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The removal of lithium from a Li-Mn(v/v)-imido cluster by ion metathesis with chloride ion results in reductive elimination of *azo-tert*-butane to give a Mn(v)-imido cubane cluster.

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Formation of the tetranuclear, tetrakis-terminalimido  $Mn_4^{IV}(N^tBu)_8$  cubane cluster by fourelectron reductive elimination of  ${}^tBuN = N^tBu$ . The role of the s-block ion in stabilization of high-oxidation state intermediates<sup>†</sup>

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 $Mn_4^{IV}(\mu_3-N^tBu)_4(N^tBu)_4$  is obtained from a previously reported asymmetric  $Mn^{IV/V}-Li-(NR)(N)$  cluster by the removal of Li from the starting cluster by ion metathesis, which triggers reductive elimination of azo-*tert*-butane to give a tetranuclear heterocubane cluster.

Reductive elimination reactions from transition metal-Lewis acid metal clusters are key to the understanding of the biological Oxygen Evolving Complex (OEC) of photosystem II, which is a Ca–Mn–O cluster that generates  $O_2$  from cluster oxide ligands by 4-electron reductive elimination. While a number of proposals exist for the molecular mechanism of this reaction,<sup>1–4</sup> scarcity of experimental examples of this reaction at metal clusters renders the proposed mechanisms experimentally inscrutable. Additionally, reductive elimination of light ligands from metal-based molecules is of interest for the generation of precursors for chemical vapor deposition of elemental solid state materials.<sup>5</sup>

Examples of reductive elimination from manganese clusters are rare. The oxygen evolving dimer from the Brudvig group releases  $O_2$ from terminal or bridging sites, but O-exchange rates are too fast to distinguish the ligand sites responsible for reductive elimination.<sup>6</sup> Experimental evidence for reductive elimination of core oxos has been reported at a synthetic  $Mn_4O_4$  cubane cluster from the group of Dismukes.<sup>7</sup>  $O_2$  evolution from reaction of a terminal manganese oxo complex with hydroxide<sup>8</sup> supports a proposed mechanism involving attack of Ca-bound hydroxide on a terminal Mn—O. The reversible oxidation of oxide to peroxide has been observed by Nam and Valentine.<sup>9</sup> We have previously reported on the twoelectron reductive elimination of azobenzene (diazenes are the



nitrene analogue of O<sub>2</sub>) from manganese aggregates in solution,

but the precise structure of the active species is not known,<sup>10,11</sup> and the four-electron reductive elimination of azoarenes by the group of

Heyduk is worthy of note.<sup>12</sup> We report here experimental evidence

for the 4-electron reductive elimination of azo-tert-butane from the

mixture of structurally analogous manganese imide clusters with the general formula  $Li_3Mn_4M(\mu_3-N^tBu)_6(\mu-N^tBu)_3(N^tBu)(N)$ 

where  $M = Mn \equiv N$  (1) or Li (1a).<sup>13</sup> This cluster, shown in

Scheme 1, possesses several ligand types:  $\mu_3$ -bridging imides,

 $\mu_2$ -bridging imides, terminal imide, and nitride. Charge counting, bond valence summation calculations<sup>14</sup> and XPS analysis reveal

the cluster possesses a mixed (*w/v*) oxidation state. This material is

a cocrystalline mixture of the nearly isostructural  $Li_3Mn_5$  (1) and

discovered that this high oxidation state is unstable in the absence

of the s-block ions. When Li<sup>+</sup> is extracted from the cluster using ion

metathesis with anhydrous Et<sub>4</sub>NCl, the result is precipitation of a

mixture of salts, of which LiCl is a primary component, and the

isolation of a new, simple  $Mn_4N_4$  heterocubane cluster (Fig. 1). This

reaction is diagrammed in Scheme 1, illustrating the lithium

cluster with four bridging tert-butyl imide ligands, and four

terminal tert-butyl imide ligands. The molecule sits on a crystallo-

graphic mirror plane (through atoms Mn(2,3), N(2,3,5,6)).

The structure of 2 is that of a tetramanganese heterocubane

In our efforts to remove the Li<sup>+</sup> from this cluster, we have

We have previously reported the synthesis of a cocrystalline

imide ligands of manganese cubane clusters.

 $Li_4Mn_4$  (1a) dicubane clusters.

metathesis from 1a (the dominant species).



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<sup>†</sup> Electronic supplementary information (ESI) available: Full experimental and synthetic procedures, NMR, UV-Vis, FT-IR, ESI mass spectra, CV of 2, full X-ray crystallographic data tables, Bond Valence Summation calculations. CCDC 930706. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc42165a

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**Fig. 1** X-ray crystal structure of  $Mn_4^{IV}(\mu_3-N^tBu)_4(N^tBu)_4$  (**2**). Thermal ellipsoids shown at 30% probability level. Symmetry equivalent atoms are generated by the (2-x, y, z) operation.

Table 1 🛛 🗠	nteratomic distances (À	A) and and	gles (deg) in	⊨Mn₄ <sup>iv</sup> (į	μ₃−Ν <sup>t</sup> Bu)₄(ľ	√ <sup>t</sup> Bu) <sub>4</sub> ( <b>2</b>
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$Mn-N(\mu_3)$	1.89-1.91	
Mn–N(term)	1.65	
Mn···Mn	2.54-2.56	
NN	2.81-2.92	
Mn–N(term)–C	176-179	

The short Mn–N terminal bond lengths (1.65 Å), and linear nitrogen atoms indicate multiple bonding to the four terminal imide ligands (Table 1). Terminal imide ligation is supported by the presence of a band at 1220 cm<sup>-1</sup> in the FT-IR spectrum consistent with a Mn—NR stretch. The terminal and bridging imides do not exchange in solution on the NMR time scale. Structurally characterized examples of terminal imide ligation on manganese are rare, limited to the monomers and linear clusters of Wilkinson<sup>15,16</sup> and the corrole-type complexes of Abu-Omar<sup>17</sup> and Goldberg.<sup>18</sup>

Though **2** is formed in approximately 81% yield based on quantification by NMR (see ESI<sup>†</sup>), isolation of pure **2** in good yield is challenging due to hypersolubility in even the most non-polar solvents such as pentane and hexamethyldisiloxane (HMDS), resulting in yield loss during crystal isolation. Purified material is obtained in 33% yield after the filtration of salt byproducts by the slow vapor diffusion of a pentane solution with HMDS in a double vial apparatus. Rinsing of the crystals briefly with cold (-30 °C) pentane results in large, pure crystals, but significant product loss. The <sup>1</sup>H NMR spectrum shows two sharp singlets in the diamagnetic region corresponding to bridging and terminal *tert*-butyl groups. The sharp, diamagnetic spectrum and magnetic measurements are indicative of a *S* = 0. Antiferromagnetic coupling has been observed in the terminal-imidecontaining iron-imido cubane cluster of Lee.<sup>19</sup>

Compound 2 is formally, and based on bond valence summation calculations,<sup>14</sup> an all-Mn(v) cluster, while the starting material 1/1a contains a mixture of Mn(v/v), implicating an overall reduction of the Mn centers. Furthermore, ligands are lost in the metathesis reaction, namely, from 1a, a nitride and two imides. Ion metathesis can explain, in part, the loss of ligands from 1a; indeed, nitride and imide ligands are present in the salt precipitate byproduct based upon ion chromatographic analysis of the acid digest. However, metathesis does not explain the overall gain of electrons by Mn. Reductive elimination of nitrogen ligands is the most plausible explanation for the change in oxidation state. The six-electron reductive elimination of nitrogen is a possibility, but would result in a product cluster with much lower oxidation state than 2. Though the reductive elimination of  $N_2$  cannot be strictly ruled out, the reductive elimination of azo-*tert*-butane, which provides four electrons to the cluster, and removes two *tert*-butyl imido ligands is most reasonable.

This proposed mechanism of cluster reduction is supported by the detection of azo-tert-butane as the sole organic byproduct of the metathesis reaction (see ESI<sup>+</sup> for data). The byproduct is separated from the reaction mixture by vacuum distillation, and analyzed by mass spectroscopy. The azo-tert-butane is also quantified using in situ NMR, and forms in 80% yield based upon eqn (1) (vide infra). The formation of azo-tert-butane as an organic byproduct of the reaction suggests reductive elimination as the mechanism for formation of 2. Thus, the lithium ions appear to serve a stabilizing role in clusters 1/1a, possibly due to the hardhard acid-base interactions among the charge-dense lithium ions, manganese(v) ions, nitride, and imide ligands. Lewis acidic ions have been previously observed to affect reduction potentials<sup>20,21</sup> or induce valence tautomerism<sup>22</sup> in manganese compounds, although it has been argued based on DFT that Ca has little effect on electronic structure in the OEC.<sup>4</sup> Thus, the stabilizing role of Li may instead be structural in nature. A similar stabilizing role of Li in preventing reductive elimination of azobenzene has been seen in hydrazide ligand chemistry at manganese.<sup>10</sup>

The conversion of  $1 (2Mn^{IV}:3Mn^V)$  or  $1a (1Mn^{IV}:3Mn^V)$  to  $2 (4Mn^{IV})$  results in the gain of three electrons, while the reductive elimination of *tert*-butyl imide ligands to give azo-*tert*-butane is a four electron process. Thus, a balanced equation cannot be written for a 1:1 molecular conversion, implicating a multistep mechanism. Furthermore, since the Mn-cube motif changes from one with imide and nitride bridges to an all-imide motif, cluster rearrangement is necessarily involved. We propose that an additional equivalent of 1 provides the 4th oxidizing equivalent for the reductive elimination reaction, resulting in the following balanced chemical equation, which is experimentally supported by quantitation of products 2 and azo-*tert*-butane, and by the detection of nitride and imide in the insoluble residue:

$$\begin{aligned} 4\text{Li}_{4}\text{Mn}_{4}(\text{N}^{t}\text{Bu})_{10}(\text{N}) \ (\textbf{1a}) + 12\text{Et}_{4}\text{NCl} \\ \rightarrow 4\text{Mn}_{4}(\text{N}^{t}\text{Bu})_{8} \ (\textbf{2}) + 3^{t}\text{Bu}\text{N} = \text{N}^{t}\text{Bu} \\ &+ (12\text{Et}_{4}\text{N}^{+}, 16\text{Li}^{+}, 12\text{Cl}^{-}, 2\text{N}^{t}\text{Bu}^{2-}, 4\text{N}^{3-} \text{ salts}) \end{aligned}$$
(1)

The cyclic voltammogram of compound 2 possesses a reversible 1-electron oxidation wave giving the formally 3-Mn(v):1-Mn(v)cubane cluster at -0.388 V *vs.* ferrocene. This oxidation state is the traditional "high oxidation state paradigm" description of the S<sub>4</sub> state, which evolves O<sub>2</sub>. In our system, the 2<sup>+</sup> state of this cluster is formed at low potential due to the extensive  $\pi$ -bonding which stabilizes high oxidation states *via*  $\pi$ -donation into the d-orbitals. A second oxidation to the formal 2-Mn(v):2-Mn(v) species occurs at 0.690 V. *vs.* ferrocene, but is quasi-reversible, leading to compound decomposition (Fig. 2).



Fig. 2 Cyclic voltammogram for **2** in 1:1 acetonitrile: tetrahydrofuran. Open circuit potential = -0.523 V Scan rate = 50 mV s<sup>-1</sup>.



Scheme 2 Two possible mechanisms for N=N bond formation in the reductive elimination of azo-*tert*-butane.

The four-electron reductive elimination of azo-tert-butane from 1a may involve core or terminal imides, or both. The involvement of core vs. terminal ligands is a topic of discussion in the mechanism of the OEC<sup>1,3,7,8,23</sup> The preparation of analogues of 1/1a with differently labelled bridging vs. terminal ligands may be of use in probing the involvement of bridging vs. terminal ligands (Scheme 2) in the reductive elimination mechanism. For instance, the analogue of 1a containing bridging *tert*-butyl groups and terminal adamantyl groups (or *vice versa*) would provide organic labels with similar electronic and steric properties for such crossover experiments. The preparation of such clusters via the controlled exchange of core vs. terminal imide ligands systems is possible due to the inherent differences in lability of terminal vs. bridging ligands, but is nevertheless an intensive synthetic challenge, which will be pursued in the further development of this chemistry.

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