Cluster-Bound Nitriles Do Not Click with Organic Azides: Unexpected Formation of Imino Complexes of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ Core-Containing Clusters[†]

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The reactions of $C_6H_5CH(CH_3)N_3$ with nitrile solvates of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core-containing cluster, $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)]^{2+}$ (**1**) and *cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(MeCN)_2]^{2+}$ (**2**), afforded the corresponding cationic imino complexes $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(PhN{=}CHCH_3)]^{2+}$ (**3**) and *cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(PhN{=}CHCH_3)_2]^{2+}$ (**4**), respectively. Both compounds were spectroscopically and crystallographically characterized. A mechanism involving a 1,2-shift of one of the groups on the azido α-C atom of the cluster−azide intermediate concerted with the photoexpulsion of dinitrogen of the azido ligand is invoked to rationalize the formation of the imino complexes. Density functional theory calculations showed that a cluster-to-ligand transition was responsible for the absorption that promotes the photodecomposition of the cluster−azide complex.

Click chemistry represents an elegant chemical philosophy guided by which a chemical reaction generates complex substances quickly and reliably by joining small modular units.[1] Arguably, most notable in this regard is 1,3-dipolar cycloaddition, the coupling reaction between a 1,3-dipole and a dipolarophile to form a five-membered heterocycle.[2] Tetrazoles, for example, a class of extremely useful building blocks and frequently targeted structures can be synthesized directly by a [2 + 3] cycloaddition between organic azides and nitriles.[3] The reaction occurs sufficiently rapidly only if it is intramolecular or the nitrile substrate is activated by an electron-withdrawing group.[3a,b,4] An interesting example exemplifying the latter point is the recent work by Szczepura and co-workers:[5] The cluster-bound and activated MeCN in $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)](BF_4)_2$ [**1**·$(BF_4)_2$] undergoes facile, room-temperature cycloaddition with N_3^- to afford the corresponding cluster−tetrazole complexes (Figure 1).

Inspired by this interesting finding and driven by the significant biological and pharmacological applications of tetrazoles,[6] we sought to extend the chemistry to the use of organic azide with the hope of developing modular synthesis of functional tetrazoles. Unexpectedly, rather than the anticipated tetrazole complex, a geometrically specific imino complex of the cluster was produced (Figure 1) using **1**·$(SbF_6)_2$[7] as the starting cluster complex. The stereoselective formation of imino groups was also observed when *cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(MeCN)_2](SbF_6)_2$ [**2**·$(SbF_6)_2$],[7] a substitutional isomer of **1**·$(SbF_6)_2$ with two cis-disposed nitrile ligands, was used. There are a large number of metal complexes with chelating imines,[8] but the number of complexes with monodentate N-bound imines is much smaller, in particular when the N atom is sterically hindered.[9] The geometrically specific imine complexes are thus expected to be useful in studying metal-mediated transformations where the imine complexes have been observed or proposed as key intermediates.[10] Herein we describe the synthesis and characterization of two novel imino complexes obtained as such. A mechanism possibly responsible for these unexpected findings, supported by computational studies, is also discussed.

[†] Dedicated to Prof. Xin-Tao Wu on the occasion of his 70th birthday.

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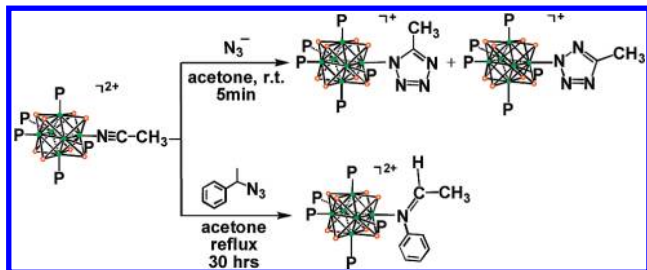
Figure 1. Distinctly different reactivity of a cluster-bound nitrile ligand toward sodium azide and (1-azidoethyl)benzene (green and brown spheres represent Re and Se atoms, respectively; P = PEt$_3$).
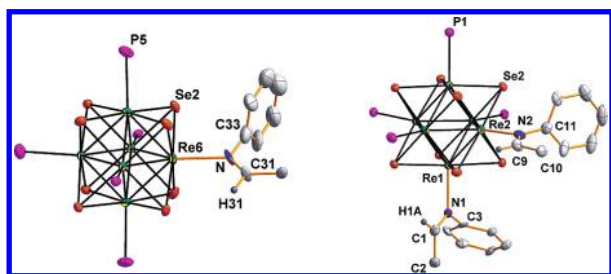

Figure 2. Crystal structures of the cationic cluster complexes, **3** (left) and **4** (right). The ethyl groups of PEt$_3$ and non-imine H atoms are omitted for clarity. Anisotropic displacement ellipsoids are drawn at the 30% probability level.

An acetone solution containing C$_6$H$_5$CH(CH$_3$)N$_3$ and the previously reported cluster solvate **1**·(SbF$_6$)$_2$ or **2**·(SbF$_6$)$_2$ was stirred under reflux for 30 h, producing respectively [Re$_6$(μ_3-Se)$_8$(PEt$_3$)$_5$(PhN=CHCH$_3$)](SbF$_6$)$_2$ [**3**·(SbF$_6$)$_2$] and *cis*-[Re$_6$(μ_3-Se)$_8$(PEt$_3$)$_4$(PhN=CHCH$_3$)$_2$](SbF$_6$)$_2$ [**4**·(SbF$_6$)$_2$], the corresponding imino complexes (Figure 2)). Anion exchange of **3**·(SbF$_6$)$_2$ with NaB(C$_6$H$_5$)$_4$ affording [**3**·(BPh$_4$)$_2$] was found necessary to obtain X-ray-quality single crystals for the structural determination of the cationic monoimine−cluster complex. The resonance of the original nitrile ligand(s) is absent from the ^{1}H NMR spectra of **3**·(BPh$_4$)$_2$ and **4**·(SbF$_6$)$_2$. Instead, a distinct resonance pattern of the PhN=C*H* proton appears, as a quartet at 8.73 and 9.10 ppm, respectively. These chemical shifts are comparable to those reported for their mononuclear analogues.[11] The ^{31}P NMR spectra of **3**·(BPh$_4$)$_2$ and **4**·(SbF$_6$)$_2$ display resonances with patterns consistent with their respective stereochemistry, two signals of 4:1 relative integration for **3**·(BPh$_4$)$_2$ and two signals of 1:1 relative integration for **4**·(SbF$_6$)$_2$.

The structures of **3**·(BPh$_4$)$_2$ and **4**·(SbF$_6$)$_2$ have been established crystallographically. However, the structure of **3**·(BPh$_4$)$_2$ suffered from some serious issues during structural refinement. Several large residual peaks remain inside and surrounding the Re$_6$Se$_8$ core, leading to large *R* values [R1 = 8.1 and wR2 = 25.7 (all data)]. An explanation is provided in the Supporting Information.). The cluster cores appear unaffected by the ligand transformation, with bond lengths and angles varying insignificantly relative to **1**·(SbF$_6$)$_2$. The Re−N bond lengths are normal, at 2.311(17) Å in **3**·(BPh$_4$)$_2$ and at 2.228(10) and 2.233(12) Å in **4**·(SbF$_6$)$_2$. Other parameters clearly suggest the identity of the coordinated imine molecules in both compounds: The N−C31 bond length

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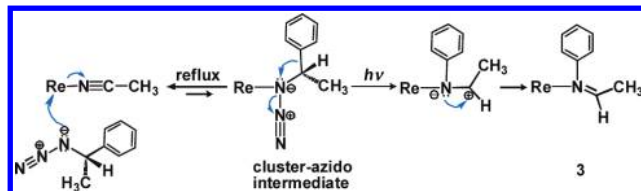

Figure 3. Mechanistic proposal for the formation of the observed imino complexes, starting with the formation of a cluster−azido intermediate followed by the stereoselective migration of one of the groups on the α-C atom of the azido ligand to its α-N atom, concerted with the photoelimination of dinitrogen. Only the N-coordinated Re site is shown for clarity.

of 1.260(3) Å in **3**·(BPh$_4$)$_2$ and the N1−C1 and N2−C9 bond lengths of 1.253(18) and 1.290(2) Å, respectively, in **4**·(SbF$_6$)$_2$ are consistent with an imine moiety. The angles about N [ranging from 112.8(19) to 127.8(17)° for **3**·(BPh$_4$)$_2$ and from 117.7(11) to 123.1(11)° for **4**·(SbF$_6$)$_2$] are close to the expected values for an sp^2 hybridization.

Because metal complexes with tetrazole-based ligands are generally thermally stable,[5,12] the formation of the present imine−cluster complexes is probably not due to the thermal decomposition of the corresponding tetrazole complexes. Rather, a mechanism schematically shown in Figure 3, modified from the one originally proposed by Abramovitch and Kyba for the photodecomposition of alkyl azides,[13] may be operative. Because the formation of the bis-imino complex **4**·(SbF$_6$)$_2$ probably follows the same mechanism, **3**·(SbF$_6$)$_2$ is used as a study model for the following mechanistic discussions. In such a mechanism, reversible substitution of the nitrile ligand for the organic azide via coordination of the α-N atom constitutes the first step of the reaction. Though not a general feature, metal complexes embracing such a coordination mode of the azido ligand are known.[14] However, the equilibrium favors the starting nitrile complex, as suggested by the difference in free energy of 13.29 kcal/mol between the cluster−azido intermediate and **1**·(SbF$_6$)$_2$, calculated using the bond energy between the cluster core and the respective ligands (Figure S8). Subsequent photodecomposition of the highly energetic cluster−azido intermediate involves the migration of the phenyl group to the α-N atom concerted with the elimination of dinitrogen. The irreversible loss of dinitrogen helps drive the initial equilibrium toward the production of the thermodynamically more favored imino complex **3**·(SbF$_6$)$_2$. Consistent with such a mechanism, control experiments performed in the dark or at room temperature failed to produce any imino complex under otherwise identical conditions.

Alkyl azides were found to undergo similar photodecomposition when irradiated using a mercury lamp. The π−π* transition (ca. 285 nm) is believed to be responsible for substrate excitation and decomposition.[13] The product mixture, generally in low overall yields, contains a number of imino derivatives whose relative concentration depends on the migration amplitude of the different alkyl groups on the

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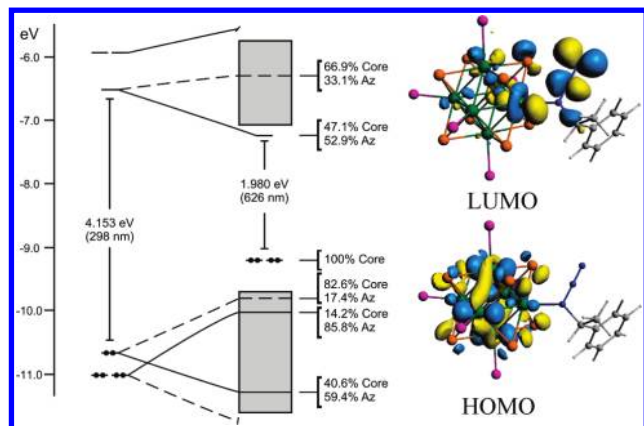
Figure 4. MO diagram denoting the contribution of the free $C_6H_5CH(CH_3)N_3$ ligand to the cluster—azido intermediate. The gray boxes indicate the MO of the total or mainly cluster core character.

α-C atom. In stark contrast, photodecomposition of the cluster—azido complex afforded only one geometrically specific imino complex in essentially quantitative yield. Even more intriguing is that the present reaction is promoted by hood illumination (400—650 nm with two comparable maxima at 550 and 620 nm; Figure S6), which is much less energetic than the mercury-lamp irradiation. These findings suggest that the cluster—azido complexes possess a drastically different electronic structure and their decomposition is promoted by a transition that is distinctly different from the aforementioned $\pi-\pi^*$ transition.

Calculations using density functional theory (DFT) were thus performed in the hopes of gaining a better understanding of the electronic structures of the reactants, the cluster—azido intermediate, and the imino complex. It has been found that, for $C_6H_5CH(CH_3)N_3$, the calculated transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is at 298 nm, very close to the wavelength reported for the $\pi-\pi^*$ transition of organic azides.[13] However, as revealed by the MO diagram of the cluster—azido intermediate shown in Figure 4, the ligand-based LUMO is somewhat stabilized, while the complex HOMO is exclusively cluster-core-based. The anticipated absorption is calculated to be at 626 nm, matching one of the emission maxima of the hood illumination. In other words, the frontier orbitals of the cluster—azido complex are so distinct that the HOMO—LUMO energy gap is effectively reduced, resulting in the shift of the photoexcitation wavelength from ultraviolet into the visible region, hence the observed facile and complete reaction under the convenient hood illumination.

The exclusive formation of a particular geometric isomer of the imino complex can be rationalized by invoking the orbital argument depicted in Figure 5.[13,15] The preferred ground-state conformation (PGSC) of the azido intermediate, the one with the least steric congestion, dictates which group is to migrate. The structures of complex $1\cdot(SbF_6)_2$, $3\cdot(SbF_6)_2$, and the cluster—azido intermediate are optimized using DFT calculations at the scalar TZP-STO/ZORA level. The calculated bond characters of $1\cdot(SbF_6)_2$ and $3\cdot(SbF_6)_2$ are in good agreement
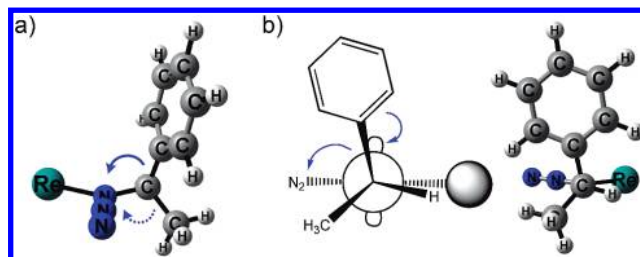
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Figure 5. Local PGSC of the cluster—azido intermediate: (a) view along the N=N=N bond; (b) view along the C—N bond. The structure was optimized using DFT calculations at the scalar TZP-STO/ZORA level.

with those obtained crystallographically (Figure S7). In the PGSC of the cluster—azido intermediate, the sp^2-hybridized α-N atom adopts a planar bonding geometry. As such, any nucleophilic attack is expected to occur only from above or under this plane (Figure 5a) in order to achieve the best overlap with the empty, unhybridized p orbital of the α-N atom; only the phenyl or methyl group is expected to be able to migrate because the H atom on the α-C atom is within the plane that contains the azido moiety. From the view of the PGSC along the C—N bond (Figure 5b), it is clear that the phenyl group is better aligned with the unhybridized p orbital, and its migration toward the α-N atom concerted with the photoexpulsion of dinitrogen leads to the exclusive formation of the observed geometric isomer of the imino complex.

In summary, two novel imino complexes of the $[Re_6-(\mu_3-Se)_8]^{2+}$ core-containing cluster have been obtained unexpectedly from the reaction between the nitrile solvates of the cluster and an alkyl organic azide originally targeting the corresponding tetrazole complexes via [2 + 3] cycloaddition. A mechanism involving a 1,2-shift of one of the groups on the azido α-C atom concerted with the photoexpulsion of nitrogen of the azido complex is invoked to rationalize the imino complexes obtained. DFT calculations were performed on the starting nitrile complex, the imino complex product, and the proposed cluster—azido intermediate in order to rationalize the high-yield synthesis of the highly stereoselective products. A cluster-to-ligand-based transition, distinctly different from the electronic transition of pure organic azide, was found to be responsible for the distinct absorption that promotes the photodecomposition of the cluster—azido intermediate complex. This report thus provides the very first definitive experimental and computational studies of the functions of metals in promoting the decomposition of azido complexes and the formation of corresponding imine complexes. With this reaction, geometrically specific and functionalized imines should be readily prepared using judiciously designed organic azides. Furthermore, because of the availability of multiple metal sites within the cluster core, site-differentiated imino complexes can be envisioned, as demonstrated by the *cis*-diimino cluster complex presented herein.

Supporting Information Available: Crystallographic data in CIF format and synthetic and characterization details of $3\cdot(BPh_4)_2$ and $4\cdot(SbF_6)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.