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Ligand-based Control of Single-Site vs Multi-Site Reactivity by a Trichromium Cluster

Amymarie K. Bartholomew, Cristin E. Juda, Jonathon N. Nessralla, Benjamin Lin, SuYin Grass Wang, Yu-Sheng Chen, and Theodore A. Betley*

Abstract: The trichromium cluster $(^{tbs}L)Cr_3(thf)$ ($[^{tbs}L]^{6-} = [1,3,5-C_6H_9(NC_6H_4-o-NSi^tBuMe_2)_3]^{6-}$) exhibits steric- and solvation-controlled reactivity with organic azides to form three distinct products: reaction of $(^{tbs}L)Cr_3(thf)$ with benzyl azide forms a symmetrized bridging imido complex $(^{tbs}L)Cr_3(\mu^3-NBn)$; reaction with mesityl azide in benzene affords a terminally-bound imido complex $(^{tbs}L)Cr_3(\mu^1-NMes)$; whereas the reaction with mesityl azide in THF leads to terminal N-atom excision from the azide to yield the nitride complex $(^{tbs}L)Cr_3(\mu^2-N)$. The reactivity of this complex demonstrates the ability of the cluster-templating ligand to produce a well-defined polynuclear transition metal cluster that can access distinct single-site and cooperative reactivity controlled by either substrate steric demands or reaction media.

Nature harnesses polynuclear reaction sites to achieve challenging small molecule activation transformations (e.g., nitrogenase, carbon monoxide dehydrogenase).^[1] While mechanistic details regarding the function of these active sites are scarce, protein side-chain mutagenesis studies have shown that the protein environment surrounding FeMoco in nitrogenase alters substrate access to the cofactor.^[2] Recent crystallographic data has demonstrated that reversibly inactivated forms of the C-cluster of CODH and FeMoco as well as a catalytically active form of FeVco feature significant structural changes to the metallocluster active sites.^[3] Synthetic chemists have begun to construct reactive polynuclear clusters aimed at recapitulating the chemistry achieved by these metallocofactors as well as potentially promoting new reactivity with small molecule substrates.^[4] However, designing cluster systems which emulate both the steric control and structural flexibility observed in biological systems is difficult, as it is challenging to control the mechanism by which transition metal clusters react with substrates. Self-assembled clusters can undergo facile changes in nuclearity under reaction conditions, while ligand-templated clusters are often sterically precluded from reactivity except at a single site.^[4a, 4c, 5] Thus, clusters exhibiting multiple controllable modes of substrate activation (e.g., site-isolated versus cooperative activation) are exceedingly rare.^[6]

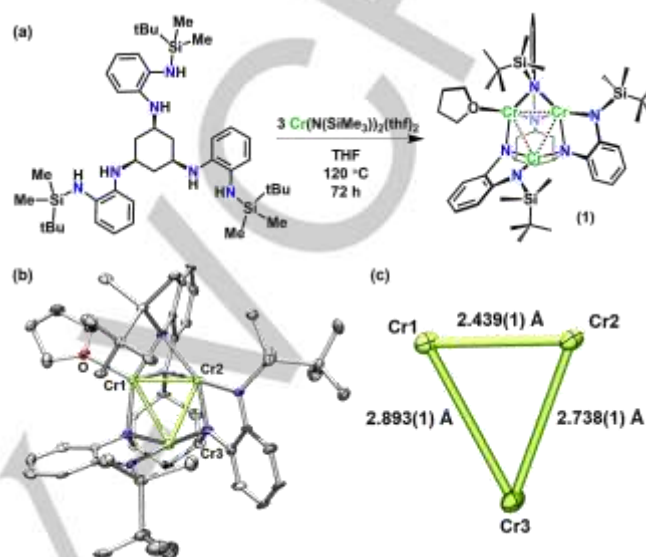


Figure 1. a) Synthesis of $(^{tbs}L)Cr_3(thf)$ (1) b) Solid-state structure of **1** at 100K with 50% probability ellipsoids^[7] c) Structural metrics of the $[Cr_3]$ core of **1**. Color Scheme: Cr, green; N, blue; O, red; Si, pink. Solvent molecules and hydrogen atoms omitted for clarity.

Previous work in our lab has achieved cooperative reactivity on triiron clusters synthesized using an *ortho*-phenylenediamine-based hexadentate ligand, $(^{tbs}L)H_6$ ($(^{tbs}LH_6 = [1,3,5-C_6H_9(NHC_6H_4-o-NHSi^tBuMe_2)_3]$).^[8] In this work we demonstrate that the same sterically demanding ligand can be used to construct a trichromium cluster whose reactivity with organic azides leads to multiple products arising from distinct mechanistic pathways. The tert-butyldimethylsilyl (tbs) protecting groups appended to the ^{tbs}L peripheral anilides modulate how the azides engage the $[Cr_3]$ core, leading to distinct products for small and large azide substituents. Furthermore, THF-dissociation from $(^{tbs}L)Cr_3(thf)$ in benzene allows for an additional mode of reactivity with large azides not observed in THF.

Metalation of $^{tbs}LH_6$ with 3 equivalents of $Cr(NTMS)_2(thf)_2$ (TMS = trimethylsilyl) at 120 °C yielded the trinuclear cluster $(^{tbs}L)Cr_3(thf)$ (**1**) (Figure 1). At lower temperatures, metalation arrests at a dinuclear form similar to those previously reported on this platform.^[9] Crystals suitable for single-crystal X-ray diffraction (SC-XRD) were grown from a concentrated diethyl ether solution of **1** at -35 °C. The structure of **1** (Figure 1a) reveals three distinct metal coordination environments: Cr1 is bound to one molecule of THF and three anilides and possesses an agostic interaction with a C-H bond from a tbs group; Cr2 is bound to four anilides; and Cr3 resides in a three-coordinate site (neglecting Cr-Cr interactions). The trinuclear core of **1** is asymmetric: the Cr1-Cr2 distance is 2.439(1) Å, while three-coordinate Cr3 is greater than 2.73 Å away from Cr1 and Cr2.

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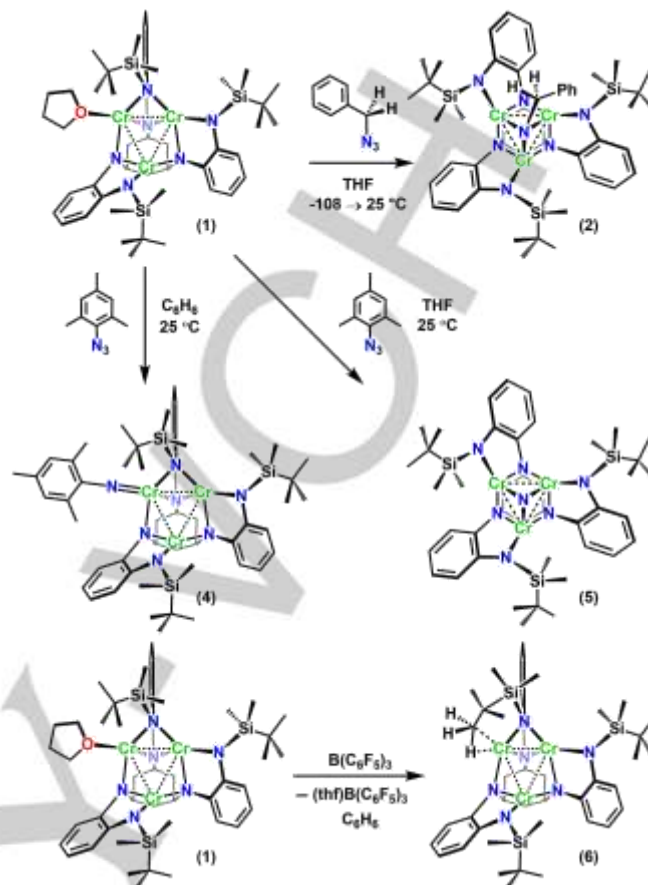
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Addition of one equivalent of benzyl azide (BnN_3) to **1** in benzene or THF at room temperature generates a mixture of $(^{\text{tbs}}\text{L})\text{Cr}_3(\mu^3\text{-NBn})$ (**2**), the bisimido product $(^{\text{tbs}}\text{L})\text{Cr}_3(\mu^3\text{-NBn})(\mu^1\text{-NBn})$ (**3**), and unreacted **1**. Cooling the reaction to $-108\text{ }^\circ\text{C}$ by performing the addition of azide in thawing THF cleanly produces **2**, while addition of two equivalents of benzyl azide cleanly generates **3**, both of which were characterized by SC-XRD (Figure 2a, Figure S3). The facile oxidation of **1** bisimido **3** is consistent with the room-temperature formation of a dichromium bisimido observed by the Theopold group.^[10]

Addition of larger mesityl azide (MesN_3) to **1** in benzene yielded a single C_7 symmetric product as revealed by ^1H NMR. Single crystals of the product were grown by storing a solution of the product in diethyl ether at $-35\text{ }^\circ\text{C}$. SC-XRD revealed the product to contain a terminally bound imido $(^{\text{tbs}}\text{L})\text{Cr}_3(\mu^1\text{-NMe})$ (**4**), rather than the expected mesityl analogue of **2**. The mesityl imido in **4** occupies the THF-bound site in **1**. The terminal imido linkage in **4** features a Cr–N bond length of $1.6858(1)\text{ \AA}$, consistent with a double bond,^[11] representing the first example of site-isolated redox reactivity on a $^{\text{tbs}}\text{L}$ -ligated cluster (Figure 2b). When the reaction of MesN_3 with **1** is performed in THF, a trace amount of **4** is formed alongside a new, pseudo- C_3 symmetric main product as observed by ^1H NMR. Crystals of the new material were formed from a concentrated hexanes solution at $-35\text{ }^\circ\text{C}$. SC-XRD revealed the new pseudo- C_3 symmetric product to be the bridging nitrido $(^{\text{tbs}}\text{L})\text{Cr}_3(\mu^3\text{-N})$ (**5**) (Scheme 1, Figure 2c).

Substituting BnN_3 with MesN_3 had a two-fold effect on reactivity with **1**: while smaller BnN_3 readily accesses the $[\text{Cr}_3]$ face leading to a bridging imido product, more sterically encumbered MesN_3 forms two distinct products (i.e., terminal imido **4** or bridging nitride **5**) as dictated by the reaction solvent. Further investigation of the mechanism of formation of **4** and **5** was undertaken to determine whether this change in reactivity could be traced to the secondary coordination sphere of $^{\text{tbs}}\text{L}$. Close inspection of a space-filling model of **1** provides insight into the possible modes of substrate association to the cluster: the bulky tbs groups significantly block access to the three-coordinate and four-coordinate sites, with THF occupying the only sterically accessible site remaining on the cluster. The tbs groups also restrict access to the trinuclear face of **1** (Figure 3c).

Given that **4** is formed cleanly in benzene solution, but suppressed in favor of **5** in THF solution, we examined the lability



Scheme 1.

of THF from **1** in benzene. Though **1** cannot be synthesized in the absence of coordinating solvent, THF was abstracted from **1** by reaction with tris(pentafluorophenyl)borane (BCF) in benzene, producing $(^{\text{tbs}}\text{L})\text{Cr}_3$ (**6**). The BCF THF complex and **6** share the same solubility properties but crystallize independently from a concentrated hexanes solution at $-35\text{ }^\circ\text{C}$. The molecular structure of **6** determined by SC-XRD confirms the removal of THF, which is replaced by strengthening of the agostic C–H interaction to Cr1 as well as a contraction of the Cr1–Cr2 distance to $2.3638(6)\text{ \AA}$

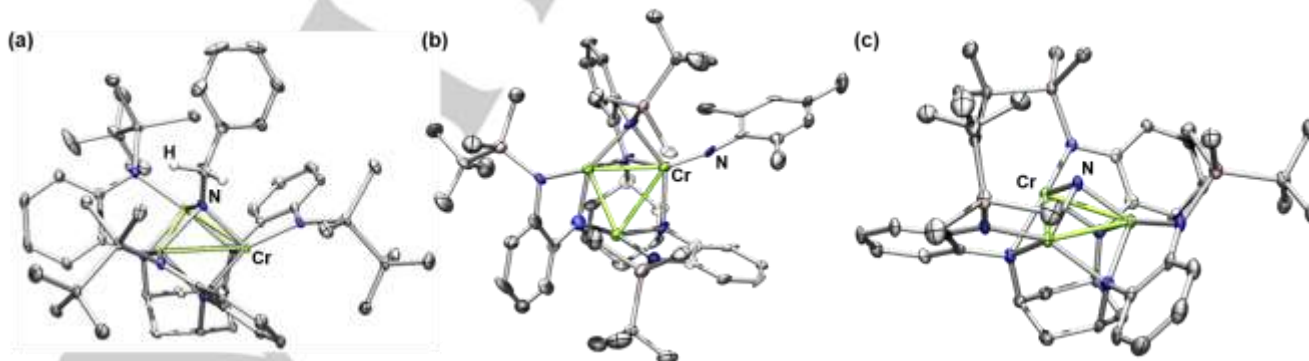


Figure 2. Solid-state structures of a) $(^{\text{tbs}}\text{L})\text{Cr}_3(\mu^3\text{-NBn})$ (**2**) b) $(^{\text{tbs}}\text{L})\text{Cr}_3(\mu^1\text{-NMe})$ (**4**) and c) $(^{\text{tbs}}\text{L})\text{Cr}_3(\mu^3\text{-N})$ (**5**) at 100K with 50% (a,c) or 35% (b) probability ellipsoids. Solvent molecules and most hydrogen atoms omitted for clarity.

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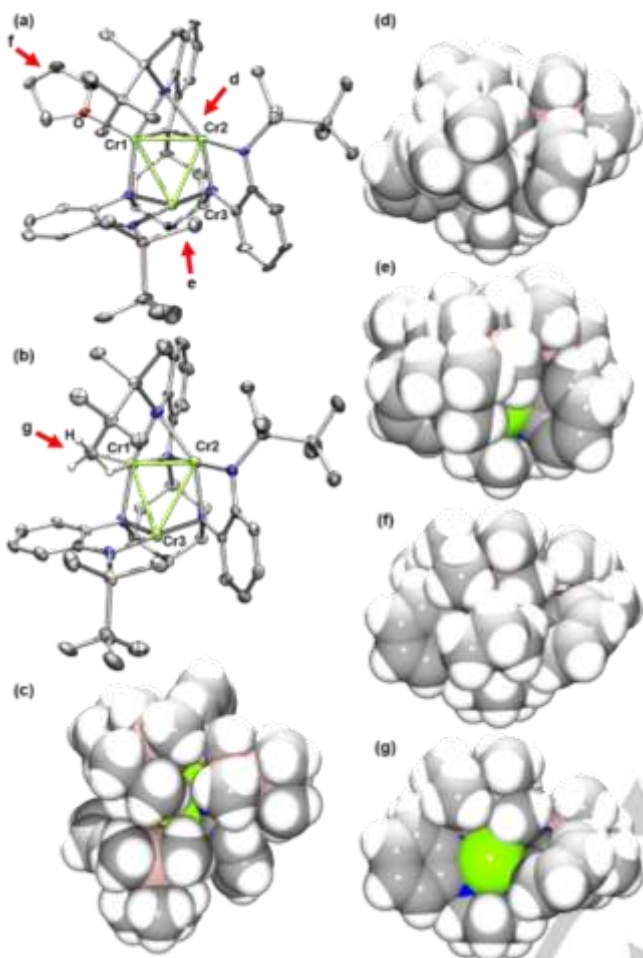


Figure 3. Solid-state structures of a) $(tbsL)Cr_3(thf)$ (**1**) and b) $(tbsL)Cr_3$ (**6**) at 100K with 50% probability ellipsoids. Space-filling models of c) top-down view of **1** d) 4-coordinate site of **1** e) 3-coordinate site of **1** f) THF-bound site of **1** g) open coordination site of **6**. Solvent molecules and most hydrogen atoms omitted for clarity.

from 2.469(1) Å. The space-filling model for **6** (Figure 3g) reveals unrestricted access to Cr1, thereby allowing access of sterically encumbered substrates.

Examination of the 1H NMR of **1** and **6** in C_6D_6 revealed that **1** exists in an equilibrium between the THF-bound and naked cluster in benzene solution (Figure S12). The THF equilibrium binding constant ($K_{eq} = 0.0028$ M) was determined by a 1H NMR titration of **6** with THF (Figure S13).^[12] We therefore conclude that unlike BnN_3 , which is small enough to react quickly with the trinuclear face of **1** to form **2** even in benzene solution where THF is labile, $MesN_3$ reacts more slowly with the face of **1** due to steric clash with the ligand *tbs* unit and instead reacts at the Cr1 site to form **4**. In THF solution, however, this pathway is inhibited by the excess of THF, leading instead to kinetically competitive reaction with $MesN_3$ at the $[Cr_3]$ face of **1** to form **5**. Consistent with this conclusion, increasing the relative concentration of THF to $MesN_3$ further disfavored the formation of **4** in THF solution. Treatment of **1** with $MesN_3$ in dilute THF solution formed **5** as the sole product.

In order to further test the hypothesis that the kinetics of

single-site vs cooperative substrate reactivity are determined by the size of the azide substrate, **1** was reacted with (2,6-diisopropyl)phenyl azide ($DippN_3$) in both benzene and THF solution. Pure $(tbsL)Cr_3(\mu^1-NDipp)$ (**7**) (Figure S7) was formed from the reaction in benzene, while the reaction in THF generated a mixture of nitrido **5** and **7**. Imido **7** is the major product of the THF reaction, whereas for $MesN_3$ **5** is the major product. These results indicate that the steric demands of the substrate affect the rate of reaction with the $[Cr_3]$ face of the cluster, making reactivity at the solvation site competitive even in THF solution for the more demanding $DippN_3$.

The formation of **5** could indicate that the secondary coordination sphere of $tbsL$ also causes divergent azide breakdown pathways to exist for facially-bound, sterically demanding azides compared to facially-bound benzyl azide. It was not possible to generate the μ^3 -mesityl imido to ensure that **5** did not result from decomposition of this species, but **4** can be heated in THF solution at 80 °C for 12 h without any decomposition or rearrangement. Addition of benzyl isocyanide ($BnNC$) induces a rearrangement of the imido to a bridging conformation, producing $(tbsL)Cr_3(\mu^3-NMes)(\mu^1-CNbn)$ (**8**) (Figure S8). The mesityl imido is therefore not sterically incompatible with the ligand conformation surrounding a μ^3 -capping unit. Addition of phenyl azide to **4** in THF solution at RT also induces rearrangement of the ligand platform, but retains the terminal binding mode of the mesityl imido, forming the mixed bisimido $(tbsL)Cr_3(\mu^3-NPh)(\mu^1-NMes)$ (**9**) (Figure S9).

Complex **1** reacts immediately with azides even in thawing THF (-108 °C), complicating our efforts to follow the reaction progress by 1H NMR. However, the coordination of phenylacetylene ($HCCPh$) to **1** forms $(tbsL)Cr_3(HCCPh)$ (**10**) at room temperature in benzene, which can provide insight into the possible interactions of azide substrates with the trinuclear face of **1**. To generate **2**, facially-bound BnN_3 would have to achieve either side-on or α -N binding to trichromium in order to release N_2 . A four-membered Bergman-like transition state would not be sterically feasible as even a benzyl group would clash with the ligand platform as the α -N approached a Cr-site for nucleophilic attack from a facially γ -N bound geometry.^[13] If side-on binding occurs, the resulting geometry would be similar to that observed for the phenylacetylene in **10**. The phenyl group of $HCCPh$ fits into the pocket formed by the surrounding ortho-phenylenediimines and *tbs* groups, but the proton at the ortho position is only 2.391(5) Å from the N-C-C plane and 2.5438(1) Å from the nearest proton on a *tbs* methyl group, indicating that the addition of a methyl group at this position as in $MesN_3$ would create a steric clash, disfavoring the side-on bound azide structure (Figure 4).

We hypothesized that in the case of facial binding of $MesN_3$ to the $[Cr_3]$ core where a side-on, α -bound, or γ -bound four-membered transition state cannot be achieved for steric reasons the strongly reducing nature of three Cr(II) sites leads to homolytic bond cleavage of the terminal N-N bond, generating mesityl diazenyl radical and **5** (Figure 4). Mesitylene is observed as a byproduct of this reaction by 1H NMR, as expected for the decomposition of the released $MesNN\cdot$ into dinitrogen and a mesityl radical.^[14] To test our hypothesis that **5** is formed by γ -N abstraction from $MesN_3$ we reacted **1** with terminally ^{15}N -labeled mesityl azide, $MesNN^{15}N$, which was synthesized following a

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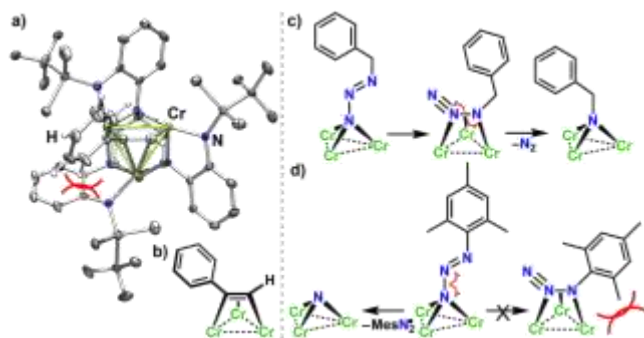


Figure 4. a) Solid-state structure of **10** at 100K with 30% probability ellipsoids. Solvent molecules and most hydrogen atoms omitted for clarity. b) Core geometry of **10**. Proposed mechanisms of formation of c) **2** and d) **4**.

procedure analogous to that used by Lešetický to synthesize PhNN¹⁵N.^[15] To determine whether the reaction of **1** with MesNN¹⁵N in THF produced (^tbsL)₃Cr₃(μ³-¹⁵N) (**5**-¹⁵N) the product of the reaction was decomposed using HCl to produce ammonium chloride and then treated with base to liberate ammonia, which was vacuum transferred into a solution of HCl in diethyl ether. ¹H NMR of the re-formed ammonium chloride in DMSO-*d*₆ showed the characteristic splitting pattern of ¹⁵NH₄Cl (Figure S16), confirming that **5** is formed from the γ-N of MesN₃. To our knowledge, the only previously reported transition metal complex to undergo this transformation is Mo(NAr)₃ (R=C(CD₃)₂CH₃, Ar = 3,5-C₆H₃Me₂) as reported by the Cummins group.^[16] It is remarkable that the steric protection afforded by the ligand results in a change from typical azide decomposition to this unusual mode of azide reactivity for larger azide substrates.

The foregoing results highlight the divergent reactivity resulting from both templating ligand and azide substrate steric control. The secondary coordination sphere control imposed by the tbs groups of the ^tbsL⁶⁻ template gates how azides can approach the reactive [Cr₃] core. While the small azide substrate BnN₃ reacts rapidly with the trinuclear face of **1** to form a μ³ imido, larger azides such as MesN₃ and DippN₃ do not afford the corresponding bridging imido products. Rather, the sterically hindered azides react faster at the THF-bound site, aided by THF dissociation in benzene solution, to form terminal imido products. When the reaction media is switched to THF and THF lability from the cluster is minimized, mesityl azide reacts with the [Cr₃] face leading to N-atom extrusion from the azide to form the neutral bridging nitride **5**. Reactivity of organic azides with **1** allows controlled access to two, three, and four-electron oxidation of the [Cr₃] core. Research is underway to understand if the divergent reaction pathways lead to fully site-isolated oxidation of the cluster.

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Ligand-based Control of Single-Site vs Multi-Site Reactivity by a Trichromium Cluster

All together now: A reactive trichromium complex synthesized using a templating ligand undergoes controllable single-site and cooperative reactivity with organic azides. By varying the steric profile of the azide substrate, it is possible to selectively form terminal and bridging imido products. Furthermore, in coordinating solvent the complex abstracts the terminal N-atom of mesityl azide to form a bridging nitrido.