Barriopedro, P. et al., 2020. Successive Protonation and Methylation of Bridging Imido and Nitrido Ligands at Titanium Complexes. Inorganic chemistry, 59(11), pp.7631–7643.

Available at https://doi.org/10.1021/acs.inorgchem.0c00550

Successive Protonation and Methylation of Bridging Imido and Nitrido Ligands at Titanium Complexes

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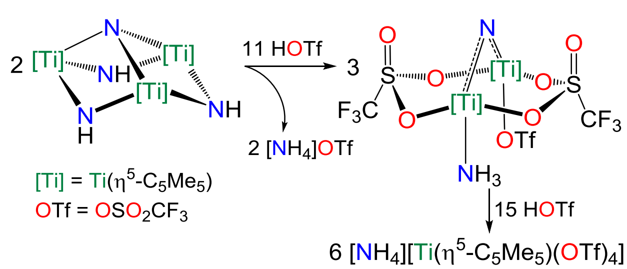
Synopsis:

Successive electrophilic attacks of ROTf (R = H, Me; OTf = OSO_2CF_3) reagents at imido and nitrido moieties of polynuclear titanium(IV) complexes enable isolation and structural characterization of a series of intermediates with nitrogen-based ligands (μ_n-N, μ_n-NH, μ-NH_2, NH_3) en route to ammonium salts $[NR_4]OTf$ or $[NR_4][Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]$ formation.



Abstract:

The reactions of nitrido complexes [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**) and [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_4$] (**2**) with electrophilic reagents ROTf (R = H, Me; OTf = OSO_2CF_3) in different molar ratios have allowed the structural characterization of a series of titanium intermediates en route to ammonium salts [NR_4]OTf or [NR_4][Ti(η^5-C_5Me_5)(OTf)$_4$] formation. The treatment of the trinuclear imido-nitrido complex **1** with 5.5 equiv of triflic acid in toluene at room temperature led to the dinuclear complex [Ti_2(η^5-C_5Me_5)$_2$(μ-N)(NH_3)(μ-O_2SOCF_3)$_2$(OTf)] (**3**) and [NH_4]OTf. Compound **3**, along with the ammonium salts [NMe_4]OTf and [NMe_4][Ti(η^5-C_5Me_5)(OTf)$_4$] (**5**), was also obtained in the reaction of **1** with 8 equiv of methyl triflate in toluene at 100 ºC. A trinuclear complex [Ti_3(η^5-C_5Me_5)$_3$(μ-N)(μ-NH)$_2$(μ-O_2SOCF_3)(OTf)] (**4**), intermediate in the formation of **3**, was isolated in the treatment of **1** with 4 equiv of MeOTf, although compound **4** was prepared in better yield by treatment of **1** with Me_3SiOTf (2 equiv). Addition of a large excess of MeOTf or HOTf reagents to solutions of **3** resulted in the clean formation of ammonium salts [NR_4][Ti(η^5-C_5Me_5)(OTf)$_4$] (R = Me (**5**), H (**6**)). Treatment of the tetranuclear nitrido complex [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_4$] (**2**) with 1 equiv of ROTf in toluene afforded the precipitation of the ionic compounds [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_3$(μ_3-NR)][OTf] (R = H (**8**), Me (**9**)), while a large excess of HOTf led to the formation of [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_3$(μ_3-NH)][Ti(η^5-C_5Me_5)(OTf)$_4$(NH_3)] (**10**) by rupture of a fraction of tetranuclear molecules. Complex **2** reacted with 1 equiv of [M(η^5-C_5H_5)(CO)$_3$H] (M = Mo, Cr) via hydrogenation of one nitrido ligand to give the molecular derivative [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_3$(μ_3-NH)] (**11**) and [{M(η^5-C_5H_5)(CO)$_3$}$_2$], while a second 1 equiv of [M(η^5-C_5H_5)(CO)$_3$H] produced

ionic compounds $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_2(\mu_3\text{-}NH)_2][M(\eta^5\text{-}C_5H_5)(CO)_3]$ (M = Mo (**12**), Cr (**13**)) by protonation of other nitrido group. The X-ray crystal structures of **3**, **4**, **5**, **9**, **10**, and **13** were determined.

Introduction

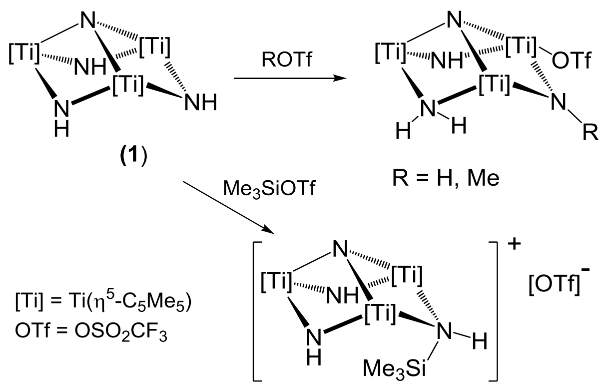
Transition metal nitrido and imido species are of interest because of their implications as key intermediates in biological and industrial dinitrogen fixation.[1,2] Since the seminal contributions of Cummins and co-workers with molybdenum(III) trisamido complexes,[3] the reductive cleavage of dinitrogen to form nitrido ligands by low-valent transition metal species is well-documented in the literature.[1,4] Most of the mid-transition metal (Groups 6-8) complexes show the nitrido ligands derived from N_2 as a terminal functionality M≡N,[5] although singular polynuclear iron species with bridging nitrido/imido ligands have been reported by Holland[6] and Murray[7] groups. In contrast, early transition metal (Groups 4 and 5) systems typically contain bridging nitrido (μ_n-N) moieties,[8,9,10] although several examples with the M≡N functionality (M = Ti,[11] Zr,[12] V,[13] and Nb[14]) have been described. In early transition metal nitrido complexes, the high stability of the resulting metal–nitrogen bonds makes difficult the subsequent functionalization and eventual release of nitrogen-containing products from the coordination sphere of the azaphilic transition element.[15] In general, those nitrido derivatives do not react with H_2, and strong acids or silylating agents are required for release of the nitrogen material. For instance, nitrido complexes are typically reacted with excess ethereal HCl to give ammonium chloride NH_4Cl as diagnostic evidence of nitrogen incorporation from N_2. Alternative methods based on hydrogenolysis of metal–nitrogen bonds by proton-coupled electron transfer (PCET) have been recently explored by Chirik.[16]

Noteworthy, Hou and co-workers have described a series of low-valent polyhydride titanium complexes capable of performing the cleavage of the N_2 molecule under mild conditions and the subsequent partial hydrogenation of the resulting μ_n-nitrido ligands to give μ_n-NH moieties.[17] The reactivity of bridging nitrido μ_n-N and imido μ_n-NH functionalities on multimetallic complexes is important to understand in the context of the mechanism of Haber-Bosch ammonia synthesis from N_2 and H_2.[6,17] In this heterogeneous catalyzed process, the rate-determining step is the N≡N bond cleavage in the surface of the catalyst to form two nitrides bridging several metal centers.[18] Subsequent hydrogenation of the nitrides produces imide NH, amide NH_2, and ammine NH_3 groups adsorbed on the metallic surfaces before ammonia elimination occurs. Well-defined species that resemble the proposed intermediates at the molecular level are relevant to the understanding of these elementary steps.

Polynuclear nitrido complexes of titanium,[19] zirconium,[20] and tantalum[21] with bridging nitrido μ_n-N, imido μ_n-NH, or amido μ-NH_2 ligands are usually obtained by the reaction of organometallic derivatives with excess ammonia. Representative examples for titanium(IV) derivatives are the trinuclear imido-nitrido $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$[22] (**1**) and the tetranuclear $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ (**2**) species,[23] which are easily prepared by ammonolysis of $[Ti(\eta^5\text{-}C_5Me_5)X_3]$ (X = Me, NMe_2) mononuclear complexes. Compounds **1** and **2** are structurally related to the systems isolated by Hou and co-workers from dinitrogen splitting,[17] as well as to those reported by us in the exposure of $[Ti(\eta^5\text{-}C_5Me_5)Me_3]$ to forming gas (H_2/N_2 mixture) under ambient conditions.[24]

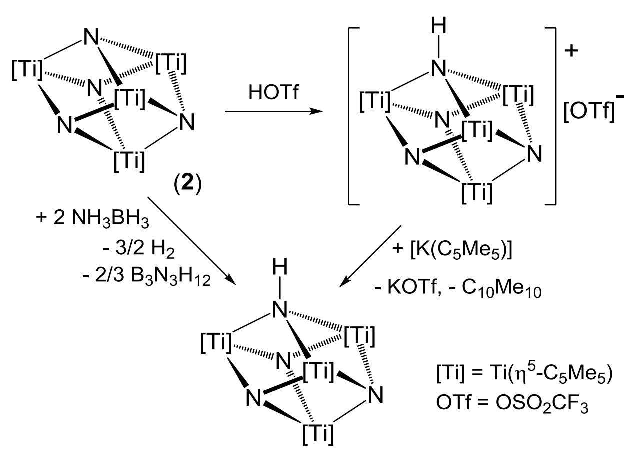
As part of a project devoted to the development of new reactivity patterns of the bridging ligands of the polynuclear complexes **1** and **2**,[25,26] we became interested in studying their reaction with electrophiles. In particular, we reported on the reaction of **1** with one equivalent of electrophilic reagents ROTf (R = H, Me, Me_3Si) to generate polynuclear complexes by selective functionalization of the imido groups (Scheme 1).[27,28]

As a logical continuation of this study, herein we describe the reactivity of **1** with higher molar ratios of ROTf reagents and the characterization of titanium nitrido intermediates en route to the ammonium salts $[NR_4]OTf$ or $[NR_4][Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]$ formation.



Scheme 1. Reaction of **1** with 1 equiv of ROTf

This study with electrophiles ROTf has been also extended to the tetranuclear nitrido complex **2**, following preliminary results on the protonation or hydrogenation of a μ_3-N nitrido ligand of this compound with one equivalent of HOTf or two equivalents of ammonia borane (Scheme 2).[29] In addition, here we report on the use of group 6 hydride derivatives $[M(\eta^5\text{-}C_5H_5)(CO)_3H]$ in the hydrogenation and protonation of the nitrido ligands in compound **2**.



Scheme 2. Protonation and hydrogenation of **2**

Experimental Section

General Considerations. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Toluene and hexane were distilled from Na/K alloy just before use. Dichloromethane was dried with P_2O_5 and distilled prior to use. Fluorobenzene was dried with CaH_2 and distilled prior to use. NMR solvents were dried with Na/K alloy (C_6D_6) or calcium hydride ($CDCl_3$, $(CD_3)_2SO$, C_5D_5N) and distilled before use. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} Torr) and subsequently filled with inert gas. $ROSO_2CF_3$ (R = H, Me, Me_3Si) were purchased from Aldrich and used as received. $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**),[22] $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ (**2**),[23] $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_3(\mu_3\text{-}NH)][OTf]$ (**8**),[29] $[Ti(\eta^5\text{-}C_5Me_5)Me_3]$,[30] and $[M(\eta^5\text{-}C_5H_5)(CO)_3H]$ (M = Mo, Cr)[31] were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as KBr pellets, and the spectra were obtained using an FT-IR Perkin-Elmer SPECTRUM 2000 or FT-IR Perkin-Elmer FRONTIER spectrophotometers. ^1H, $^{13}C\{^1H\}$ and ^{19}F NMR spectra were recorded on a Varian Unity-300, Mercury-300 and/or Unity-500 spectrometers. Chemical shifts (δ, ppm) in the ^1H and $^{13}C\{^1H\}$ NMR spectra are given relative to residual protons or to carbon of the solvent, C_6D_6 (^1H: δ = 7.15; ^{13}C: δ = 128.0), $CDCl_3$ (^1H: δ = 7.24; ^{13}C: δ = 77.0), $(CD_3)_2SO$ (^1H: δ = 2.49; ^{13}C: δ = 39.0) or C_5D_5N (^1H: δ = 8.71; ^{13}C: δ = 149.9). Chemical shifts (δ, ppm) in the ^{19}F NMR spectra are given relative to $CFCl_3$ as external reference. The effective magnetic moments were determined by the Evans NMR method at 293 K (using a 300 MHz instrument with a field strength of 7.05 Tesla).[32] Microanalyses (C, H, N, S) were performed in a Leco CHNSO-932 or Perkin Elmer CHNS/O 2400 microanalyzers.

Synthesis of [$Ti_2(\eta^5$-$C_5Me_5)_2(\mu$-N)(NH_3)(μ-$O_2SOCF_3)_2$(OTf)] (3). *Method A:* A 100 mL Schlenk tube was charged with **1** (0.20 g, 0.33 mmol), HOTf (0.25 g, 1.67 mmol), and toluene (25 mL). The reaction mixture was stirred at room temperature for 2 days to give a dark orange solution and a fine white solid. The solid (0.043 g) was isolated by filtration onto a glass frit and characterized as [NH_4]OTf by ^{1}H NMR spectroscopy in DMSO-d_6, δ = 7.06 (t, ^1J(H,^{14}N) = 51.2 Hz, 4H; NH_4). The volatile components were removed from the filtrate under reduced pressure to afford **3** as an orange solid (0.34 g, 81%). *Method B:* A 100 mL ampule (Teflon stopcock) was charged with **1** (0.20 g, 0.33 mmol), MeOTf (0.43 g, 2.62 mmol), and toluene (20 mL). The reaction mixture was stirred at 100 ºC for 2 days to give a dark orange solution and a light violet solid. The solid (0.31 g) was isolated by filtration onto a glass frit and subsequently characterized as a 1:1 mixture of [NMe_4]OTf and [NMe_4][Ti(η^5-C_5Me_5)$(OTf)_4$] (**5**), according to analysis by ^{1}H NMR spectroscopy of a solution of this solid in DMSO-d_6. The volatile components were removed from the filtrate under reduced pressure to afford **3** as an orange solid (0.26 g, 93%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3344 (w), 3267 (w), 3183 (w), 2962 (w), 2917 (m), 1607 (w), 1489 (w), 1431 (m), 1382 (m), 1331 (vs), 1312 (vs), 1230 (vs), 1208 (vs), 1187 (vs), 1145 (s), 1029 (vs), 1008 (vs), 879 (vs), 857 (vs), 791 (m), 731 (w), 632 (vs), 513 (m), 444 (m). ^{1}H NMR (300 MHz, C_6D_6, 20 ºC): δ 2.07 (s, 15H; C_5Me_5), 1.76 (s, 15H; C_5Me_5), 1.68 (s br., 3H; NH_3). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 ºC): δ 131.9 (C_5Me$_5$), 128.9 (C_5Me$_5$), 12.4 (C$_5$$Me_5$), 12.0 (C$_5$$Me_5$), the CF$_3$ carbon atom resonances were not detected. ^{19}F NMR (282 MHz, C_6D_6, 20 ºC): δ –76.8

(s), –77.6 (s). Anal. Calcd for $C_{23}H_{33}F_9N_2O_9S_3Ti_2$ (M_w = 844.43): C 32.71, H 3.94, N 3.32, S 11.39. Found: C 33.03, H 3.79, N 3.52, S 11.24.

Synthesis of [$Ti_3(\eta^5$-$C_5Me_5)_3(\mu$-N)(μ-NH$)_2(\mu$-O_2SOCF_3)(OTf)] (4). A 100 mL ampule (Teflon stopcock) was charged with **1** (0.30 g, 0.49 mmol), Me_3SiOTf (0.22 g, 0.99 mmol), and toluene (30 mL). After stirring at room temperature for 24 h, the reaction mixture was heated at 85 ºC for 2 d to give a dark orange solution. After filtration, the volatile components of the solution were removed under reduced pressure to afford **4** as an orange solid (0.31 g, 70%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3358 (m), 3261 (w), 3184 (w), 2915 (s), 2863 (m), 2731 (w), 1614 (w), 1495 (w), 1434 (m), 1382 (m), 1337 (vs), 1312 (vs), 1236 (vs), 1196 (vs), 1139 (s), 1068 (w), 1011 (vs), 927 (vs), 906 (vs), 788 (s), 720 (m), 633 (vs), 571 (w), 518 (m), 435 (m). ^{1}H NMR (300 MHz, C_6D_6, 20 ºC): δ 14.19 (s br., 2H; NH), 2.04 (s, 30H; C_5Me_5), 1.87 (s, 15H; C_5Me_5). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 20 ºC): δ 124.2 (C_5Me$_5$), 122.9 (C_5Me$_5$), 11.7 (C_5Me_5), 11.6 (C_5Me_5), the CF_3 carbon atom resonances were not detected. ^{19}F NMR (282 MHz, C_6D_6, 20 ºC): δ –76.4 (s). Anal. Calcd for $C_{32}H_{47}F_6N_3O_6S_2Ti_3$ (M_w = 891.47): C 43.11, H 5.31, N 4.71, S 7.19. Found: C 43.07, H 5.63, N 4.34, S 6.96.

Reaction of 1 with 4 equiv of MeOTf. A 100 mL ampule (Teflon stopcock) was charged with **1** (0.20 g, 0.33 mmol), MeOTf (0.22 g, 1.34 mmol), and toluene (20 mL). The reaction mixture was stirred at 60 ºC for 16 h to give a dark orange solution and a fine white solid. The solid (0.063 g) was isolated by filtration onto a glass frit and characterized as $[NMe_4]$OTf. The volatile components were removed from the filtrate under reduced pressure to afford an orange solid (0.28 g). Analysis by NMR spectroscopy of a solution of this solid in benzene-d_6 showed it to be a 1:1 mixture of compounds **3** and **4.**

Spectroscopic and analytical data for $[NMe_4]OTf$:[33] IR (KBr, cm^{-1}): $\tilde{\nu}$ 3047 (w), 2973 (m), 1493 (s), 1420 (w), 1252 (vs), 1229 (vs), 1154 (vs), 1033 (vs), 953 (s), 793 (w), 757 (w), 639 (vs), 573 (m), 519 (m), 459 (w). ^1H NMR (300 MHz, DMSO-d_6, 20 ºC): δ 3.08 (s; NMe_4). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 20 ºC): δ 120.2 (q, ^1J(C,F) = 320.3 Hz; CF_3), 53.9 (t, ^1J(C,^{14}N) = 4.0 Hz; NMe_4). ^{19}F NMR (282 MHz, DMSO-d_6, 20 ºC): δ –81.9 (s). Anal. Calcd for $C_5H_{12}F_3NO_3S$ (M_w = 223.21): C 26.91, H 5.42, N 6.28, S 14.37. Found: C 26.36, H 5.02, N 6.31, S 14.60.

Synthesis of $[NMe_4][Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]$ (5). A 100 mL Schlenk tube was charged with **7** (0.10 g, 0.16 mmol), $[NMe_4]OTf$ (0.035 g, 0.16 mmol), and toluene (25 mL). The reaction mixture was stirred at room temperature for 24 h to give a dark violet solid and a violet solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **5** as a dark violet powder (0.080 g, 57%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2923 (w), 1491 (m), 1364 (m), 1243 (s), 1201 (vs), 1197 (vs), 1193 (vs), 1148 (m), 1033 (m), 1009 (m), 974 (s), 766 (w), 631 (s), 596 (w), 508 (w), 451 (w), 412 (w). ^1H NMR (300 MHz, DMSO-d_6, 20 ºC): δ 3.08 (s, 12H; NMe_4), 2.08 (s, 15H; C_5Me_5). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, 20 ºC): δ 140.0 (C_5Me$_5$), 120.2 (q, ^1J(C,F) = 320.3 Hz; CF_3), 53.9 (t, ^1J(C,^{14}N) = 3.8 Hz; NMe_4), 13.3 (C_5Me_5). ^{19}F NMR (282 MHz, DMSO-d_6, 20 ºC): δ –77.7 (s). Anal. Calcd for $C_{18}H_{27}F_{12}NO_{12}S_4Ti$ (M_w = 853.51): C 25.33, H 3.19, N 1.64, S 15.03. Found: C 24.89, H 3.01, N 2.05, S 15.46.

Synthesis of $[NH_4][Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]$ (6). A 100 mL Schlenk tube was charged with **3** (0.20 g, 0.24 mmol), HOTf (0.19 g, 1.27 mmol), and toluene (30 mL). The reaction mixture was stirred at room temperature for 24 h to give a dark violet solid and a violet solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **6** as a dark violet powder (0.34 g, 89%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3259 (m, broad), 1489 (w), 1435 (m), 1351 (s), 1248 (vs), 1211 (vs), 1192 (vs), 1157 (s), 1033 (s), 988 (vs), 769 (w), 634 (s), 623 (s), 598 (w), 506 (w), 449 (w). ^{1}H NMR (300 MHz, DMSO-d_6, 20 ºC): δ 7.06 (t, $^{1}J(H,^{14}N)$ = 51.2 Hz, 4H; NH_4), 2.08 (s, 15H; C_5Me_5). $^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO-d_6, 20 ºC): δ 140.0 (C_5Me$_5$), 120.2 (q, ^{1}J(C,F) = 320.0 Hz; CF_3), 13.3 (C_5*Me*$_5$). ^{19}F NMR (282 MHz, DMSO-d_6, 20 ºC): δ –77.8 (s). Anal. Calcd for $C_{14}H_{19}F_{12}NO_{12}S_4Ti$ (M_w = 797.40): C 21.09, H 2.40, N 1.76, S 16.08. Found: C 20.84, H 2.50, N 1.83, S 16.15.

Synthesis of [Ti(η^5-C_5Me_5)(OTf)$_3$] (7). A 100 mL Schlenk tube was charged with [Ti(η^5-C_5Me_5)Me_3] (0.20 g, 0.88 mmol), HOTf (0.40 g, 2.67 mmol), and toluene (40 mL). The reaction mixture was stirred at room temperature for 24 h to give a violet solid and a violet solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **7** as a violet powder (0.37 g, 67%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2923 (w), 1489 (w), 1432 (w), 1374 (s), 1358 (s), 1340 (s), 1238 (vs), 1198 (vs), 1141 (vs), 1013 (s), 981 (vs), 947 (s), 769 (w), 636 (s), 622 (s), 598 (m), 510 (w), 453 (w), 419 (w). ^{1}H NMR (300 MHz, $CDCl_3$, 20 ºC): δ 2.63 (s, C_5Me_5). ^{1}H NMR (300 MHz, DMSO-d_6, 20 ºC): δ 2.08 (s; C_5Me_5). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 20 ºC): δ 149.9 (C_5Me$_5$), 118.3 (q, ^{1}J(C,F) = 320.1 Hz; CF_3), 14.7 (C_5*Me*$_5$). $^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO-d_6, 20 ºC): δ 140.0 (C_5Me$_5$), 120.2 (q, ^{1}J(C,F) = 320.1 Hz; CF_3), 13.3 (C_5*Me*$_5$). ^{19}F NMR (282 MHz, $CDCl_3$, 20 ºC): δ –75.9 (s). ^{19}F NMR (282 MHz, DMSO-d_6, 20 ºC): δ –77.7 (s). Anal. Calcd for $C_{13}H_{15}F_9O_9S_3Ti$ (M_w = 630.30): C 24.77, H 2.40, S 15.26. Found: C 24.72, H 2.50, S 15.16.

Synthesis of [{Ti(η^5-C_5Me_5)}$_4$(μ$_3$-N)$_3$(μ$_3$-NMe)][OTf] (9). A 100 mL ampule (Teflon stopcock) was charged with **2** (0.20 g, 0.25 mmol), MeOTf (0.042 g, 0.26 mmol), and toluene (20 mL). The system was allowed to react at 100 ºC without any stirring for 3 days.

After decantation, the resultant dark red needles were vacuum-dried to afford **9** (0.18 g, 72%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2909 (s), 1602 (w), 1489 (m), 1437 (s), 1378 (s), 1275 (vs), 1221 (s), 1144 (vs), 1062 (w), 1032 (vs), 953 (w), 869 (w), 802 (m), 750 (w), 732 (w), 648 (vs), 619 (vs), 571 (s), 548 (m), 517 (m), 463 (vs), 434 (m). ^{1}H NMR (300 MHz, $CDCl_3$, 20 ºC): δ 4.39 (s, 3H; NMe), 2.08 (s, 45H; C_5Me_5), 2.07 (s, 15H; C_5Me_5). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 20 ºC): δ 126.6 (C_5Me$_5$), 125.3 (C_5Me$_5$), 55.3 (NMe), 12.7 (C$_5$*Me*$_5$), 12.5 (C$_5$*Me*$_5$), the *C*F$_3$ carbon atom resonance was not detected. ^{19}F NMR (282 MHz, $CDCl_3$, 20 ºC): δ –78.0 (s). Anal. Calcd for $C_{42}H_{63}F_3N_4O_3STi_4$ (M_w = 952.51): C 52.96, H 6.67, N 5.88, S 3.37. Found: C 53.04, H 6.38, N 6.06, S 3.19.

Synthesis of [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_3$(μ_3-NH)][Ti(η^5-C_5Me_5)(OTf)$_4$(NH_3)] (10). *Method A:* A 100 mL Schlenk tube was charged with **2** (0.20 g, 0.25 mmol), HOTf (0.16 g, 1.07 mmol), and toluene (20 mL). The reaction mixture was stirred at room temperature for 24 h to give a dark red solid and a red solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **10** as a dark red powder (0.29 g, 73%). *Method B:* A 100 mL Schlenk tube was charged with **2** (0.10 g, 0.13 mmol), **6** (0.10 g, 0.13 mmol), and toluene (25 mL). The reaction mixture was stirred at room temperature for 24 h to give a dark red solid and a red solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **10** as a dark red powder (0.16 g, 80%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3360 (w), 3215 (w, broad), 2916 (m), 1653 (w), 1620 (w), 1494 (w), 1442 (m), 1381 (m), 1348 (s), 1236 (s), 1200 (vs), 1032 (s), 1001 (vs), 790 (m), 736 (m), 636 (vs), 514 (w), 468 (w), 446 (w). ^{1}H NMR (300 MHz, $CDCl_3$, 20 ºC): δ 12.42 (s br., 1H; NH), 2.40 (s br., 15H; C_5Me_5), 2.06 (s, 15H; C_5Me_5), 2.05 (s, 45H; C_5Me_5), the resonance signal for the NH_3 ligand was not detected. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 20 ºC): δ 147.2 (C_5Me$_5$), 126.2 (C_5Me$_5$), 125.1 (C_5Me$_5$), 13.7 (C$_5$*Me*$_5$), 12.7 (C$_5$*Me*$_5$), 12.2 (C$_5$*Me*$_5$), the *C*F$_3$ carbon atom resonance was not detected. ^{19}F NMR (282 MHz, CDCl$_3$, 20 ºC): δ –76.1 (s). Anal. Calcd for $C_{54}H_{79}F_{12}N_5O_{12}S_4Ti_5$ (M_w = 1585.81): C 40.90, H 5.02, N 4.42, S 8.09. Found: C 40.22, H 4.72, N 4.51, S 7.90.

Synthesis of [{Ti(η^5-C$_5$Me$_5$)}$_4$(μ$_3$-N)$_3$(μ$_3$-NH)] (11).[29] A 100 mL Schlenk tube was charged with **2** (0.30 g, 0.38 mmol), [Mo(η^5-C$_5$H$_5$)(CO)$_3$H] (0.094 g, 0.38 mmol), and toluene (25 mL). The reaction mixture was stirred at room temperature for 24 h to give a dark blue solution and a fine dark blue solid. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **11** as a dark blue powder (0.26 g, 88%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3333 (w) (ν_{NH}). ^{1}H NMR (300 MHz, CDCl$_3$, 20 ºC): δ 10.0 (s br., $\Delta\nu_{1/2}$ = 45 Hz, 15H; C$_5$Me$_5$), 8.7 (s br., $\Delta\nu_{1/2}$ = 33 Hz, 45H; C$_5$Me$_5$). The effective magnetic moment of **11** was determined to be 1.70 μ_B (based on a unit formula of $C_{40}H_{61}N_4Ti_4$) on a CDCl$_3$ solution.

Synthesis of [{Ti(η^5-C$_5$Me$_5$)}$_4$(μ$_3$-N)$_2$(μ$_3$-NH)$_2$][Mo(η^5-C$_5$H$_5$)(CO)$_3$] (12). A 100 mL Schlenk tube was charged with **2** (0.25 g, 0.32 mmol), [Mo(η^5-C$_5$H$_5$)(CO)$_3$H] (0.078 g, 0.32 mmol), and toluene (20 mL). The reaction mixture was stirred at room temperature for 2 h and a second 1 equiv of [Mo(η^5-C$_5$H$_5$)(CO)$_3$H] (0.078 g, 0.32 mmol) was added to the resultant dark suspension. After stirring at ambient temperature for 16 h, a dark green precipitate was isolated by filtration onto a glass frit and vacuum-dried to afford **12** (0.27 g, 82%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3277 (m), 3264 (m), 2910 (s), 2858 (m), 1895 (vs), 1781 (vs), 1747 (vs), 1494 (m), 1427 (s), 1377 (s), 1023 (w), 788 (vs), 782 (m), 697 (w), 642 (w), 617 (w), 515 (m), 496 (m), 445 (m), 421 (m). ^{1}H NMR (300 MHz, C$_5$D$_5$N, 20 ºC): δ 9.3 (s br., $\Delta\nu_{1/2}$ = 61 Hz, 30H; C$_5$Me$_5$), 8.0 (s br., $\Delta\nu_{1/2}$ = 55 Hz, 30H; C$_5$Me$_5$), 5.51 (s, 5H; C$_5$H$_5$). Anal. Calcd for $C_{48}H_{67}MoN_4O_3Ti_4$ (M_w = 1035.48): C 55.68, H 6.52, N 5.41. Found: C 55.45, H

6.12, N 5.37. The effective magnetic moment of **12** was determined to be 1.64 μ_B (based on a unit formula of $C_{48}H_{67}MoN_4O_3Ti_4$) on a C_5D_5N solution.

Synthesis of [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_2$(μ_3-NH)$_2$][Cr(η^5-C_5H_5)(CO)$_3$] (13). In a fashion similar to the preparation of **12**, the treatment of **2** (0.20 g, 0.25 mmol) with [Cr(η^5-C_5H_5)(CO)$_3$H] (0.10 g, 0.50 mmol) in toluene (15 mL) for 2 days afforded **13** as a dark green powder (0.19 g, 38%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3289 (m), 3266 (m), 3101 (w), 2911 (s), 2858 (m), 1936 (m), 1890 (vs), 1778 (vs), 1746 (vs), 1487 (m), 1427 (s), 1377 (s), 1261 (w), 1112 (w), 1066 (w), 1023 (m), 786 (s), 747 (s), 695 (m), 652 (s), 509 (s), 445 (s). ^1H NMR (300 MHz, C_5D_5N, 20 ºC): δ 9.3 (s br., $\Delta\nu_{1/2}$ = 70 Hz, 30H; C_5Me_5), 8.0 (s br., $\Delta\nu_{1/2}$ = 57 Hz, 30H; C_5Me_5), 5.02 (s, 5H, C_5H_5). Anal. Calcd for $C_{48}H_{67}CrN_4O_3Ti_4$ (M_w = 991.53): C 58.14, H 6.81, N 5.65. Found: C 57.46, H 6.61, N 5.92. The effective magnetic moment of **13** was determined to be 1.62 μ_B (based on a unit formula of $C_{48}H_{67}CrN_4O_3Ti_4$) on a C_5D_5N solution.

X-ray structure determination of 3, 4, 5, 9, 10, and 13. Orange crystals of **3** were grown at room temperature by slow diffusion of hexane into a fluorobenzene solution of this compound. Orange crystals of **4**·C_7H_8 and dark red crystals of **9**·C_7H_8 were obtained from toluene solutions at –30 ºC. Dark violet crystals of **5** were grown by slow cooling at room temperature of a toluene solution heated at 110 ºC. Dark red crystals of **10** were obtained at room temperature by diffusion of hexane into a dichloromethane solution of this compound. Dark green crystals of **13**·C_6D_6 were grown by slow cooling at room temperature of a benzene-d_6 solution heated at 80 ºC in a NMR tube. The crystals were removed from the Schlenk or NMR tubes and covered with a layer of a viscous perfluoropolyether (Fomblin®Y). A suitable crystal was selected with the aid of a microscope, mounted on a cryoloop, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 or 150 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for all the complexes are presented in Table S1 of the Supporting Information.

The structures were solved, using the WINGX package,[34] by direct methods (**13**) (SHELXS-2013)[35] or intrinsic phasing methods (the rest) (SHELXT)[36], and refined by least-squares against F^2 (SHELXL-2014/7).[37] It was not possible to obtain crystals of better quality for compounds **3**–**5** and **9,** and therefore some disorder problems could not be solved in those structures.

The asymmetric unit of **3** was formed by two independent molecules associated through hydrogen bonds, but there were no significant differences between these molecules. Crystals of **3** showed disorder for one bridging triflate ligand (S(2), O(21), O(22), O(23), C(2), F(21), F(22) and F(23)). This disorder was treated by using the PART tool of the SHELXL program and allowing free refinement of the occupancy factor with the FVAR command. The final values of occupancy were 89.9 and 10.1%. All non-hydrogen atoms were anisotropically refined, except the atoms corresponding to the minor position of the disordered triflate group (S(2)’, O(21)’, O(22)’, O(23)’, C(2)’, F(21)’, F(22)’ and F(23)’), which were refined isotropically. All the hydrogen atoms were placed geometrically and refined by using a riding model, except those of the ammine ligands (H(21), H(22), H(23), H(41), H(42) and H(43)), which were found in the difference Fourier map and refined isotropically.

In the difference Fourier map for compound **4**, a distorted molecule of toluene was found, so it was constrained to be constituted by a regular hexagon. Crystals of **4** presented disorder for the non-bridging triflate ligand (S(3), O(31), O(32), O(33), C(3), F(31), F(32) and F(33)). This disorder was also treated by using the PART tool with final values of 75.6 and 24.4%. Additionally, SADI restraints were employed for the CF_3 moiety of the minor position of this disordered triflate group. All non-hydrogen atoms were anisotropically refined, whereas all the hydrogen atoms were positioned geometrically and refined using a riding model. Moreover, the atoms of the pentamethylcyclopentadienyl ring linked to Ti(2) were restrained with DELU and SIMU instructions.

In the crystallographic study of **5**, all non-hydrogen atoms were anisotropically refined, whereas all the hydrogen atoms were positioned geometrically and refined by using a riding model.

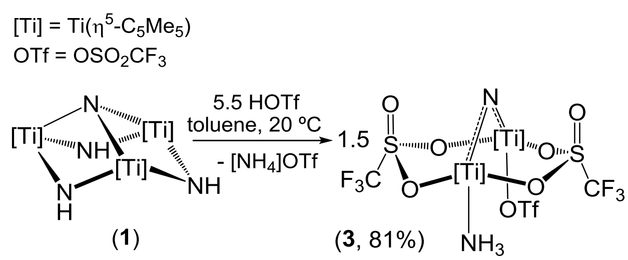
Complex **9** crystallized with a toluene molecule. Crystals of **9** presented disorder for the atoms of the triflate group (S(1), O(1), O(2), O(3), C(2), F(1), F(2) and F(3)) and the carbon atoms of the pentamethylcyclopentadienyl ligand linked to Ti(3) (C(31)-C(40)). These disorders were also treated conventionally affording occupancy factors of 60.2 and 39.8% for the triflate anion, and 79 and 21% for the C_5Me_5 moiety. All non-hydrogen atoms were anisotropically refined, while all the hydrogen atoms were positioned geometrically and refined using a riding model. The minor position for the disordered C_5Me_5 ring was constrained to retain a regular geometry, and DELU and SIMU restraints were used with the carbon atoms of this fragment. Atoms N(1) and C(1) were also restrained with DELU and SIMU commands, and SADI restraints were employed with the triflate group. Additionally, FREE instruction was applied to the atoms C(1) and O(1)' to avoid problems on calculated hydrogen atoms.

In the study of compound **10**, all non-hydrogen atoms were anisotropically refined. All hydrogen atoms were placed geometrically and refined using a riding model, except those linked to nitrogen (H(11), H(51), H(52) and H(53)), which were found in the difference Fourier map and refined isotropically. Moreover, distance restraints were applied to constrain the distance N(1)–H(11).

Compound **13** crystallized with a benzene molecule, which was located in the difference Fourier map, although it was constrained to be a regular hexagon. All non-hydrogen atoms were anisotropically refined. All hydrogen atoms were positioned geometrically and refined by using a riding model, except hydrogen H(1) and H(3) which were also found in the Fourier map, and refined isotropically.

Results and Discussion

Reaction of complex 1 with excess ROTf electrophilic reagents. The treatment of [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**) with 5.5 equiv of triflic acid in toluene at room temperature led to the precipitation of ammonium triflate and a dark orange solution from which the dinuclear complex [Ti_2(η^5-C_5Me_5)$_2$(μ-N)(NH_3)(μ-O_2SOCF_3)$_2$(OTf)] (**3**) was isolated in 81% yield (Scheme 3). Reactions of **1** with lower ratios (1:2, 1:3 or 1:4) of HOTf gave complicated mixtures of products, where only compounds [Ti_3(η^5-C_5Me_5)$_3$(μ_3-N)(μ-NH)$_2$(μ-NH_2)(OTf)] (Scheme 1)[28] and **3** were identified by NMR spectroscopy.



Scheme 3. Synthesis of the dinuclear complex **3**.

Complex **3** was characterized by analytical and spectroscopic methods, as well as by an X-ray crystal structure determination. The IR spectrum (KBr) of **3** shows three bands for the ν_{NH} vibrations, between 3344 and 3183 cm^{-1}, and one absorption at 1607 cm^{-1} assignable to the NH_3 bending mode.[38] In addition, the spectrum reveals several strong absorptions in the range 1331-1008 cm^{-1} for the coordinated triflato ligands.[39] The ^{1}H NMR spectrum of **3** in benzene-d_6 at room temperature shows two singlets in a 1:1 ratio for the η^5-C_5Me_5 groups, and a broad resonance for the ammine ligand at δ = 1.68. The ^{19}F NMR spectrum of **3** in benzene-d_6 reveals two resonance signals, assigned to bridging and terminal triflato ligands, in accord with its solid-state structure. The solid-state structural study of a single crystal of **3** shows two molecules associated through hydrogen bonding interactions between the terminal triflato group of one molecule and the ammine ligand of the other molecule in the asymmetric unit (vide infra). There are no substantial differences between the two molecules (see Figure 1 and Table 1 for one molecule, and Figure S1 and Table S2 in the Supporting Information for the second one). Compound **3** shows a dinuclear structure with two asymmetric moieties "Ti(η^5-C_5Me_5)L" held together by one bridging nitrido ligand and two μ-O_2SOCF_3 groups. The titanium atoms have classical four-legged piano-stool arrangements, where the legs are occupied by one nitrido, one terminal triflato, and two bridging triflato ligands for Ti(1) and Ti(3); and one nitrido, one ammine, and two bridging triflato ligands for Ti(2) and Ti(4). The bridging nitrido ligand of **3** is characterized by titanium–nitrogen bond lengths of averaged 1.797(2) Å, which is consistent with a Ti=N=Ti unit, based in the few examples found in the literature containing that fragment.[19a,40] The narrow Ti–N(nitrido)–Ti angle (av. 133.4(1)º) is likely due to the existence of two additional triflato ligands bridging the metal centers. The titanium–oxygen distances of 2.100(3)–2.185(3) Å are in the normal range for triflato ligands in complexes such as [{Ti(η^5-C_5Me_5)(μ-OH)(μ-O_2SOCF_3)(OTf)}$_2$],[41] and the titanium–nitrogen(ammine) bond length (av. 2.194(9) Å) compares well with those found in the few examples of titanium organometallic complexes with NH_3 ligands.[16a,19 a,42]

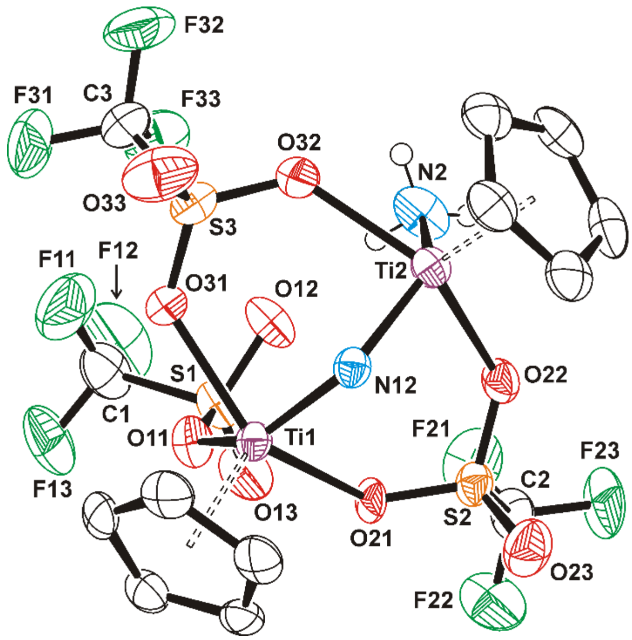


Figure 1. Perspective view of one of the two associated molecules in the asymmetric unit of complex **3** (thermal ellipsoids at the 50% probability level). The methyl groups of the pentamethylcyclopentadienyl ligands are omitted for clarity.

Table 1. Selected Lengths (Å) and Angles (deg) for One of the Two Associated Molecules of **3**

Ti(1)–N(12)	1.796(3)	Ti(1)–O(11)	2.100(3)
Ti(1)–O(21)	2.173(5)	Ti(1)–O(31)	2.149(3)
Ti(2)–N(12)	1.798(3)	Ti(2)–N(2)	2.188(4)
Ti(2)–O(22)	2.159(6)	Ti(2)–O(32)	2.127(3)
S(2)–O(21)	1.439(6)	S(2)–O(22)	1.458(6)
S(3)–O(31)	1.465(3)	S(3)–O(32)	1.460(3)
Ti(1)···Ti(2)	3.301(1)		
N(12)–Ti(1)–O(11)	134.8(1)	N(12)–Ti(1)–O(21)	85.6(2)
N(12)–Ti(1)–O(31)	86.0(1)	O(11)–Ti(1)–O(21)	77.9(2)
O(11)–Ti(1)–O(31)	78.2(1)	O(21)–Ti(1)–O(31)	136.3(2)
N(12)–Ti(2)–N(2)	125.2(2)	N(12)–Ti(2)–O(22)	86.1(2)
N(12)–Ti(2)–O(32)	86.3(1)	N(2)–Ti(2)–O(22)	77.0(2)
N(2)–Ti(2)–O(32)	75.8(2)	O(22)–Ti(2)–O(32)	140.1(2)
Ti(1)–N(12)–Ti(2)	133.4(2)	Ti(1)–O(21)–S(2)	125.2(4)
Ti(1)–O(31)–S(3)	128.4(2)	Ti(2)–O(22)–S(2)	125.0(3)
Ti(2)–O(32)–S(3)	129.0(2)	O(21)–S(2)–O(22)	113.6(3)
O(31)–S(3)–O(32)	113.0(2)		

As mentioned above, analysis of the crystal structure of **3** reveals the existence of several N–H···O and N–H···F hydrogen bonds (Figure 2, Table 2). Within each molecule, there is an intramolecular hydrogen bonding interaction between an oxygen atom of the terminal triflato and one hydrogen atom of the ammine ligand, which can be classified as strong according to the criteria on the donor–acceptor distances.[43] In addition, the two molecules of the asymmetric unit are associated by weaker hydrogen bonding interactions between oxygen or fluorine atoms of the terminal triflato ligand of one molecule and the hydrogen atoms on the ammine group of the other molecule.

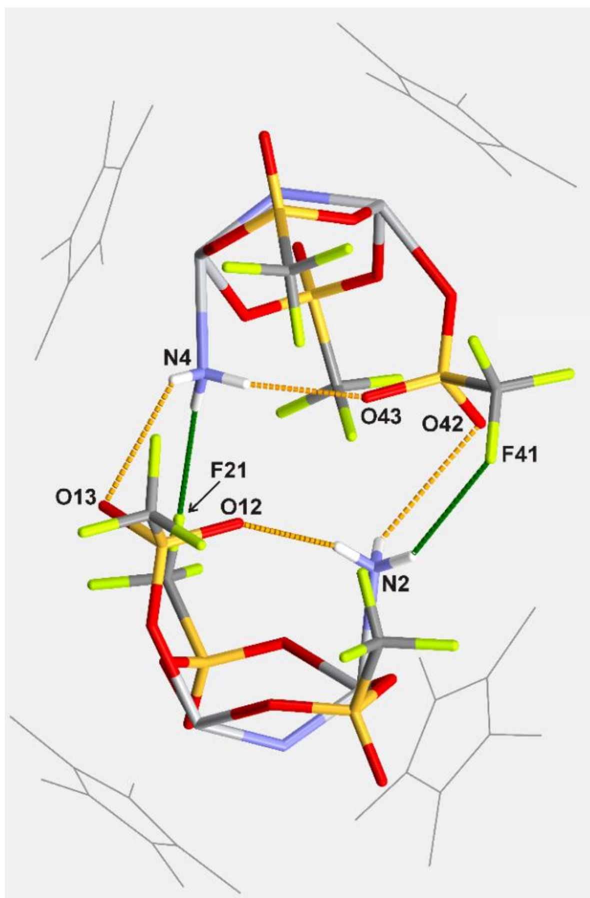


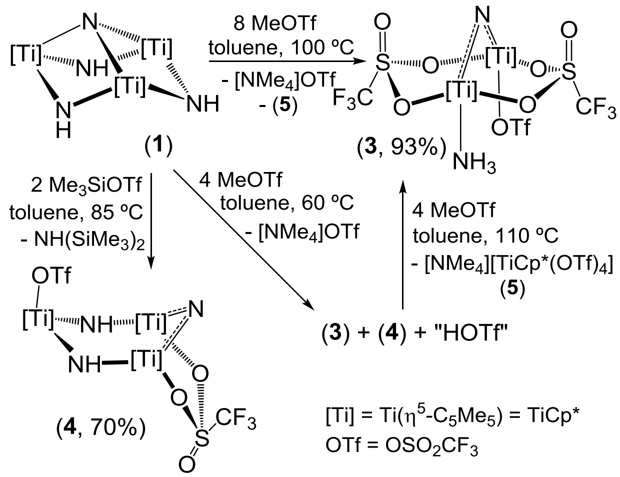
Figure 2. Simplified view of the most relevant intra- and intermolecular hydrogen bonding interactions present in complex **3** (N–H···O hydrogen bonds are drawn in orange, whereas N–H···F interactions are in green).

Table 2. Relevant Hydrogen Bonds[a] for Compound **3**

D–H···A	D···A/Å	H···A/Å	D–H···A/deg
N(2)–H(21)···O(42)	3.275(6)	2.77(7)	124(6)
N(2)–H(22)···F(41)	3.548(8)	2.75(6)	154(6)
N(2)–H(23)···O(12)	2.961(6)	2.09(6)	165(6)
N(4)–H(41)···O(43)	2.972(7)	2.18(6)	164(5)
N(4)–H(42)···O(13)	3.164(6)	2.60(7)	126(6)
N(4)–H(43)···F(21)	3.259(7)	2.34(5)	159(5)

[a]A = acceptor; D = donor.

Compound **3** was also isolated in 93% yield from the orange solution resulting of the treatment of **1** with 8 equiv of methyl triflate in toluene at 100 ºC for 2 days (Scheme 4). Along with this solution, a light violet precipitate was obtained in the reaction. This solid was only soluble in dimethylsulfoxide-d_6, and its composition was analyzed by NMR spectroscopy. The spectra revealed a 1:1 mixture of the tetramethylammonium salts $[NMe_4]OTf$ and $[NMe_4][Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]$ (**5**), which were independently synthetized by other procedures. Thus, the reaction of **1** with 4 equiv of MeOTf in toluene at 60 ºC for 16 h afforded an orange solution and a white precipitate. Spectroscopic and analytical data of this solid were consistent with the ionic compound $[NMe_4]OTf$,[33] whereas the orange solution obtained in the reaction was shown to contain a 1:1 mixture of **3** and the trinuclear derivative $[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}N)(\mu\text{-}NH)_2(\mu\text{-}O_2SOCF_3)(OTf)]$ (**4**) according to ^1H NMR spectroscopy. Compounds **3** and **4** exhibit a similar solubility in toluene, but crystallization at –30 ºC gave a few orange crystals of **4**·C_7H_8 suitable for a single crystal X-ray diffraction determination (vide infra). Interestingly, addition of 4 equiv of MeOTf to the toluene solution containing derivatives **3** and **4**, and subsequent heating at 110 ºC for 16 h, cleanly afforded an orange solution of complex **3** along with violet crystals characterized as $[NMe_4][Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]$ (**5**) by X-ray crystallography.



Scheme 4. Reactions of **1** with excess ROTf (R = Me, $SiMe_3$).

The synthesis of **4** in a pure form and good yield (70%) was achieved by treatment of **1** with 2 equiv of trimethylsilyl triflate in toluene at 85 ºC (Scheme 4). The first step in the formation of **4** involves the reaction of one equivalent of Me_3SiOTf with **1** at room temperature to give the previously reported complex $[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)(\mu\text{-}NH)_2(\mu\text{-}NHSiMe_3)][OTf]$ (Scheme 1).[28] Subsequent silylation of the $NHSiMe_3$ amido ligand of this ionic compound with an additional equivalent of Me_3SiOTf at higher temperatures would result in formation of the amine $NH(SiMe_3)_2$, which is eventually released with concomitant coordination of the triflato groups to give compound **4**.

The ^1H NMR spectrum of **4** in benzene-d_6 at room temperature shows two sharp singlets in a 2:1 ratio for the η^5-C_5Me_5 ligands and a broad resonance at δ = 14.19 for the imido groups. While the ^1H and $^{13}C\{^1H\}$ NMR spectra are consistent with a C_s symmetry in solution, the ^{19}F NMR spectrum showed only one resonance for the triflato groups, even though the solid-state structure reveals inequivalent terminal and bridging triflato ligands. This could be due to coincidence of the resonance signals or the existence of a rapid dynamic exchange involving terminal and bridging sites of the triflato groups in solution. The X-ray crystal structure consists of a [Ti_3N_3] six-membered ring in boat conformation (Figure 3). The titanium atoms have classical three-legged piano-stool arrangements, where the legs are occupied by two imido and a terminal triflato ligands in the case of Ti(3), and one of the oxygen atoms of the bridging triflato group, one imido and one nitrido ligands for Ti(1) and Ti(2). The trifluoromethanesulfonato ligand that links these two titanium atoms closes a second six-membered [Ti_2NO_2S] ring in chair conformation. The Ti–N(imido) distances (Table 3) in **4** range from 1.880(5) to 1.894(5) Å, and resemble the values found in complexes **1** (av. 1.930(7) Å)[22] and [$Ti_3(\eta^5$-$C_5Me_5)_3(\mu_3$-N)(μ-NH)(μ-NH_2)(μ-NR)(OTf)] (1.831(3)–1.858(3) Å)[28]. However, the Ti–N(nitrido) distances of 1.791(5) and 1.797(4) Å are clearly shorter and agree with the higher titanium-nitrogen bond order expected for a Ti=N=Ti unit.[40] Those Ti–N lengths compare well with the averaged value of 1.797(2) Å found in the dinuclear compound **3**. In a fashion similar to this derivative, the narrow Ti–N(nitrido)–Ti angle (125.1(3)°) in complex **4** can be explained by the existence of two additional bridging systems, a triflato ligand and a [(μ-$NH)_2Ti(\eta^5$-C_5Me_5)(OTf)] fragment, between the Ti(1) and Ti(2) atoms. Lastly, the crystal structure of **4** shows two different types of bonded triflato ligands. The terminal triflato ligand is coordinated to Ti(3) with a titanium–oxygen bond distance of 2.038(10) Å, which compares well with those found in other compounds such as [$Ti(\eta^5$-C_5Me_5)(OMe)(μ-O_2SOCF_3)(OTf)]$_2$ (2.039(4) Å) and [$Ti(\eta^5$-C_5Me_5)(μ-OH)(μ-O_2SOCF_3)(OTf)]$_2$ (2.071(3) Å).[41a] The Ti–O distances associated with the bridging triflato ligand (averaged 2.088(9) Å) are logically longer than that of the terminal ligand, but they are shorter than those (2.125(2)–2.164(3) Å) found in the bridging ligands of the aforementioned examples.[41a]

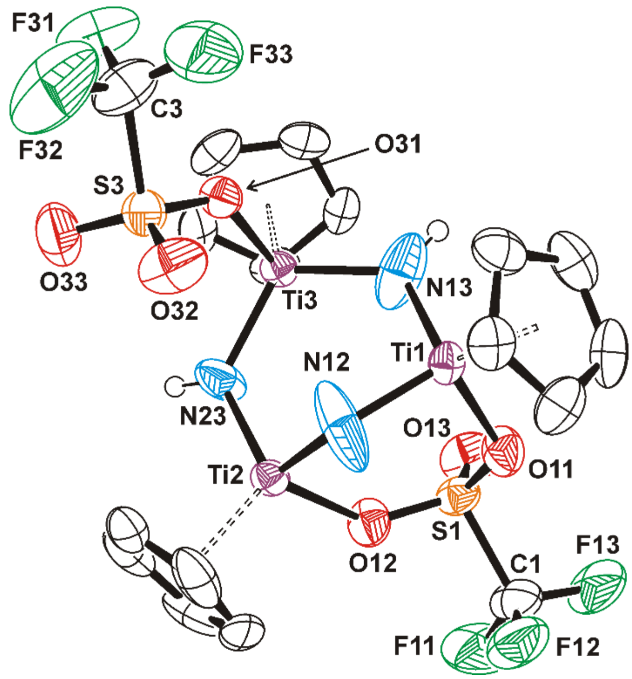
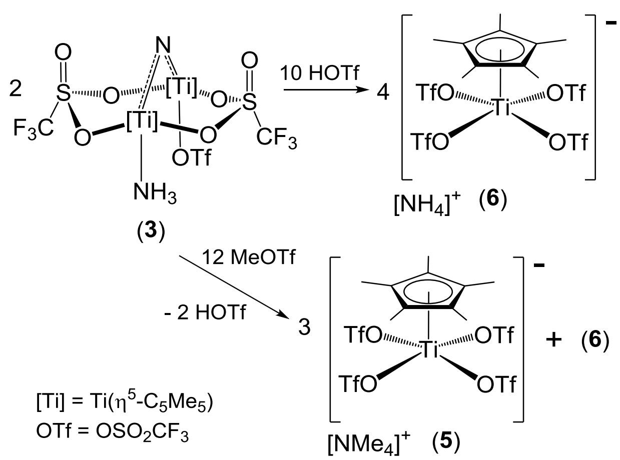


Figure 3. Perspective view of complex **4**·C_7H_8 (thermal ellipsoids at the 50% probability level). The methyl groups of the η^5-C_5Me_5 ligands and the toluene solvent molecule are omitted for clarity.

Table 3. Selected Lengths (Å) and Angles (deg) for Complex **4**

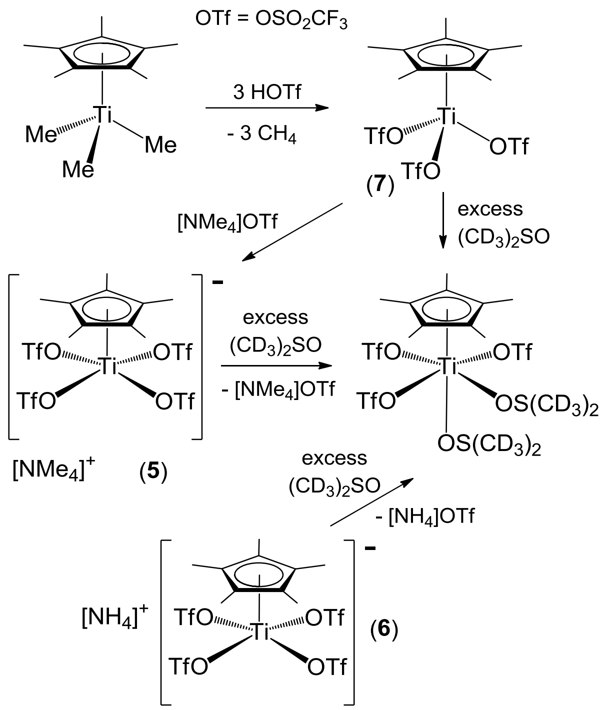
Ti(1)–N(12)	1.797(4)	Ti(1)–N(13)	1.880(5)
Ti(1)–O(11)	2.082(3)	Ti(2)–N(12)	1.791(5)
Ti(2)–N(23)	1.888(4)	Ti(2)–O(12)	2.095(3)
Ti(3)–N(13)	1.894(5)	Ti(3)–N(23)	1.892(4)
Ti(3)–O(31)	2.038(10)	Ti(1)···Ti(2)	3.184(1)
Ti(1)···Ti(3)	3.276(1)	Ti(2)···Ti(3)	3.198(1)
N(12)–Ti(1)–N(13)	101.6(3)	N(12)–Ti(1)–O(11)	100.4(2)
N(13)–Ti(1)–O(11)	101.8(2)	N(12)–Ti(2)–N(23)	104.7(3)
N(12)–Ti(2)–O(12)	99.6(2)	N(23)–Ti(2)–O(12)	103.5(2)
N(13)–Ti(3)–N(23)	116.5(2)	N(13)–Ti(3)–O(31)	100.3(3)
N(23)–Ti(3)–O(31)	107.9(2)	Ti(1)–N(12)–Ti(2)	125.1(3)
Ti(1)–N(13)–Ti(3)	120.5(3)	Ti(2)–N(23)–Ti(3)	115.6(2)

The reactivity of the dinuclear complex $[Ti_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}N)(NH_3)(\mu\text{-}O_2SOCF_3)_2(OTf)]$ (**3**) with a large excess of electrophilic reagents ROTf (R = H, Me) was also examined (Scheme 5). The treatment of **3** with 5 equiv of HOTf in toluene at room temperature afforded the precipitation of a violet solid characterized as $[NH_4][Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]$ (**6**) in good yield (89%). However, the analogous reaction of **3** with excess MeOTf leads to a mixture of complexes $[NMe_4][Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]$ (**5**) and **6**. Compounds **5** and **6** are only soluble in dimethylsulfoxide but **5** could not be isolated in a pure form by fractional crystallization of this mixture.



Scheme 5. Reactions of **3** with excess ROTf (R = H, Me).

To isolate the ionic compound $[NMe_4][Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]$ (**5**) in a pure form and good yield, we first synthetized the hitherto unknown neutral derivative $[Ti(\eta^5\text{-}C_5Me_5)(OTf)_3]$ (**7**). Complex **7** was obtained in 67% yield by reaction of $[Ti(\eta^5\text{-}C_5Me_5)Me_3]$ with 3 equiv of triflic acid in toluene at room temperature (Scheme 6). Subsequent treatment of **7** with $[NMe_4]OTf$ in toluene at room temperature afforded compound **5** in high purity. While ionic compounds **5** and **6** are only soluble in dimethylsulfoxide-d_6, the molecular complex **7** is also soluble in chloroform-d_1. Complexes **5-7** were characterized by spectroscopic and analytical methods, as well as by an X-ray crystal structure determination for **5**. IR spectra (KBr) show several strong absorptions between 1364 and 1009 cm^{-1} for the coordinated trifluoromethanesulfonato groups.[39] In addition, the IR spectrum of **6** displays a very broad band at 3259 cm^{-1} for the ν_{NH} vibration of the $[NH_4]^+$ cation. The ^1H NMR spectrum of a violet solution of **7** in chloroform-d_1 exhibits a singlet at δ = 2.63 for the η^5-C_5Me_5 group. The resonance for the *ipso* carbons of the C_5Me_5 group (δ = 149.9) in the $^{13}C\{^1H\}$ NMR spectrum of **7** in chloroform-d_1 is shifted downfield with respect those found in analogous 12-electron complexes $[Ti(\eta^5\text{-}C_5Me_5)X_3]$ (X = Cl, δ = 137.2; Br, δ = 138.2; OEt, δ = 120.5; OPh, δ = 126.5).[44] This deshielding effect is consistent with the strong electron withdrawing character of the triflato ligand. Noteworthy, the violet compound **7** readily dissolves in dimethylsulfoxide-d_6 to give a brown solution, and the $^{13}C\{^1H\}$ NMR spectrum shows a resonance signal at δ = 140.0 for the *ipso* carbons of the C_5Me_5 group. The color change and significant high-field shift of this resonance signal when compared with those in chloroform-d_1 suggest the coordination of dimethylsulfoxide molecules to the titanium atom of compound **7** (Scheme 6). Furthermore, the ^1H and $^{13}C\{^1H\}$ NMR spectra of brown solutions of compounds **5** and **6** in dimethylsulfoxide-d_6 show resonance signals for the η^5-C_5Me_5 ligands (δ_H = 2.08, and δ_C = 140.0 and 13.3) which are identical to those of complex **7** in that solvent. In addition, the NMR spectra of **5** and **6** shows the same resonance signals assignable to the $[NR_4]^+$ groups that those found for the $[NR_4]OTf$ salts. These data suggest that compounds **5**–**7** reacts with dimethylsulfoxide-d_6 to give the same species in solution via displacement of the corresponding salts $[NR_4]OTf$ in compounds **5** and **6**. This species could be tentatively formulated as the 16-electron complex $[Ti(\eta^5\text{-}C_5Me_5)(OTf)_3\{OS(CD_3)_2\}_2]$ (Scheme 6), but ionic derivatives with triflate anions (e.g., $[Ti(\eta^5\text{-}C_5Me_5)(OTf)_2\{OS(CD_3)_2\}_3][OTf]$) cannot be ruled out.



Scheme 6. Synthesis of **5** and plausible behavior of **5**-**7** in DMSO-d_6.

The solid-state structure of **5** shows well-separated tetrahedral $[NMe_4]^+$ cations and mononuclear titanium anions $[Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]^-$. The titanium atom exhibits a four-legged piano-stool arrangement, with the legs occupied by an oxygen atom of the terminal trifluoromethanesulfonato groups (Figure 4 and Table S3). The Ti–O bond lengths of averaged 2.014(7) Å are similar to those found in complexes **3**, **4** and other examples with terminal triflato ligands.[41] Furthermore, the distance from the titanium atom to the centroid of the pentamethylcyclopentadienyl group of 2.045 Å is comparable to those reported for the analogous derivatives [Ti(η^5-C_5Me_5)Cl_3][45] and [Ti(η^5-C_5Me_5)(OC_6F_5)$_3$][46].

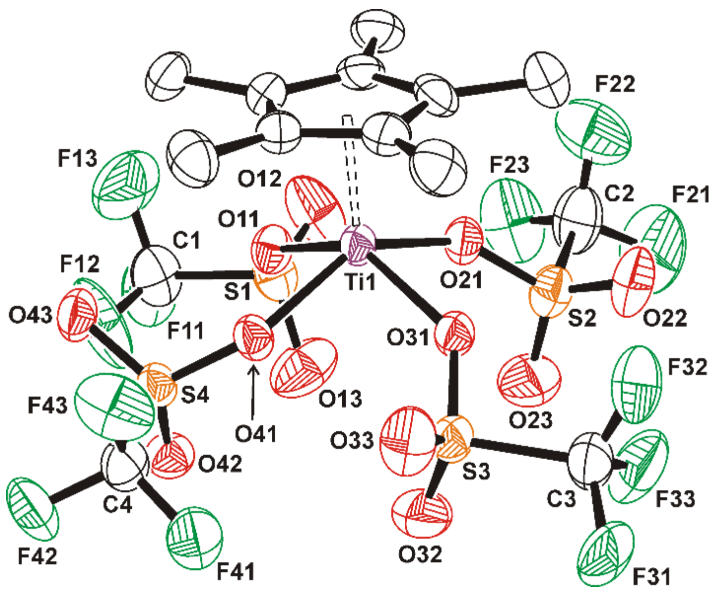
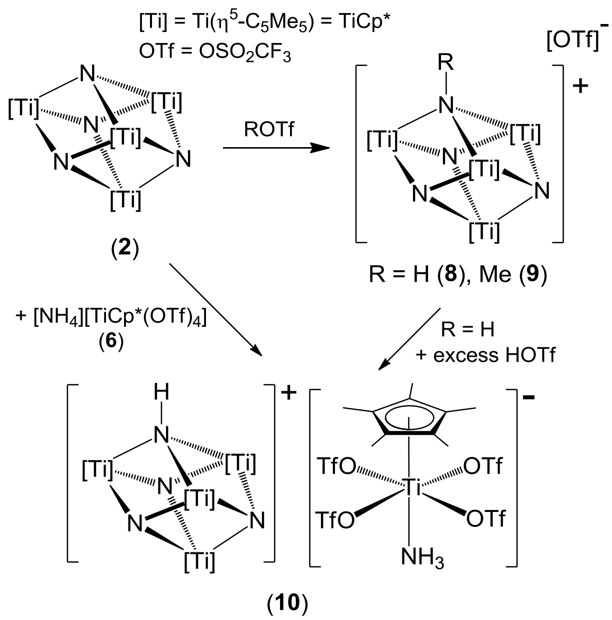


Figure 4. Perspective view for the anion of compound **5** (thermal ellipsoids at the 50% probability level). Hydrogen atoms of the methyl groups are omitted for clarity. Selected averaged bond lengths (Å) and angles (deg): Ti(1)–O 2.014(7), Ti(1)–Cm 2.045, O–Ti(1)–Cm 109(1), O–Ti(1)–O_{cis} 83.7(7), O–Ti(1)–O_{trans} 141(2). Cm = Centroid of the pentamethylcyclopentadienyl ring.

Reactions of complex 2 with ROTf and [M(η^5-C_5H_5)$(CO)_3$H] reagents.

We have also studied the reactivity of the tetranuclear nitrido complex [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_4$] (**2**) with electrophilic ROTf (R = H, Me, Me_3Si) reagents (Scheme 7). Treatment of **2** with 1 equiv of triflic acid or methyl triflate in toluene afforded the precipitation of the ionic complexes [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_3$(μ_3-NR)][OTf] (R = H (**8**),[29] Me (**9**)). Interestingly, no reaction was observed in the treatment of **2** with the larger trimethylsilyl fragment of Me_3SiOTf even at high temperatures. While compound **9** did not react with higher ratios of MeOTf even upon heating the reaction mixture at 100 ºC, the treatment of **2** with excess HOTf in toluene at room temperature led to the formation of $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_3(\mu_3\text{-}NH)][Ti(\eta^5\text{-}C_5Me_5)(OTf)_4(NH_3)]$ (**10**). We speculate that triflic acid could produce the complete rupture of a fraction of a tetranuclear aggregate to form 4 equiv of $[NH_4][Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]$ (**6**), and this salt subsequently reacts with the remaining tetranuclear molecules to give **10**. Indeed, compound **10** was isolated in 80% yield by treatment of a toluene solution of **2** with 1 equiv of the ionic derivative **6** at room temperature (Scheme 7).



Scheme 7. Reactions of **2** with ROTf (R = H, Me).

Compounds **8-10** were obtained in good yields (72-80%) as red solids, which are not soluble in hydrocarbon solvents but exhibit a good solubility and stability in halogenated solvents. The compounds were characterized by spectroscopic and analytical methods, as well as by X-ray crystal structure determinations. The IR spectra (KBr) of derivatives **8** and **10** show one and two bands, respectively, for the ν_{NH} vibrations of the NH and NH_3 ligands. In addition, the IR spectrum of **10** reveals one band at 1620 cm^{-1} assignable to the NH_3 bending mode. However, the most important difference among the IR spectra of the three compounds is found in the trifluoromethanesulfonato group $\nu_{as}(SO_3)$ vibrations. In complex **9** there is only one band at 1275 cm^{-1} assignable to the $CF_3SO_3^-$ ion,[39b] whereas in **8** this vibration splits into two bands, at 1285 and 1255 cm^{-1}, due to the hydrogen bonding interaction between the triflate ion and the NH imido group of the cation $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_3(\mu_3\text{-}NH)]^+$.[39c] The ^1H NMR spectra in chloroform-d_1 at room temperature of compounds **8**-**10** reveal two singlets in a 3:1 ratio for the C_5Me_5 ligands of the cation, which are consistent with C_{3v}-symmetric structures in solution. In addition to the resonances due to the C_5Me_5 ligands of the cation, the $^{13}C\{^1H\}$ NMR spectrum of **10** displays one resonance signal at δ = 147.2 for the *ipso* carbons of the η^5-C_5Me_5 group of the anionic fragment. This value is slightly shifted to high-field compared to that of the neutral complex $[Ti(\eta^5\text{-}C_5Me_5)(OTf)_3]$ (**7**) in chloroform-d_1 (δ = 149.9), but clearly downfield with respect to that of complexes **5**-**7** in dimethylsulfoxide-d_6 (δ = 140.0). These data further support the incorporation of dimethylsulfoxide molecules into the coordination sphere of the titanium center in complexes **5**-**7** in that solvent (see above), because the 16-electron complex $[Ti(\eta^5\text{-}C_5Me_5)(OTf)_4(NH_3)]^-$ should give a resonance at higher field than the 14-electron anion $[Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]^-$.

The X-ray diffraction studies on complexes **8**-**10** confirm their ionic nature. There are no substantial differences in the cations of these compounds, except the substitution of the μ_3-NH group in **8** and **10** for a μ_3-NMe ligand in **9**. The solid-state structure of **8** shows a weak[43] N–H···O hydrogen bonding interaction between the triflate anion and the NH imido group of the cationic fragment.[29] The structure for the cation of **10** is shown in Figure 5 and selected averaged distances and angles for the cations of the three complexes are compared in Table 4. The crystal structure of these ions consist of almost perfect [Ti_4N_4] cube cores, with the Ti–N–Ti and the N–Ti–N angles very close to 90º, in an analogue disposition of the parent complex **2**.[23] Each titanium center is bound to one pentamethylcyclopentadienyl ligand and three bridging nitrogen atoms in a three-legged piano-stool arrangement. The protonation or methylation of one nitrido ligand results in a lengthening of ca. 0.1 Å of the Ti–N distances of the {$Ti_3(\mu_3$-NR)} fragments compared with the Ti–N separations of the {$Ti_3(\mu_3$-N)} units. An analogous lengthening in those distances has been found in the {$Ti_3(\mu_4$-N)MX} fragments of the Lewis acid-base adducts [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_{4-n}${(μ_4-N)MX}$_n$] previously prepared in our group.[26]

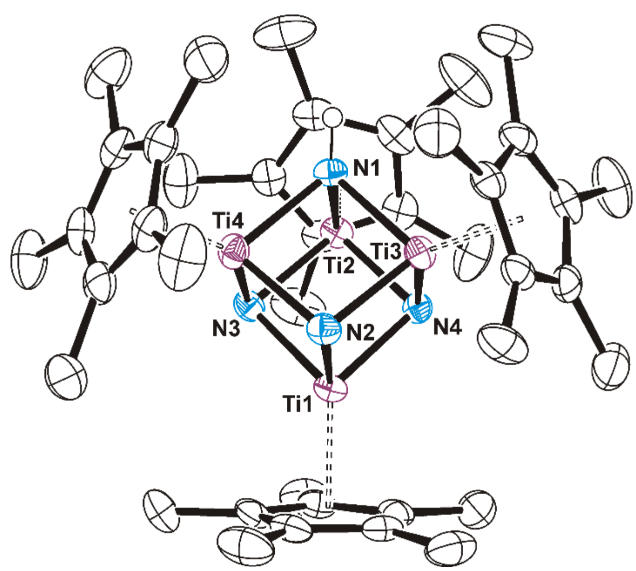


Figure 5. Perspective view for the cation of **10** (thermal ellipsoids at the 50% probability level). Hydrogen atoms of the η^5-C_5Me_5 ligands are omitted for clarity.

Table 4. Selected Averaged Lengths (Å) and Angles (deg) for the Cations of **8–10**

	8·$3C_6H_5F$[29]	**9**·C_7H_8	**10**
Ti–N_{imido}	2.044(6)	2.040(2)	2.010(8)
Ti–$N_{nitrido}$	1.937(12)	1.932(13)	1.944(11)
Ti···Ti	2.782(1)–2.876(1)	2.782(1)–2.867(1)	2.797(1)–2.862(1)
N(1)–C(1)	–	1.394(10)	–
Ti–N_{imido}–Ti	89.4(2)	89.2(2)	90.7(1)
Ti–$N_{nitrido}$–Ti	91.3(1)–96.7(1)	91.6(2)–96.3(2)	91.8(1)–95.2(1)
N–Ti–N	87.6(7)	87.6(6)	87.5(6)
C(1)–N(1)–Ti	–	123.7(5)–127.9(5)	–

The anionic fragment of complex **10** (Figure 6) is similar to the titanate anion of $[NMe_4][Ti(\eta^5\text{-}C_5Me_5)(OTf)_4]$ (**5**) with the incorporation of an ammine ligand. If the centroid of the pentamethylcyclopentadienyl ring is considered, the titanium atom exhibits a distorted octahedral geometry, with the η^5-C_5Me_5 and ammine groups located in *trans* positions and four oxygen atoms of the triflato ligands occupying the rest of the sites in the octahedron. The Ti–Cm distance of 2.128 Å in **10** is clearly longer than that found in the anion of **5** (2.045 Å) most likely due to the electron donation of the NH_3 ligand and the steric repulsions about the more crowded titanium center. The Ti(5)–N(5) bond length of 2.231(4) Å is similar to that found in the Ti–NH_3 fragment of the dinuclear complex **3** (av. 2.194(9) Å), while the Ti(5)–O bond lengths have an averaged value of 2.073(4) Å and are slightly longer than in **5** (av. Ti–O 2.014(7) Å).

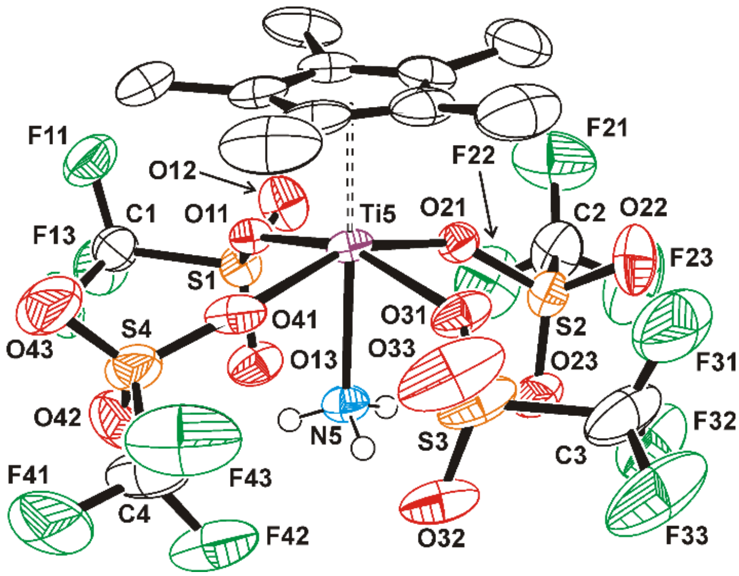
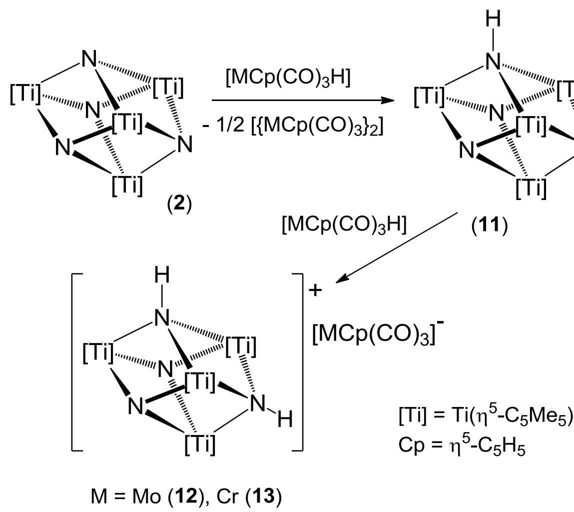


Figure 6. Perspective view for the anion of **10** (thermal ellipsoids at the 50% probability level). Hydrogen atoms of the η^5-C_5Me_5 ligands are omitted for clarity. Selected averaged bond lengths (Å) and angles (deg) for the anion: Ti(5)–N(5) 2.231(4), Ti(5)–O 2.073(4), Ti(5)–Cm 2.128, N(5)–Ti(5)–Cm 177.7, O–Ti(5)–Cm 101.7(5), O–Ti(5)–O_{cis} 88(2), O–Ti(5)–O_{trans} 156.6(9), N(5)–Ti(5)–O 78(2). Cm = Centroid of the pentamethylcyclopentadienyl ring.

We have also explored the reaction of complex $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ (**2**) with weakly acidic group 6 hydride derivatives $[M(\eta^5\text{-}C_5H_5)(CO)_3H]$ (M = Mo, pK_a = 13.9; M= Cr, pK_a = 13.3)[47] (Scheme 8). The chromium hydride compound is a weak acid and reducing agent that has been applied to N–H bond formation in titanium compounds by PCET pathways.[16b] Indeed, complex **2** reacted with $[M(\eta^5\text{-}C_5H_5)(CO)_3H]$ (1 equiv) in toluene at room temperature to give the paramagnetic molecular derivative $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_3(\mu_3\text{-}NH)]$ (**11**) via hydrogenation of one nitrido ligand. Compound **11** has been previously prepared by treatment of **2** with 2 equiv of ammonia borane (65% yield) or by stepwise proton and electron transfer with HOTf and [K(C_5Me_5)] (Scheme 2).[29] However, the synthesis with [Mo(η^5-C_5H_5)$(CO)_3$H] gave **11** in a higher isolated yield (88%) since the [{Mo(η^5-C_5H_5)$(CO)_3$}$_2$] by-product of this reaction is easily separated from **11** due to its enhanced solubility in hydrocarbon solvents.



Scheme 8. Reactions of **2** with [M(η^5-C_5H_5)$(CO)_3$H] (M = Mo, Cr).

In contrast to this hydrogenation reaction of a nitrido group in **2**, the treatment of **11** with an additional equivalent of [M(η^5-C_5H_5)$(CO)_3$H] afforded the ionic compounds [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_2$(μ_3-NH)$_2$][M(η^5-C_5H_5)$(CO)_3$] (M = Mo (**12**), Cr (**13**)) by protonation of other nitrido group. Compounds **12** and **13** were isolated in 82 and 38% yields as dark green solids, which are not soluble in hydrocarbon solvents but exhibit a good solubility in pyridine-d_5. The compounds are also soluble in chloroform-d_1 but readily react with this solvent to give [Ti(η^5-C_5Me_5)Cl_3] and other unidentified species. Complexes **12** and **13** were characterized by spectroscopic and analytical methods, as well as by an X-ray crystal structure determination for **13**. The IR spectra (KBr) show two N–H stretching modes, between 3289 and 3264 cm^{-1}, as the absorptions expected for C_{2v} symmetry (A_1 and

B_2 vibrations) of the cationic fragment. These two bands are similar to those found in the neutral complex $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}CH)_2(\mu_3\text{-}NH)_2]$,[24] while one absorption is observed in the spectra of **11** (3333 cm^{-1}) and **8** (3237 cm^{-1}).[29] In addition, the IR spectra of compounds **12** and **13** show strong bands, between 1936 and 1746 cm^{-1}, for the ν(CO) vibrations of the $[M(\eta^5\text{-}C_5H_5)(CO)_3]^-$ anions. The ^1H NMR spectra of **12** and **13** in pyridine-d_5 reveal two far-downfield (δ = 9.3 and 8.0) and broad resonances for the η^5-C_5Me_5 ligands in a 1:1 ratio in accord with a C_{2v} symmetry in solution. These resonance signals are comparable to those found in the spectrum of complex **11** in chloroform-d_1 (δ = 10.0 and 8.7 in a 1:3 ratio) which is paramagnetic with a μ_{eff} = 1.70 μ_B according to the Evans method[32] determination of the magnetic susceptibility in this solvent. Similarly, compounds **12** and **13** in pyridine-d_5 solutions gave μ_{eff} values of 1.64 and 1.62 μ_B, which are consistent with the presence of one unpaired electron in the complexes.

The crystal structure of compound **13** contains $[Cr(\eta^5\text{-}C_5H_5)(CO)_3]^-$ and $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_2(\mu_3\text{-}NH)_2]^+$ ions. The cationic fragment shows an almost perfect $[Ti_4N_4]$ cube core (Figure 7), with the Ti–N–Ti and N–Ti–N angles very close to 90º, similar to those found in the neutral complexes $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$[23] (**2**) and $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_3(\mu_3\text{-}NH)]$ (**11**).[29] The titanium–nitrogen(imido) lengths (av. 2.02(2) Å) are longer than titanium–nitrogen(nitrido) separations (av. 1.964(8) Å). The averaged Ti···Ti (2.85(3) Å) and Ti–N (1.99(3) Å) separations in **13** are slightly longer than those found in complex **2** (2.783(2) and 1.938(7) Å).

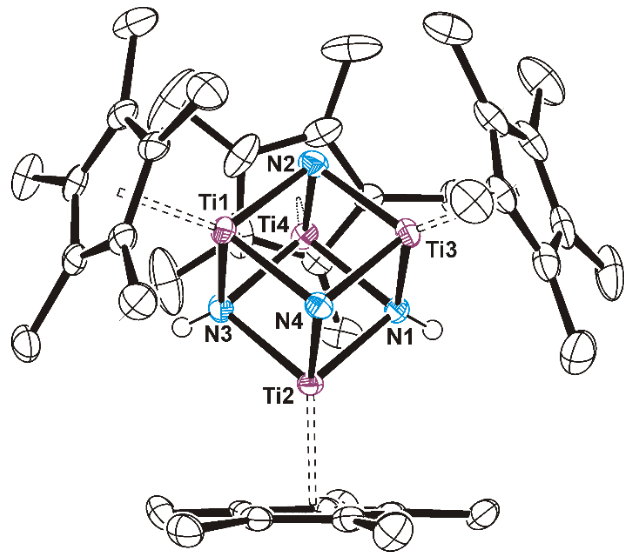


Figure 7. Perspective view of the cation of **13** (thermal ellipsoids at the 50% probability level). Hydrogen atoms of the η^5-C_5Me_5 ligands are omitted for clarity. Selected averaged lengths (Å) and angles (deg): Ti–N(1) 2.032(8), Ti–N(2) 1.962(5), Ti–N(3) 1.998(3), Ti–N(4) 1.965(12), Ti···Ti 2.824(1)–2.904(1), N–Ti–N 87.8(1)–89.2(1), Ti–N–Ti 88.8(1)–93.6(1).

Conclusion

We have shown the isolation and structural characterization of several polynuclear nitrido titanium(IV) derivatives through the reaction of complexes [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] and [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_4$] with different molar ratios of electrophilic reagents ROTf (R = H, Me, Me_3Si; OTf = OSO_2CF_3). The electrophilic attacks with low ratios of electrophiles occur selectively at the imido ligands of [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] to give trinuclear or dinuclear species while the nitrido ligand remains unaltered. The functionalization of the bridging nitrido unit was only observed with a large excess of electrophiles to afford the ammonium salts $[NR_4][Ti(\eta^5-C_5Me_5)(OTf)_4]$ (R = H, Me). Similarly, one of the nitrido groups of $[\{Ti(\eta^5-C_5Me_5)\}_4(\mu_3-N)_4]$ reacts with triflic acid or methyl triflate to form a μ_3-NR imido ligand, but a higher ratio of triflic acid produces the rupture of a fraction of the tetranuclear complex with formation of the ionic species $[\{Ti(\eta^5-C_5Me_5)\}_4(\mu_3-N)_3(\mu_3-NH)][Ti(\eta^5-C_5Me_5)(OTf)_4(NH_3)]$. Initial stoichiometric studies of the tetranitrido $[\{Ti(\eta^5-C_5Me_5)\}_4(\mu_3-N)_4]$ with group 6 hydride complexes $[M(\eta^5-C_5H_5)(CO)_3H]$ (M = Mo, Cr) results in the hydrogenation of one nitrido ligand but a second equivalent of $[M(\eta^5-C_5H_5)(CO)_3H]$ leads to protonation of other nitrido group and not electron transfer occurs. We are currently evaluating the redox potentials of our titanium polynuclear species as well as the use of other hydride compounds in order to establish mild pathways for N–H bond formation.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.xxxxxx.

Experimental crystallographic data of complexes **3**, **4**, **5**, **9**, **10**, and **13**; perspective view of the crystal structures of complexes **3** and **9**; tables for selected lengths and angles of the crystal structures of **3**, **5**, **9**, **10** and **13**; selected NMR spectra (PDF).

Accession Codes

CCDC 1977628-1977633 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

Acknowledgments.

We are grateful to the Spanish MCIU (PGC2018-094007-B-I00) and the Universidad de Alcalá (CCG2018/EXP-008) for financial support of this research. P.B. and J.C. thank the UAH and MEC for fellowships.

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