A polymeric ionic liquid catalyst for the $N$-formylation and $N$-methylation of amines using CO$_2$/PhSiH$_3$

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A R T I C L E  I N F O

Keywords:
Polymeric ionic liquids
Carbon dioxide (CO$_2$)
$N$-formylation
$N$-methylation
Phenylsilane (PhSiH$_3$)

A B S T R A C T

We describe a polymeric ionic liquid (PIL) derived from trimethyl(p-vinylbenzyl)ammonium chloride ([VBTAm]Cl) that efficiently catalyzes the $N$-formylation of amines employing CO$_2$ and PhSiH$_3$ at room temperature with low catalyst loadings in near-quantitative yield. Under more forcing conditions $N$-methylated products can be selectively obtained. The PIL catalyst can be easily recovered and reused repeatedly without a decrease in activity. The reaction mechanism was studied in situ using high-pressure NMR spectroscopy and a tentative mechanistic cycle has been proposed.

1. Introduction

Carbon dioxide is a cheap, nontoxic, and renewable (C1) building block gaining importance as a substrate in the synthesis of new C–C, C–O and C–N bonds. [1–3] Due to the high thermodynamic and kinetic stability of CO$_2$, the non-catalytic reduction of CO$_2$ necessitates the application of stoichiometric amounts of strong reducing agents, e.g. NaBH$_4$ and LiAlH$_4$ [4–6]. However, these reagents usually react with many (reducible) functional groups which makes them unsuitable for many reactions. Consequently, the development of effective catalytic routes that can be used to reduce CO$_2$ in combination with milder reducing agents, e.g. hydrosilanes, [7–14] formic acid [15] or molecular hydrogen [16], has attracted attention. To activate H$_2$, metal catalysts are usually required, [17–19] and for these reasons hydrosilanes represent a more activated source of hydrogen, but less aggressive than borohydrides and other reductants. Among the hydrosilanes, phenylsilane (PhSiH$_3$) is liquid at room temperature and easy to handle. [20] Phenylsilane composites such as PhSiH$_3$-cesium fluoride, [21,22] and diphenylsilane-cesium fluoride [23], have been applied as reducing agents in a range of reactions. The combination of PhSiH$_3$ and CO$_2$ may be used in the $N$-formylation of amines employing base catalysts such as 1,8-diazabicycloundec-7-ene and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), [24] and in the $N$-methylation of amines using ruthenium-based [25] or metal-free [26,27] catalysts. The reaction was subsequently broadened to the $N$-methylation of amines, [28,29] the synthesis of aminals [30,31], amine-aldehyde couplings (formation of imines), [32] and other related C–N coupling reactions [33–35].

The mechanism for the $N$-formylation/$N$-methylation of amines using PhSiH$_3$/CO$_2$ has been extensively studied [33–36] and theoretical studies show that the pathway varies according to the catalytic conditions [36–38]. However, $N$-methylation is always preceded by $N$-formylation, [8,39,40] and the selectivity of the reaction can be controlled by both the nature of the catalyst [29,41,42], and the reaction conditions [28,43]. In salt catalyzed reactions, it is widely accepted that a key five-coordinated Si-intermediate in the form PhSiH$_3$X is generated that leads to facile nucleophilic attack of CO$_2$ by the hydride. The formation of hypervalent five-coordinated Si-intermediate requires only a nucleophile (X$^-$) to activate the hydrosilanes. Thus, salts with nucleophilic anions such as chlorides, [44] fluorides, hydroxides [45], carboxylate anions, [10,21,46] and carboxylate-based zwitterions [35,36], are excellent catalysts. While these salts are generally convenient to use, their separation from the reaction product is not straightforward and hampers reuse.

To overcome this limitation we hypothesized that polymeric ionic liquids (PILs) [47,48] with a (free) nucleophilic anion would facilitate catalyst separation and recycling. [49] Herein, we report the synthesis of a cationic polymer derived from an inexpensive commercially available with chloride counter-ions that catalyzes the $N$-formylation of amines under ambient conditions at low catalyst loadings or $N$-methylation under more forcing conditions. A broad substrate scope has

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https://doi.org/10.1016/j.jcou.2020.101240
Received 22 April 2020; Received in revised form 23 June 2020; Accepted 1 July 2020
Available online 08 July 2020
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been demonstrated and mechanistic insights have been acquired from in situ spectroscopic studies.

2. Results and discussion

Trimethyl(p-vinylbenzyl)ammonium chloride, [VBTAm]Cl, undergoes facile radical polymerization [50] in the presence of 2,2′-azobis(2-methylpropionitrile) to afford a polymer termed p[VBTAm]Cl as shown in Scheme 1 (see Figures S1 – S3 in the Supporting Information for a comparison of the 1H and 13C NMR and UV–vis spectra of the monomer [VBTAm]Cl and polymer p[VBTAm]Cl).

The monomer is soluble in water, ethanol, methanol, acetonitrile, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), ethyl acetate, chloroform, and dichloromethane, whereas p[VBTAm]Cl is soluble in water, ethanol, and methanol, and sparingly soluble in DMSO, DMF and ionic liquids. Scanning electron microscopy (SEM) of p[VBTAm]Cl shows that p[VBTAm]Cl comprises a non-porous globular structure with diameters in the range c.a. 200 – 300 nm (Fig. 1). Ionic polymers based on the [VBTAm] cation with different anions adopt similar globular structures, but are usually larger in size, i.e. 1000 – 3000 nm in diameter. [51–56]

Scheme 1. Synthesis of p[VBTAm]Cl.

[VBTAm]Cl and p[VBTAm]Cl were evaluated as catalysts for the N-formylation of N-methylaniline in the presence of CO2 and PhSiH3 in dimethylformamide (DMF) solution. The selection of DMF as the solvent is based on previous reports showing that the reaction hardly proceeds in non-polar solvents, [57] and in polar solvents such as DMF, dimethyl sulphoxide (DMSO) and to a lesser extent acetonitrile, the nucleophilicity and basicity of amines is enhanced which activates organosilanes via Lewis acid–base N–Si interactions. [36,57–60] N-formylation of N-methylaniline takes place at room temperature under 1 bar of CO2 using a catalyst loading of 1% mol affording N-methyl formanilide in near-quantitative yield, i.e. 96 and 99 %, respectively (Table 1, entries 1 and 2). Increasing the catalyst loading and/or the reaction pressure and temperature reduces the selectivity of the reaction with the additional formation of N,N-dimethyl aniline. However, by increasing the pressure of CO2 to 10 bar and the temperature to 100 °C the N-methylated product can be obtained in near-quantitative yield (Table 1, entries 3 and 4). Other hydrogen sources were evaluated (see Table S1), including molecular hydrogen, which is ineffective, and diphenylsilane and polymethylhydrosiloxane (PMHS), which result in lower conversions and poorer selectivities compared to PhSiH3. Under equivalent conditions both [VBTAm]Cl and p[VBTAm]Cl catalyze the reaction to essentially the same extent, as can be appreciated from the data presented in Table 1.

The substrate scope of the N-formylation reaction was evaluated using the p[VBTAm]Cl catalyst (Table 2). Aniline is readily N-formylated under the standard conditions affording N-phenyl-formamide in almost quantitative yield (Table 2, entry 1). Substituted anilines with electron-donating groups (−OH, −OCH3) on the phenyl ring at the para-position are slightly less reactive, but still afford the N-formylated product in >90 % yield (Table 2, entries 2–3). However, N-formylation

![Fig. 1. SEM images of p[VBTAm]Cl at different magnifications.](image)

Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Catalyst loading (mol%)</th>
<th>Pressure (bar)</th>
<th>Time (h)</th>
<th>Yield A [%]</th>
<th>Yield B [%]</th>
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<tr>
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<td>1</td>
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Yield determined by GC using n-decane as the internal standard. Reaction conditions: N-methylaniline (1 mmol), PhSiH3 (1 mmol), DMF (0.75 mL).
when one H-atom on the NH₂ group in aniline is replaced by a benzyl reactive, even under harsher conditions (Table 2, entry 4). Likewise, of aniline with a chloride at the para-position of the phenyl ring undergo N-formylation in high yield (Table 2, entries 6–10), whereas the yield is reduced when the ortho-position of the ring is substituted, as in o-trifluoromethyl-N-methylaniline (Table 2, entry 11).

Table 2: Substrate scope for the N-formylation reaction employing the p[VBTAm]Cl catalyst.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Substrate</th>
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<th>Isolated yield (%)</th>
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Reaction conditions: p[VBTAm]Cl (1 mol%), amine (1 mmol), DMF (0.75 mL), PhSiH₃ (1 mmol) and CO₂ (10 bars).* Yield determined by GC using n-decane as the internal standard. NMR spectra of the isolated products are shown in Figures S4–S17.

of aniline with a chloride at the ortho-position of the ring is much less reactive, even under harsher conditions (Table 2, entry 4). Likewise, when one H-atom on the NH₂ group in aniline is replaced by a benzyl group the yield of the N-formylation product is reduced (Table 2, entry 5). However, N-methylated aniline derivatives with substituents at the para-position of the phenyl ring undergo N-formylation in high yield (Table 2, entries 6–10), whereas the yield is reduced when the ortho-position of the ring is substituted, as in o-trifluoromethyl-N-methylaniline (Table 2, entry 11).

N-formylation of alkylamine substrates can also be achieved. Both primary and secondary alkyl amines can be N-formylated in generally high yield in the range 81–91% (Table 2, entries 12–16). In addition, cyclic (Table 2, entries 17–21) and heterocyclic (Table 2, entries 22 and 23) amines undergo N-formylation in high yield, i.e. 88–97%.

The performance of p[VBTAm]Cl was compared with 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), a benchmark ionic liquid that has been previously reported as catalyst for N-formylation of amines. [44] Under conditions in which p[VBTAm]Cl transforms N-methylaniline into N-methyl formanilide in 99% yield, i.e. 1 mol% catalyst, 1 bar CO₂ and 25 °C, [Bmim]Cl affords N-methyl formanilide in only 86% yield. The lower activity may be attributed to stronger ion pairing between the [Bmim]+ cation and the chloride anion which reduces the nucleophilicity of the anion and hence the reduced catalytic activity. [44] The reaction mechanism of the [VBTAm]Cl catalyzed N-formylation of N-methylaniline was probed by ¹H NMR spectroscopy under 10 bar of CO₂ (Figs. 2 and S18).

The mechanism of N-formylation and N-methylation employing CO₂ with silane reducing agents in the presence of metal-free (salt) catalysts has been previously studied. [35,36,44–46] The key step of this catalytic cycle is the activation of the PhSiH₃ by nucleophilic attack of the chloride anion 1 to afford a hypervalent silicon intermediate 2 (Scheme 2) as evidenced by the downfield shift of the PhSiH₃ protons in the ¹H NMR spectra from 4.15 ppm to 4.45 ppm (Figure S18). This intermediate then reacts with CO₂ to afford a formoxysilane intermediate 4, tentatively assigned to the low intensity signal at ~8.2 ppm for the O-CHO moiety in the ¹H NMR spectra (Fig. 2) and also in the ¹³C NMR spectra taken in CD₂CN solvent by the signal at ~164.1 ppm for the C-atoms of the O-CHO group (Figure S19), in accordance with previous observations. [10,44,45] Subsequent reaction of 4 with N-methylaniline gives the desired N-formylated product 6 (Scheme 2) as evidenced by gradually increasing signal at 8.55 ppm for the N-CHO moiety in the ¹H NMR spectrum (Fig. 2). The released chlorosilane 3 and silanol S are presumably too reactive and can undergo rapid dimerization to 1,3-diphenyl-disiloxane, or even oligomerization as already proposed previously. [28] The broad peaks between 4.60–5.35 ppm in the ¹H NMR spectra possibly correspond to these species (Figure S18). [61,62] However, they are too broad and too weak to be confidently assigned.

The same intermediates are obtained with p[VBTAm]Cl, based on a related in situ ¹³C NMR spectroscopic study (Figure S20, a). The formation of the N-formylated product 6, identified by a gradually increasing peak at 33.5 ppm (N-CH₂) (Figure S20, b) and the consumption of phenylsilane evidenced by gradually decreasing peaks at 132.6 and 138.3 ppm can be observed (Figure S20, c). As DMSO-D₆ is used as the solvent for the polymer, the peak corresponding to the formoxysilane 4 intermediate appears at 165.1 ppm (Figure S20, d) along with a gradually increasing peak at 164.6 ppm for the -CHO in the product 6. In a similar catalytic system when [BMim]Cl is used as catalyst, it has been reported that the formation of formoxysilane 4 can be observed as represented by the peak at 163.0 ppm for the O-CHO in the product 6 (Scheme 2) as evidenced by the downfield shift of the PhSiO moiety in the ¹H NMR spectra (Fig. 2) and also in the ¹³C NMR spectra taken in CD₂CN solvent by the signal at ~164.1 ppm for the C-atoms of the O-CHO group (Figure S19), in accordance with previous observations. [10,44,45] Subsequent reaction of 4 with N-methylaniline gives the desired N-formylated product 6 (Scheme 2) as evidenced by gradually increasing signal at 8.55 ppm for the N-CHO moiety in the ¹H NMR spectrum (Fig. 2). The released chlorosilane 3 and silanol S are presumably too reactive and can undergo rapid dimerization to 1,3-diphenyl-disiloxane, or even oligomerization as already proposed previously. [28] The broad peaks between 4.60–5.35 ppm in the ¹H NMR spectra possibly correspond to these species (Figure S18). [61,62] However, they are too broad and too weak to be confidently assigned.

The recyclability and scalability of p[VBTAm]Cl was investigated in the N-formylation of N-methylaniline on a 10 mmol (1.08 g) scale, carried out in an autoclave under CO₂ (10 bar) at room temperature, affording the product in very high yield over several cycles with only a slight decrease in activity observed (Fig. 3).

2.1. Concluding remarks

Both the monomer [VBTAm]Cl and the polymer p[VBTAm]Cl catalyze the N-formylation of amines using the PhSiH₃/CO₂ system. In situ NMR spectroscopy confirms the mechanism of the catalytic process, revealing the formation of the five-coordinated silicon-intermediate as the key step. The activity of the [VBTAm]Cl and p[VBTAm]Cl catalysts are comparable or superior to other reported catalysts. [41–44] The availability of monomer and polymer catalysts is also advantageous.
compared to catalysts such as metal complexes [25], frustrated Lewis pairs [63] and covalent organic frameworks [64]. Most importantly, the polymer catalyst p[VBTAm]Cl can be recovered and reused multiple times.

3. Experimental

All chemicals were obtained commercially and used without further purification. Technical grade CO$_2$ gas was obtained from Carbagas AG. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance instrument (400 MHz). In situ NMR spectroscopic studies were performed using a sapphire NMR tube (10 mm) on a Bruker DRX 400 NMR spectrometer. The general procedure of sample preparation for the in situ NMR study comprises monomer [VBTAm]Cl or polymer p[VBTAm]Cl (1.76 mg, 1 mol%), N-methylaniline (107 mg, 1 mmol) and PhSiH$_3$(108 mg, 1 mmol) dissolved in CD$_3$CN or DMSO-d$_6$ (2 mL) in a 10 mm sapphire NMR tube. This solution was pressurized at room temperature to 10 bar with CO$_2$. $^1$H NMR and $^{13}$C NMR spectroscopy of the reaction mixture were recorded at regular intervals. SEM images were obtained on a Zeiss Merlin Scanning electron microscope fitted with a Gemini II column. UV-vis spectra were recorded on a Cary-60 spectrometer (Agilent Technologies) in the wavelength range 200 – 400 nm in absolute ethanol. GC-FID-MS characterization of the organic products were performed on a Gas Chromatograph- Agilent 7890B equipped with an Agilent 7000C MS triple quad detector and a capillary column from Agilent (1 × d × f: 30 m × 0.25 mm × 0.25 mm) using N$_2$ as the carrier gas and the following setup: heating to 50°C for 3 min, then heating to 230°C at a rate of 10°C/min and holding for 3 min at 230°C. High boiling point products were subjected to an additional holding time of 15 min. Prior to analysis, a drop of the reaction mixture (diluted with EtOAc and internal standard n-decane) was removed from the reaction flask/autoclave, filtered (using Chromafil syringe filters) and added to a GC vial, and completed with EtOAc.

3.1. Preparation of p[VBTAm]Cl

The polymer was prepared according to a literature protocol. [50] NMR spectra of p[VBTAm]Cl are shown in Figures S1 and S2 and UV–vis spectra are shown in Figure S3.

3.2. Experimental procedure for the N-formylation and N-methylation reactions

[VBTAm]Cl or p[VBTAm]Cl (2.11 mg, 0.01 mmol) was added to a septum-sealed 50 ml two-neck round-bottom Schlenk flask that was connected to a CO$_2$ balloon and Schlenk line. CO$_2$-vacuum purging was performed at least three times before adding the amine substrate (1 mmol), and dry DMF solvent (0.75 mL). The resulting mixture was stirred at 300 rpm. PhSiH$_3$ (108 mg, 1 mmol) was then added to the solution mixture using a syringe, and the reaction was monitored by GC-FID-MS. For the reactions performed under pressure of 10 bar CO$_2$, the same procedure was carried out in a 75 ml glass vial in a steel-lined Parr autoclave with the CO$_2$ purging cycles carried out after mixing all the contents.

After completion of the reaction, 5–10 mL of EtOAc was added, and the organic phase was washed with water (3 × 30 mL). The products were purified with technical grade EtOAc, hexane, dichloromethane and methanol system as the eluents on 0.1 % Et$_3$N deactivated silica gel using a Combiflash Rf + IGZ automatic column chromatography instrument.
3.3. Catalyst recycling

The recyclability of p[VBTAm]Cl as catalyst for the N-formylation of N-methylaniline on a 10 mmol scale in an autoclave using CO₂ (10 bar), PhSiH₃ (10 mmol i.e., 1.08 g), dry DMF (7.5 mL) at room temperature with a catalyst loading of 1 mol% (21.1 mg, 0.1 mmol) for a period of 11 h. On completion of the reaction, the p[VBTAm]Cl catalyst was recovered by centrifugation, washed with ethyl acetate (3x5 mL) and then dried under vacuum at room temperature for a period of 24 h. An additional catalyst amount of 10% was added in every recycling step to compensate for any catalyst loss due to the very low quantity of catalyst employed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We thank the EPFL, the Swiss National Science Foundation, the Swiss Competence Center for Energy Research (SCCER) and the Commission for Technology and Innovation (CTI) for financial support.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jcou.2020.101240.

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