition-metal complexes that contain aminopyridinato ligands. Since they tend to bind early transition metals in a C_3-symmetric fashion,[6] we were interested in using potentially hexadentate trianionic chelating ligands (Chart 1). By doing so, a more stable ligand set can be obtained in comparison to the propeller-like arrangement of three aminopyridinato ligands. Furthermore, a variable ligand periphery might be established, where an additional coordination site can be provided for substrate binding via metal−pyridine bond cleavage.[7] Variable denticity would be an indication of such a behavior. We report here the synthesis and structure of titanium and niobium complexes that contain tris(aminopyridinato) ligands and display variable denticity (penta- or hexadentate) of such ligands.

Chart 1. Schematic Representation of a Tris(aminopyridinato) Ligand (M = Early Transition Metal, X = Additional Ligand)



Results and Discussion

The reactions of 3 equiv of 4-methyl-2-aminopyridine and 4,6-dimethyl-2-aminopyridine with tris(bromodimethylsilyl)methane[8] in the presence of 3 equiv of triethylamine gave respectively (trisAP-4)H_3 (**1a**) in 84% yield and (trisAP-4,6)H_3 (**1b**) in 99% yield. The purification of both ligand precursors (**1a**,**b**) remains quite difficult due to their oily consistency, sensitivity toward moisture, and outstandingly good solubility in hydrocarbons. Impurities of 4-methyl-2-aminopyridine and 4,6-dimethyl-2-aminopyridine, respectively, can be crystallized from a pentane solution at −78 °C. The purity, as shown in the ^{1}H NMR spectra provided as Supporting Information, allows successful complex synthesis. Com-

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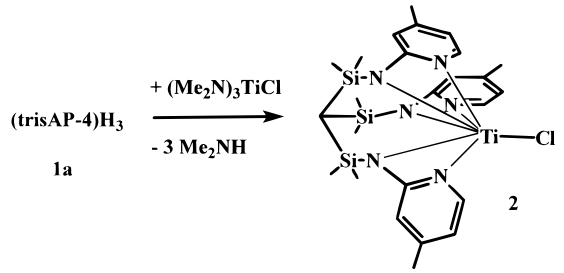
Table 1. Crystallographic Details of the X-ray Crystal Structure Analyses of 2 and 3

	2	3
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	10.485(2)	12.364(2)
b, Å	22.228(3)	20.093(3)
c, Å	12.903(2)	17.972(3)
β, deg	95.600(13)	91.790(12)
V, Å^3	2992.8(7)	4462.6(12)
Z	4	4
cryst size, mm	0.5 × 0.4 × 0.3	0.4 × 0.3 × 0.2
fw	589.23	815.18
ρ_{calcd}, g cm^{-3}	1.308	1.213
μ(Mo Kα), cm^{-1}	5.21	4.10
F(000)	1240	1720
T, K	293	293
θ range, deg	1.8−24.3	1.5−22.7
no. of rflns	8801	10 875
no. of unique rflns	4799	5632
no. of obsd rflns ($I > 2\sigma(I)$)	2700	3745
no. of params	325	451
R_w^2 (all data)	0.113	0.123
R value ($I > 2\sigma(I)$)	0.048	0.042

pound **1a** reacts with $(Me_2N)_3TiCl$[9] to give the dark red, crystalline material (trisAP-4)TiCl (**2**) in 40% yield.

The reaction of trilithiated **1a** (*in situ*) with $TiCl_4$ or $TiCl_4(THF)_2$ failed. In general, salt elimination routes have been found to be difficult in the preparation of titanium aminopyridinato complexes in general.[6,10] Therefore, we have at the moment two possible explanations. First, reduction of the titanium center may occur, and second, the amide functions of the lithiated ligands may be sterically hindered. Molecular structures of lithiated (silylamino)pyridines[11] show a perfect steric shielding of the amide function and a coordinative saturation of the lithium atoms; thus, they might be kinetically too inert to react with nonactivated metal chlorides.



Room-temperature NMR data for **2** as well as the low-temperature NMR spectra reveal a monomeric and C_3-symmetric complex due to the observation of a single signal set. An X-ray crystal structure analysis was carried out to investigate the binding mode of the ligand in the solid state. Crystallographic details are listed in Table 1. The molecular structure presented in Figure 1 with selected bond lengths and angles shows a mononuclear titanium complex with a hexadentate ligand. The coordination geometry is best described as a distorted pentagonal bipyramid similar to that in an

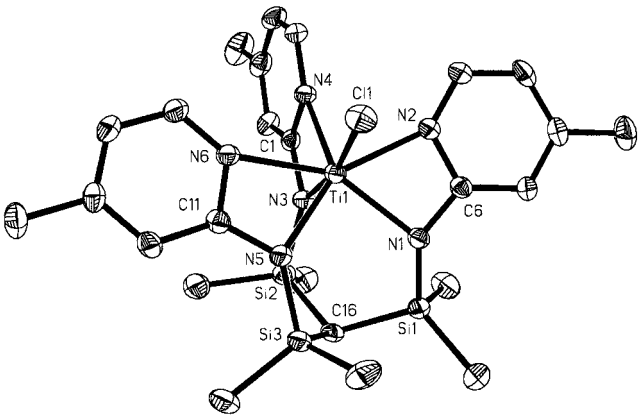
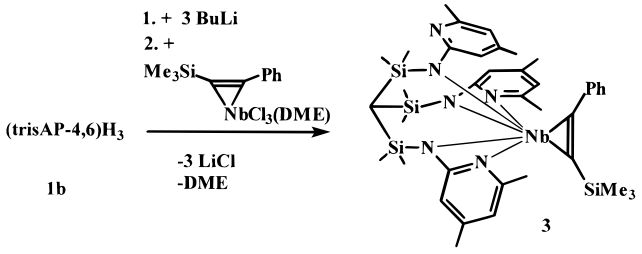


Figure 1. Structural diagram of **2**. Non-hydrogen atoms are represented as thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): N(1)−Ti(1), 2.131(3); N(2)−Ti(1), 2.162(3); N(3)−Ti(1), 2.020(3); N(4)−Ti(1), 2.223(3); N(5)−Ti(1), 2.070(3); N(6)−Ti(1), 2.179(3); Cl(1)−Ti(1), 2.3799(13); N(1)−Ti(1)−N(2), 62.29(12); N(3)−Ti(1)−N(4), 63.28(13); N(5)−Ti(1)−N(6), 62.98(12).

yttrium complex reported recently.[5] Two of the three aminopyridinato arms occupy the central plane (N(1), N(2), N(5), and N(6)) together with the pyridine nitrogen of the third arm (N(4)). The corresponding amido nitrogen binds perpendicular to this plane (out of plane) and opposite to the chloro ligand (almost C_m symmetry). Compound **2** can be considered analogous to MeSi{$SiMe_2N(2\text{-}C_5H_4N)$}$_3$ZrCl, except for the fact that the zirconium complex is not described as a heptacoordinated species.[12]

The reaction of trilithiated **1b** (*in situ*) with $NbCl_5$, $NbCl_4(THF)_2$, and $NbCl_3$(DME) did not lead to a well-defined, homogeneous product. Similar observations were reported recently, concerning unsuccessful reactions of lithiated 2-(phenylamino)pyridine with $NbCl_5$.[13] Refluxing of a 3:1 ratio of 2-(phenylamino)pyridine and $NbCl_5$ yielded a bis(aminopyridinato)niobium complex.[13] Due to the presence of Si−N bonds in **1a**,**b** such an approach was not taken. The compounds $NbCl_3$(DME)(η^2-RC≡CR)[14] have been found to react smoothly with (tris(pyrazolyl)borato)potassium via salt elimination to give the corresponding niobium alkyne complexes.[15] Accordingly, the reaction of $NbCl_3$(DME)(η^2-PhC≡CSiMe_3) with trilithiated **1b** (*in situ*) gave (trisAP-4,6)Nb(η^2-PhC≡CSiMe_3) (**3**), a red, crystalline material.



The IR spectrum of **3** (coordinated alkyne at $\nu = 1624$ cm^{-1}) and ^{13}C NMR data suggest a four-electron-donor

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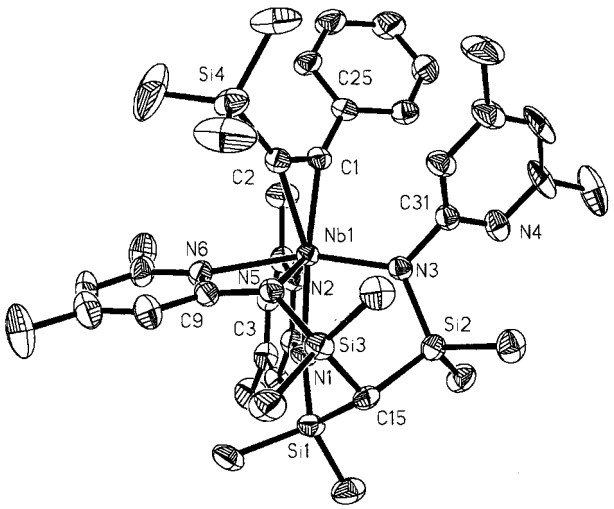

Figure 2. Structural representation of **3**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): C(1)−C(2), 1.321(7); C(1)−Nb(1), 2.103(5); C(2)−Nb(1), 2.125(5); N(1)−Nb(1), 2.222(4); N(2)−Nb(1), 2.223(4); N(3)−Nb(1), 2.023(4); N(5)−Nb(1), 2.196(4); N(6)−Nb(1), 2.285(4); C(1)−Nb(1)−C(2), 36.4(2); C(2)−C(1)−Nb(1), 72.7(3); C(1)−C(2)−Nb(1), 70.9(3); N(3)−Nb(1)−N(5), 89.5(2); N(1)−Nb(1)−N(2), 60.18(14); N(5)−Nb(1)−N(6), 59.7(2).

alkyne ligand.[16] The ^{1}H NMR spectrum reveals a highly dynamic system with a single but very broad signal set for the tris(aminopyridinato) ligand and sharp signals for the coordinated alkyne at room temperature. Low-temperature NMR data show splitting of the tris(aminopyridinato) ligand signal in a 2:1 ratio. A temporary cleavage of the pyridine−metal bond of one of the three aminopyridinato arms could explain this observation, which can be understood as due to the overcrowded coordination sphere of the complex. The result of an X-ray analysis confirms this. Crystallographic details are listed in Table 1. The molecular structure of **3** is shown in Figure 2 as well as selected bond lengths and angles. One of the three aminopyridinato arms coordinates only via the amido nitrogen (without pyridine coordination) and the other two are bound in a strained η^2 fashion. Thus, **3** confirms the opportunity of such tris(aminopyridinato) ligands to change denticity via metal−pyridine bond cleavage. The C−C bond distance of the coordinated alkyne (1.321(7) Å) agrees very well with the standard value of a C(sp^2)=C(sp^2) double bond (1.321(13) Å).[17] The coordinated alkyne has to be considered as a four-electron donor in a niobacyclopropene ring, which is also in accordance with the Nb−C distances.

Group 5 metal complexes are known to polymerize and cyclooligomerize alkynes.[18] The tendency to do so strongly depends on the steric properties of the ancillary ligands. The reaction of **3** with acetylene was examined. ^{1}H NMR spectroscopy[19] showed that no significant alkyne exchange occurred in the temperature range between 20 and 50 °C. Nevertheless, traces of an acetylene complex must have been formed, because traces of polyacetylene were observed. The fact that **3** does not catalyze benzene formation most likely is due to the steric demand of the tris(aminopyridinato) ligand and the stability of the niobacyclopropene ring.

Experimental Section

Materials and Procedures. Tris(bromodimethylsilyl)-methane,[8] tris(dimethylamino)titanium(IV) chloride,[20] and (1-phenyl-2-(trimethylsilyl)acetylene)niobium(III) chloride[14] were prepared according to literature procedures. 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 dried Schlenk-type glassware on a dual-manifold Schlenk line, interfaced to a high-vacuum line, or in an argon-filled glovebox (Braun Labmaster 130) with a high-capacity recirculator (<1.5 ppm of O_2). Solvents (Aldrich) and NMR solvents (Cambridge Isotope Laboratories, all 99 atom % D) were freshly distilled from sodium tetraethylaluminate.

Physical Measurements. NMR spectra were recorded on a Bruker ARX 400 instrument with a variable-temperature unit. ^{1}H and ^{13}C chemical shifts are referenced to the solvent resonances and reported relative to tetramethylsilane. Melting points were determined in sealed capillaries on a Büchi 535 apparatus. Elemental analyses were performed with a Leco CHNS-932 elemental analyzer. X-ray diffraction data were collected on a Stoe-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The crystals were mounted under a cold nitrogen stream or sealed inside a capillary. The structure was solved by direct methods (SHELXS-86)[21] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[22] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

(trisAP-4)H$_3$ (1a). To a solution of 4.76 g (44.0 mmol) of 4-methyl-2-aminopyridine in 40 mL of ether was added 6.13 mL (4.45 g, 44.0 mmol) of triethylamine and, over a period of 2 h, a solution of 6.27 g (14.7 mmol) of tris(bromodimethylsilyl)-methane in 60 mL of ether at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, stirring was continued for 48 h at room temperature. The reaction mixture was filtered and the solvent removed *in vacuo* to yield a colorless, viscous residue (**1a**). Yield: 6.23 g, 84%. ^{1}H NMR (303 K, C_6D_6): δ 0.62 (s, 18 H, $SiMe_2$), 1.16 (s, 1H, CH), 1.84 (s, 9 H, Ap-CH_3), 4.59 (s, 3 H, NH), 5.81 (s, 3 H, 3-H), 6.21(d, J = 5.2 Hz, 3 H, 5-H), 8.12 (d, J = 5.3 Hz, 3 H, 6-H). ^{13}C NMR (303 K, C_6D_6): δ 3.2 ($SiMe_2$), 5.7 (CH), 20.8 (Ap-CH_3), 112.1, 114.6 (C-3, C-5), 147.9 (C-6), 148.1 (C-4), 160.8 (C-2). MS (78.5 eV): *m/z* (%) 400 (51) [M − Ap$^+$], 399 (67), 385 (93), 309 (67), 295 (61), 108 (100) [Ap$^+$], 80 (71). Anal. Calcd for $C_{25}H_{40}N_6Si_3$: C, 59.01; H, 7.92; N, 16.51. Found: C, 58.64; H, 7.85; N, 16.13.

(trisAP-4,6)H$_3$ (1b). To a solution of 3.70 g (30.3 mmol) of 4,6-dimethyl-2-aminopyridine in 40 mL of ether was added 4.22 mL (3.07 g, 30.3 mmol) of triethylamine and, over a period of 2 h, a solution of 4.31 g (10.1 mmol) of tris(bromodimethylsilyl)methane in 60 mL of ether at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, stirring was continued for 48 h at room temperature. The reaction mixture was filtered and the solvent removed *in vacuo* to yield a colorless, viscous residue (**1b**). Yield: 5.53 g, 99%. ^{1}H NMR (303 K, C_6D_6): δ 0.63 (s, 18 H, $SiMe_2$), 1.01 (s, 1H, CH), 1.88 (s, 9 H, Ap-CH_3),

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2.34 (s, 9 H, Ap-CH_3), 4.23 (s, 3 H, NH), 5.58 (s, 3 H, 3-H), 6.12 (s, 3 H, 5-H). ^{13}C NMR (303 K, C_6D_6): δ 3.0 ($SiMe_2$), 5.5 (CH), 20.7 (Ap-CH_3), 24.2 (Ap-CH_3), 107.9, 113.6 (C-3, C-5), 148.0, 156.4 (C-4, C-6), 160.1 (C-2). MS (78.5 eV): *m*/*z* (%) 551 (15) [M + 1$^+$], 535 (21), 503 (14), 485 (38), 471 (60), 461 (39), 459 (48), 430 (41) [M − Ap$^+$], 429 (100), 123 (93) [Ap + 1$^+$]. Anal. Calcd for $C_{28}H_{46}N_6Si_3$: C, 61.04; H, 8.42; N, 15.25. Found: C, 60.72; H, 8.60; N, 14.52.

(trisAP-4)TiCl (2). To 238 mg (1.10 mmol) of tris(dimethylamido)titanium(IV) chloride in 20 mL of ether was slowly added 562 mg (1.10 mmol) of **1a** in 5 mL of ether. After the mixture was stirred for 6 h at room temperature, the obtained red solution was crystallized at room temperature to afford a dark red crystalline material (**2**). Yield: 261 mg (40%). Mp: 223 °C dec. ^{1}H NMR (303 K, THF-d_8): δ −0.26 (s, 1 H, CH), 0.25 (s, 18 H, $SiMe_2$), 2.20 (s, 9 H, Ap-CH_3), 6.05 (s, 3 H, 3-H), 6.39 (d, J = 5.41 Hz, 3 H, 5-H), 7.71 (d, J = 5.41 Hz, 3 H, 6-H). ^{13}C NMR (303 K, THF-d_8): δ 4.2 ($SiMe_2$), 9.9 (CH), 21.6 (Ap-CH_3), 111.1, 114.6 (C-3, C-5), 141.6 (C-6), 151.7 (C-4), 169.2 (C-2). Anal. Calcd for $C_{25}H_{37}N_6Si_3TiCl$: C, 50.96; H, 6.33; N, 14.26. Found: C, 50.72; H, 6.18; N, 14.09.

(trisAP-4,6)Nb[PhCCSi(Me)$_3$] (3). To a slurry of 1.15 g (3.07 mmol) of (η^2-1-phenyl-2-(trimethylsilyl)acetylene)niobium chloride in 30 mL of hexane was added slowly over a period of 2 h a solution of 1.75 g (3.07 mmol) of previously trilithiated tris((4,6-dimethyl-2-aminopyridinato)dimethylsilyl))methane (*in situ*) in 20 mL of hexane. After it was stirred for 2 days at room temperature, the solution was filtered, the precipitate was washed with hexane, and the volume of the filtrate was reduced *in vacuo*. Crystallization at room temperature afforded red crystals of **3**. Yield: 336 mg (13%). Mp: 210 °C. ^{1}H NMR (303 K, THF-d_8): δ 0.00 (s, 1 H, CH), 0.39 (s, 15 H, $SiMe_2$), 0.45 (s, 3 H), 0.45 (s, 3 H), 0.73 (s, 6 H, $SiMe_3$), 2.31 (s, 12 H, Ap-CH_3), 2.37 (s, 3 H, Ap-CH_3), 2.57 (s, 3 H, Ap-CH_3), 6.11 (s, 1 H), 6.35 (br s, 4 H), 6.53 (s, 1 H) (3-H, 5-H), 7.30−7.35 (m, 3 H, Ph), 7.39−7.43 (m, 2 H, Ph). ^{13}C NMR (303 K, THF-d_8): δ 0.0 ($SiMe_3$), 2.4 ($SiMe_2$), 5.3 (CH), 20.4 (Ap-CH_3), 23.8 (Ap-CH_3), 107.9, 113.6 (C-3, C-5), 127.4, 128.4, 130.9, 141.3, 147.9, 156.3 (C-4, C-6), 160.1 (C-2), 232.8 (alkyne C), 235.2 (alkyne C). Anal. Calcd for $C_{39}H_{57}N_6Si_4Nb$: C, 57.46; H, 7.05; N, 10.31. Found: C, 57.43; H, 7.02; N, 10.11. IR (KBr): ν (cm^{-1}) 1624.8 (alkyne, coordinated).

Reaction of 3 with Acetylene. A sample of **3** (120 mg, 0.15 mmol) in toluene-d_8 (5 mL) was loaded into a special NMR tube.[19] The NMR tube was not spun, to allow acetylene addition during the NMR experiment. No change of the ^{1}H NMR spectrum of **3** was observed during the addition. After the acetylene addition was complete, the temperature was increased to 50 °C and subsequently decreased again to room temperature. No changes of the signals due to **3** were observed. The intensity of the ^{1}H NMR signal of acetylene decreased. No benzene formation could be detected. The NMR tube was removed from the NMR spectrometer. A black polymer (polyacetylene, 1.6 mg) precipitated from solution. This was filtered and characterized by elemental analysis.

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Supporting Information Available: Figures giving ^{1}H NMR spectra of the compounds **1a**,**b** and experimental details of the X-ray crystal structure analyses, including tables of atomic coordinates, bond lengths and angles, and anisotropic displacement factors of the compounds **2** and **3** (20 pages). Ordering information is given on any current masthead page.

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