Electronic Supplementary Information for:

Electrophilic Attack on Trinuclear Titanium Imido-Nitrido Systems

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Experimental Details and Characterization Data:

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. NMR solvents were dried with Na/K alloy (C_6D_6) or calcium hydride ($CDCl_3$) and vacuum-distilled. Dichloromethane-d_2 was dried over activated molecular sieves and stored under argon. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1 × 10^{-3} Torr) and subsequently filled with inert gas. $MeOSO_2CF_3$, $[M\{N(SiMe_3)_2\}]$ (M = Li, K) and $HOSO_2CF_3$ were purchased from Aldrich and used as received. $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) was prepared according to a published procedure.[1]

Samples for infrared spectroscopy were prepared as KBr pellets. ^1H, $^{13}C\{^1H\}$ and ^{19}F NMR spectra were recorded on a Varian Unity-300 and/or Unity-500 Plus 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. Chemical shifts (δ, ppm) in the

^{19}F NMR spectra are given relative to $CFCl_3$ as external reference. Microanalyses (C, H, N, S) were performed in a Leco CHNS-932 microanalyzer.

Reaction of 1 with one equiv of MeOTf in a NMR Tube-Scale Experiment. A 5 mm valved NMR tube was charged with **1** (0.015 g, 0.025 mmol), $MeOSO_2CF_3$ (0.004 g, 0.025 mmol) and benzene-d_6 (1.00 mL). The reaction course at room temperature was monitored by NMR spectroscopy. After 5 min, the spectra showed complete consumption of **1** and complex $[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)(\mu\text{-}NH)_2(\mu\text{-}NHMe)(OTf)]$ (**2**) was characterized by ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectroscopy. Spectra taken after 2 h revealed a mixture (3:1 ratio) of compounds **2** and **3**. Upon leaving the tube at room temperature for 24 h, orange crystals of **3** precipitated at the bottom of the tube and the ^{1}H NMR spectrum of the orange solution only showed resonances for **3**.

NMR data for $[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)(\mu\text{-}NH)_2(\mu\text{-}NHMe)(OTf)]$ (**2**): ^{1}H NMR (300 MHz, C_6D_6, 20 ºC): δ 12.64 (s br., 2H; NH), 2.97 (q, ^3J(H,H) = 6.6 Hz, 1H; N*H*Me), 2.63 (d, ^3J(H,H) = 6.6 Hz, 3H; NH*Me*), 1.91 (s, 15H; C_5Me_5), 1.81 (s, 30H; C_5Me_5). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 ºC): δ 124.8 (C_5Me$_5$), 118.5 (C_5Me$_5$), 42.7 (NH*Me*), 12.7 (C$_5$*Me*$_5$), 11.5 (C$_5$*Me*$_5$), the *C*F$_3$ carbon atom resonance was not detected. ^{19}F NMR (282 MHz, C_6D_6, 20 ºC): δ -77.3.

Synthesis of $[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)(\mu\text{-}NH)(\mu\text{-}NH_2)(\mu\text{-}NMe)(OTf)]$ (3). A solution of $MeOSO_2CF_3$ (0.14 g, 0.82 mmol) in toluene (2 mL) was carefully added to **1** (0.50 g, 0.82 mmol) in toluene (5 mL). The system was allowed to react without any stirring at room temperature for 24 h. After decantation, the resultant orange crystals were vacuum-dried to afford **3** (0.49 g, 78%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3350 (s), 3265 (m), 2909 (s), 2858 (s), 1590 (w), 1491 (w), 1437 (s), 1376 (s), 1308 (vs), 1230 (vs), 1203 (vs), 1175 (vs), 1122 (s), 1067 (w), 1011 (vs), 779 (vs), 757 (s), 705 (vs), 673 (vs), 635 (vs), 604 (s), 564 (s), 516 (s), 481 (m), 438 (m), 419 (w). ^{1}H NMR (300 MHz, C_6D_6, 20 ºC): δ

13.26 (s br., 1H; NH), 3.94 (s, 3H; NMe), 3.53 (m br., 1H; N*H*H), 2.28 (m br., 1H; NH*H*), 1.88 (s br., 15H; C_5Me_5), 1.84 (s, 15H; C_5Me_5), 1.83 (s br., 15H; C_5Me_5). ^{1}H NMR (300 MHz, $CDCl_3$, 20 ºC): δ 12.94 (s br., 1H; NH), 3.80 (s, 3H; NMe), 3.28 (m br., 1H; N*H*H), 2.49 (m br., 1H; NH*H*), 2.03 (s br., 15H; C_5Me_5), 2.00 (s, 15H; C_5Me_5), 1.88 (s br., 15H; C_5Me_5). ^{1}H NMR (300 MHz, CD_2Cl_2, 20 ºC): δ 13.03 (s br., 1H; NH), 3.82 (s, 3H; NMe), 3.27 (m br., 1H; N*H*H), 2.78 (m br., 1H; NH*H*), 2.05 (s br., 15H; C_5Me_5), 2.03 (s, 15H; C_5Me_5), 1.92 (s br., 15H; C_5Me_5). ^{1}H NMR (500 MHz, CD_2Cl_2, -30 ºC): δ 12.84 (s br., 1H; NH), 3.74 (s, 3H; NMe), 3.17 (d, ^2J(H,H) = 8.5 Hz, 1H; N*H*H), 2.65 (d, ^2J(H,H) = 8.5 Hz, 1H; NH*H*), 2.00 (s, 15H; C_5Me_5), 1.98 (s, 15H; C_5Me_5), 1.84 (s, 15H; C_5Me_5). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 ºC): δ 124.2 (br., C_5Me_5), 118.3 (C_5Me_5), 117.7 (br., C_5Me_5), 52.5 (N*Me*), 12.2 ($C_5\mathit{Me}_5$), 11.8 ($C_5\mathit{Me}_5$), 11.5 ($C_5\mathit{Me}_5$), the *C*F_3 carbon atom resonance was not detected. ^{19}F NMR (282 MHz, $CDCl_3$, 20 ºC): δ -78.0. Anal. Calcd for $C_{32}H_{51}F_3N_4O_3STi_3$ (M_w = 772.44): C 49.76, H 6.65, N 7.25, S 4.15. Found: C 50.01, H 6.55, N 7.25, S 4.21.

Synthesis of [(F_3CSO_2O)Li{(μ_3-NH)$_2$(μ_3-NMe)Ti_3(η^5-C_5Me_5)$_3$(μ_3-N)}]$_2$ (4). A 100 mL Schlenk flask was charged with **3** (0.20 g, 0.26 mmol), [Li{N($SiMe_3$)$_2$}] (0.043 g, 0.26 mmol) and toluene (25 mL). The reaction mixture was stirred at room temperature for 24 h to give an abundant yellow solid and an orange solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **4** as a yellow powder (0.17 g, 85%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3356 (w), 2914 (s), 2859 (m), 1490 (w), 1430 (m), 1377 (s), 1295 (vs), 1279 (vs), 1229 (s), 1162 (vs), 1103 (m), 1042 (s), 950 (w), 744 (s), 667 (vs), 637 (s), 595 (w), 514 (w), 474 (w), 431 (w). Anal. Calcd for $C_{64}H_{100}F_6Li_2N_8O_6S_2Ti_6$ (M_w = 1556.75): C 49.38, H 6.47, N 7.20, S 4.12. Found: C 49.29, H 6.90, N 7.03, S 3.98.

Solutions of **4** in chloroform-d$_1$ immediately undergo partial dissociation (ca. 25 %) to give complex **5** and presumably [Li(O$_3$SCF$_3$)]. Spectra taken after 24 h at room temperature showed a 1:1 mixture of **4** and **5** in solution. This mixture remains unaltered for weeks at room temperature. NMR data for **4**: ^{1}H NMR (300 MHz, CDCl$_3$, 20 ºC): δ 12.89 (s br., 4H; NH), 4.00 (s, 6H; N*Me*), 2.03 (s, 30H; C$_5$Me$_5$), 2.01 (s br., 60H; C$_5$Me$_5$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 20 ºC): δ 120.1 (*C*$_5$Me$_5$), 117.5 (*C*$_5$Me$_5$), 51.8 (N*Me*), 11.8 (C$_5$*Me*$_5$), 11.5 (C$_5$*Me*$_5$).^{19}F NMR (282 MHz, CDCl$_3$, 20 ºC): δ -78.3.

Synthesis of [Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)(μ-NH)$_2$(μ-NMe)] (5). A 100 mL ampule (Teflon stopcock) was charged with **3** (0.70 g, 0.91 mmol), [K{N(SiMe$_3$)$_2$}] (0.18 g, 0.91 mmol) and toluene (20 mL). The reaction mixture was stirred at 50 ºC for 24 h to give an orange solution and a white fine solid. After filtration, the volatile components of the solution were removed under reduced pressure to afford **5** as an orange solid (0.51 g, 91%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3355 (w), 2906 (vs), 2854 (s), 2754 (w), 1493 (w), 1431 (m), 1396 (w), 1374 (s), 1124 (s), 1067 (w), 1024 (w), 949 (w), 786 (s), 711 (vs), 677 (vs), 662 (vs), 626 (s), 606 (m), 530 (m), 501 (w), 449 (m), 418 (m). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 ºC): δ 14.09 (s br., 2H; NH), 3.94 (s, 3H; N*Me*), 2.04 (s, 30H; C$_5$Me$_5$), 1.99 (s, 15H; C$_5$Me$_5$). ^{1}H NMR (CDCl$_3$, 20 ºC): δ 13.71 (s br., 2H; NH), 4.03 (s, 3H; N*Me*), 2.02 (s, 15H; C$_5$Me$_5$), 2.00 (s, 30H; C$_5$Me$_5$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 20 ºC): δ 116.9 (*C*$_5$Me$_5$), 116.7 (*C*$_5$Me$_5$), 50.2 (N*Me*), 11.5 (C$_5$*Me*$_5$), 11.3 (C$_5$*Me*$_5$). Anal. Calcd for C$_{31}$H$_{50}$N$_4$Ti$_3$ (M_w = 622.36): C 59.83, H 8.10, N 9.00. Found: C 59.77, H 7.94, N 8.65.

Synthesis of [Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)(μ-NH)(μ-NHMe)(μ-NMe)(OTf)] (6). A 100 mL Schlenk flask was charged with **5** (0.20 g, 0.32 mmol), MeOSO$_2$CF$_3$ (0.052 g, 0.32 mmol) and hexane (25 mL). The reaction mixture was stirred at room temperature for 10 min to give an orange solid and a light brown solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **6** as an orange powder (0.19 g, 74%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3340 (m), 3306 (w), 2908 (s), 1495 (w), 1438 (m), 1378 (m), 1315 (s), 1232 (vs), 1207 (vs), 1168 (s), 1015 (vs), 955 (w), 787 (s), 754 (s), 711 (s), 678 (s), 634 (s), 590 (m), 516 (w), 482 (w), 464 (w), 436 (w). ^{1}H NMR (300 MHz, C_6D_6, 20 ºC): δ 13.20 (s br., 1H; NH), 3.90 (s, 3H; NMe), 2.70 (m, 1H; N*H*Me), 2.60 (d, ^3J(H,H) = 6.6 Hz, 3H; NH*Me*), 1.91 (s, 15H; C_5Me_5), 1.81 (s, 15H; C_5Me_5), 1.80 (s, 15H; C_5Me_5). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 ºC): δ 124.7 (C_5Me_5), 118.1 (C_5Me_5), 117.3 (C_5Me_5), 52.9 (NMe), 41.8 (NHMe), 12.5 ($C_5\mathit{Me}_5$), 11.6 ($C_5\mathit{Me}_5$), 11.3 ($C_5\mathit{Me}_5$), the *C*F_3 carbon atom resonance was not detected. ^{19}F NMR (282 MHz, C_6D_6, 20 ºC): δ -77.3. Anal. Calcd for $C_{33}H_{53}F_3N_4O_3STi_3$ (M_w = 786.45): C 50.39, H 6.79, N 7.12, S 4.07. Found: C 50.21, H 6.42, N 7.22, S 4.01.

X-ray structure determination of 3 and 4. Orange crystals of **3** were grown in toluene at room temperature as described in the Experimental Section. Yellow crystals of **4** were obtained by slow diffusion of a toluene solution of [Li{N($SiMe_3$)$_2$}] (5 mL) in a toluene solution of **3** (20 mL). The crystals were removed from the Schlenk 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 200K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit.

Crystallographic data for complexes **3** and **4** are presented in Table 1. The structures were solved, using the WINGX package,[2] by direct methods (SHELXS-97)[3] and refined by least-squares against F^2 (SHELXL-97).[3] Crystals of compound **3** presented disorder for the atoms S(1), O(1), O(2), O(3), C(2), F(1), F(2) and F(3) of the triflato ligand, and for two of the C_5Me_5 groups (C(11)-C(20) and C(21)-C(30)). The disorder of the triflato moiety was treated by using the PART tool and allowing free refinement of the occupancy factors with the FVAR command of the SHELXL-97 program. The final values were 91 and 9% for each position. Moreover the triflato ligand was restrained with SADI and DFIX instructions to hold a tetrahedral form. However it was not possible to resolve the disorder of the pentamethylcyclopentadienyl groups, although it did not affect the location of the core of the molecule. All non-hydrogen atoms were anisotropically refined, except C(2)’, F(1)’, F(2)’, F(3)’, O(1)’, O(2)’ and O(3)’, which were refined isotropically. The hydrogen atoms were positioned geometrically and refined using a riding model, except for those of the amido group, H(13)A and H(13)B, which were located in the difference Fourier map and refined isotropically.

The crystal structure of **4** was studied with the *C*2*/m*, *C*2 and *Cm* space groups, but only *C*2*/m* led to a sensible chemical model. The molecule lies on a crystallographic inversion center located on the midpoint between the two lithium atoms, and also presents a mirror plane containing the Li(1), Ti(2), N(1), N(11) and C(1) atoms. The triflato groups are located close to the mentioned symmetry elements leading each triflato ligand to be in two sites with an occupancy of 50% for the S(1), C(2), F(2) and O(2) atoms. This disorder prevents from clarifying the conformation of the [$Li_2O_4S_2$] eight-membered ring. SADI and DFIX restraints have been employed to hold a more reasonable geometry for the triflato groups, and DELU restraints have been also used for the CF_3 moiety. On the other hand, the C_5Me_5 ligand C(21)-C(28), which is located close to the mirror plane mentioned above, presents disorder too, but it was not possible to resolve it. However it does not affect the location of the molecule core. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined using a riding model, except that of the imido group, H(12), which was located in the difference Fourier map and refined isotropically.

References

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(2) L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837-838.

(3) G. M. Sheldrick, *SHELX97, Program for Crystal Structure Analysis (Release 97-2)*, Universität Göttingen, Germany, 1998.

Table 1.- Crystallographic data for complexes **3** and **4**.

Compound	**3**	**4**
Empirical formula	$C_{32}H_{51}F_3N_4O_3STi_3$	$C_{64}H_{100}F_6Li_2N_8O_6S_2Ti_6$
Formula weight	772.53	1556.92
Temperature (K)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P\ 2_1/c$	$C\ 2/m$
a(Å); α(°)	17.020(2)	16.296(1)
b(Å); β(°)	13.646(1); 115.16(1)	19.247(3); 97.98(1)
c(Å); γ(°)	17.195(2)	11.924(1)
Volume (Å^3)	3614.8(7)	3703.7(7)
Z	4	2
Density (calculated) (Mg/m^3)	1.420	1.396
Absorption coefficient (mm^{-1})	0.757	0.739
F(000)	1616	1624
Crystal size (mm^3)	0.20 × 0.15 × 0.13	0.33 × 0.23 × 0.22
Theta range for data collection	3.01 to 27.50°	3.25 to 27.50°
Index ranges	-22 to 20, -17 to 17, 0 to 22	-21 to 20, -24 to 24, 0 to 15
Reflections collected	78766	36784
Independent reflections	8300 [R(int) = 0.061]	4387 [R(int) = 0.047]
Reflections [$I>2\sigma(I)$]	4958	3239
Completeness to theta = 27.5°	99.9%	99.8%
Goodness-of-fit on F^2	1.062	1.060
Final R indices [$I>2\sigma(I)$]	R1 = 0.061, wR2 = 0.155	R1 = 0.052, wR2 = 0.141
R indices (all data)	R1 = 0.114, wR2 = 0.181	R1 = 0.079, wR2 = 0.157
Largest diff. peak and hole (e Å^{-3})	0.660 and -0.511	0.665 and -0.500

Table 2.- Selected lengths (Å) and angles (º) for complex **3**.

Ti(1)-N(1)	1.868(3)	Ti(1)-N(12)	1.831(3)
Ti(1)-N(13)	2.102(3)	Ti(2)-N(1)	2.084(3)
Ti(2)-N(12)	1.983(3)	Ti(2)-N(23)	2.000(3)
Ti(2)-O(1)	2.167(4)	Ti(3)-N(1)	1.868(3)
Ti(3)-N(13)	2.098(3)	Ti(3)-N(23)	1.856(3)
N(23)-C(1)	1.468(5)	Ti(1)···Ti(2)	2.866(1)
Ti(1)···Ti(3)	2.905(1)	Ti(2)···Ti(3)	2.853(1)
N(1)-Ti(1)-N(12)	88.7(1)	N(1)-Ti(1)-N(13)	85.1(1)
N(12)-Ti(1)-N(13)	102.2(1)	N(1)-Ti(2)-N(12)	78.9(1)
N(1)-Ti(2)-N(23)	80.5(1)	N(1)-Ti(2)-O(1)	145.2(1)
N(12)-Ti(2)-N(23)	118.8(1)	N(12)-Ti(2)-O(1)	81.7(2)
N(23)-Ti(2)-O(1)	83.9(2)	N(1)-Ti(3)-N(13)	85.2(1)
N(1)-Ti(3)-N(23)	90.3(1)	N(13)-Ti(3)-N(23)	101.2(1)
Ti(1)-N(1)-Ti(2)	92.8(1)	Ti(1)-N(1)-Ti(3)	102.1(1)
Ti(2)-N(1)-Ti(3)	92.3(1)	Ti(1)-N(12)-Ti(2)	97.3(1)
Ti(1)-N(13)-Ti(3)	87.5(1)	Ti(2)-N(23)-Ti(3)	95.4(1)
Ti(2)-N(23)-C(1)	124.4(3)	Ti(3)-N(23)-C(1)	140.2(3)

Table 3. Relevant hydrogen bonds[a] for complex **3**.

D-H···A	D···A/Å	H···A/Å	D-H···A/º
N(13)-H(13)A···O(3)	3.417(6)	2.54(5)	159(4)
N(12)-H(12)···O(2)	3.130(4)		

[a] A = acceptor; D = donor.

Table 4.- Selected lengths (Å) and angles (º) for complex **4**.

Li(1)-N(11)	2.356(10)	Li(1)-N(12)	2.313(6)
Li(1)-O(1)	1.994(6)	Ti(1)-N(1)	1.911(2)
Ti(1)-N(11)	1.947(2)	Ti(1)-N(12)	1.936(3)
Ti(2)-N(1)	1.943(3)	Ti(2)-N(12)	1.924(3)
N(11)-C(1)	1.473(6)	Ti(1)···Ti(1)a	2.802(1)
Ti(1)···Ti(2)	2.822(1)		
N(11)-Li(1)-N(12)	79.6(2)	N(12)-Li(1)-N(12)a	80.2(3)
N(11)-Li(1)-O(1)	112.0(3)	N(12)-Li(1)-O(1)	90.9(1)
N(12)-Li(1)-O(1)a	164.1(5)	O(1)-Li(1)-O(1)a	94.5(4)
N(1)-Ti(1)-N(11)	86.8(1)	N(1)-Ti(1)-N(12)	86.1(1)
N(11)-Ti(1)-N(12)	100.7(1)	N(1)-Ti(2)-N(12)	85.6(1)
N(12)-Ti(2)-N(12)a	101.6(2)	Ti(1)-N(1)-Ti(2)	94.1(1)
Ti(1)-N(1)-Ti(1)a	94.3(1)	Li(1)-N(11)-Ti(1)	88.8(2)
Ti(1)-N(11)-Ti(1)a	92.0(1)	Ti(1)-N(11)-C(1)	133.9(1)
Li(1)-N(11)-C(1)	95.5(4)	Li(1)-N(12)-Ti(1)	90.4(2)
Li(1)-N(12)-Ti(2)	88.4(2)	Ti(1)-N(12)-Ti(2)	93.9(1)

Symmetry code: (a) x, 1 – y, z