A mononuclear, and terminal titanium(III) imido

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We report the first mononuclear Ti^{III} complex possessing a terminal imido ligand. Complex $[Tp^{tBu,Me}Ti\{\equiv NSi(CH_3)_3\}(THF)]$ (2) ($Tp^{tBu,Me}$ = hydridotris(3-tert-butyl-5-methylpyrazol-1-yl)borate) is prepared by reduction of $[Tp^{tBu,Me}Ti\{\equiv NSi(CH_3)_3\}(Cl)]$ (1) with KC_8 in high yield. The connectivity and metalloradical nature of 2 were confirmed by single crystal X-ray diffraction studies (scXRD), Q- and X-band EPR as well as UV-Vis and ^1H NMR spectroscopies. The d^1 complex $[(Tp^{tBu,Me})TiCl(OEt_2)][B(C_6F_5)_4]$ (3), was prepared in order to spectroscopically compare it to 2. Electrochemical studies of 1 and 2 reveal a reversible $1e^-$ process, whereas chemical oxidants $ClCPh_3$ or ½ eq. XeF_2 cleanly yield 1 or the fluoride derivative $[Tp^{tBu,Me}Ti\{\equiv NSi(CH_3)_3\}(F)]$ (4), respectively, with the latter being fully characterized including a scXRD study.

Early transition metal (group III-VI) imidos (RN^{2-}) have been studied extensively for the past 60 years due to their utility in stoichiometric[1] and catalytic reactions.[2] Specifically, titanium imidos have shown great utility in Ziegler-Natta polymerization,[2b,3] cycloaddition,[4] group transfer,[1b,5] hydroamination,[5b,6] C-H bond activation,[7] carboamination,[8] and hydrogenation reactions.[7b,9] The earliest reports of Ti^{IV} imidos, by Bradley *et al.*, date back to 1963 followed by the first structural characterization of a polymeric Ti^{IV} imido complex containing bridging imido and chloride ligands, $[Ti\{\mu\text{-}NSi(CH_3)_3\}(\mu\text{-}Cl)Cl]_n$, reported by Alcock *et al.* in 1974.[10] Not until 1990 when Hill *et al.* reported a terminal, mononuclear Ti^{IV} imido did two distinct classes of Ti imidos displaying either bridging or terminal coordination emerge.[9b,11] Both coordination modes of Ti imidos are dominated by diamagnetic, Ti^{IV} centers with mononuclear and terminal Ti^{III} imidos entirely eluding isolation, in spite of being isoelectronic with the ubiquitous vanadyl ion, $\{V\equiv O\}^{2+}$, a system which helped establish the present-day understanding of metal-ligand multiple bonds.[9b,12] Dinuclear Ti^{III} imido systems, however, have been reported in both coordination modes. Cummins *et al.* showed the reduction of complex $[(^tBu_3SiNH)(THF)(R)Ti\equiv NSi^tBu_3]$ (R = Me, ^{t}Bu) with H_2 yielded $[(^tBu_3SiNH)Ti\{\mu\text{-}NSi^tBu_3\}]_2$, **Fig 1A**, representing the first example of $Ti_2^{III,III}$ bridging imidos.[7b] Later, Bai *et al.* reported the ligand fragmentation product $K_2[\{\eta^2\text{-}ArNC(CH_3)CHC(CH_3)\}(ArN)Ti(\mu\text{-}H)]_2$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$, **Fig 1B**), representing a $Ti_2^{III,III}$ complex containing terminal imidos.[13] Other examples include the mixed valence $Ti_2^{III,IV}$ complex $[CoCp_2][(C_5R_5)Ti(Cl)\{\mu\text{-}NAr\}]_2$ (R = H, Me; Ar = 3,5-$(CF_3)_2C_6H_3$) by Tsurugi *et al.* containing two bridging imidos (**Fig 1C**),[14] and, more recently, the $Ti_2^{III/III}$ complex $[K(18\text{-crown-}6)(THF)_2][(NIm^{Ar})(NAd)Ti(\mu\text{-}NAd)_2Ti(NIm^{Ar})(K)]$ (NIm^{Ar} = 1,3-bis(Ar)imidazolin-2-iminato; Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; Ad = adamantyl) containing one terminal and two bridging imidos by Gómez-Torres, *et al* (**Fig 1D**).[15] Inspired by these advances, and given our recent success in isolating a pseudo-tetrahedral Ti^{II} center,[16] we sought to expand the chemistry of Ti imidos by synthesizing and fully characterizing a mononuclear and terminal Ti^{III} imido as described herein.

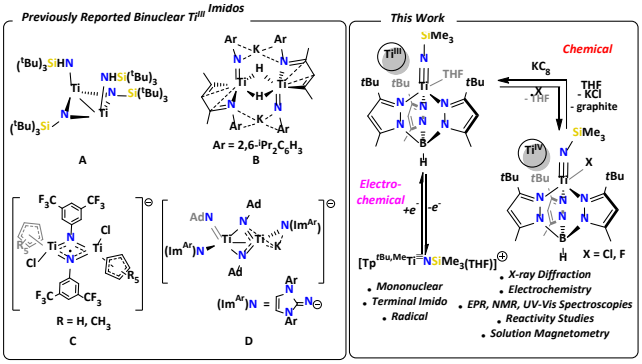

Fig 1. Left: Previous examples of isolated and structurally characterized dinuclear Ti^{III} imido complexes **A**-**D**. Cations for **C** ($CoCp_2^+$), and **D** ($K(18\text{-crown-}6)(THF)_2^+$) are omitted for clarity. Right: This work: a mononuclear, terminal Ti^{III} imido displaying redox reactivity.

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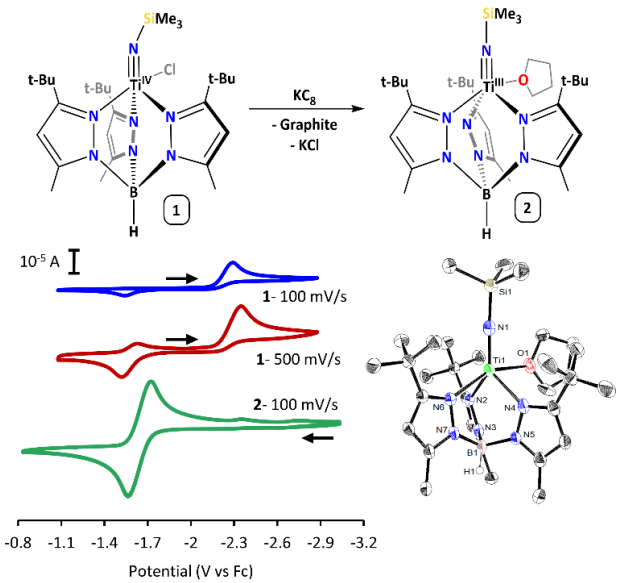


Fig 2. Top: Reduction of **1** to **2**. Bottom Left: CV of **1** (3.0 mM **1**, 0.215 M [^{n}Bu$_4$N][PF$_6$] in THF) collected at various scan rates and **2** (3.4 mM **2**, 0.271 M [^{n}Bu$_4$N][PF$_6$] in THF) collected at a scan rate of 100 mV/s. All referenced to Fc$^{0/+}$ couple at 0.0 V. Bottom Right: Thermal ellipsoid plot of **2** (50% probability level) with hydrogen atoms (except for H1) and residual Et$_2$O omitted for clarity.

Previously, our group reported the Ti^{IV} imido complex [(Tp^{tBu,Me})Ti{≡NSi(CH$_3$)$_3$}(Cl)] (**1**) (Tp^{tBu,Me} = hydridotris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate) formed upon deazotation of (CH$_3$)$_3$SiN$_3$ by [(Tp^{tBu,Me})TiCl].[16] Cyclic voltammetry studies (CV) of **1** at slow scan rates (50 and 100 mV/s) revealed an irreversible reduction event at -2.32 V as well as an irreversible oxidation event at -1.53 V vs Fc$^{+/0}$, **Fig 2** (blue trace). The latter oxidation feature becomes quasi-reversible at faster scan rates (≥150 mV/s, $E_{1/2red}$ = -1.61 V, $E_{1/2ox}$ = -1.53 V, **Fig 2**, red trace). These quasi-reversible features are dependent on the reduction event at -2.32 V and thus not observed in CV scans sweeping potentials >-1.9 V (see SI for details). We initially assigned the reduction event at -2.32 V to a [(Tp^{tBu,Me})Ti{≡NSi(CH$_3$)$_3$}(Cl)]$^{0/-}$ redox couple, for which a subsequent chloride dissociation step leads to electrochemical irreversibility and the quasi-reversible features at -1.61/-1.53 V to a [(Tp^{tBu,Me})Ti{≡NSi(CH$_3$)$_3$}(THF)]$^{+/0}$ redox couple. To probe this, 1-4 eq. [^{n}Bu$_4$N][Cl] were added to the electrolyte solution causing the quasi-reversible reduction event (-1.61 V) to disappear. This suggests a hypothetical cationic species such as "[(Tp^{tBu,Me})Ti{≡NSi(CH$_3$)$_3$}(THF)]$^+$" to rapidly associate with Cl$^-$ to form complex **1** with high concentrations of Cl$^-$ and with PF$_6^-$ under low concentrations of chloride (See SI and discussion below for details). It also suggests that the PF$_6^-$ coordinated "[(Tp^{tBu,Me})Ti{≡NSi(CH$_3$)$_3$}(THF)]$^+$" is easier to reduce than **1** (*vide infra*). In any case, the reduction event at -2.32 V suggested the possibility of chemical reduction of **1** to a Ti^{III} species, which under electrochemical conditions seemed unstable.

Accordingly, chemical reduction of **1** with one equivalent of KC$_8$ in THF yielded a yellow-brown microcrystalline material in 91% yield after work-up, identified as [(Tp^{tBu,Me})Ti{≡NSi(CH$_3$)$_3$}(THF)] (**2**), **Fig 2**, on the basis of structural and spectroscopic studies (*vide infra*). Room temperature ^{1}H-NMR spectroscopy revealed significantly broadened and paramagnetic shifts for the pyrazolyl, B-H, and trimethylsilyl resonances (ESI, Fig S3.1.1). Solution state magnetometry determined *via* Evans method[17] (300 K in benezene-d_6) revealed μ_{eff} = 1.85 μ_B consistent with a spin-only d^1 system.

Single crystal X-ray diffraction studies (scXRD) of **2**, **Fig 2**, revealed an unprecedented, terminally-bound, and mononuclear Ti^{III} imido with a short Ti≡NR length of 1.766(6) Å. The Ti≡NR bond length is only ~0.06 Å longer than the same metrical parameter found in the Ti^{IV} precursor **1**, 1.692(1)-1.700(2) Å,[16,18] in line with the larger ionic radius of Ti^{III} versus the Ti^{IV} ion (0.67 vs 0.42 Å, respectively).[19] The Ti≡NR bond distance in **2** is in good agreement with the Ti≡NR bond distance of 1.770(4) Å in the Ti$_2^{III,III}$ terminal imido and the difference from its Ti^{IV} analogue (~0.04 Å) reported by Bai *et al.*, **Fig 1B**.[13] The Ti≡NR bond length in complex **2** is however, longer than the terminal Ti≡NR bond distance of 1.729(3) Å reported recently by Gomez-Torres *et. al.*[15] Additionally, the ∠Ti≡N-Si in **2** was found to be 172.6(4)°, which is more obtuse than the same angles of 158.94(10)-160.24(9)° found in precursor **1**.[16,18] We attribute the near-linear topology of the {Ti≡N-Si} core in **2** to the increase in the size of and change of geometry (**1**: τ_5 = 0.47-0.59, **2**: τ_5 = 0.29) about the Ti-center which lies an average of 0.17 Å further from the tris-pyrazole (NNN) plane (see SI for details)[16,18] and enables the imido ligand to minimize steric repulsion with the bulky Tp^{tBu,Me} ligand and become almost perfectly linear in **2**.

To better understand why **1** gave rise to two separate redox events and to determine if indeed the Cl$^-$ was interfering with reversibility, we collected CV data for **2**. We found that **2** possesses a fully reversible redox event at $E_{1/2}$ = -1.64 V vs Fc$^{0/+}$, which we attribute to the Ti^{III}/Ti^{IV} redox couple, **Fig 2** (green trace in Figs 2 and S7.2.2). No significant features were observed around -2.3 V (Fig S7.2.3). The reversible feature at -1.64 V for **2** coincides with the irreversible oxidation/reduction peaks observed at -1.53/-1.61 V for **1** (*vide supra*), which suggests that one-electron oxidation of **2** to form a hypothetical "[**2**$^+$][PF$_6^-$]" salt becomes reversible when chloride ions are absent and a background of [PF$_6^-$] is present and suggests that "[(Tp^{tBu,Me})Ti{≡NSi(CH$_3$)$_3$}(THF)]$^+$" is more easily reduced than **1** (see SI for details). This feature also suggests that one-electron oxidation of **2** at the electrode surface to form hypothetical "[**2**$^+$][PF$_6^-$]" involves minimal reorganization energy due to the weakly coordinating nature of PF$_6^-$ unlike with Cl$^-$ (*vide supra*).

To better understand the electronic structure of **2**, we prepared a close structural and electronic analogue [(Tp^{tBu,Me})TiCl(OEt$_2$)][B(C$_6$F$_5$)$_4$] (**3^{Et_2O}**) independently from oxidation of [(Tp^{tBu,Me})TiCl][16] with [Tl][B(C$_6$F$_5$)$_4$] in Et$_2$O in 65.7% yield (ESI, Section 2.3). The THF complex, [(Tp^{tBu,Me})TiCl(THF)][B(C$_6$F$_5$)$_4$], (**3^{THF}**), was analogously prepared but proved more challenging to purify. These cationic chloride complexes were chosen as close structural analogues of **2** to assess the perturbation of the electronic structure of the d^1 ion caused by the multiple bond character of the imido group and to assess the role of a dative ligand such as THF. Akin to **2**, the solution magnetic susceptibility measurement of **3^{Et2O}** yielded

μ_{eff} = 1.86μ_B at 300 K in THF-d_8 in good agreement with a spin-only d^1 species. To further probe the electronic structure of **2**, we turned to UV-vis spectroscopy, **Fig 3**. The d^0 precursor, **1**, unsurprisingly, displays no absorption bands in the range 500-750 nm (THF or toluene solvent). In contrast, **2** and **3** (**3^{THF}**) each display a low-intensity feature consistent with a *d-d* transition: **2**: 618 nm (ε = 225 $cm^{-1}\cdot M^{-1}$) in toluene and 659 nm (ε = 110 $cm^{-1}\cdot M^{-1}$) in THF (pink and green traces in **Fig 3** respectively); **3** (**3^{THF}**): 574 nm (ε = 30 $cm^{-1}\cdot M^{-1}$) in THF and (**3^{Et_2O}**): 584 nm (ε = 56 $cm^{-1}\cdot M^{-1}$) in Et_2O (black and blue trace in **Fig 3** respectively).

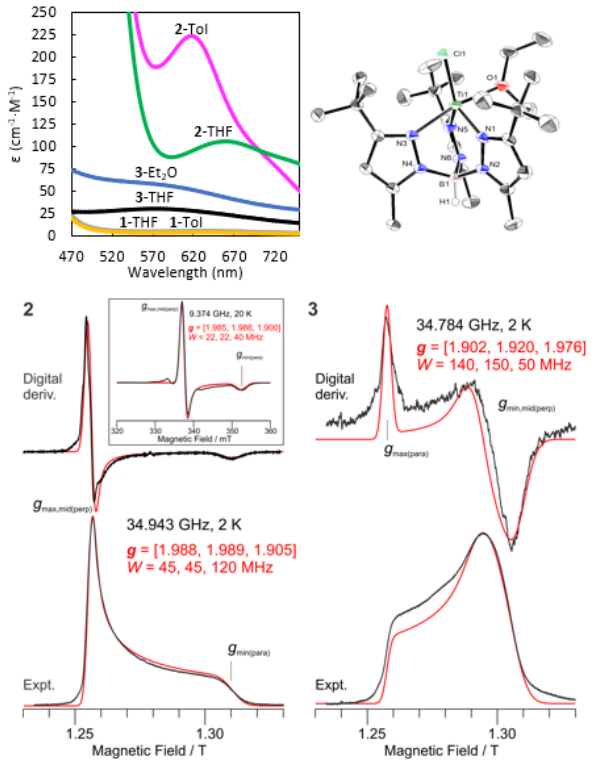


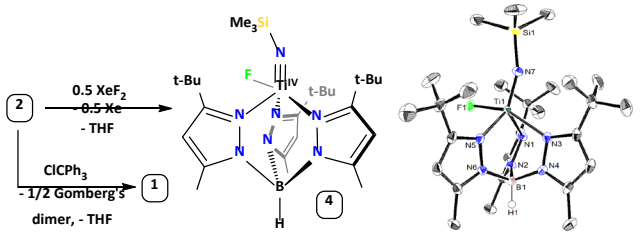
Fig 3: Top left: UV-vis spectrum of **1**, **2**, and **3** in solvents listed (Tol = toluene). Top right: X-ray structure of **3^{Et_2O}** (50% probability level) with H atoms (except for H1), residual Et_2O, and $[B(C_6F_5)_4]^-$ omitted for clarity. Bottom Left: EPR spectra of **2** in Tol/THF frozen solution (black traces; simulations as red traces with S = 1/2 parameters as shown). Main figure: Q-band (34.943 GHz, 2 K) spectrum. Experimental spectrum is in absorption mode due to rapid passage effects and is shown with a digital derivative above for comparison with conventional (first derivative) EPR. Inset: X-band (9.374 GHz, 20 K) spectrum in first derivative (slow passage) mode. Features not reproduced in the simulations are due to ^{47,49}Ti hyperfine coupling (See SI for details). Bottom right: EPR spectrum of **3^{Et_2O}** in Tol frozen solution.

The solvent-dependence in the intensity and absorption energy for electronic transitions in complex **2** are consistent with dissociation of the THF ligand in toluene to form a putative four-coordinate Ti^{III} imido [($Tp^{tBu,Me}$)Ti{≡NSi(CH_3)$_3$}]. In a previous study, it was found that an isoelectronic V^{IV} nitrido complex, [($Tp^{tBu,Me}$)V{≡N}(THF)], readily expels THF in weakly coordinating solvents.[20] The near order of magnitude increase in molar absorptivity between **3** and **2** reflects the forbidden nature of *d-d* transitions occurring in **3** (selection rule for orbital quantum number: Δl = ±1), versus the more allowed $d_{xy}\rightarrow\pi^*_{Ti\equiv NR}$ transitions in **2** (excitations to molecular orbitals with titanium and nitrogen parentage), which is consistent with the bonding and spectroscopic properties for a d^1 systems having metal-ligand multiple bonds developed by Ballhausen and Gray for the isoelectronic vanadyl ion, $\{V\equiv O\}^{2+}$.[12]

Further spectroscopic evidence for the presence of a Ti-centric radical in **2** was obtained through continuous wave (CW) X- and Q-band EPR spectroscopy. Surprisingly, **2** exhibited an axial S = 1/2 spectrum ($g_{x(max)} \approx g_{y(mid)} \approx g_\perp > g_{z(min)} = g_\parallel$) in toluene and toluene/THF glasses, **Fig 3**, (X-band, $g_{x,y,z}$ = [1.985, 1.986, 1.900; g_{avg} = 1.957], 20 K; Q-band, $g_{x,y,z}$ = [1.988, 1.989, 1.905], 2 K) despite its low symmetry observed in the solid state by scXRD. This axial EPR, as would be expected for a trigonally symmetric four-coordinate complex, is however consistent with the results of UV-Vis spectroscopy (*vide supra*). The g values observed for **2** display a pattern similar to $\{V\equiv O\}^{2+}$, in which $g_\perp$ is closer to g_e (2.00) than $g_\parallel$ due to the energetic ordering of the V 3d orbitals in triply-bonded $\{V\equiv O\}^{2+}$, and in line with the electronic structure of **2** being strongly defined by $\{Ti\equiv NSiMe_3\}$ bonding.[12,24] In contrast to UV-vis spectral studies (*vide supra*), there is no change in the g-values when CW-X-band EPR was collected using 1:1 THF:toluene glass or toluene glass. Hence, the periphery of the $\{Ti\equiv NR\}^+$ fragment have minimal effect on the magnetic properties of **2**. No hyperfine coupling to the imido nitrogen was detected by EPR indicating that the unpaired electron is metal centered and in a d_{xy} orbital orthogonal to the Ti≡NR bond. In comparison, the EPR spectrum of **3^{Et2O}** is also roughly axial, but with ($g_{x(min)} \approx g_{y(mid)} \approx g_\perp < g_{z(max)} = g_\parallel$; Q-band, $g_{x,y,z}$ = [1.902, 1.920, 1.976], 2 K) and is thus similar, albeit less rhombic, to the neutral, five-coordinate complex [$Tp^{tBu,Me}Ti^{III}Cl_2$] reported previously.[16] We propose the EPR differences between **2** and **3** to result from the stronger π-donation of the imido compared to the chloride.[21] Further comparisons among EPR spectra of **3** as a function of temperature and solvent are given in the SI.

Taking advantage of the radical nature of **2**, we chemically probed its electrochemical features (*vide supra*); oxidation of **2** with $ClCPh_3$ quantitatively formed **1** along with Gomberg's dimer as evidenced by ^{1}H-NMR spectroscopy (Fig S3.2.1).[22] In an attempt to desilylate **2** with 0.5 equivalents of XeF_2, we instead observed the formation of the imido-fluoride [($Tp^{tBu,Me}$)Ti{≡NSi(CH_3)$_3$}(F)], (**4**), in 86% yield, **Fig 4**. Complex **4** is resistant to $FSiMe_3$ elimination even under forcing conditions (70 °C, 18 hrs) and metrically, the structures of **1** and **4** are quite similar with a short $Ti\equiv NSiMe_3$ bond distance and slightly bent ∠Ti≡N-Si (Table in **Fig 4**). The geometries at Ti are also quite similar when judged by their τ_5 values (Table in **Fig 4**). The room temperature ^{19}F-NMR spectrum of **4** exhibits one sharp resonance at +131.4 ppm, and unlike **1**, complex **4** undergoes rapid Berry pseudo-rotation on the NMR time scale (300 K) resulting in equivalent pyrazolyl moieties in solution (ESI, Fig S3.4.1).[23] Unsurprisingly and akin to **1**, complex **4** displays no absorption bands in the 500-750 nm range (Fig S5.4.1).

We have provided conclusive evidence for the synthesis of the first mononuclear, Ti^{III} complex containing a terminal imido ligand, $\{Ti\equiv NR\}^+$. Electrochemical and chemical reversibility of the interconversion between Ti^{IV} imido **1** and Ti^{III} imido **2** were probed electrochemically (CV) and chemically *via* reduction



	1[a]	2	4
∠Ti≡N-Si (°)	158.94(10) - 160.24(9)	172.6(4)	157.2(1)
Ti≡NSi(CH$_3$)$_3$ (Å)	1.692(1) - 1.700(2)	1.766(6)	1.706(2)
τ_5	0.59 - 0.47	0.29	0.51

Figure 4: Top left: Reactivity of **2** with $ClCPh_3$ and XeF_2 to form **1** and **4** respectively. Bottom Top right: Thermal ellipsoid plot of **4** (50% probability level) with hydrogen atoms (except for H1) and residual Et_2O omitted for clarity. Bottom: Table of the structural parameters of compounds **1**, **2**, and **4**. [a]Previously reported.[16]

(oxidation) with potassium graphite (trityl chloride). We observed no evidence for desilylation of the imido upon treatment of the Ti^{III} center with an electrophilic fluoride source (XeF_2) and instead form a {Ti-F} bond, **4**. In probing the radical nature of **2**, we provided evidence from EPR of {Ti≡NSiMe$_3$} bonding of a Ti-centered radical having axial symmetry, where the unpaired electron resides in a d-orbital perpendicular to the orbitals involved in π-donation from the imido ligand $\{V{\equiv}NR\}^{2+}$ and resembling the well-known vanadyl unit, $\{V{\equiv}O\}^{2+}$.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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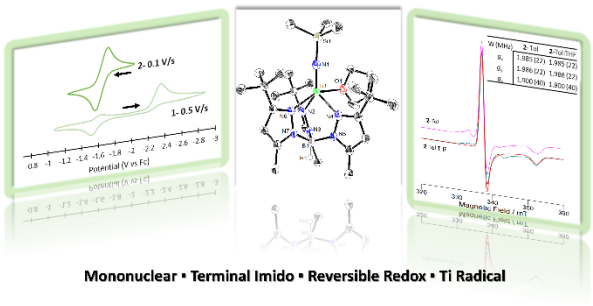
TOC Graphic



Mononuclear ▪ Terminal Imido ▪ Reversible Redox ▪ Ti Radical