Metal-support interactions in molecular single-site cluster catalysts

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Supporting Information Placeholder

Abstract. This study provides atomistic insights into the interface between a single-site catalyst and a transition metal chalcogenide support and illustrates how their cooperativity can be harnessed to modulate catalytic activity. A molecular platform $MCo_6Se_8(PEt_3)_4(L)_2$ (1-M, M = Cr, Mn, Fe, Co, Cu, Zn) was designed in which the active site (M)/support (Co_6Se_8) interactions are interrogated by systematically probing the electronic and structural changes that occur as the identity of the metal varies. All 3d transition metal 1-M clusters display remarkable catalytic activity for coupling tosyl azide and *tert*-butyl isocyanide, with Mn and Co derivatives showing the fastest turnover in the series. Detailed structural, electronic, and magnetic characterization of the clusters was performed using single crystal X-ray diffraction, ¹H and ³¹P nuclear magnetic resonance spectroscopy, electronic absorption spectroscopy, cyclic voltammetry, and computational methods. Distinct metal/support redox regimes can be accessed in 1-M based on the energy of the edge metal's frontier orbitals with respect to those of the cluster support. As the degree of electronic interaction between the edge and the support increases, a cooperative regime is reached wherein the support can deliver electrons to the catalytic site, increasing the reactivity of key metal-nitrenoid intermediates.

Tuning metal/support interactions represents a powerful strategy to modulate catalytic activity, making supported single-site catalysts that harness these effects an active frontier of research.^{1–7} The electronic and geometric interactions with the atoms of the support can critically impact the performance of the active site, particularly when the support is chemically non-innocent as is the case for transition metal chalcogenides.⁸ For instance, the coordination environment of single Rh atoms installed at edge vacancies of MoS₂ nanosheets, as well as charge transfer between the active sites and the support impart optimal stability and high selectivity for aldehyde hydrogenation.⁹ In a more molecularly-inspired approach, tuning the number of bonds between surface-anchored Co active sites and the WS₂ nanosheet support facilitates increased activity for electrochemical oxygen reduction.¹⁰ More broadly, the interaction between surface or edge metal dopants and layered transition metal dichalcogenide supports has been extensively investigated in the context of identifying catalysts for industrially relevant processes, such as hydrotreatment and hydrogen evolution (Figure 1A).¹¹ In these materials metal dopants can serve as new catalytic centers,^{9,10} or alter the activity of native sites indirectly, for example by engaging in charge transfer^{12–14} or by inducing structural changes within the support.¹⁵ However, the role of the metal dopant is complex and varies with the chemical transformation,^{16,17} substrate identity,¹⁸ and material morphology,^{19–22} among other factors^{23,24} precluding the determination of clear-cut structure-function relationships.

In contrast, coordinative non-innocence and electronic cooperativity between the ligand sphere and an active site have been extensively utilized and studied in molecular platforms.^{25,26} For example, systematically tuning the identity of the metals in a



Figure 1. A) Types of edge and surface-supported active sites on a layered transition metal chalcogenide support. B) Single-site, atomically precise platform designed to study the electronic and structural changes at the metal/support interface, and their effects on catalytic activity.

simplified, bimetallic platform enabled exquisite insights into the role of the supporting metal center in modulating substrate binding, activation, and catalytic performance at the active site.^{27,28} Extending this molecular approach to investigate constructs that embody the complexities of a heterogenous active site could offer new perspectives for controlling catalytic activity or selectivity using metal/support interactions.

Due to their synthetic tunability and homogeneous nature, atomically precise nanoclusters are advantageous for this purpose and can serve as both functional models and as platforms for new catalyst development.^{29,30} Examples of molecular clusters that feature metal/support architectures exist,^{31–35} such as the catalytically competent $Au_n(SR)_m$ clusters in which the reactive surface gold atoms are chemically distinguished from those of the cluster core.³⁶ While tuning cluster size^{37–39} and the coordination environment⁴⁰ of the active sites has been shown to modulate their catalytic activity, studies that identify the active site and systematically correlate how its identity impacts the metal/support interaction and the emerging catalytic activity have yet to materialize. To this end, our group has developed a class of nanoclusters (M_3 ; $M_3Co_6Se_8L_6$, M = Cr, Fe, Co, Zn, $SnMe_2$, $L = PPh_2N^{(-)}Tol$, Ph = phenyl, Tol = 4-tolyl) which feature three edge metals, M, anchored on the atomically precise Co_6Se_8 cluster.^{41–45} This construct resembles edge- and surface-metals supported on transition metal chalcogenides, but their homogeneity enables the use of molecular characterization techniques. In M_3 , the substrate-accessible edges facilitate not only catalytic activity^{41,44} and dimensional control over nanomaterial growth,^{42,43} but also provide atomic level insights into the evolution of the active sites under catalytic conditions, and their interconnected reactivity.⁴⁴

Herein, the metal (M)/support (Co₆Se₈) interactions are interrogated by systematically probing the electronic and structural changes that occur at this interface as the identity of the metal varies in the 3d period. The role of the metal/support cooperativity in modulating reactivity is explored in the context of catalytic nitrene transfer. To this end, a single-site cluster platform $MCo_6Se_8(PEt_3)_4(L)_2$ (1-M, M = Cr, Mn, Fe, Co, Cu, Zn) was designed to i) circumvent the complexities of multi-site dynamics present in M_3 , and ii) enable systematic modification of the edge metal identity (Figure 1B). This study reveals that distinct metal/support redox regimes can be accessed in 1-M based on the energy of the edge metal's frontier orbitals with respect to those of the cluster support. As the degree of electronic interaction between the edge and the support increases, a cooperative regime is reached wherein the support can deliver electrons to the catalytic site, increasing the reactivity of key metal-nitrenoid intermediates. By using a cluster as a support, this work provides an atomic level picture into how these effects manifest in a heterogenous single-site catalyst, and illustrates how metal/support interactions can be used to facilitate catalysis.

Synthesis of single-site clusters 1-M (M = Cr, Mn, Fe, Co, Cu, Zn)

Site-differentiation of a cluster with chemically degenerate surface sites is a challenging synthetic pursuit. Successful strategies to accomplish this include stoichiometric control of reagents,^{46–49} engineering sophisticated or very bulky ligand frameworks,^{31,50,51} or by relying on allosteric effects between multiple edge sites.⁴³ Here, the synthesis of clusters with a single active site relies on access to isomerically pure samples of the site-differentiated cluster *cis*-Co₆Se₈(PEt₃)₄(CO)₂, in which two carbonyl groups localized on *cis*-cobalt sites can be precisely displaced by nucleophiles without scrambling on the cluster surface.⁵² Photolysis of the *cis*-

Scheme 1. Synthesis of single-site clusters.





carbonyl cluster in the presence of excess aminophosphine Ph₂PN(H)Tol (L^H) results in the formation of *cis*-Co₆Se₈(PEt₃)₄(L^H)₂ (**1**-H₂; 84% isolated yield; Scheme 1). The metalloligand **1**-H₂ features one well-defined binding site poised to anchor a single metal to the surface of the Co₆Se₈ support via amide chelation and up to two hemilabile M–Se interactions. Deprotonation of the aminophosphines of **1**-H₂ with *n*-butyllithium and subsequent treatment with the salt of a divalent metal (M²⁺ = Cr²⁺, Mn²⁺, Fe²⁺, Co²⁺, Cu²⁺ or Zn²⁺) leads to the formation of a single new species identified as the monometallated cluster MCo₆Se₈(PEt₃)₄(L)₂ (**1**-M; 71-96% yield). With the exception of **1**-Cr(Sol) (Sol = THF, py) the monometallated clusters are isolated without bound exogenous ligands, which is in contrast to their trimetallated counterparts, typically isolated as solvent adducts **M**₃(Sol)_x (M = Cr, Fe, Co, Zn) despite their identical coordination environment at M.⁴¹⁻⁴⁴ This apparent lower affinity for ligands is likely a consequence of the more electron rich Co₆Se₈ core in the **1**-M series,⁵³ which features just one Lewis acidic metal on its surface, and four electron donating triethylphosphine groups.

Trends in catalytic activity

Transition metal catalyzed N-group transfer is an attractive method to selectively and efficiently form carbon-nitrogen bonds.^{54,55} We previously discovered that Fe_3 and $Cr_3(py)_3$ are excellent catalysts for the coupling of tosyl azide (TsN₃) and tert-butyl isocyanide ('BuNC) to form the asymmetric carbodiimide TsNCN'Bu, therefore this transformation was used to benchmark the relative reactivity of the 1-M series. Here, we discovered that all the monometallated clusters catalyze this transformation at room temperature with 1 mol% catalyst loading, whereas 1-H₂ shows negligible activity (Figure 2; Figure S29). Inspecting the kinetic profiles of the homologues, 1-Mn stands out as the most efficient catalyst with 50% conversion $(t_{1/2})$ achieved in just 5 min, followed by 1-Co (10 min), 1-Fe (22 min), 1-Cr(py) (53 min) and 1-Cu (66 min), respectively. In contrast to the other clusters, the conversion profile of 1-Zn features a slow induction period followed by a very active catalytic regime, suggesting a different catalytic pathway is at play than in the



Figure 2. Catalytic conversion of carbodiimide (TsNCN'Bu) with 1 mol% loading of 1-M cluster. Conversion determined by ¹H NMR integrations of the product and reactants.

other clusters. To assess the stability of the 1-M clusters during this transformation, we analyzed the post-catalytic reaction mixtures using ¹H NMR spectroscopy at 10% 1-M loading (Figure S31). Under these conditions, 1-Co is completely regenerated. Although only ca. 60% of 1-Fe is recovered upon substrate depletion, the remaining 40% is accounted for by the formation of a single new species, ostensibly the iron amido complex 1-Fe(NHTs) (Figure S30). Some cluster fragmentation likely occurs for 1-Zn and 1-Cu where NMR analysis indicates that the resulting reaction mixture contains multiple unidentified species in addition to some recovered 1-M cluster (17 and 23%, respectively). The spectroscopic analysis of the 1-Cr and 1-Mn samples does not suggest cluster degradation, but the broad, paramagnetic features of these clusters make a quantitative NMR analysis unreliable. While an extensive investigation into the speciation of the clusters under catalytic conditions is beyond the scope of this study, we point out that the trimetallated derivatives **Fe**₃ and **Cr**₃(py)₃ catalyze this transformation without any observable cluster decomposition.^{41,44} Carbodiimide formation typically occurs via the formation of metal-nitrenoid intermediates.^{54,56–58} The recent isolation of catalytically competent metal-imido nanocluster intermediates (e.g. **Cr**₃(NTs)₃) demonstrated this is the case for the chromium derivative, confirming that the three edge sites are indeed catalytically active and that the edge/support construct is viable under catalytic conditions.⁴⁴

Structural analysis via single crystal X-ray diffraction

Single crystal X-ray diffraction analysis of the 1-M cluster series reveals that three different coordination geometries can be distinguished at the edge sites depending on the chemical identity of M (Figure 3A, B). The Mn, Fe, Co, and Zn edges feature distorted tetrahedral geometries, and are chelated κ^4 by the cluster via two amides and two Se atoms. Although the Ni congener has proven challenging to isolate experimentally, its geometry and electronic structure were modeled in silico and found to adopt a similar pseudo-tetrahedral edge coordination (Section S.7). In the Cr variant, characterized in the solid state as a THF adduct, the edge site features a pseudo-square pyramidal geometry similar to that observed for the trimetallated analogue $Cr_3(py)_3$, with one short and one long Cr–Se bond (2.581(6) and 2.772(7) Å).⁴⁴ In contrast, the edge site does not engage in bonding with Se in 1-Cu (Cu....Se > 2.792(5) Å). The nearly linear N–Cu–N bond angle (ca. 173°) is a mark of Cu¹⁺ and suggests that upon metallation with the Cu^{2+} salt an intramolecular electron transfer occurs between the edge and the support that gives rise to a $Cu^{1+}/Co_6Se_8^{1+}$ complex. A contraction in the Co...Co distances within the Co_6Se_8 core, typically associated with mono-oxidation,⁵⁹ is indeed observed in 1-Cu (Figure 3C). Electrochemical, magnetic and nuclear magnetic resonance (NMR) data, as well as density functional theory (DFT) analysis also support this interpretation, as discussed in later sections. Monometallation gives rise to systematic distortions within the Co_6Se_8 core (Figure 3C, Table S4). These are primarily localized at the MCo₂Se₂ edge where the most striking change brought upon installing the edge site is an increased interatomic separation of the two Se atoms. The MCo₂Se₂ edge features elongated Co-Se bonds and contracted Co...Co distances compared to the rest of the Co_6Se_8 core, where the distortion trends are reversed such that overall the average metrics of the

nonmetallated clusters (i.e. $Co_6Se_8L^{H_6}$ and $Co_6Se_8(PEt_3)_4(CO)_2$) are preserved.^{41,52} Comparison of the M...Se interatomic distances in the **1**-M series to the average distance for M–Se single bond in the Cambridge Structural Database suggests that the edge metal is bound strongest to the Se in the Mn and Co derivatives, followed by the Cr, Fe and Zn complexes, whereas no Cu...Se bonding interactions are present in **1**-Cu.^{60–62}



Figure 3. A) Single crystal X-ray structure of 1-Cr(THF), 1-Mn, 1-Fe, 1-Co, 1-Cu, and 1-Zn. B) Zoom ins on the edge site first coordination sphere. Ellipsoids are plotted at 50% probability, and carbon backbones are depicted as wireframes. Disorder, hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. C) (i-iii) Edge (MCo_2Se_2) and core (Co_6Se_8) structural distortions upon monometallation. (iv) The deviation of M-Se interatomic distances from the average M-Se value reported in the Cambridge Structural Database.

Electronic structure investigations: magnetic moments, electronic absorption, and cyclic voltammetry

The magnetic response of the 1-M nanoclusters was probed by solution phase magnetic susceptibility measurements using the Evans method.⁶³ The parent 1-H₂ cluster is diamagnetic,⁶⁴ and remains closed-shell upon monometallation with zinc. 1-Cr(py), 1-Mn, 1-Fe and 1-Co are paramagnetic with effective magnetic moments of 4.6(3), 5.4(3), 4.9(3), and 3.8(3) μ_B , respectively, close to those expected for high-spin M²⁺ edge sites with S = 2, 5/2, 2 and 3/2. The high-spin state of the edge metals in 1-Mn, 1-Fe and 1-Co is consistent with the pseudo-tetrahedral coordination environment enforced by the cluster support, and is in agreement with earlier investigations into the electronic structure of Fe₃ and Co₃(py)₃ reported by our group.^{41,42,53} DFT calculations predict that while most of the spin (64-90%) is localized on the edge metal's 3*d* orbitals in 1-Cr(py), 1-Mn, 1-Fe, 1-Co, and 1-Ni, there is a non-negligible contribution from the cobalt core (5-19%) which indicates the presence of some spin mixing between the paramagnetic edge metals and the Co₆Se₈ support (Figure 4, Table S5).⁶⁵ In contrast, the entirety of the spin density calculated for 1-Cu is localized on the Co₆Se₈ support, observation that is in line with the proposed redistribution of charge between the edge and support that results in a diamagnetic Cu¹⁺ site and a mono-oxidized S = 1/2 [Co₆Se₈]¹⁺ cluster core. Experimentally, 1-Cu has an effective magnetic moment of 1.8(3) μ_B , which cannot be used to distinguish between

 $Cu^{1+}/[Co_6Se_8]^{1+}$ and $Cu^{2+}/[Co_6Se_8]^0$. It is interesting to note that the predicted distribution of the unpaired electrons in **1**-Cu is not uniform in the cluster core but is concentrated on the cobalt centers closest to the copper edge site. The localization of lattice distortion and spin closest to the edge site mirrors experimental observations and theoretical models for the interfacial perimeter in heterogeneous metal/support constructs.⁴



Figure 4. Mulliken spin density (α - β) plots of 1-M series calculated at uB3LYP+/cc-pVTZ level of theory. Spin density values for the edge "M" and Co₆Se₈ core are included. Surfaces plotted at an isovalue of 0.004.

Electronic absorption spectroscopy and electrochemical measurements reveal that the electronic interaction between the edge and core is greatest in 1-Fe, 1-Co, and 1-Cu, whereas metallation with Cr, Mn and Zn does not perturb the electronic structure of the metalloligand 1-H₂ significantly (Figure 5). In 1-Fe, 1-Co, and 1-Cu, the three characteristic UV absorption bands of the Co_6Se_8 core broaden, and the absorption in the visible and near IR spectral range intensifies significantly. For example, at 650 nm, the 1-Cu derivative has an absorption coefficient of 6400 cm⁻¹ M⁻¹, more than double that of 1-H₂ (Figure 5C). Similar, but more pronounced electronic changes associated with edge/core interactions have been observed in the trimetallated analogues.⁴¹ The increased absorption in the visible and IR range indicates decreased HOMO/LUMO gaps, which is corroborated by electrochemical analysis (Figure 5A). In contrast, the electronic absorption spectra of 1-Cr(py), 1-Mn, and 1-



Figure 5. A) Cyclic voltammograms of 1-M series recorded in 0.1 M solutions of $[(nBu)_4N]PF_6$ in tetrahydrofuran (THF), dichloromethane (DCM), or 1,2-difluorobenzene (DFB) at a scan rate of 200 mV/s and referenced to ferrocene/ferrocenium redox couple. B) Relative potentials of the HOMO/LUMO levels for each of the homologues in the 1-M series, estimated from the 0/+1 and 0/-1 events in THF. C) Electronic absorption spectra collected in THF for the 1-M series (left, M = Cr(py), Mn, Zn; right, M = Fe, Co, Cu) plotted vs the spectrum of 1-H₂. Insets feature zoom-ins of the absorption in the visible and near-IR range. The extinction coefficient of 1-Co was not measured.

Zn trace closely with that of 1-H₂, with only a very small redshift in the absorption (< 5 nm) suggesting these metals have minimal influence on the electronic structure of the cobalt core.

Electrochemical analysis reinforces the trends observed in the optical spectra (Figure 5A, B). Cyclic voltammetry reveals that monometallation induces a narrowing of the HOMO/LUMO gap in 1-Fe, 1-Co and especially in 1-Cu, whereas in 1-Zn, 1-Cr(py) and 1-Mn it remains nearly identical to that of 1-H₂. Here, the HOMO/LUMO gaps are estimated from the energetic difference between the first oxidation and first reduction events in tetrahydrofuran (THF). Overall, the 1-M clusters retain rich redox profiles that are reminiscent of the metalloligand 1-H₂, itself featuring four chemically reversible one-electron oxidations and one irreversible reduction. Notably, upon metallation the first reduction becomes chemically reversible for all derivatives except 1-Mn and is stabilized in the series Mn < Fe < Co << Cu.

Overall, the effect of monometallation on the electronic structure is proportional to the extent of structural distortion the edge site inflicts on the Co/Se cluster (Figure 3C). Thus, little electronic and structural distortions are observed for 1-Cr, whereas in 1-Fe and 1-Co the decreased HOMO/LUMO gaps and redshift in the electronic absorption compared to $1-H_2$ are accompanied by pronounced structural distortions and increased M–Se interaction strength. Exceptions to this trend are the d^5 and d^{10} derivatives 1-Mn and 1-Zn, which feature structural distortions and relatively short M—Se bonding interactions but have HOMO/LUMO gaps and electronic absorption spectra resembling those of the parent ligand.

Paramagnetic ³¹P NMR spectroscopy reports on the electronic structure of 1-M clusters

The chemically differentiated phosphines in 1-M make them excellent reporters on the local electronic microenvironments. The ${}^{31}P$ NMR chemical shifts of the triethylphosphine ligands capping four of the six cobalt sites in Co₆Se₈ report directly on the support. The amidophosphines cap the remaining two cobalt centers in the cluster, but also directly anchor the surface metal, therefore informing on both the edge and the support.

While no ³¹P NMR signals were detected for the Cr and Mn derivatives, 1-Fe, 1-Co, 1-Cu, and 1-Zn display diagnostic chemical shifts. The observed experimental chemical shift of a paramagnetic compound (δ_T^{obs}) is the sum contribution of the diamagnetic (δ^{dia}) and paramagnetic (δ_{T}^{para}) components, of which only the latter is temperature (1/T) and spin dependent (Equation S1).^{66–68} The diamagnetic 1-Zn cluster has chemical shifts similar to those of the free ligand. Meanwhile, the paramagnetic variants reveal a linear dependence of the ³¹P NMR chemical shifts with the inverse of temperature (Figure 6). As the spin state of the clusters increases in the 1-Cu (S = $\frac{1}{2}$), 1-Co (S = $\frac{3}{2}$), 1-Fe (S = 2) series, the ³¹P chemical shifts associated with the amidophosphine become more negative (-663, -796, and -956 ppm, respectively). Spatially removed from high spin metal edge sites, the chemical shifts of the PEt₃ capping ligands are very similar for 1-Fe and 1-Co (-113, -98 ppm, respectively) where the Co₆Se₈ core is expected to stay diamagnetic. In contrast, they shift dramatically in



Figure 6. Curie behavior of 1-Fe, 1-Co and 1-Cu reflected in the linear dependence of the 31 P NMR chemical shifts with inverse temperature in the 290 to 330 K range.

1-Cu (-354, -400 ppm), corroborating our hypothesis that the cluster core is mono-oxidized (S = $\frac{1}{2}$). While the C_{2v} cluster symmetry gives rise to two distinct PEt₃ environments in 1-M, these are only resolved by ³¹P NMR spectroscopy for the 1-Cu derivative. We attribute this to the localization of the charge on the cobalt atoms proximal to the edge site, as predicted by DFT (Figure 4).

Calculated electronic structures

DFT calculations carried out at the uB3LYP+/cc-pVTZ level of theory closely reproduce structural and electrochemical experimental data of 1-M (Figures S45).^{69–72} Considering the large number of electronic states, the energetic overlap and relative

contributions of the edge and core atoms to the valence orbitals and lowest energy unoccupied levels in the **1**-M clusters are more clearly visualized using density of states plots.⁷³ Inspecting Figure 7, we note that the energy of the d orbitals decreases in the atomic series Cr, Mn, Fe, Co and Ni.^{12,74,75} This manifests at the LUMO levels where the edge metal contribution increases across the series, eventually peaking at Ni, where the first reduction is predicted to be primarily nickel, not Co_6Se_8 -centered. The predicted increase in the edge metal contribution at the LUMO level correlates directly with the lowering in energy observed experimentally for the 0/–1 electrochemical reduction (Figure 5A). As expected, calculations reveal that there is no contribution to the LUMO levels from the d¹⁰ Zn²⁺ and Cu¹⁺ edges. **1**-Cu is electronically different from the rest of the series. Corroborating the structural, magnetic, NMR, and electrochemical data, DFT calculations predict that the HOMO level is localized on the Cu¹⁺ edge site. Additionally, they reveal that the low-lying LUMO level is associated with the mono-oxidized core [Co₆Se₈]¹⁺, explaining the markedly lower 0/–1 reduction potential measured for **1**-Cu.



Density of States

Figure 7. Partial density of states plots of 1-M series calculated at uB3LYP+/cc-pVTZ level of theory.

Deconstructing edge/core cooperativity in 1-M: M-Se interaction strength and redox regimes

The Co₆Se₈ cluster core ostensibly modulates the reactivity of the edge site by engaging in hemilabile edge–Se interactions on demand, or by providing electrons (or holes) to the reaction site. Empirically, the strength of the edge/core interaction in the 1-M pre-catalysts is found to track linearly with the catalytic activity, such that the species with the shortest M-Se bonds in the solid state are also the most active catalysts (1-Mn > 1-Co > 1-Fe > 1-Cr > 1-Cu). This apparent trend in reactivity is illustrated in Figure S44 where the deviation of the edge M-Se bond lengths from the corresponding average values extracted from the Cambridge Structural Database, 60-62 is plotted against the observed catalytic activity for carbodilimide formation. We hypothesize that as the edge/support (M-Se) interaction becomes stronger, the edge/nitrenoid (M-NTs) interaction weakens thereby becoming more reactive. Earlier studies into the trimetallated M_3 nanoclusters corroborate this claim by revealing a strong interdependence in the substrate/edge site/support interaction dynamics.41,43 For example, in the trichromium nanocluster Cr₃, a catalyst for carbodiimide formation, edge sites that engage in stronger Cr-Se bonding interactions with the support form weaker edge/substrate (Cr-NTs) interactions,⁴⁴ although for this system the kinetic implications of this coordinative interplay could not be separated from isocyanide binding equilibria at the Cr(NTs) edge. Ultimately, however, it is important to note that this trend in reactivity (Mn > Co > Fe > Cr > Cu) could also reflect the intrinsic periodic differences in reactivity of the 3d edge metal. For example, experimentally determined bond dissociation energies for metal-oxo fragments, isoelectronic with the putative metal-nitrenoid intermediates in azide activation, also increase in the series Mn < Co < Fe < Cr.⁷⁶

The redox activity of the cobalt selenide support positions it to become electronically involved during a multielectron transformation such as azide activation and nitrene transfer, modulating the reactivity of the edge site. To identify the distinct regimes of edge/support redox cooperativity as a function of edge site identity, the calculated electronic structures of **1**-M were used to assess which derivatives energetically favor redox cooperativity. When M = Cr or Fe, the HOMO level is predicted to be primarily localized on the edge site, suggesting the cluster core is minimally involved with oxidation. When M = Cu, the edge metal has low-lying empty orbitals to which the core spontaneously transfers an electron, reducing the edge site. As in the case of Cr and Fe, here, the first oxidation is expected to be localized strictly on the edge metal (Cu¹⁺), with no cluster core participation. Finally, when M = Co, Mn, Ni, the similar energy of the edge atom and Co/Se core orbitals at the HOMO level positions the core to become electronically involved and, together with the strong M–Se interactions, facilitate edge/core charge redistribution during a redox reaction. This regime is therefore one of redox cooperativity, and its implication for the electronic structure of the metal-nitrenoid intermediate is contrasted below with that in which the edge site is redox independent from the cluster core.

Role of edge/core electronic interactions in modulating the M-NTs multiple bonds

To evaluate the role of the edge/support cooperativity in modulating the reactivity of **1**-M, the electronic structure of two metalnitrenoid intermediates, ostensibly the key intermediates in azide activation and nitrene transfer, were investigated in silico. Two clusters were selected to illustrate the distinct regimes of electronic edge/support interactions, **1**-Cr(NTs), in which the Cr edge site is expected to be redox independent of the cluster core, and **1**-Co(NTs), in which the cobalt core is poised to become electronically involved. Electronic structure calculations of **1**-Cr(NTs) (S = 1) reproduce the experimental metrics for Cr(NTs) edge sites (Table S6),⁴⁴ and indicate that upon azide activation the oxidation is indeed localized on the chromium edge. This is reflected in the density of states plot of **1**-Cr(NTs) by the large Cr contribution at the LUMO levels, and the exclusive Co₆Se₈ contribution at the HOMO frontier levels (Figure 8C). Spin density plots reveal that the resulting Cr^{IV}-imido confines the unpaired spin on the Cr edge, while cobalt selenide core remains largely unaffected (Figure 8A and B).

In contrast to the edge/support redox independence in 1-Cr, calculations suggest that the Co₆Se₈ support contributes an electron to activating tosyl azide in 1-Co. The resulting 1-Co(NTs) (S = 5/2) cluster features a Co²⁺-iminyl edge on a mono-oxidized [Co₆Se₈]⁺, whereas a Co³⁺-iminyl might be expected in the absence of the cluster core participation. The density of states plot of 1-Co(NTs) reveals the LUMO level is completely localized on the Co₆Se₈ core, while the Co edge metal contributes to the HOMO levels (Figure 8C). Metal-nitrenoid Cr,^{58,77,78} Mn,^{79,80} Fe,^{81–84} Co,^{85–88} Ni,^{89–91} and Cu^{92,93} species exist in a variety of electronic configurations,^{56,94} and while no Co²⁺-iminyl has yet been isolated, one has recently been implicated.⁹⁵ In general, metal centers with high oxidation states and low spin configurations impart stability to a metal-nitrenoid fragment. In contrast, lower oxidation states and high spin intermediates as those likely at play in 1-Co are more reactive due to the population of antibonding orbitals and the increased electron-electron repulsion, both of which destabilize and weaken the M…N bond.^{96,97} We therefore hypothesize that when M = Co, the cluster core localizes some of the charge created upon N₂ extrusion (+1), enabling the edge metal to retain a relatively lower oxidation state. In turn, this Co²⁺-iminyl electronic structure is expected to



Figure 8. Mulliken spin density (α - β) plots of A) 1-Cr(NTs), and B) 1-Co(NTs) calculated at uB3LYP+/cc-pVTZ level of theory. Spin density values for the edge, NTs fragment, and Co₆Se₈ core are included. Surfaces plotted at an isovalue of 0.004. C) Corresponding partial density of states plots of 1-Cr(NTs) and 1-Co(NTs).

feature a decreased bond order, and hence display higher reactivity.⁹⁴ Therefore, in the case of **1**-Co, the edge/support cooperativity is poised to increase the reactivity of the M–NTs multiple bond fragment.

Conclusions

1-M is a molecular cluster that incorporates the complexities of a heterogeneous single-site catalyst in a tunable and monodisperse platform. Leveraging a molecular approach, this study provides atomistic insights into the metal/support interface, and how the ensuing cooperativity can be harnessed to dramatically alter catalytic activity in a redox transformation.

As a ligand, the Co_6Se_8 cluster is structurally and electronically responsive to the chemical identity of the edge site. The structural versatility is captured by the variety of coordination environments adopted by the edge metals in the solid-state: two coordinate linear (Cu), four-coordinate pseudo-tetrahedral (Mn, Fe, Co, Zn), or five-coordinate square pyramidal (Cr). The electronic effects of the metal/support interactions are probed by cyclic voltammetry, magnetic measurements, electronic absorption spectroscopy, paramagnetic ³¹P NMR, and DFT calculations. The most obvious change observed is the narrowing of the HOMO/LUMO gaps, which is proportional to the degree of structural distortion inflicted by the edge site on the Co_6Se_8 cluster. Periodic trends in the valence orbital energies across the 3d series manifest in a stabilization of the LUMO levels across the 1-M series up to copper, where edge/support charge redistribution occurs spontaneously to form a reduced Cu^{1+} edge and a mono-oxidized to $[Co_6Se_8]^+$ core. Ultimately, the use of molecular characterization techniques provides an atomic-level picture of the edge/cluster interface.

Metal/support interactions have been shown to enhance the catalytic activity of single-site heterogeneous catalysts. In **1**-M, the edge/support construct imparts remarkable activity for nitrene transfer across the 3d transition metal series, chemical versatility that is reserved to few molecular ligands.^{98,99} The identity of the edge metal effectively tunes the observed catalytic rates, which peak for the Mn and Co derivatives. Empirically, the strength of edge/core (M–Se) bonding interaction correlates linearly with the catalytic activity of the 3d series. We hypothesize that due to dynamic push-pull substrate/active site/support interactions, the strength of the M–Se bonds and M–NTs multiple bonds are inversely related. Hence, the stronger the edge/core interaction, the weaker and more reactive the M(NTs) fragment in key metal nitrenoid catalytic intermediates. Identifying redox regimes wherein electronic cooperativity can occur between the active site and the cluster support provides a method to tune the reactivity of metal-ligand multiple bonds. The electronic interaction between the edge metal and the cluster support ranges from fully independent (Cr) to cooperative (Co, Mn). In the latter, electron transfer from the cluster core to the edge site is predicted to increase the reactivity of the metal nitrenoid intermediate by ensuring a relatively lower oxidation state of the active site and weakening the M(NTs) bond.

In aggregate, this study provides an atomic level picture into the key structural and electronic factors underpinning metal/support interactions and their role in facilitating reactivity in a molecular single-site cluster, ultimately illustrating how their cooperativity can be leveraged to modulate catalytic performance.

ASSOCIATED CONTENT

Supporting Information

Synthetic protocols, experimental characterization for all compounds, including crystallographic data, catalytic nitrene transfer studies, as well as computational investigations is available online.

Accession Codes

CCDC 2113026, 2113027, 2113028, 2113029, 2113030 and 2113031 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <u>www.ccdc.cam.ac/uk/data_request/cif</u>, or by emailing <u>data_request@ccdc.cam.ac.uk</u>, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CD2 1EZ, UK; fac; +44 1223 336033.

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Notes

The authors declare no competing financial interests

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