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Electrophilic attack on trinuclear titanium imido-nitrido systems

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Abstract:

Alkylation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ with MeOTf occurs at the imido ligands to produce the methylamido derivative $[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)(\mu\text{-}NH)_2(\mu\text{-}NHMe)(OTf)]$ which readily rearranges to form the methylimido complex $[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)(\mu\text{-}NH)(\mu\text{-}NH_2)(\mu\text{-}NMe)(OTf)]$.

While an extensive chemistry has been developed with mononuclear transition metal complexes bearing imido or nitrido ligands as a terminal functionality, M=NR or M≡N,[1] the study of polynuclear derivatives containing bridging (μ_n-NR or μ_n-N) ligands remains comparatively scarce.[2,3] The reactivity of terminal imido or nitrido ligands has received increasing attention because of their potential to show either electrophilic or nucleophilic character.[1,4] When imido or nitrido ligands react with electrophiles the net result is a reduced bond order between the metal and the nitrogen atom, to produce amido and imido derivatives respectively, with no change in the oxidation state of the metal.

Over the last few years we have been involved in the study of the reactivity of the trinuclear imido-nitrido titanium(IV) derivative $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$[5] (**1**). This molecule contains two potentially reactive functionalities: the three μ-NH imido groups and the μ_3-N nitrido ligand. While complex **1** is capable of acting as a Lewis base through the imido groups toward many metal derivatives to give cube-type adducts $[L_nM\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$,[6] the Lewis base behavior of the apical μ_3-N nitrido ligand has been only documented with copper and silver MX Lewis acids.[7] This nitrido ligand is quite chemically unreactive, and only recently we have reported the "apparent" nucleophilic attack of an acetylide $[C\equiv CR]^-$ at this site to yield alkynylimido μ_3-NCCR ligands.[8] We were interested in studying the reactivity of **1** toward electrophiles and here we report the preliminary results on the reaction with methyltrifluoromethanesulfonate (MeOTf) to generate polynuclear complexes by selective functionalization of the imido groups.

The reaction of **1** with one equivalent of methyl triflate in benzene-d_6 at room temperature was monitored by NMR spectroscopy (Scheme 1). After 5 min, complete consumption of **1** was observed and complex $[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)(\mu\text{-}NH)_2(\mu\text{-}$

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NHMe)(OTf)] (**2**) was characterized by ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectroscopy. Spectra taken after 2 h showed a new set of resonance signals assignable to compound [Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)(μ-NH)(μ-NH$_2$)(μ-NMe)(OTf)] (**3**) (*ca.* 25% conversion) along with those due to **2**. Upon standing at room temperature for 24 h, orange crystals of **3** were grown at the bottom of the NMR tube while analysis of the orange solution only showed resonances for **3**. While complex **3** was isolated as orange crystals in 78% yield by treatment of **1** with one equiv of MeOTf in toluene at room temperature, the intermediate **2** could not be obtained in a pure form and was only characterized by NMR spectroscopy. The ^{1}H NMR spectrum of **2** in benzene-d$_6$ at room temperature reveals two resonance signals for the η^5-C$_5$Me$_5$ ligands in a 1:2 ratio, one resonance for two equivalent NH imido groups and those assigned to one NHMe methylamido ligand. The NMR data are consistent with a *C*$_s$ symmetric structure with the methylamido and triflato ligands in the mirror plane of the molecule.
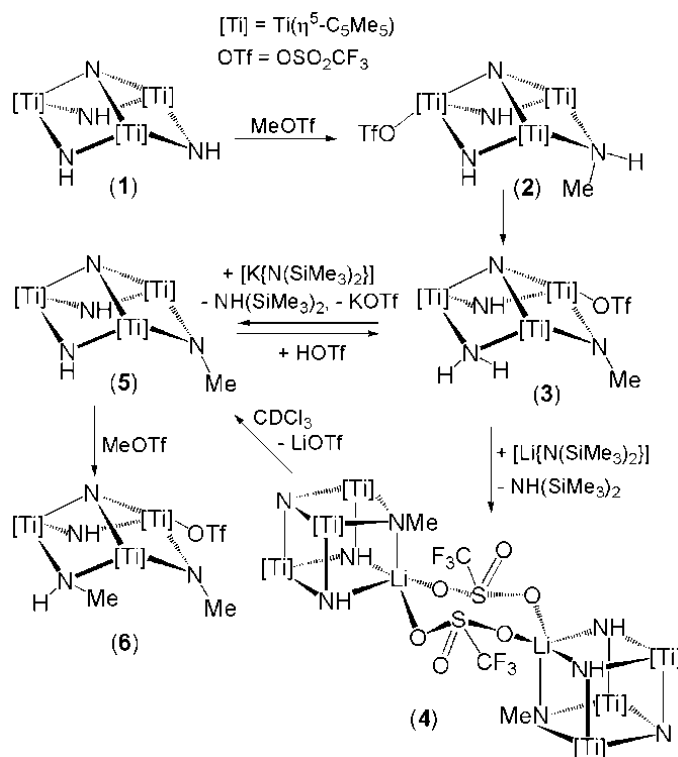
Scheme 1 Reaction of **1** with MeOTf.

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Compound **3** was characterized by analytical and spectroscopic methods, as well as by an X-ray crystal structure determination.‡ The solid-state structure of **3** reveals a six-membered Ti_3N_3 ring in chair conformation with the three titanium atoms also bridged by a further nitrogen atom (Fig. 1). The Ti(1) and Ti(3) atoms have classical three-legged piano-stool arrangements, where the legs are occupied by one μ-NH_2 amido, one $μ_3$-N nitrido and either a μ-NH or μ-NMe imido ligands. The Ti(2) atom exhibits a classical four-legged piano-stool arrangement, in which the legs are occupied by one triflato, one nitrido, and two imido ligands. The Ti(2)-N bond lengths of 1.983(3) to 2.084(3) Å are clearly longer than the titanium-nitrogen distances associated with the nitrido and imido groups bonded to the Ti(1) and Ti(3) atoms (1.831(3)-1.868(3) Å). The terminal triflato ligand is linked to Ti(2) with a rather long Ti(2)-O(1) bond length (2.167(4) Å),[9] and also shows intramolecular hydrogen bonding interactions between O(3) and the inner hydrogen of the NH_2 amido ligand (O(3)···N(13) = 3.417(6) Å), and between O(2) and the NH imido group (O(2)···N(12) = 3.130(4) Å).
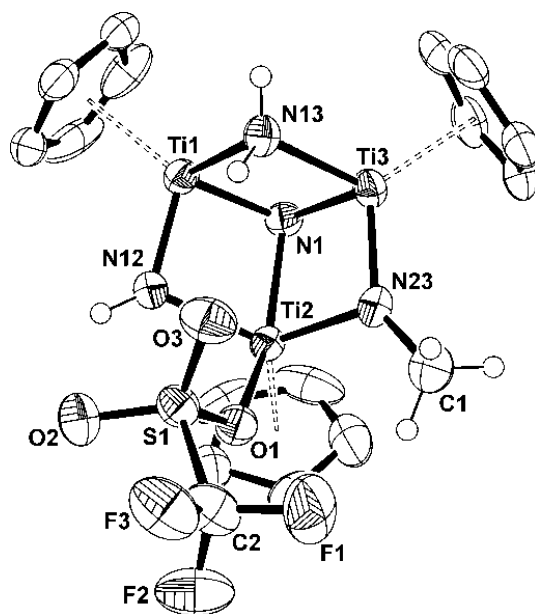

Fig. 1 Crystal structure of complex **3** (thermal ellipsoids at the 50% probability level). The methyl groups of the pentamethylcyclopentadienyl ligands are omitted for clarity. The

disorder of the triflato ligand is not shown. Selected bond lengths (Å): 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).

The IR spectrum (KBr) of **3** shows two ν_{NH} vibrations, at 3350 and 3265 cm^{-1}, and one δ_{NH} vibration at 1590 cm^{-1} for the NH and NH_2 groups. Also the IR spectrum reveals several strong absorptions in the range 1308-1011 cm^{-1} for the coordinated triflato ligand.[10] In accord with the C_1 symmetry determined in the solid-state structure, the ^{1}H NMR spectra of **3** in benzene-d_6 or chloroform-d_1 at room temperature reveals resonance signals for three different η^5-C_5Me_5 ligands, two singlets for the NMe and NH imido groups, and two resonances for the NH_2 amido ligand. However, the resonance signals for two η^5-C_5Me_5 ligands and those assigned to the NH and NH_2 groups are broad, suggesting a dynamic exchange process in solution. Indeed, the ^{1}H NMR spectrum of a solution of **3** in dichloromethane-d_2 at -30 ºC revealed three sharp resonances for the η^5-C_5Me_5 ligands, two well-defined doublets ($^2J(H,H)$ = 8.5 Hz) for the NH_2 group and one resonance signal for the NH ligand. The dynamic behavior is probably the result of proton transfer from the NH_2 group to the hydrogen-bonded triflato ligand and generation of HOTf, which then delivers that proton to the NH imido group with concomitant coordination of the triflato ligand at the opposite titanium atom, creating time-averaged C_s symmetry by ^{1}H NMR spectroscopy at high temperatures. Studies are underway to clarify the fluxional process occurring on complex **3** and the conversion of the intermediate **2** to compound **3**, which apparently involves an analogue but irreversible HOTf rearrangement.

In several NMR experiments, we tried to trap triflic acid by addition of bases to benzene-d_6 solutions of **3**. Complex **3** did not react with pyridine or triethylamine, and the NMR spectra did not show any changes in the resonance signals of **3**. However, upon addition of one equiv of lithium bis(trimethylsilyl)amide to a benzene-d_6 solution of **3**, there is an immediate precipitation of a yellow solid, and the NMR spectra only show resonances for free $NH(SiMe_3)_2$. The lithium triflate adduct $[(F_3CSO_2O)Li\{(\mu_3\text{-}NH)_2(\mu_3\text{-}NMe)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2$ (**4**) was isolated as a yellow solid in 85% yield by treatment of **3** with one equiv of $[Li\{N(SiMe_3)_2\}]$ in toluene at room temperature (Scheme 1). The presence of coordinated LiOTf in **4** was unambiguously established by an X-ray crystal structure determination (Fig. 2).‡ The solid-state structure of **4** consists of two cube-type $[LiTi_3N_4]$ cores connected by two μ-triflato-$\kappa O{:}\kappa O'$ ligands between the lithium atoms. The two bridging triflato ligands, along with the two lithium atoms, form a $[Li_2O_4S_2]$ puckered eight-membered ring.[11] The geometry around the lithium centers is best described as distorted square-pyramidal with two NH and two bridging triflato ligands at the planar base, and the NMe imido group in the apical position. The tridentate coordination of the $\{(\mu_3\text{-}NH)_2(\mu_3\text{-}NMe)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$ metalloligand to lithium in **4** (Li-N bond lengths are 2.313(6) and 2.356(10) Å) resembles that found in many cube-type adducts $[L_nM\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ prepared from **1**.[6]
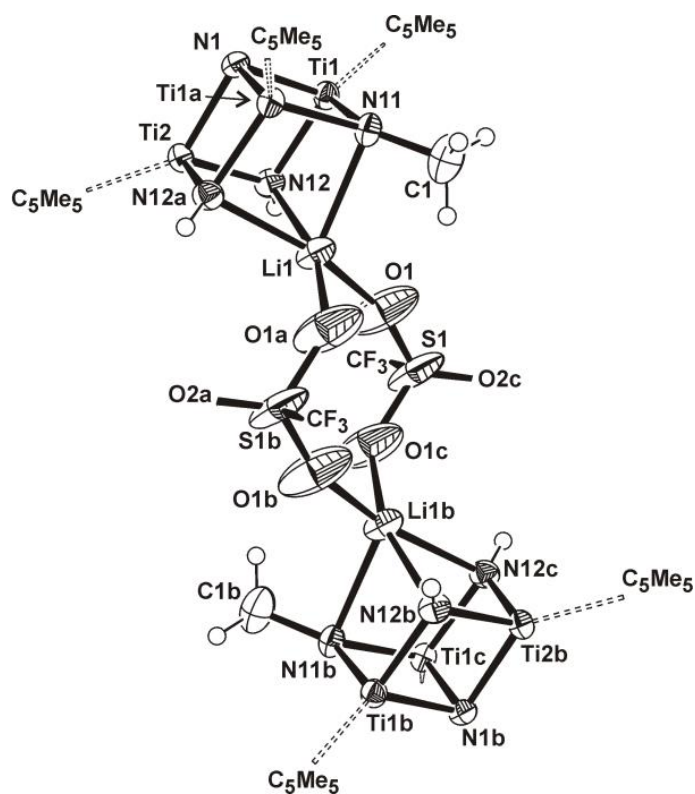
Fig. 2 Crystal structure of complex **4** (thermal ellipsoids at the 50% probability level). The pentamethylcyclopentadienyl ligands are not shown for clarity. The CF$_3$ groups of the triflato ligands are also omitted. The disorder of the triflato ligands is not shown. Selected bond lengths (Å): Li(1)-N(11) 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). Symmetry transformations used to generate equivalent atoms (a) x, 1 − y, z; (b) –x, 1 − y, –z; (c) –x, y, –z.

Complex **4** is not soluble in hydrocarbon solvents and undergoes partial dissociation (*ca.* 50% conversion after 24 h at room temperature) in chloroform-d$_1$ solution to give [Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)(μ-NH)$_2$(μ-NMe)] (**5**) and LiOTf. The free titanium metalloligand **5** was prepared by the reaction of **3** with [K{N(SiMe$_3$)$_2$}] in toluene at 50 ℃. Compound **5** was isolated as an orange solid in good yield (91%), which is very soluble in benzene-d$_6$ or

chloroform-d_1. The ^{1}H and ^{13}C{^{1}H} NMR spectra in those solvents indicate C_s symmetry and are consistent with an incomplete cube structure similar to that of **1**. Noteworthy, the addition of one equiv of HOTf to a benzene-d_6 solution of **5** regenerated complex **3**, while the reaction with MeOTf gave the analogue [Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)(μ-NH)(μ-NHMe)(μ-NMe)(OTf)] (**6**) by selective methylation of a NH imido group. Compound **6** was isolated as an orange precipitate in 74% yield by reaction of **5** with one equiv of MeOTf in hexane. Complex **6** is soluble in toluene or benzene, and its ^{1}H and ^{13}C{^{1}H} NMR spectra in benzene-d_6 at room temperature are consistent with a C_1 symmetric structure similar to that of **3**. However, in contrast with the dynamic behavior of **3,** the ^{1}H NMR spectrum of **6** at room temperature shows sharp resonance signals for the three η^5-C$_5$Me$_5$ ligands.

In summary, we have shown that the selective methylation of [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] with MeOTf occurs at the imido groups to produce an unstable methylamido intermediate [Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)(μ-NH)$_2$(μ-NHMe)(OTf)], which readily rearranges to form a methylimido complex [Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)(μ-NH)(μ-NH$_2$)(μ-NMe)(OTf)]. We are currently investigating the mechanism of the HOTf rearrangement occurring in those complexes, as well as the reactivity of **1** with a variety of electrophiles in different molar ratios.

Notes and references

‡ Crystal data for **3**: $C_{32}H_{51}F_3N_4O_3STi_3$, M = 772.53, monoclinic, a = 17.020(2), b = 13.646(1), c = 17.195(2) Å, β = 115.16(1)º, U = 3614.8(7) Å^3, T = 200(2) K, space group $P2_1/c$ (no. 14), Z = 4, μ(Mo-Kα) = 0.757 mm^{-1}, 78766 reflections measured, 8300 unique (R_{int} = 0.061) which were used in all calculations. $R1$(F^2) = 0.061 (for 4958 reflections with F$_o$ > 4σ(F$_o$)) and $wR2$ = 0.181 for all data.

Crystal data for **4**: $C_{64}H_{100}F_6Li_2N_8O_6S_2Ti_6$, M = 1556.92, monoclinic, a = 16.296(1), b = 19.247(3), c = 11.924(1) Å, β = 97.98(1)º, U = 3703.7(7) Å^3, T = 200(2) K, space group $C2/m$ (no. 12), Z = 2, μ(Mo-Kα) = 0.739 mm^{-1}, 36784 reflections measured, 4387 unique (R_{int} = 0.047) which were used in all calculations. $R1$(F^2) = 0.052 (for 3239 reflections with F$_o$ > 4σ(F$_o$)) and $wR2$ = 0.157 for all data. CCDC XXXXXX, and XXXXXX. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x

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