CCDC-185168 (**1**) and CCDC-185167 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Ionic Liquids Containing Anionic Selenium Species: Applications for the Oxidative Carbonylation of Aniline**

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Non-phosgene processes for the synthesis of carbamates and/or substituted ureas have attracted increasing interest in recent years, particularly in the area of green chemistry because of the environmental concern regarding the use of highly toxic phosgene.[1] Of the various non-phosgene processes, one approach involves the catalytic oxidative carbonylation of an amine in the presence of an appropriate catalyst or catalytic system.[2]

In previous reports, we have demonstrated that alkali metal-containing selenium compounds, obtained from the reaction of SeO_2 and M_2CO_3 (M = alkali metal) in methanol, are effective catalysts for the oxidative carbonylation of aniline to produce phenyl carbamate and diphenylurea.[3] The major disadvantage of using these selenium compounds is the difficulty in separating the product and the catalyst from the reaction mixture, which arises from the coproduction of insoluble diphenylurea and soluble alkyl phenyl carbamate, with high conversion of aniline. A further disadvantage is the formation of small quantities of unknown, highly volatile, malodorous, and possibly toxic selenium species at relatively high reaction temperatures.

Recently, there have been a considerable number of papers regarding ionic liquids and their use in immobilizing volatile, precious, and/or toxic homogeneous catalysts, thereby improving the stability and facilitating the recovery of the catalyst.[4]

In this context, the alkali metal-containing selenium compound $[KSeO_2(OCH_3)]$ can be reacted with 1-alkyl-3-methylimidazolium chlorides to prepare new imidazolium-based ionic liquids containing anionic selenium species. The ionic liquids are found to show surprisingly high activity for the

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carbonylation of aniline, even at temperatures as low as 40 °C. Furthermore, malodorous selenium species are not formed when the immobilized selenium compound is used as a catalyst for carbonylation.

We now report, for the first time, the synthesis and reactivity of a series of new, room-temperature ionic liquids consisting of imidazolium cations (1-R-3-methylimidazolium, $R = CH_3$, C_2H_5, n-C_4H_9) and selenium-containing anions $[SeO_2(OR')]^-$ ($R' = CH_3$, CH_2CH_3, CH_2CF_3, C_6H_5), which are highly active, easily recyclable, and air and moisture stable.

The reaction of SeO_2 with 0.5 equiv of K_2CO_3 in methanol for 1 h at room temperature, followed by the addition of THF into the resulting solution produced $[KSeO_2(OCH_3)]$ (**1**) as an extremely hygroscopic white precipitate [Eq. (1)], which was characterized by elemental analysis and ^{1}H NMR spectroscopy.

$$2\,SeO_2 + K_2CO_3 + 2\,CH_3OH \rightarrow 2\,KSeO_2(OCH_3) + H_2O + CO_2 \quad (1)$$

The ambiguous spectroscopic data of **1** led us to carry out a single-crystal X-ray diffraction study to elucidate its structure, which revealed that **1** was, indeed, potassium methyl selenite, $[KSeO_2(OCH_3)]$, in which the methoxy group is bonded to the selenium center (Figure 1).[5]

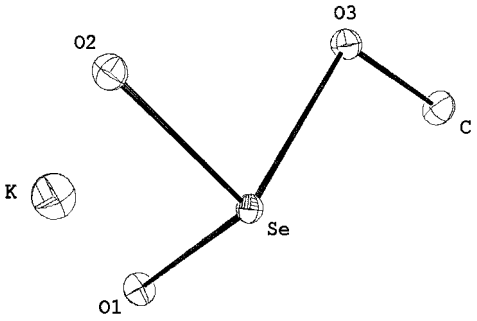
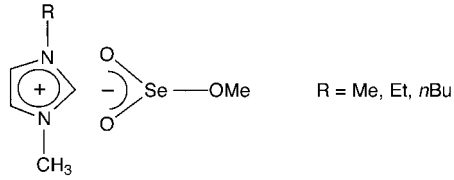


Figure 1. Single-crystal X-ray structure of **1**. Selected bond lengths [Å] and angles [°]: Se···K 3.7364(9), Se-O1 1.6590(19), Se-O2 1.6579(19), Se-O3 1.8460(19), O3-C 1.438(4); O2-Se-O1 106.27(10), O2-Se-O3 95.31(9), O1-Se-O3 101.44(10), C-O3-Se 112.74(16).

To immobilize the selenite anion within an imidazolium-based ionic liquid, (bmim)Cl (bmim = 1-n-butyl-3-methylimidazolium) and **1** were reacted in methanol at room temperature for 6 h. Filtration of KCl and subsequent removal of methanol under reduced pressure afforded an air-stable yellow liquid, which was characterized as $[bmim][SeO_2(OCH_3)]$ (**2a**) by ^{1}H NMR spectroscopy, elemental analysis, and mass spectrometry. Similarly, $[emim][SeO_2(OCH_3)]$ (**3a**) and $[dmim][SeO_2(OCH_3)]$ (**4a**) were prepared by reacting **1** with (emim)Cl (emim = 1-ethyl-3-methylimidazolium) and (dmim)Cl (dmim = 1,3-dimethylimidazolium), respectively. Although the melting points of **2a**, **3a**, and **4a** were not precisely established, they were all liquids at -10 °C.



Interestingly, reactions of **3a** with various alcohols produced a series of new selenium-containing ionic liquids, as shown in Equation (2).

$$[emim][SeO_2(OCH_3)] + ROH \rightarrow [emim][SeO_2(OR)] + CH_3OH \quad (2)$$
(**3b**: R = CH_3CH_2, **3c**: R = CF_3CH_2, **3d**: R = Ph)

The viscosity and conductivity of **2a**, $[bmim][SeO_2(OCH_2CF_3)]$ (**2c**), and $(bmim)BF_4$ were measured. Ionic liquid **2c** surprisingly exhibits lower viscosity (15 cP) and higher conductivity (4.33 mS cm^{-1}) than both **2a** (viscosity: 6055 cP, conductivity: 0.14 mS cm^{-1}) and $(bmim)BF_4$ (viscosity: 233 cP, conductivity: 1.73 mS cm^{-1}).[6] These results demonstrate that the physical properties of the ionic liquids could be significantly altered by replacing the alkoxide group in the anionic moiety.

The activities of various ionic liquids consisting of imidazolium cations and selenium-based anions were evaluated as catalysts for the oxidative carbonylation of aniline, and compared with the activities of **1** and 5% Pd/C–KI (a catalyst for the Asahi process).[7]

The results in Table 1 show that the activities of the ionic-liquid catalysts **2a**, **3a–c**, and **4** are significantly higher than those of **1** and 5% Pd/C–KI at 40 °C. The reason for the enhanced activities of ionic liquid-immobilized selenium catalysts cannot be fully explained at the moment, but it is likely that the imidazolium cation plays an important role in the catalytic process by electronically communicating with the anionic selenium species. This is partially supported by

Table 1. Activities of various catalysts for the oxidative carbonylation reactions of aromatic amines.[a]

Amine	Catalyst	T [°C]	Conversion [%]	Selectivity [%][b]	TOF [h^{-1}][c]
$PhNH_2$	**1**	40	5.1	100	18
$PhNH_2$	**2a**	40	51.3	100	93
$PhNH_2$	**3a**	40	53.6	100	97
$PhNH_2$	**4a**	40	52.6	100	96
$PhNH_2$	**3b**	40	52.4	100	95
$PhNH_2$	**3c**	40	54.5	100	99
$PhNH_2$	Pd/C–KI[d]	40	7.2	100	26
$PhNH_2$	**3a**	60	97.4	98.9	177
$PhNH_2$	**3a**[e]	120	36.8	99.3	3680
o-Tolu[f]	**3a**	60	28.0	100	51
p-Tolu	**3a**	60	95.2	100	173
MDA[g]	**3a**	60	81.8	100	149
$PhCH_2NH_2$	**3a**	60	92.4	100	168

[a] amine (40 mmol), catalyst (0.11 mmol), methanol (25 mL), $P = 1.36$ MPa (O_2/CO, 20:80 v/v), $t = 2$ h. [b] *N*,*N*′-diphenylurea for aniline; $(CH_3C_6H_4NH)_2CO$ for toluidine, $(NH_2C_6H_4CH_2C_6H_4NH)_2CO$ for MDA; $(C_6H_5CH_2NH)_2CO$ for $PhCH_2NH_2$. [c] TOF = (moles of aniline consumed/moles of catalyst) h^{-1}. [d] 5% Pd/C (234 mg, 0.11 mmol Pd), KI (90 mg, 0.55 mmol). [e] $t = 1$ h, aniline (160 mmol), **3a** (0.016 mmol). [f] Tolu = toluidine. [g] MDA = 4,4′-methylenedianiline.

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comparing the cyclic voltammograms (CVs) of [dmim][$SeO_2(OCH_3)$], (dmim)Cl, and [$KSeO_2(OCH_3)$] (Figure 2), where the reversibility of the oxidation wave of [dmim][$SeO_2(OCH_3)$] at $+0.3$ V (versus Ag/AgCl) is pronounced, while such a reversible wave is not observed in the CVs of **1** and (dmim)Cl.

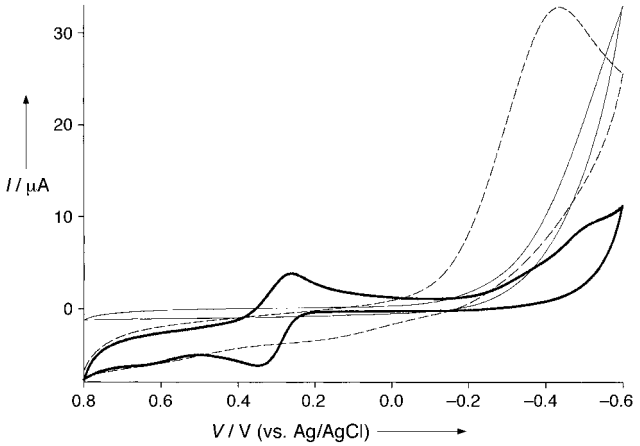

Figure 2. Cyclic voltammograms of 0.12 M solutions of **4a** (——), (dmim)Cl (——), and **1** (– – –) in CH_3OH at a platinum disk with a Ag/AgCl reference electrode at a scan rate of 0.05 $V s^{-1}$.

Compound **3a** was also found to be a highly active catalyst for the carbonylation of other substrates including toluidines (both *ortho* and *para*), benzylamine, and 4,4-methylenedianiline. Interestingly, *p*-toluidine shows much higher conversion than *o*-toluidine, possibly as a result of the steric hindrance of the methyl group next to the $-NH_2$ group. Only one amino group in 1,4-methylenedianiline is carbonylated to give $(NH_2C_6H_4CH_2C_6H_4NH)_2CO$ under the reaction conditions.

The catalytic activity of **3a** for the carbonylation of aniline increases with increasing temperature, resulting in a high turnover frequency (TOF) of 3680 h^{-1} at 120 °C. It should be mentioned that TOFs for the selenium-based catalyst systems reported by other groups are usually lower than 100 h^{-1}.[8]

During the oxidative carbonylation of aniline, **3a** is likely to react with aniline to form an intermediate species, [emim][$SeO_2(NHC_6H_5)$], which in turn reacts with CO to give [emim][$SeO_2(CONHC_6H_5)$]. The in situ ^{1}H NMR spectrum of the reaction mixture in [d_4]methanol clearly demonstrates the transformation of **3a** into two other selenium species that contain the imidazolium cation (see Figure 3); there is no evidence that selenium species without imidazolium cations are present.

To investigate the possibility of recycling these novel catalyst systems, experiments have been conducted with aniline and **3a** at 60 ° and 1.4 MPa of O_2/CO (20:80 v/v) for 2 h, at which time the reaction mixture was filtered off to remove diphenylurea and the solution containing the ionic liquid was reused for further carbonylation reactions with a fresh charge of consumed aniline and methanol. As can be seen in Table 2, **3a** retains most of its original activity even after five cycles, which indicates that **3a** is, indeed, a recyclable catalyst.

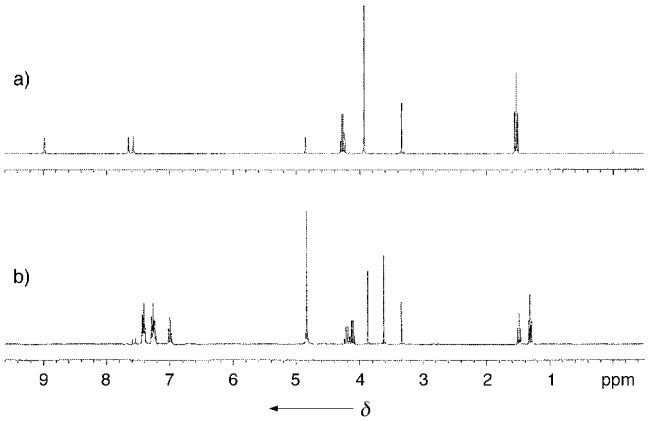

Figure 3. ^{1}H NMR spectra: a) **3a** in [d_4]methanol; b) after the carbonylation reaction with 2 equiv of $PhNH_2$ at 100 °C and 1.0 MPa of O_2/CO (20:80 v/v) for 2 h.

Table 2. Catalyst recycling studies with **3a**.[a]

Cycle	Conversion [%]	Selectivity [%][b]	TOF [h^{-1}]
1	97.0	99.1	176
2	96.8	99.4	176
3	95.3	99.0	173
4	94.2	98.9	171
5	93.9	99.3	170

[a] aniline (40 mmol), **3a** (0.11 mmol), methanol (25 mL), $P = 1.36$ MPa (O_2/CO 20:80 v/v), $t = 2$ h. [b] *N*,*N*′-diphenylurea.

As a consequence of the possible toxicity of the selenium-based ionic liquids, the level of selenium contamination in the isolated urea was measured using induced coupled plasma (ICP) analysis. When **3a** was used as the catalyst for the carbonylation of aniline, the isolated diphenylurea was found to contain 45.4 ppm of selenium, which was significantly reduced to 2.5 ppm after additional washing with methanol (2×10 mL). After this treatment, the isolated diphenylurea was found not to have an unpleasant odor. This was in contrast to similar experiments using **1** as the catalyst, in which the isolated urea did exhibit a strong, unpleasant odor even after additional washing with methanol (2×10 mL), and showed higher levels of selenium contamination (54.3 ppm after filtration and 13.2 ppm after additional washing).

There are many advantages to selenium-containing ionic-liquid catalyst systems. In addition to the improved catalytic performance and the absence of species responsible for potentially foul odors, they are recyclable without losing their initial activity. Furthermore, they are air stable and highly soluble in various organic solvents including CH_2Cl_2, $CHCl_3$, and CH_3CN. Spectroscopic and electrochemical investigations to elucidate the mechanism for the oxidative carbonylation of amines are now in progress.

Experimental Section

The imidazolium salts (bmim)Cl, (emim)Cl, and (dmim)Cl were prepared according to the literature procedure.[9] Aniline, *o*-toluidine, *p*-toluidine, benzylamine, and 4,4′-methylenedianiline were purchased from Aldrich Chemical Co. and used as received.

1: A solution of SeO_2 (3.3 g, 30 mmol) in methanol (30 mL) was treated with K_2CO_3 (2.0 g, 15 mmol) in a 100-mL 2-neck flask at room temperature

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for 1 h. As soon as K_2CO_3 was added, CO_2 started to evolve. Addition of THF into the resulting colorless solution produced a white solid (yield 92%). Elemental analysis calcd (%) for CH_3KSe: C 6.6, H 1.7, K 21.5, Se 43.6; found: C 6.8, H 1.8, K 21.4, Se 42.7; ^{1}H NMR (300 MHz, [D$_4$]methanol, 25°C): $\delta = 3.35$ (s).

Single crystals of **1** suitable for X-ray diffraction studies were grown inside a dry-box (under argon). Compound **1** (0.5 g) was dissolved in methanol (3 mL) in a vial which was contained within a larger vial charged with approximately 2 mL of diethyl ether. The diethyl ether was allowed to slowly diffuse into the methanol solution by maintaining the vials at room temperature for several days.

2a: A solution of (bmim)Cl (3.1 g, 18 mmol) in methanol (30 mL) was treated with 1.1 equiv of **1** (3.6 g, 19.8 mmol) in methanol (30 mL) at room temperature. After stirring for 6 h, the solution was filtered to remove KCl and the solvent was evaporated under reduced pressure to give a yellow liquid. The resulting liquid was further purified by adding CH_2Cl_2 and filtering to remove excess **1** and KCl, followed by drying under high vacuum for 12 h (yield 85%). Elemental analysis calcd (%) for $C_9H_{18}N_2Se$: C 38.45, H 6.41, N 9.97, Se 28.09; found: C 38.18, H 6.30, N 9.60, Se 28.10; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 0.91$ (t, ^3J(H,H) = 7.5 Hz, 3H; CH_3), 1.34 (m, 2H; CH_2), 1.83 (m, 2H; CH_2), 3.45 (s, 3H; OCH_3), 4.06 (s, 3H; NCH_3), 4.27 (t, ^3J(H,H) = 7.2 Hz, 2H; NCH_2), 7.23 (d, ^3J(H,H) = 1.5 Hz, 1H; $C_3H_3N_2$), 7.33 (d, ^3J(H,H) = 1.5 Hz, 1H; $C_3H_3N_2$), 10.58 ppm (s, 1H; $C_3H_3N_2$); LC-MS (CH_3OH): positive ion: 139 $[bmim]^+$; negative ion: 143 $[SeO_2(OCH_3)]^-$.

3a and **4a** were prepared in a similar manner to that of **2a**, by replacing (bmim)Cl with (emim)Cl and (dmim)Cl, respectively.

3a: Yield 86%; elemental analysis calcd (%) for $C_7H_{14}N_2Se$: C 33.21, H 5.54, N 11.07, Se 31.20; found: C 32.90, H 5.50, N 11.50, Se 29.70; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 1.51$ (t, ^3J(H,H) = 7.8 Hz, 3H; CH_3), 3.47 (s, 3H; OCH_3), 4.04 (s, 3H; NCH_3), 4.35 (q, ^3J(H,H) = 7.5 Hz, 2H; NCH_2), 7.28 (s, 1H; $C_3H_3N_2$), 7.30 (s, 1H; $C_3H_3N_2$), 10.88 ppm (s, 1H; $C_3H_3N_2$). LC-MS (CH_3OH): Positive ion: 111 $[emim]^+$; Negative ion: 143 $[SeO_2(OCH_3)]^-$.

4a: Yield 87%; elemental analysis calcd (%) for $C_6H_{12}N_2Se$: C 30.14, H 5.02, N 11.72, Se 33.03; found: C 30.00, H 5.00, N 11.90, Se 32.10; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 3.45$ (s, 3H; OCH_3), 3.98 (s, 6H; $2(NCH_3)$), 7.31 (s, 2H; $C_3H_3N_2$), 10.83 ppm (s, 1H; $C_3H_3N_2$). LC-MS (CH_3OH): Positive ion: 97 $[dmim]^+$; Negative ion: 143 $[SeO_2(OCH_3)]^-$.

Transformation reactions of **3a** to give **3b** and **3c:**[10] A solution of **3a** (0.1 g, 0.4 mmol) in CH_3CH_2OH (3 mL) or CF_3CH_2OH (3 mL) was stirred at room temperature for 6 h, followed by removal of the solvent under high vacuum for 12 h to give a yellow liquid (yield 99%).

Transformation of **3a** to give **3d:**[10] A solution of **3a** (0.1 g, 0.4 mmol) in CH_2Cl_2 (3 mL) was treated with 1.3 equiv of PhOH (0.05 g, 0.52 mmol) at room temperature for 6 h. The subsequent removal of the solvent and excess PhOH under high vacuum for 12 h gave a yellow liquid (yield 99%).

Catalysis reaction: All of the carbonylation reactions were conducted in a 100-mL Parr reactor with a magnetic drive stirrer and an electrical heater. The reactor was charged with an aromatic amine, methanol, an appropriate catalyst and toluene (1 mL) as an internal standard. The reactor was pressurized with a gaseous mixture of O_2 and CO (20:80 v/v), and then heated to a specified temperature. The pressure was maintained at 1.4 MPa throughout the reaction using a reservoir tank equipped with a high-pressure regulator and a pressure transducer. After the reaction was completed, the reactor was cooled to room temperature and the reaction mixture was filtered off to remove the solid diaryl urea. The resulting solution and the isolated urea were analyzed by GC, HPLC, and GC-MS.

Recycling experiment: The 100-mL reactor was charged with aniline (40 mmol), methanol (25 mL), **3a**, and toluene (1 mL) as the internal standard, and then reacted at 60°C for 2 h under pressure of 1.4 MPa of O_2/CO (20:80 v/v). When the reaction was completed, diphenylurea was removed by filtration and the solution that contained the ionic liquid was reused for further carbonylation reactions with a fresh charge of consumed aniline.

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[5] X-ray single-crystal diffraction data for **1** was collected on a Siemens SMART CCD diffractometer. Crystal data for **1**: monoclinic, space group $P2_1/c$, $a = 10.2502(16)$, $b = 7.3115(12)$, $c = 6.4330(10)$ Å, $\beta = 103.012(2)°$, $V = 469.74(13)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.561$ g cm^{-1}, $\mu(Mo_{K\alpha}) = 8.746$ mm^{-1}, $R1 = 0.0332$, $wR2 = 0.0886$, ($I > 2\sigma I$); $R1 = 0.0340$, $wR2 = 0.0893$ (all data). CCDC-185119 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[10] See the Supporting Information for the ^{1}H NMR data of the transformation reactions of **3a** into **3b**, **3c**, and **3d**.

Spatially Directed Protein Adsorption by Using a Novel, Nanoscale Surface Template**

Patricia Moraille and Antonella Badia*

Phase-separated, ultrathin organic films can serve as surface templates for the selective and patterned deposition of macromolecules on the submicron scale.[1–6] Deposition is generally directed by chemical differences in the domains or domain edges generated by phase separation. We demonstrate herein that a chemically *homogeneous* surface exhibiting solid/fluid-phase coexistence can also be used as an

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