# Room Temperature Liquid Salts of Cr and Mo as Self-Supported Oxidants

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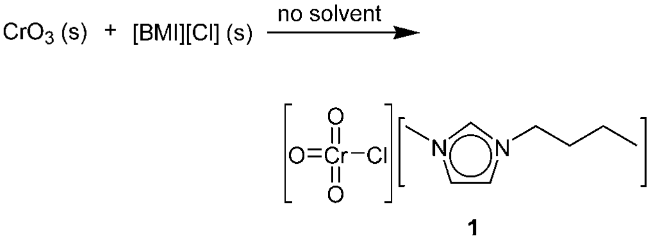
**Abstract:** Room temperature liquid salts of Cr and Mo were synthesized and fully characterized including cyclic voltammetry of the neat Mo salt. These liquid salts were used as self-supported reagents for the oxidation of alcohols (under solvent-free and biphasic conditions) and their potential for biphasic self-supported catalytic applications was demonstrated.

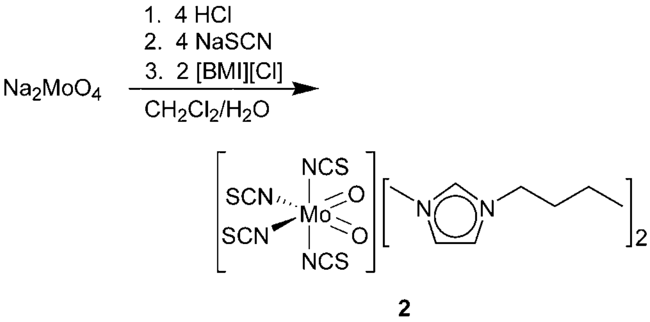
**Keywords:** biphasic catalysis; chromium; cyclic voltammetry; molybdenum; oxidation; room temperature ionic liquids

Room temperature ionic liquids (RTILs) are an attractive (often "green") alternative to classic organic solvents for stoichiometric and catalytic reactions as well as separation processes.[1] Furthermore, due to their ionic nature, RTILs form ideal "immobilization" media for polar and charged reagents, including catalysts, thus offering the advantage of easy product separation. RTILs are also emerging as competent solvents for oxidation reactions.[2] On the other hand, relatively few examples of RTILs which integrate the function of solvent and reagent have been published so far.[3] Despite the fact that transition metals exert crucial functions in synthesis and catalysis, examples of transition metal salts that are liquid at room temperature are still rare.[4] We present here the synthesis and full characterization of Cr and Mo salts that are liquid at room temperature and their use as self-supported molecular (catalytic) oxidants of alcohols and $PPh_3$.

Pyridinium chlorochromate (Corey's reagent)[5] is a widely used oxidant[6] which prompted us to synthesize an imidazolium[7] analogue. Upon mixing solid $CrO_3$ with solid 1-butyl-3-methylimidazolium chloride ([BMI][Cl]) in a glove-box immediately a dark red brownish melt formed which was identified as **1** [Eq. (1)]. Compound **1** turned out to be insoluble in alkanes, aromatics, ethers, and chloroform and, although it is slightly soluble, it forms two phases with water contrasting the high water solubility of the starting materials. Liquid **1** displayed Newtonian behavior with a viscosity of $\eta_0 = 0.1065$ Pa·s (over a shear velocity range between 0.5 and 300 $s^{-1}$)[8] and a conductivity of 2.54 mS $cm^{-1}$. The IR spectrum of neat **1** revealed two characteristic bands at 898 $cm^{-1}$ (s) and 945 $cm^{-1}$ (vs)[9] and the $^1$H NMR spectrum showed broadened signals of the imidazolium cation.



(1)



(2)

The molybdate $[PPh_4]_2[Mo(O)_2(NCS)_4]$ was shown to be a reversible oxo transfer agent.[10] The corresponding room temperature liquid imidazolium molybdate **2** was synthesized by metathetical exchange of the cations in a biphasic $H_2O/CH_2Cl_2$ system [Eq. (2)]. Compound **2** is a deep red viscous oil with a constant viscosity of $\eta_{8-500} =$ 0.865 Pa·s for a shear velocity ranging from 8 to 500 $s^{-1}$. The considerably higher viscosity of **2** as compared to **1** may explain the lower conductivity of pure **2** (0.42 mS $cm^{-1}$). Salt **2** formed two phases with alkanes, aromatic solvents, ethers, chloroform, and water while it was soluble in $CH_2Cl_2$ and DMSO. The NMR spectra were as expected and the carbon atoms of the NCS ligands resonated at 139.8 and 146.6 ppm. The IR spec-

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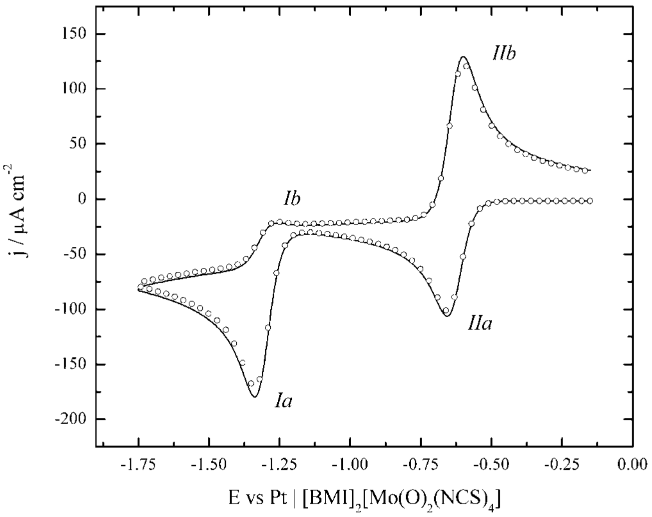

**Figure 1.** Cyclic voltammogram of neat **2** at a Pt electrode[12] and a scan rate $\nu = 10\ \mathrm{mV\,s^{-1}}$. Dots: numerical simulation of an ECE mechanism. Potentials are referred to a pseudo-reference Pt electrode.

trum confirmed the presence of the terminal *cis*-dioxo function exhibiting two absorption bands at $893\ \mathrm{cm^{-1}}$ (s) and $928\ \mathrm{cm^{-1}}$ (s).[10] Both salts showed shelf-lives of at least several weeks at room temperature so far.

The steady state cyclic voltammogram of neat **2** is shown in Figure 1, where two waves *I* and *II* are observed. Negative going scans were initiated at the open circuit potential (*ca.* $-0.15$ V). Peak *IIa* was not observed in the first scan, because it was necessary to reach potentials below $-1.25$ V to observe the appearance of waves *IIa* and *IIb*. Process *Ia* is irreversible, and a net cathodic current is present in the reverse scan up to *ca.* $-0.75$ V. This overall behavior could be explained by an ECE mechanism in which the first reduction occurs at more negative potentials, followed by a fast irreversible chemical step that renders wave *I* practically irreversible. The product of the intermediate chemical step undergoes further oxidation and reduction leading to waves *IIa* and *IIb*. Numerical simulation of the proposed ECE mechanism was performed with the Digisim® 3.03 package, and a fairly consistent result was obtained, as shown in Figure 1. The diffusion coefficient of **2**, dissolved in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMI][$PF_6$]), was obtained from j *vs.* ν½ analysis as $D = 6.2 \cdot 10^{-9}\ \mathrm{cm^2\,s^{-1}}$. This value is consistent with previously reported data[11] and reflects strong ionic interactions which explain the low current values observed in neat **2**. To the best of our knowledge this is the first example of a well-behaved electroactive RTIL.

RTILs **1** and **2** were tested for the solvent-free oxidation of alcohols to carbonyl compounds (Table 1). During the course of the reaction the homogeneous mixtures turned more viscous (mechanical stirring is advisable). At the end, the reaction mixtures were extracted with diethyl ether in which the spent oxidants were completely insoluble. In order to demonstrate the feasibility of a truly solvent-free oxidation, 1.5 g of benzyl alcohol were oxidized using **1** as a solvent-reagent (36 h, 400 rpm, room temperature, homogeneous solution) followed by direct fractional high vacuum distillation affording 1.1 g of pure benzaldehyde.

**Table 1.** Solvent-free oxidations of alcohols over 24 h with equimolar amounts of **1** or **2**.

| Oxidant | Substrate | Product | Yield |
|---|---|---|---|
| **1**[a] | Benzyl alcohol (**3**) | Benzaldehyde (**4**) | 62% |
| **2**[a] | Benzyl alcohol (**3**) | Benzaldehyde (**4**) | 40% |
| **2**[b] | Cyclohexanol (**5**) | Cyclohexanone (**6**) | 46% |
| **2**[b] | *n*-Octanol (**7**) | *n*-Octanal (**8**) | 30%[c] |

[a] At room temperature.
[b] At 70 °C in sealed vials.
[c] 66% as hemiacetal.

**Table 2.** Biphasic oxidations with equimolar amounts of **2**.[a]

| Entry | Substrate | Product | Partition [%][b] | |
|---|---|---|---|---|
| | | | Organic phase | Ionic phase |
| 1[c] | **3** | **4** | 7 (**3**), 10 (**4**) | 50 (**3**), 33 (**4**) |
| 2[c, d] | **5** | **6** | 29 (**5**), 38 (**6**) | <1 (**5**), 33 (**6**) |
| 3[c, d] | **7** | **8** | 66 (**7**), 33 (**8**)[e] | <1 (**7**), <1 (**8**) |
| 4[f] | $PPh_3$ (**9**) | $OPPh_3$ (**10**) | 39 (**9**), 4 (**10**) | <1 (**9**), 57 (**10**) |

[a] At room temperature, 500 rpm.
[b] Numbers are percent, bold numbers identify substrates and products.
[c] In toluene/alcohol = 3 (w/w), 24 h.
[d] At 67 °C in sealed vials.
[e] 42% as hemiacetal.
[f] 25% solution of **9** in benzene/heptane = 2 (w/w), 10 h.

RTIL **2** was then tested as a self-supported biphasic oxidant (Table 2). The initial biphasic system consisted of the heavier ionic phase of **2** and the lighter organic solutions of the substrates. Table 2 presents the yields and partitions as percentage of substrate and product molecules in the two phases at the end of the reactions. As in Table 1, we note that **2** more readily oxidized cyclohexanol (**5**) than benzyl alcohol (**3**) and that none of alcohol **5** was detected in the ionic phase (entry 2). Likewise, lipophilic octanol and octanal were not detected in the ionic phase (entry 3). Oxygen atom transfer (OAT) from **2** to $PPh_3$ (**9**, entry 4) was quite efficient and 94% of the product oxide **10** accumulated in the ionic phase, while 99% of $PPh_3$ partitioned into the organic phase. We wondered if reoxidation of the reduced RTIL (thought to be $[BMI]_2[Mo^{IV}(O)(SCN)_4]$) with DMSO would regenerate RTIL **2** and thus lead to the biphasic self-supported catalytic system as outlined in Eq. (3).[13] Indeed, a $PPh_3$ solution (25% w/w in benzene/heptane) was completely oxidized by 10 mol % **2** in the presence of 2 equivalents of DMSO in 48 h at room temperature.[14]

This catalytic OAT model reaction effectively and completely removed $PPh_3$ from the organic phase and may serve as a model reaction for the catalytic oxidative removal of contaminants from organic phases (e.g., desulfurization of fuels). Clearly, this model reaction suggests that adequate design of the biphasic system allows one to control the relative affinities of substrate and product molecules for the ionic and organic phases. An RTIL catalyst such as salt **2** can conveniently be tailored (e.g., by modifying the cation) to suit specific applications.

$$PPh_3 + O{=}S(CH_3)_2 \xrightarrow[\{\mathbf{2}\}]{n\text{-}C_7H_{16}/C_6H_6} O{=}PPh_3 + S(CH_3)_2 \quad (3)$$

In summary, we showed that chromate- and molybdate-based RTILs are accessible through Lewis acid-base and cation metathesis reactions, respectively. The neat RTIL **2** was shown to be electrochemically well-behaved. Liquids **1** and **2** were used as self-supported oxidants of alcohols. Finally, the RTIL molybdate **2** showed good potential to act as a self-supported biphasic OAT catalyst. We are currently investigating the electrochemical re-oxidation of such liquid metallate phases and their use as biphasic self-supported oxidation catalysts.

## Experimental Section

### [1,3-Butylmethylimidazolium][$CrClO_3$] (1)

Powdered [BMI][Cl] (2.97 g, 17.0 mmol) was added to powdered $CrO_3$ (1.70 g, 17.0 mmol) in a nitrogen-filled glovebox. This resulted in the immediate formation of a brown oil (4.66 g, 99%) which was stirred for 2 h and then kept at $-10\,°C$. Elemental analysis (calculated for $C_8H_{15}ClCrN_2O_3 \cdot 0.6\,H_2O$): C 33.46 (33.66), H 5.74 (5.72), N 9.80 (9.81), Cl 13.00 (12.42); $d = 1.36$ g·cm$^{-3}$; $\kappa = 2.54 \pm 0.07$ mS cm$^{-1}$; $\eta_0 = 0.1065$ Pa·s (all values at 25 °C); $^1H$ NMR (300.13 MHz, DMSO-$d_6$, broadened signals): $\delta = 0.90$ (s, 3H), 1.25 (s, 2H), 1.76 (m, 2H), 3.85 (s, 3H), 4.16 (s, 2H), 7.71 (s, 1H), 7.77 (s, 1H), 9.16 (s, br, 1H); $^{13}C$ NMR (75.47 MHz, $CD_2Cl_2$): $\delta =$ 13.82, 19.34, 31.93, 36.34, 49.10, 122.83, 124.19, 137.13.

### [1,3-Butylmethylimidazolium]$_2$[$Mo(NCS)_4O_2$] (2)

Aqueous HCl (1.00 M, 166.1 mL) was added dropwise with a burette over 15 min to a colorless solution of $Na_2MoO_4 \cdot 2\,H_2O$ (10.044 g, 41.518 mmol) and NaSCN (14.47 g, 178.5 mmol) in water (110 mL) affording a yellow solution. After stirring for another 30 min, a solution of [BMI][Cl] (14.502 g, 83.025 mmol) in $CH_2Cl_2$ (200 mL) was added dropwise under vigorous stirring giving a yellow emulsion which separated into a bright orange organic phase and a yellowish aqueous phase. The organic phase was separated, washed with $H_2O$ (150 mL, colorless washing), and dried over $Na_2SO_4$. Filtration and evaporation of the volatiles under vacuum afforded a bright red oil; yield: 21.4 g (81%). Elemental analysis (calculated for $C_{20}H_{30}MoN_8O_2S_4$): C 38.20 (37.61), H 4.88 (4.73), N 17.14 (17.54); $d = 1.38$ g·cm$^{-3}$; $\kappa = 0.42 \pm 0.01$ mS·cm$^{-1}$; $\eta_{8-500} = 0.865$ Pa·s (all values at 25 °C); $^1H$ NMR (300.13 MHz, $CD_3OD$): $\delta = 0.99$ (t, $J = 7.4$ Hz, 3H), 1.30–1.45 (m, 2H), 1.80–1.95 (m, 2H), 3.94 (s, 3H), 4.23 (t, $J = 7.3$ Hz, 3H), 7.55–7.60 (m, 1H), 7.60–7.65 (m, 1H), 8.91 (s, br, 1H); $^{13}C$ NMR (75.47 MHz, $CD_2Cl_2$): $\delta = 14.99$, 21.12, 33.61, 38.58, 51.81, 124.28, 125.80, 137.50, 139.85, 146.57.

### Typical Biphasic Oxidation Procedure

To **2** (640 mg, 1.00 mmol) in a Schlenk tube were added 435 mg (1.01 mmol) of a solution of **3** in toluene (1 : 3 w/w). The biphasic reaction mixture was stirred at 500 rpm for 24 h. The $^1H$ NMR spectrum of the organic phase showed the presence of 10% aldehyde and 7% alcohol (internal toluene reference) while the spectrum of the diamagnetic ionic phase gave 33% aldehyde and 50% alcohol (internal reference: $BMI^+$). No benzoic acid was detected.

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