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## Destruction of chemical warfare agent **simulants** by air and moisture stable metal NHC complexes

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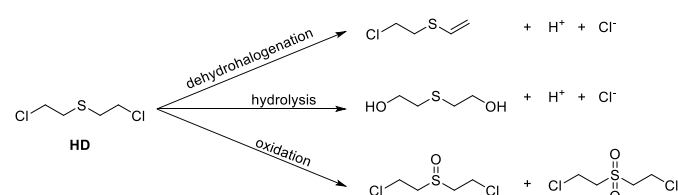
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The cooperative effect of both NHC and metal centre has been found to destroy chemical warfare agents (CWA) simulants. Choice of both the metal and NHC is key to these transformations as simple, monodentate N-heterocyclic carbenes in combination with silver or vanadium can promote stoichiometric destruction, whilst bidentate, aryloxide-tethered NHC complexes of silver and alkali metals promote breakdown under mild heating. Iron-NHC complexes generated *in-situ* are competent catalysts for the destruction of each of the three targeted CWA simulants.

### Introduction

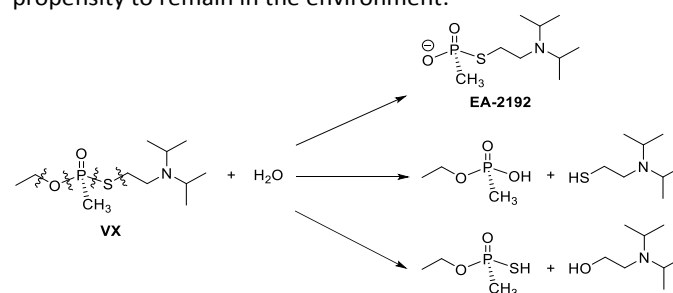
Since the first deployment of chemical warfare agents (CWAs) during the First World War, research into efficient decontamination routes has become necessary for immediate applications, and also for the destruction of CWA stockpiles as set out in the 1992 Chemical Weapons Convention Treaty (demilitarisation).<sup>1-5</sup> Whilst a variety of fast and effective decontamination routes have been identified, these generally contain a mixture of flammable solvents and corrosive reagents and can be impractical for transportation or decontamination of expensive equipment. For example, DS2 is a combination of nucleophilic diethylenetriamine/ethylene glycol/monomethyl ether/sodium hydroxide mixtures and whilst it is a broadband decontaminant it is highly corrosive towards many materials.<sup>6</sup> Alternate decontamination solutions containing basic hypochlorite (bleach)-based microemulsions are very effective for sulfur mustard decontamination<sup>7,8</sup> however these are also deemed too corrosive and environmentally unacceptable for widespread use.<sup>9</sup> Therefore new reagents that have a low environmental impact and can be used in different situations on different classes of warfare agents are desired.<sup>10</sup>



Scheme 1. Three pathways for sulfur-mustard destruction

Sulfur mustard (**HD**), bis-2-chloroethyl sulfide, is a potent vesicant with a long environmental persistence that makes decontamination challenging.<sup>6,11-13</sup> Generally destruction of **HD** can occur via three different pathways (Scheme 1). Currently known dehydrohalogenation procedures can be problematic due to the reversible addition of HCl<sup>14,15</sup> and considered too slow in comparison to the other decontamination pathways<sup>16</sup> whilst at ambient temperatures hydrolysis is limited by the low aqueous solubility of **HD**.<sup>17</sup> Oxidation is currently one of the most effective pathways of decontamination; however care must be taken to selectively form the mono-oxidation product, the sulfone, is a potent vesicant in its own right.

The other major class, nerve agents, are organophosphonate compounds that were originally developed as pesticides until their highly toxic nature was recognised. Nerve agents can be divided into two main classes: non-persistent G- (eg. Sarin) and persistent V- (eg. VX) series, where the persistence relates to the relative ease of degradation or propensity to remain in the environment.



Scheme 2. Pathways for VX destruction by hydrolysis

Traditional routes for decontamination of **VX** have centred around its susceptibility towards nucleophilic attack, but again the control of product formation is imperative. In the simplest case addition of H<sub>2</sub>O yields several products,<sup>18,19</sup> but the formation of **EA-2192** is of concern as it is nearly as toxic as **VX** and is less reactive towards further nucleophilic attack.<sup>10</sup>

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Electronic Supplementary Information (ESI) available: Synthetic details for the compounds; kinetic data for the catalysis. Crystal structure data for the vanadium-NHC decomposition product. CCD code 1580495. See DOI: 10.1039/x0xx00000x

N-heterocyclic carbenes (NHCs) have transformed modern organometallic chemistry.<sup>20</sup> The strongly Lewis basic  $\sigma$ -donor ligands have been shown to bind to many metals leading to widespread applications, notably their use in homogeneous catalysis with late transition metals for alkene metathesis and C-C coupling reactions.<sup>21</sup> In relation to decontamination and demilitarisation of CW agents, the range of reactivity available to NHCs and their highly tuneable nature makes them attractive candidates for these processes due to their ability to act as strong nucleophiles in organocatalysis, as well as organic bases.<sup>22</sup> Oxidative CWA destruction pathways can also be considered in combination with right choice of metal centre. Many coinage metal NHC complexes made for medicinal applications display very high water stability,<sup>23</sup> while homogeneous catalysts based on Pd and V show both a high stability towards oxidation<sup>24-28</sup> and great effectiveness as oxidation catalysts,<sup>29-31</sup> in particular vanadium doped silica has been previously shown to be effective for the oxidation of CEES. The redox couple of  $\text{VO}_2^+/\text{VO}^{2+}$  (vanadyl) complexes is +1.00 V,<sup>32</sup> and it has been demonstrated that the complex  $\text{VOCl}_3(\text{IMes})$  is air-stable.<sup>33</sup>

We have been studying the cooperative reactivity of metal-NHC complexes in which the metal-C bond is relatively labile, and can give rise to reactions of both the metal and NHC. We have previously shown a range of carbon-element bond formation and cleavage reactions.<sup>34-36</sup>

Herein we report the effectiveness of a range of air and moisture stable metal NHC complexes for the stoichiometric and catalytic destruction of both H- (mustards) and V- (nerve) type chemical warfare agent (CWA) simulants shown in Fig. 1. The use of simulants is required due to strictly controlled production, acquisition, retention or use of warfare agents under Schedule 1 of the Chemical Weapons Convention (CWC). Previous research has shown 2-Chloroethyl ethyl sulphide (CEES, referred to as half mustard) is an effective simulant for HD,<sup>37</sup> whilst Paraoxon-ethyl and Profenofos are used to simulate VX as these contain the desirable P-O and P-S bond cleavages, respectively. Whilst these simulants are less toxic than the actual CWAs, they are still considered to be very toxic (Paraoxon-ethyl: LD50 in Rat = 0.716 mg/kg) and must be handled with great care. Reactions are carried out on a small scale with no more than 5  $\mu\text{L}$  of the chosen CWA simulant, to manage the risks associated with these compounds.

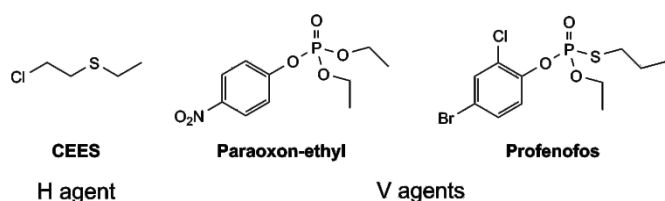


Figure 1. CWA simulants targeted for decontamination

## Results and Discussion

### Candidate metal-NHC complexes

Copper and silver NHC complexes were initially targeted due to their high water-stability and ability to undergo redox reactions, thus providing a good baseline for how metal-NHC complexes may react with CWA simulants. This focused on the use of previously reported, commercially available unsaturated NHCs (denoted (IR) and derived from the imidazolium chloride salts  $\text{IPr.HCl}$ ,  $\text{IMes.HCl}$  and  $\text{ICy.HCl}$ ) and saturated NHCs (denoted (SIR) and derived from the imidazolium salts  $\text{SIPr.HCl}$ , and  $\text{SIMes.HCl}$ ) and a bidentate aryloxo-functionalised imidazolium salt ( $\text{HOArIPr.HCl}$ ), Figure 2. The silver NHC complexes  $\text{AgCl}(\text{IR})$  ( $\text{R} = \text{Dipp}$  **1-Ag**,  $\text{Mes}$  **2-Ag**,  $\text{Cy}$  **3-Ag**),  $\text{AgCl}(\text{SIR})$  ( $\text{R} = \text{Dipp}$  **4-Ag**,  $\text{Mes}$  **5-Ag**)<sup>38</sup> and corresponding copper NHC complexes  $\text{CuCl}(\text{IR})$  ( $\text{R} = \text{Dipp}$  **1-Cu**,  $\text{Mes}$  **2-Cu**,  $\text{Cy}$  **3-Cu**),  $\text{CuCl}(\text{SIR})$  ( $\text{R} = \text{Dipp}$  **4-Cu**,  $\text{Mes}$  **5-Cu**)<sup>39</sup> are readily obtained through reaction with the corresponding metal oxide. Due to the potential for oxidation destruction pathways the use of the highly oxidising but remarkably air-stable vanadyl NHC complexes  $\text{VOCl}_3(\text{IR})$  ( $\text{R} = \text{Dipp}$  **1-V**,  $\text{Mes}$  **2-V**,  $\text{Cy}$  **3-V**), Fig. 2, (**1-3-V**) were isolated from the stoichiometric addition of  $\text{VOCl}_3$  to the free carbene.<sup>33, 40</sup> It is of note that whilst the saturated analogues of the vanadium NHC complexes were also isolated they were found to be unstable towards moisture, and therefore were not used in this study (see SI).

In addition, metal complexes of the bidentate aryloxo NHC were also made; **6-Ag** was made from silver(I)oxide,<sup>41</sup> and the sodium (**6-Na**) and potassium (**6-K**) complexes were made from the corresponding  $\text{MO}^t\text{Bu}$  ( $\text{M} = \text{Na}$  or  $\text{K}$ ) salt *in situ* prior to use.

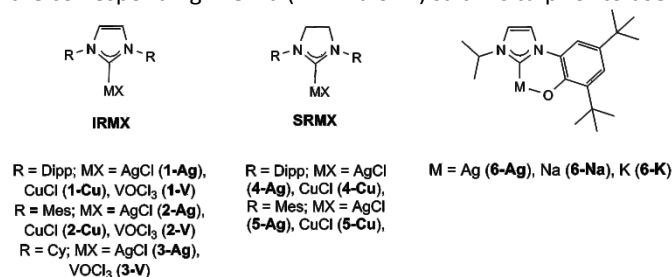


Figure 2. M-NHC complexes used in this study.

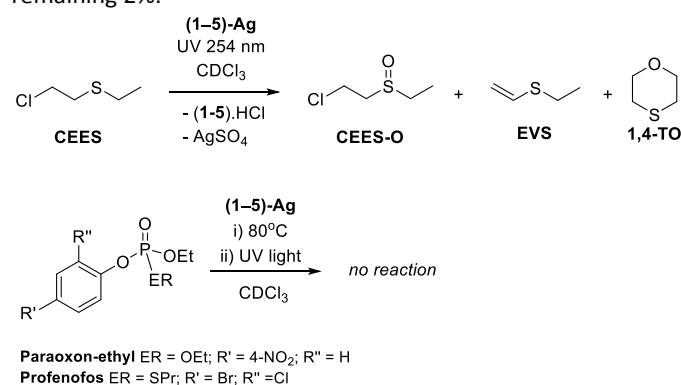
Reactions of each compound shown in Fig. 2 with each of the three CWA simulants were monitored by  $^1\text{H}$  NMR spectroscopy. Reactions used stoichiometric, excess, or catalytic amounts of the complexes and were accelerated by either heat or photolysis.

### Destruction by Group 11 metal-NHC complexes

Stoichiometric simulant degradation reactions were followed in 0.5 mL of  $\text{CDCl}_3$ . Reactions were monitored at intervals by a combination of NMR spectroscopy ( $^1\text{H}$  and  $^{31}\text{P}$  where relevant), UV-Vis spectroscopy and GC mass spectrometry. As shown in Scheme 3, complexes (**1-5**)-Ag showed no reactivity at room temperature or after prolonged heating at 80  $^\circ\text{C}$  with any of the simulants. However, upon exposure to low-intensity UV light (254 nm, 6 W) the reactions with CEES showed the conversion of CEES into new compounds after 1 hr, according to  $^1\text{H}$  NMR spectroscopic analysis. No

reaction of the V agent simulants was observed even after prolonged exposure to either 254 nm or 364 nm UV radiation.

Full destruction of **CEES** was observed after 5 hrs when using an excess of **1-Ag** (5 eq.). The  $^1\text{H}$  NMR spectra show several new species in solution. Through a combination of HSQC, HMBC, COSY and DOSY 2D NMR spectroscopy experiments the major product was identified as the mono-oxidation product, **CEES-O** (Scheme 3). The two other major products are attributed to the dehydrohalogenation of **CEES** and include ethyl(vinyl)sulfide (**EVS**) and 1,4-thioxane (**1,4-TO**) which results from the dehydrohalogenation of partially hydrolysed **CEES**<sup>10</sup>. An approximate product distribution was 80% **CEES-O** : 8% **EVS** : 10% **1,4-TO**, with several minor products accounting for the remaining 2%.



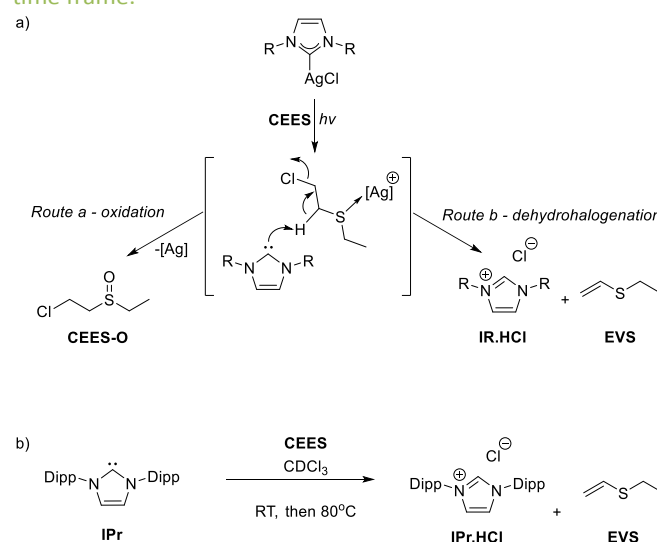
**Scheme 3.** Reactions of **(1–5)-Ag** with CWA simulants showing the major decontamination products.

The fate of complex **1-Ag** was also determined by NMR spectroscopy and ICP-OES spectrometry as the imidazolium chloride salt **IPr.HCl**, and a silver- and sulfur-containing material which was observed to precipitate during the reaction. The scale of these reactions (demanded for safety reasons) make unambiguous analysis difficult, but it is most likely to be silver sulfate.

Kinetic analyses of the reactions of **(1–5)-Ag** with **CEES** were carried out to examine the influence of the sterics and electronics of the NHC on the reaction. Reactions between **(1–5)-Ag** and **CEES** in  $\text{CDCl}_3$  in a quartz tube were monitored by  $^1\text{H}$  NMR spectroscopy with mesitylene as an internal standard. NMR spectra were recorded for each sample after 30-minute periods of UV (254 nm) radiation. The data fitted to a first-order dependence on **CEES** (Figure 3), show that **1-Ag** is the fastest of all the silver NHC complexes (Figs S6-10).

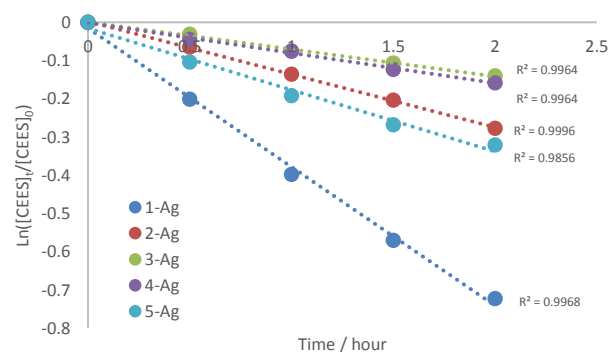
It is proposed that the photolysis cleaves the silver-NHC bond, thus releasing the silver ion, a potent oxidant for **CEES**, and the free carbene which is active for the dehydrohalogenation of **CEES**, giving two routes for the destruction of the CWA simulant, Scheme 4a. Reactions of equimolar amounts of  $\text{Ag}_2\text{O}$  and  $\text{AgCl}$  and **CEES** were also carried out as control reactions, however they were insoluble in the reaction medium and no decomposition was observed at 80 °C or under photolysis. It is suggested that the NHC plays an important role by both helping solubilise the metal cation whilst also acting as a reagent in its own right.

This hypothesis is backed up by the products formed from the reaction of the free base NHC (Scheme 4b). The equimolar reaction between **IPr** and **CEES** at room temperature shows 10 % conversion to **EVS**, the dehydrohalogenation product, within 5 minutes. However, storage for a further hour at room temperature or at 80 °C for 24 hr showed no further destruction of **CEES**, presumably because the remaining NHC decomposed during prolonged contact with air and moisture. A trial reaction using artificial sunlight from a commercially available SAD lamp provided ca. 40% decomposition of **CEES** within the same 5 hr time frame.



**Scheme 4.** Destruction of **CEES** mediated by the silver cation (oxidation, route a) or by the released NHC **IPr** (dehydrohalogenation, route b)

The analysis of observed rates gives a reactivity in decreasing order for the NHC of  $\text{IPr} > \text{ICy} > \text{IMes} > \text{SIPr} > \text{SIMes}$ . Saturated NHCs (SIR) are better  $\sigma$ -donors than the unsaturated (IR) analogues.<sup>42</sup> Thus although the free (SIR) carbene could be considered more reactive for the dehydrohalogenation reaction, the efficacy of complexes **(1–5)-Ag** appears to be dominated by the reaction that cleaves the Ag-NHC bond.



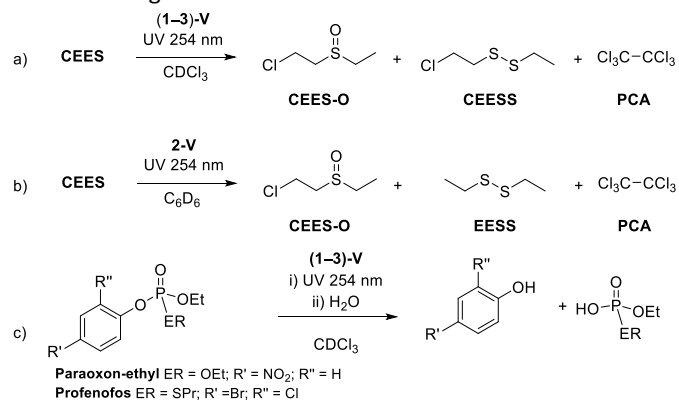
**Figure 3.** Kinetic rate data for the decomposition of **CEES** by **(1–5)-Ag** showing first order dependence on **CEES** and that **1-Ag** is by far the fastest reagent for its destruction.

To further confirm this cooperative effect reactions between the metal and the NHC reactions were carried out

using the analogous copper NHC complexes. Following the same protocol for the silver complexes, the Cu(I) analogues (**1–5**)-Cu were combined with 1 equivalent of **CEES** in the presence of UV light (254 nm). After 1 hr the  $^1\text{H}$  NMR spectra confirm that the Cu-NHC bonds have been broken, showing broad, paramagnetically-shifted resonances which are attributed to the formation of Cu(II) ions arising from aerobic oxidation after release into solution. GC-MS data indicate that no degradation of **CEES** has occurred in any of the reactions studied. Prolonged exposure of the reactions to UV light show only background reactivity, *ca.* 10% decomposition of **CEES**. Since the  $\text{Cu}^+/\text{Cu}^0$  redox couple is significantly less oxidising than the  $\text{Ag}^+/\text{Ag}^0$  couple (+0.52 V vs. +0.80 V),<sup>32</sup> these observations suggest that both the oxidising metal and the basic NHC are responsible for the **CEES** destruction. We note that the degradation products arise from both oxidation and dehydrohalogenation, suggesting that the metal cation also plays a role in facilitating dehydrohalogenation. Presumably coordination of the sulfur to the silver cation renders the **CEES** active towards attack by the liberated NHC.

### Destruction by vanadium NHC complexes

Complexes (**1–3**)-V produce efficient stoichiometric destruction of **CEES** in 5 hours under UV light (254 nm), Scheme 4a. The reactions appear to involve reduction by the vanadium centre as the  $^1\text{H}$  NMR spectra of the reaction mixtures show contact-shifted resonances due to the paramagnetic vanadium centre, and must be separated from vanadium-containing materials for identification. Reactions monitored by GC-MS also show the conversion of **CEES** to new products (Scheme 5a). The major decomposition product is **CEES-O** (60 %), with 2-chloroethylethylidene disulfide (**CEESS**) a minor product. Two features are notable: there is no evidence of dehydrohalogenation, and hexachloroethane (**PCA**) is also formed during the reaction.



Scheme 5. Reactions of (**1–3**)-V with CWA simulants showing the major decontamination products.

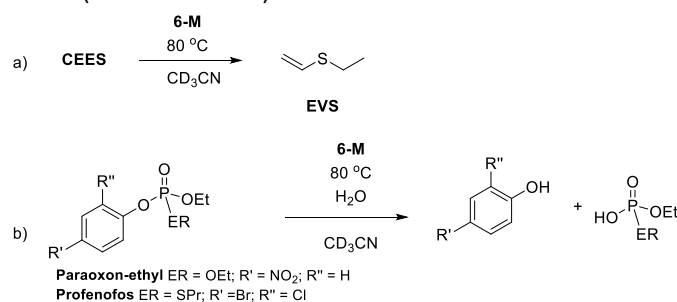
The observation of **PCA** production is notable since it is usually observed to form in samples of **CEES** that have been stored for long periods of time (tens of years to the best of our knowledge),<sup>17</sup> although there are only a few literature reports of the chlorination of **CEES**. In these cases the di, tri, and tetrachlorinated sulfides are reported to form, along with

hexachloroethane which results from the reaction with excess chlorine radicals.<sup>43</sup> Here however, repetition of the reactions between **2-V** and **CEES** in  $\text{C}_6\text{D}_6$  confirm the **PCA** derives from solvent decomposition, as after 3 hrs, the new decomposition product diethyldisulfide (**EESS**) is formed (Scheme 5b).  $\text{VOCl}_3$  has been recently shown to effect the oxychlorination of cyclohexane,<sup>44</sup> but if anything, is only a minor contributor here (see SI for proposed mechanism).

The complexes (**1–3**)-V also react with the two V-agent simulants shown in Figure 1. Scheme 5c shows the reaction of (**1–3**)-V with both **paraoxon-ethyl** and **profenofos** yield substituted phenol products arising from P-OAr bond cleavage and subsequent hydrolysis through trace moisture in the reaction mixture. These were identified by GC-MS trace after 3 hrs of exposure to UV light (254 nm) (Scheme 4c), with complete decomposition of both V agent simulants observed after 24 hrs.

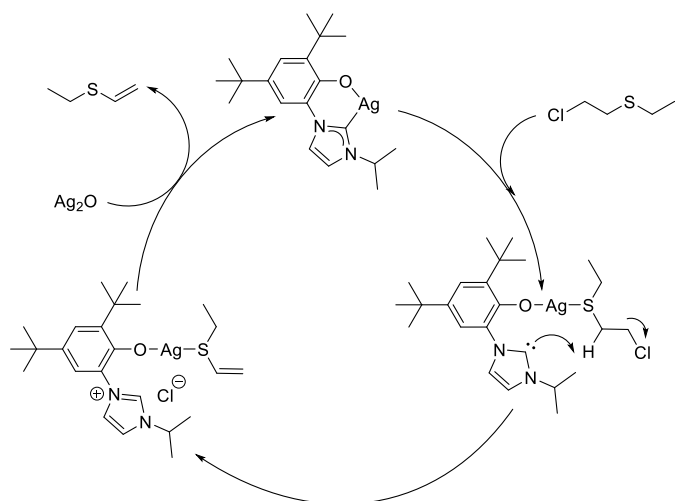
### Destruction by complexes of tethered-NHCs

To test the hypothesis that a combination of metal and NHC afford enhanced dehydrohalogenation of the H-agent, three different metal complexes of a hemilabile, bidentate aryloxy-NHC, **6-Ag**, **6-Na** and **6-K** shown in figure 2, were made and tested (see SI for details).



Scheme 6. Reactions of **6-M** with CWA simulants showing the major decontamination products

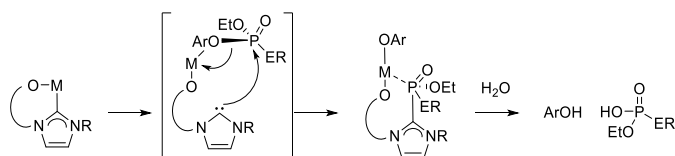
No reaction between stoichiometric quantities of **6-Ag** and **CEES** was observed at room temperature by  $^1\text{H}$  NMR spectroscopy, but after 1 hr at 80 °C, 25% conversion to the product of dehydrohalogenation, **EVS**, was observed. This was characterised by the characteristic alkene hydrogens of the product (Scheme 6a). The complete conversion of **CEES** to **EVS** can be achieved using a catalytic amount of **6-Ag** if additional  $\text{Ag}_2\text{O}$  is added within 5 hrs, thus rendering the system catalytic in NHC. The proposed mechanism for this reaction is outlined in Scheme 7, showing how the combination of the silver centre and the NHC can be effective for the destruction of **CEES**.



**Scheme 7.** Proposed mechanism for the destruction of **CEES** catalysed by **6-Ag**

Furthermore, similar reactivity can be obtained with the alkali metal NHC complexes **6-Na** and **6-K**, which give 30% and 15% destruction of **CEES** in 1 hr, respectively (at 80 °C). Again, the selective formation of **EVS** was identified by  $^1\text{H}$  NMR spectroscopy. The kinetic data (Fig. S27) suggest a small induction period (possibly due to complex formation) and first order dependence on base. It is possible to double the rate of reaction by doubling the amount of alkali metal base. Once formed, these Group 1 salts show moderate moisture instability; decomposition of **6-K** occurs over one hour after exposure to air so whilst cheaper, they are less desirable as decontamination reagents than the silver complexes.

The reactivity of complexes **6-M** towards both **paraoxon-ethyl** and **profenofos** nerve simulants under analogous reaction conditions also proved successful; cleavage of P-OAr bond was identified by  $^{31}\text{P}$  NMR spectroscopy after 20 hrs at 80 °C (Scheme 6b). A proposed mechanism is outlined in Scheme 8, in which the nucleophilic carbene attacks the phosphorus centre, leading to M-OAr bond formation then P-OAr bond cleavage.



**Scheme 8.** Proposed mechanism for the destruction of nerve agents with **6-M** complexes

### Catalytic CWA destruction

NHC complexes of earth-abundant iron and nickel have shown widespread uses in homogeneous catalysis. Their combination with the simple bases  $\text{KO}^t\text{Bu}$  was studied as a potential destruction method. Thus, a series of catalytic reactions in which the active catalyst is generated *in situ*, from the use of air stable components ( $\text{NiCl}_2$ ,  $\text{FeBr}_2$  and  $\text{FeCl}_3$ ) with imidazolium salts ( $\text{IPr.HCl}$ ,  $\text{IMes.HCl}$  and  $\text{ICy.HCl}$ ) was carried out. Use of equimolar amounts of  $\text{MCl}_n$  and  $\text{IR.HCl}$  with a fourfold excess of  $\text{KO}^t\text{Bu}$  leads to the formation of  $\text{NHC-MX}_n$

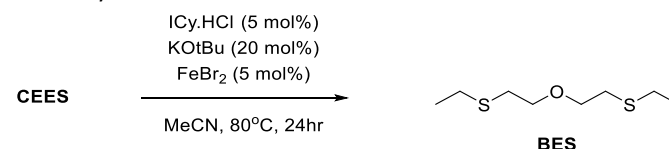
(where  $\text{X} = \text{Cl}$  or  $\text{O}^t\text{Bu}$ ) *in situ*, to which each of the chosen CWA simulants were then added 20-fold excess (i.e. 5 mol% catalyst loading w.r.t. simulant) and monitored over a period of 24 hrs at 80 °C using a combination of UV/vis, GC-MS and NMR spectroscopy.

**Table 1.** Catalytic destruction of CWA simulants with *in-situ* catalyst formation from air stable components showing the major products from each reaction

ENTRY	IR.HCL	$\text{MX}_n$	CWA SIMULANT	
			CEES	Paraoxon-ethyl profenofos
1	IPr.HCl	$\text{NiCl}_2$	EESS	<p>Paraoxon ER = OEt; R' = <math>\text{NO}_2</math>; R'' = H Profenofos ER = SPr; R' = Br; R'' = Cl</p>
2	IPr.HCl	$\text{FeBr}_2$	EESS	
3	IPr.HCl	$\text{FeCl}_3$	CEES-O	
4	IMes.HCl	$\text{NiCl}_2$	EESS	
5	IMes.HCl	$\text{FeBr}_2$	EESS	
6	IMes.HCl	$\text{FeCl}_3$	CEES-O	
7	ICy.HCl	$\text{NiCl}_2$	EESS	
8	ICy.HCl	$\text{FeBr}_2$	BES	
9	ICy.HCl	$\text{FeCl}_3$	CEES-O	

Reaction conditions used 1  $\mu\text{mol}$  of  $\text{NHC.HCl}$  and metal salt, with 4  $\mu\text{mol}$  of  $\text{KO}^t\text{Bu}$  and 20  $\mu\text{mol}$  of CWA simulant in 1 mL of MeCN at 80 °C.

In all cases catalytic destruction of the chosen simulants was observed after mild heating at 80 °C for 24 hours. In terms of **CEES** destruction, use of the  $\text{Fe(III)}$  complex results in oxidation to **CEES-O** as the major product (Table 1, entries 3, 6 and 9) whilst **EESS** and **PCA** were identified as the major products for  $\text{Ni(II)}$  and  $\text{Fe(II)}$  reactions (Table 1, entries 1,2, 4, 5, and 7), except for  $\text{FeBr}_2$  reactions in which oxybis(ethylsulfane) (**BES**) was identified (Scheme 9). In the case of the nerve simulants P-OAr cleavage was identified as the major product through GC-MS analysis.



**Scheme 9.** Catalytic breakdown of **CEES** using an *in-situ* generated  $\text{NHC-Fe(II)}$  catalyst.

Attempts to render the **(1–3)-V** systems catalytic proved to be unsuccessful, but the reactions underline the capability of the oxidising metal in these CWA destructions.

### Conclusions

Air- and moisture stable NHC complexes have been shown to be effective for the destruction of CWA simulants. The cooperative effect of both the NHC and metal centre is vital to the success of these decontamination reactions. Comparison of the simple commercially available imidazoline/imidazolium silver NHC complexes, **(1–5)-Ag**, these were found to provide efficient destruction under UV conditions in 5 hrs, primarily to the oxidation product, **CEES-O**, and also to the



dehydrohalogenation product. The choice of metal centre is key for these transformations as reactions with complexes **(1-3)-V** provide complete destruction of CEES within 5 hrs and allowed for destruction of nerve simulants through cleavage of P-OAr bond to form substituted phenols. Preliminary studies using artificial sunlight (from a commercially available SAD lamp) also show reasonable levels of CEES decomposition within the same 5 hr timeframe, presumably a result which could be improved with suitable ligand tuning.

Examination of the cooperative effect of metal centre and NHC through use of a hemi-labile bidentate aryloxide tethered NHC complex **(6-M)** shows clean destruction to **EVs** at 80 °C within a few hours. The rate of destruction is increased, and the reaction rendered catalytic in NHC via addition of further equivalents of alkali metal base or silver (I) oxide. Catalytic destruction of all three CWA simulants can also be achieved using *in-situ* generated iron or nickel NHC complexes. This new class of CWA simulant degradants show promise, and further work is in progress to improve reactivity while retaining the air-stability of the metal-NHC complexes.

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