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1-Butyl-3-methylimidazolium cobalt tetracarbonyl [bmim][Co(CO)$_4$]: a catalytically active organometallic ionic liquid

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An ambient temperature liquid transition metal carbonyl anion has been prepared in a metathesis reaction between [bmim]Cl ([bmim]$^+$ = 1-butyl-3-methylimidazolium cation) and Na[Co(CO)$_4$]; the ionic liquid catalyses the debromination of 2-bromoketones.

Transition metal carbonyl compounds have attracted considerable attention since the discovery of the highly toxic pale yellow liquid Ni(CO)$_4$.[1] Landmarks in the field of transition metal carbonyl cluster chemistry include the preparation of compounds with metal–metal bonds leading to high nuclearity clusters,[2] super-reduced anions[3] and most recently, the synthesis of counter-intuitive cationic complexes.[4] Transition metal carbonyl chemistry remains an active field of research largely due to their role in catalysis[5] and stoichiometric organic synthesis.[6] Certain aspects of transition metal carbonyl chemistry remain controversial, such as the mechanism by which carbonyl rearrangements take place.[7] Apart from Ni(CO)$_4$, the only other transition metal carbonyl compound that is liquid at room temperature is Fe(CO)$_5$, which is widely used in organic synthesis and catalysis.[8] In this communication we report on a new transition metal carbonyl compound that is liquid at ambient temperatures, furthermore, the transition metal carbonyl complex is anionic.

The reaction of the white solids Na[Co(CO)$_4$] and [bmim]Cl ([bmim]$^+$ = 1-butyl-3-methylimidazolium cation) in propanone afforded a blue-green suspension. After 24 h the precipitate (NaCl) was removed by filtration, and the propanone was removed under reduced pressure affording an intense blue-green coloured liquid. The liquid was initially confirmed to be the [bmim][Co(CO)$_4$] molten salt as it has no detectable vapour pressure since vacuum pumping over a period of 48 h did not result in a change in mass.[9] A photograph of the liquid is shown in Fig. 1. While we have not established a precise melting point for [bmim][Co(CO)$_4$] it remains a liquid, *albeit* quite viscous, even at 0 °C.

The spectroscopic characterisation of [bmim][Co(CO)$_4$] has been achieved using a combination of techniques,[10] most notably the IR (υ_{CO}) spectrum of the liquid diluted in dichloromethane shows a strong peak at 1890 cm^{-1} which is characteristic of the tetrahedral [Co(CO)$_4$]$^-$ anion.[11] The UV-VIS absorption spectrum of the liquid diluted in propanone shows absorptions at 664 with a shoulder at 645, 605, and 230 with a shoulder at 275 nm.

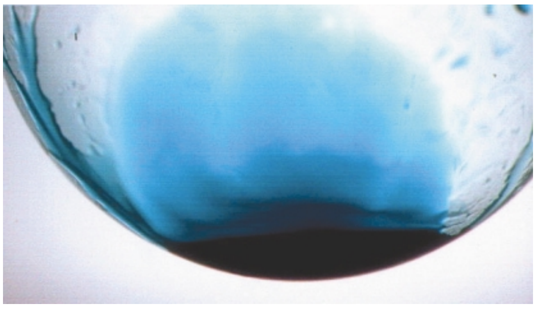

Fig. 1

The [bmim][Co(CO)$_4$] ionic liquid has also been investigated using cyclic voltammetry.[12] The main features of the electrochemistry are the large anodic (oxidative) peak at +0.9 V and the much smaller cathodic (reductive) peak at −0.1 V (see Fig. 2). The peaks at +0.9 V and −0.1 V are not of a totally conventional shape, however, this is not surprising given the unusual electrochemical conditions. It is important to realise that the electrochemistry is being performed on the neat ionic liquid which, by definition, is at a very high concentration. The ionic liquid can be considered to be acting as both the background electrolyte and the active electrochemical species and may be subject to both diffusional and migrational processes. It is proposed that the peaks represent the Co [−1]/[0] couple. The noisy response from +2 V back to +0.5 V is a reproducible phenomenon. Since this electrochemical noise is only seen on the backwards sweep it is thought unlikely that this is owing to a turbulence effect caused by the bulk oxidation and more likely that some form of passivating layer has been formed on the electrode surface. As shown in Fig. 3 the peak

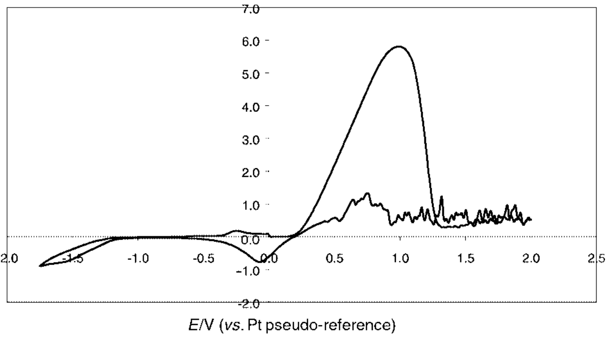

Fig. 2 CV for the ionic liquid at a Pt working electrode with Pt pseudo-reference, 50 mV s^{-1}.

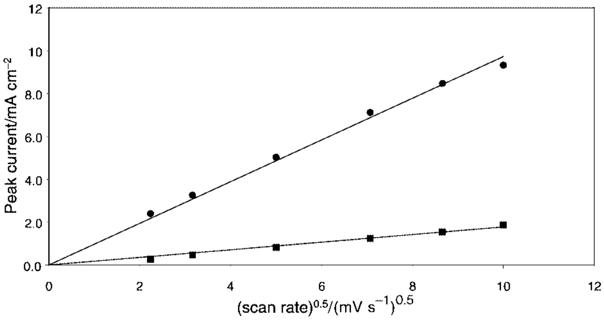

Fig. 3 Graph of peak current against (scan rate)$^{0.5}$ for the ionic liquid; anodic peak, (●); cathodic peak, (■).

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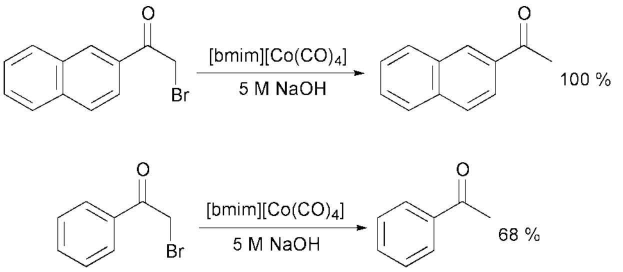
currents of the two main peaks are directly proportional to the square root of the scan rate; this could be a sign of a diffusion controlled solution phase process within the ionic liquid (no adsorption to the electrode surface). However in light of the previous proposal of formation of a passivating layer of the electrode surface, it is also possible that the peak current to scan rate relationship could be attributable to a diffusion controlled process within such a film on the electrode surface. The relative sizes of the two main peaks indicate that this is probably an EC process, *i.e.* an electrochemical oxidation followed by a chemical process occurring on the same time scale as the sweep time of the voltammetry. In this way less oxidised material is available for re-reduction. The potential window of the material is extremely large as expected for an ionic liquid. Reductive decomposition seems to occur after about −3 V. The positive limit (although the response is noisy) is above +4 V. The width of the anodic peak increases dramatically with time (with a slight peak current increase), presumably as the ionic liquid starts to decompose.

Ionic liquids based on imidazolium cations have recently attracted much interest as green solvents for catalysis.[13] Two main methodologies have been explored in catalysis. First, where the ionic liquid is itself catalytically active, for example those with chloroaluminate anions have been shown to catalyse Friedel–Craft reactions[14] and depolymerisation.[15] Second, where the ionic liquid is essentially inert and is used to dissolve/support homogeneous catalysts. This latter technique has been used in reactions such as hydrogenation,[16] hydroformylation,[17] C–C coupling[18] and many others.[13] The anion $[Co(CO)_4]^-$, generated from $Co_2(CO)_8$, and NaOH, has previously been shown to catalyse dehalogenation and coupling reactions.[19] Sodium hydroxide is soluble in the $[bmim][Co(CO)_4]$ ionic liquid and the solution was found to catalyse the debromination of 2-bromo-2′-acetonaphthone and 2-bromoacetophenone to their corresponding ketones (see Scheme 1). The melting point of 2-bromo-2′-acetonaphthone is *ca.* 83 °C and was therefore dissolved in benzene. In contrast, the lower melting point of 2-bromoacetophenone (−50 °C) meant it could be added directly to the catalyst without the need for organic solvents or other reagents. Extraction of the product into an organic solvent also removed the bromine generated during the reaction from the ionic liquid, which was recovered with the characteristic blue colour with the same spectroscopic properties.



Scheme 1

We have prepared $[bmim][HFe(CO)_4]$ and $[bmim][Mn(CO)_5]$ in an analogous manner to that described for $[bmim][Co(CO)_4]$ and they are also intensely coloured and liquid at room temperature, although much more viscous than the cobalt liquid. Presumably, the colour is due to charge transfer from the transition metal carbonyl anion to the bmim cation. The $[HFe(CO)_4]^-$ anion is an active hydroformylation catalyst[20] and we will report on these ionic liquids in due course.

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10 Spectroscopic data: IR (υ_{CO}, CH_2Cl_2) 1890 cm^{-1}. Electrospray mass spectrum ($CHCl_3$): Positive ion: 139 $[bmim]^+$, Negative ion: 171 $[Co(CO)_4]^-$, 143 $[Co(CO)_3]^-$. UV-VIS (Me_2CO) 664, 645 (sh), 605 (sh), 275 (sh), 230 nm. ^1H NMR (neat): δ9.49 (br s, 1H), 6.17 (br s, 1H), 6.05 (br s, 2H), 3.88 (br s, 1H), 3.19 (br s, 1H), 3.44 (br s, 2H). ^{13}C NMR (neat): δ133.08, 121.00, 119.63, 47.15, 34.13, 29.07, 16.37, 10.46. The carbonyl carbon atoms were not observed.

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