Imidazolium and Phosphonium Alkylselenites for the Catalytic Oxidative Carbonylation of Amines: Mechanistic Studies

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The reactions of $KSeO_2(OCH_3)$ (**1**) in methanol with [Rmim]Cl (Rmim = 1-alkyl-3-methylimidazolium) at room temperature give imidazolium-based ionic liquids containing methylselenite anion, $[Rmim][SeO_2(OCH_3)]$ (**2a**, R = *n*-C_4H_9; **3a**, R = C_2H_5; **4a**, R = CH_3), respectively. Similarly, phosphonium methylselenites, $[R_4P][SeO_2(OCH_3)]$ (**6a**, R = *n*-butyl; **7a**, R = ethyl) were prepared by reacting **1** with tetraalkylphosphonium bromides. The methoxy groups in imidazolium and phosphonium methylselenites were easily replaced by other alkoxy groups upon interaction with various alcohols. [1,3-dimethylimidazolium]$[SeO_2(OCH_3)]$ (**4a)** is slowly transformed into [1,3-dimethylimidazolium]$_2[Se_2O_5]$ (**5a)** in the absence of methanol. An X-ray study reveals that **5a** is a dimeric selenium complex consisting of two 1,3-dimethylimidazolium cations and $Se_2O_5^{2-}$ anion. All the ionic liquid compounds containing methylselenite anion show surprisingly high activity for the oxidative carbonylation of aniline, even at temperatures as low as 40 °C, to give diphenylurea in high yield. The effects of molar ratio of aniline to catalyst, temperature, and solvent have been investigated. The plausible mechanism for the carbonylation reaction of aniline based on the ^1H and ^{13}C NMR studies using **3a** is presented.

Introduction

Interest in ureas has recently increased, because ureas can be used as intermediates to many biologically important compounds, several pesticides, herbicides, medicines, pigments, and resins.[1] Ureas can also be easily converted to carbamates (eq 2), which are used for important precursors for preparing isocyanates by thermal cracking.[2] The conventional methods for preparing ureas involve the reaction of amines with phosgene. However, the toxicity of phosgene, the formation of corrosive hydrogen chloride as a byproduct, and difficulties in the removal of hydrolyzable chlorine compounds make the process cumbersome with respect to both industrial and environmental viewpoints. During the last two decades, much effort has been made to develop alternative methods for the preparation of substituted ureas by non-phosgene routes.[3] One of the approaches is the catalytic oxidative carbonylation of an amine with carbon monoxide and oxygen in the presence of an alcohol with an appropriate catalyst or catalytic system as shown in eq 1.[4]

$$2RNH_2 + CO + {}^1/_2O_2 \rightarrow (RNH)_2CO + H_2O \quad (1)$$

$$(RNH)_2CO + R'OH \rightarrow RNH(C{=}O)OR' + RNH_2 \quad (2)$$

Group 8−10 transition metals are commonly used as catalysts for this purpose, but most of these catalytic systems suffer from either low reaction yield or severe reaction conditions such as high temperatures and pressures.[5] Alkali-metal-containing selenium compounds have also been successfully employed in the oxidative carbonylation of aromatic amines to give diarylureas and/or arylcarbamates.[6] However, the major disadvan-

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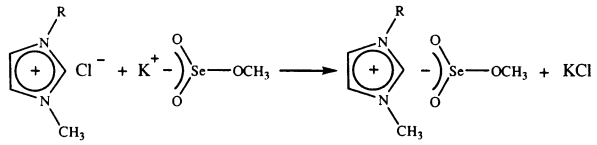
Scheme 1



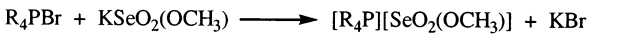
(**2**: R = *n*-C_4H_9; **3**: R = C_2H_5; **4**: R = CH_3)

tage of using these selenium compounds is the difficulty in separating product and catalyst from the reaction mixture, which arises from the coproduction of insoluble *N*,*N*′-diphenylurea and soluble alkyl *N*-phenylcarbamate, at 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 has been considerable interest in the potential application of ionic liquids to immobilize volatile, precious, and/or toxic homogeneous catalysts and, thereby, to improve the stability and to facilitate the recovery of the catalysts.[7] In a previous communication,[8] we have demonstrated that the catalytic activity and stability of selenium compounds such as [$KSeO_2$-(OCH_3)] can be significantly improved by immobilizing with 1-alkyl-3-methylimidazolium chlorides. In the present paper, we describe in detail the synthesis, characterization, and catalytic activities of imidazolium- and phosphonium-immobilized alkyl selenite anions. The mechanistic investigation of the oxidative carbonylation of an amine in the presence of an imidazolium-immobilized methylselenite anion is also presented.

Results and Discussion

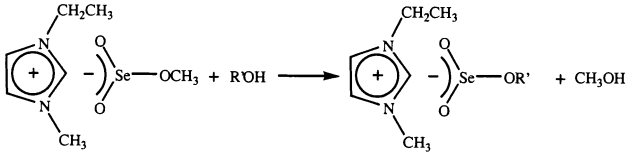
Synthesis of 1-Alkyl-3-methylimidazolium Methylselenites and Their Derivatives. The reactions of $KSeO_2(OCH_3)$ (**1**) with [Rmim]Cl (Rmim = 1-alkyl-3-methylimidazolium) produced imidazolium-based ionic liquids containing methylselenite anion in high yield, as shown in Scheme 1.

Scheme 2



(**6a**: R = *n*-butyl; **7a**: R = ethyl)

Scheme 3



(**3a**: R′ = CH_3; **3b**: R′ = C_2H_5; **3c**: R′ = CH_2CF_3; **3d**: R′ = Ph)

Similarly, phosphonium-immobilized methylselenites were prepared by reacting **1** with tetraalkylphosphonium bromides (Scheme 2).

Interestingly, the methoxy groups in imidazolium and phosphonium methylselenites were easily replaced by other alkoxy groups upon interaction with various alcohols to produce a series of new imidazolium- and phosphonium-immobilized selenium complexes containing alkyl- or phenylselenite anions. For example, as shown in Scheme 3, 1-ethyl-3-methylimidazolium methylselenite (**3a**) reacts with ethanol, 1,1,1-trifluoroethanol, and phenol to give **3b**−**d**, respectively. Unlike complex **1**, complexes **2**−**7** are fairly air-stable and highly soluble in most polar organic solvents, including $CHCl_3$, CH_2Cl_2, CH_3CN, DMF, DMSO, NMP, propylene carbonate (PC), and CH_3OH.

X-ray Crystallographic Structure of [1,3-Dimethylimidazolium]$_2$[diselenite] (5a). Interestingly, when **4a** was placed in a flask for several days, it was slowly transformed into the new compound **5a**, as a white crystalline solid. The ^{1}H NMR spectrum of the white solid shows two sets of resonances, implying that the new compound may exist as an isomeric mixture (see Figure 2B). The ambiguous spectroscopic data of the white solid led us to carry out an X-ray diffraction study to elucidate the structure of **5a**, which was recrystallized in propylene carbonate. The single-crystal structure and crystallographic data of **5a** are presented in Figure 1 and Table 1, respectively.

The X-ray structural analysis reveals that **5a** is a dimeric selenium complex consisting of two 1,3-dimethylimidazolium cations and $Se_2O_5^{2-}$ in which two SeO_2 anions are bridged by oxygen atoms. The two imidazolium cations are located perpendicular to each other. All the oxygen atoms of the two SeO_2 anions form strong hydrogen bonds to hydrogen atoms of the surrounded imidazolium rings. Hydrogen coordinates and the local structure around $Se_2O_5^{2-}$ are presented in the Supporting Information. The formation of **5a** from **4a** can be rationalized by assuming the slow release of dimethyl ether during the dimerization of **4a**, as shown in Scheme 4.

However, as shown in Scheme 4, there is a possibility of the presence of an isomer with both imidazolium cations arranged below the Se(1)−O−Se(2) plane (structure B). The presence of an isomer is somewhat supported by the ^{1}H NMR spectrum and following in situ ^{1}H NMR study, as shown in Figure 2. Figure 2A is the NMR spectrum of **4a** in $CDCl_3$, and Figure 2B is the NMR spectrum of **5a** in $CDCl_3$. The larger peaks (▽) in

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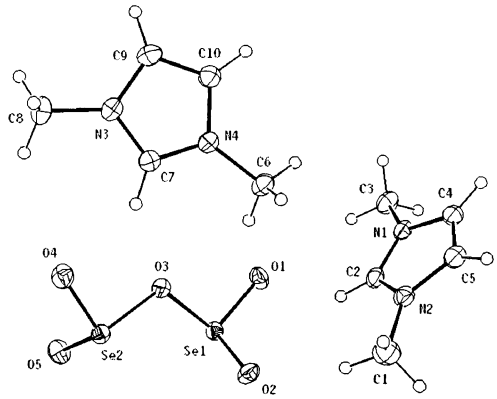


Figure 1. ORTEP drawing of **5a** with atom labeling. Ellipsoids show 50% probability levels. Selected bond lengths (Å) and angles (deg): Se(1)−O(1) = 1.6418(18), Se(1)−O(2) = 1.6509(18), Se(1)−O(3) = 1.8566(18), Se(2)−O(5) = 1.6502(19), Se(2)−O(4) = 1.6505(18), Se(2)−O(3) = 1.8391(18); O(1)−Se(1)−O(2) = 107.56(10), O(1)−Se(1)−O(3) = 98.26(9), O(2)−Se(1)−O(3) = 100.49(9), O(5)−Se(2)−O(4) = 107.02(10), O(5)−Se(2)−O(3) = 101.65(9), O(4)−Se(2)−O(3) = 97.63(9), Se(2)−O(3)−Se(1) = 115.09(9).

Table 1. X-ray Crystal Data and Structure Refinement for 5a

formula	$C_{10}H_{18}N_4O_5Se_2$
fw	432.20
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	7.3171(6)
b (Å)	8.8046(7)
c (Å)	13.4556(11)
α (deg)	106.658(2)
β (deg)	100.678(2)
γ (deg)	95.497(2)
V (Å^3)	805.83(11)
Z	2
color	colorless
cryst size (mm^3)	0.37 × 0.20 × 0.04
D_{calcd} (g/cm^3)	1.781
F(000)	428
μ (mm^{-1})	4.613
transmissn min/max	0.8370/0.2801
temp (K)	173(2)
type of diffr	Siemens SMART CCD
radiation	Mo Kα (0.710 73 Å)
θ range (deg)	2.45−28.29
h, k, l collected	$-9 \le h \le 5$
	$-11 \le k \le 11$
	$-12 \le l \le 17$
no. of rflns	5040
no. of indep rflns	3609 (R(int) = 0.0181)
no. of data/restraints/params	3609/0/194
final R indices ($I > 2\sigma(I)$)	R1 = 0.0256, wR2 = 0.0630
R indices (all data)	R1 = 0.0350, wR2 = 0.0666

Figure 2B are likely to be associated with structure A and smaller peaks (▼) can be ascribed to structure B.

When 0.8 equiv of methanol was added to the NMR tube containing **5a**, the two sets of signals (▽, ▼) merged into one with the appearance of new peaks at 3.42 (★) and 3.25 (●) ppm, which can be assigned to the free methanol and Se−OCH_3, respectively. The easy transformation of **5a** into the single monomeric selenium complex **4a** in the presence of methanol is a clear indication that the dimeric selenium complex **5a** exists as an isomeric mixture (see Scheme 4). $K_2Se_2O_5$, having a structure similar to that of **5a**, has already been suggested and used as an active catalyst for the carbonylation of aromatic amine.[6]

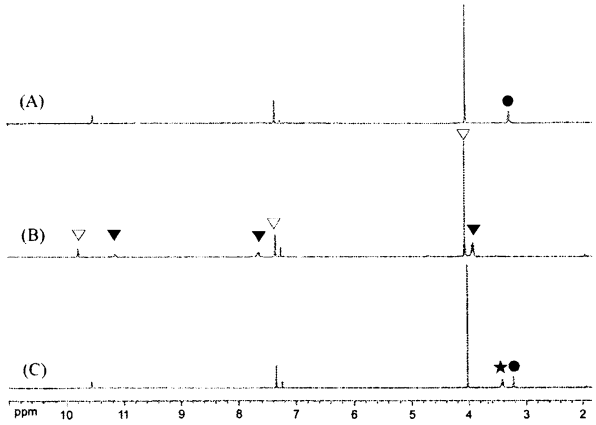


Figure 2. In situ ^{1}H NMR spectra for the transformation reaction of **5a** into **4a**: (A) **4a** in $CDCl_3$; (B) **5a** in $CDCl_3$; (C) solution in (B) after addition of 0.8 equiv of CH_3OH Legend: (★) free CH_3OH; (●) SeOCH_3).

Scheme 4. Reaction Scheme for the Reversible Reaction between Monomer (4a) and Dimer Complexes (5a)

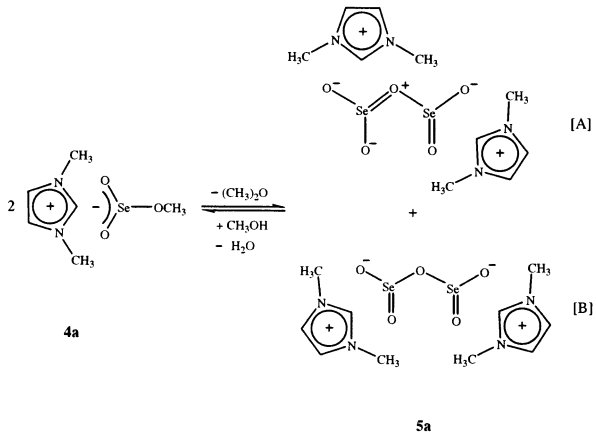


Table 2. Activities of Various Catalysts for the Oxidative Carbonylation of Amines[a]

amine	catalyst	conversn (%)	selectivity[b] (%)	TOF[c] (h^{-1})
aniline	**1**	18.3	99.4	23
aniline	**2a**	98.1	99.8	122
aniline	**3a**	98.3	99.9	121
aniline	**4a**	98.2	99.4	123
aniline	**3b**	97.9	99.4	124
aniline	**3c**	98.5	99.6	124
aniline	**3d**	97.2	99.7	122
aniline	**5a**	95.6	99.6	120
aniline	**6a**	60.3	99.5	76
aniline	**7a**	58.6	99.4	73
n-BuNH$_2$	**3a**	95.2	97.5	119
CyNH$_2$[d]	**3a**	80.1	99.8	100

[a] Conditions: amine 40 mmol, catalyst 0.16 mmol, methanol 25 mL, T = 60 °C, P = 1.4 MPa (O_2/CO = 20:80 v/v), t = 2 h. [b] N,N′-Disubstituted urea. [c] TOF = (mol of amine consumed) (mol of catalyst)$^{-1}$ h^{-1}. [d] Cy = cyclohexyl.

Catalytic Activities. The catalytic activities of **2**−**7** were tested for the oxidative carbonylation of aromatic, alicyclic, and aliphatic amines. The results in Table 2 show that imidazolium and phosphonium alkylselenites **2**−**7** exhibit significantly higher activity for the oxidative carbonylation of aniline than **1**. The dimeric selenium compound **5a** also shows activity similar to that of **2**−**4** in the carbonylation reaction in methanol at 60 °C and 1.4 MPa for 2 h. The comparable activity of **5a**

Table 3. Oxidative Carbonylation of Various Aromatic Amines[a]

amine	conversn (%)	selectivity[b] (%)	TOF[c] (h^{-1})
aniline	99.6	98.6	125
o-toluidine	98.9	100	124
2,4-DMA[d]	99.5	100	124
2,6-DMA[d]	99.7	100	125
2,4,6-TMA[e]	99.9	100	125

[a] Conditions: substrate 40 mmol, **3a** 0.16 mmol, methanol 25 mL, T = 80 °C, P = 1.4 MPa (O_2/CO = 20/80 v/v), t = 2 h. [b] N,N′-Disubstituted urea. [c] TOF = (mol of amine consumed) (mol of catalyst)$^{-1}$ h^{-1}. [d] DMA = dimethylaniline. [e] TMA = trimethylaniline.

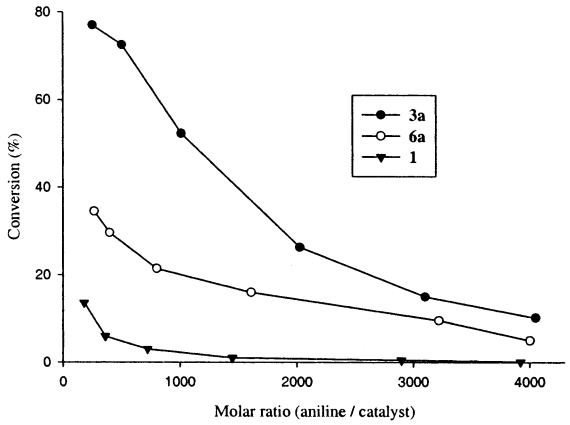


Figure 3. Effect of molar ratio (aniline/catalyst) on the conversions in the oxidative carbonylation of aniline performed with catalysts **3a**, **6a**, and **1**. Conditions: aniline 40 mmol, methanol 25 mL, T = 60 °C, P = 1.4 MPa (O_2/CO = 20/80 v/v), t = 1 h.

can be ascribed to the fact that **5a** can be converted to **4a** in the presence of methanol.

Oxidative carbonylation of aniline and substituted anilines were performed using **3a** in methanol at 1.4 MPa (O_2/CO = 20/80 v/v) for 2 h, and the results are listed in Table 3. Aromatic amines including aniline, *p*-toluidine, benzylamine, and 4,4′-methylenedianiline were easily carbonylated to produce corresponding ureas at 60 °C in high yields,[8] whereas substituted anilines at the 2- or 2,6-positions such as *o*-toluidine, 2,4-dimethylaniline, 2,6-dimethylaniline, and 2,4,6-trimethylaniline were carbonylated only at the elevated temperature, 80 °C, to give the corresponding ureas, implying that the steric effect is an important factor in the carbonylation reaction.

Effect of Aniline/Catalyst Molar Ratio. The effect of the aniline/catalyst molar ratio on the carbonylation of aniline was studied with **3a**, **6a**, and **1** at 60 °C and 1.4 MPa (O_2/CO = 20/80 v/v) for 1 h. The molar ratio of aniline to catalyst was varied in the range 180−4050, and the results are shown in Figure 3. The catalytic activities of ionic liquid catalysts **3a** and **5a** are significantly higher than that of **1** throughout the full range of molar ratios performed. The conversions of aniline decreased continuously with the increase of the molar ratio. The highest turnover frequency of 545 h^{-1} was obtained with catalyst **3a** at the molar ratio of 2025.

Effect of Temperature. Figure 4 shows the effect of temperature on the oxidative carbonylation of aniline performed with catalysts **3a**, **6a**, and **1** in the temperature range 40−120 °C at 1.4 MPa (O_2/CO = 20/80 v/v) for 1 h. Figure 5 shows the change of product composition with temperature in the **3a**-catalyzed carbonylation of aniline. The catalytic activities of **3a** and **6a** are significantly higher at the temperature range of 40−60 °C compared with **1**, but this is not much pronounced at the range of 80−120 °C. The conversions of aniline increased with increasing temperature, but, as shown in Figure 5, the selectivity to diphenylurea started to decrease above 60 °C due to the alcoholysis of diphenylurea to phenylcarbamate (see eq 2). The major disadvantage of carbonylation of aniline using homogeneous catalysts is the difficulty in separating product and catalyst from the reaction mixture as a result of coproduction of insoluble urea and soluble carbamate at high temperatures. Therefore, it is desirable to perform the carbonylation reaction at 60 °C or lower to depress the formation of soluble phenylcarbamate, thereby facilitating the recovery of catalyst from the reaction mixture by simple filtration.

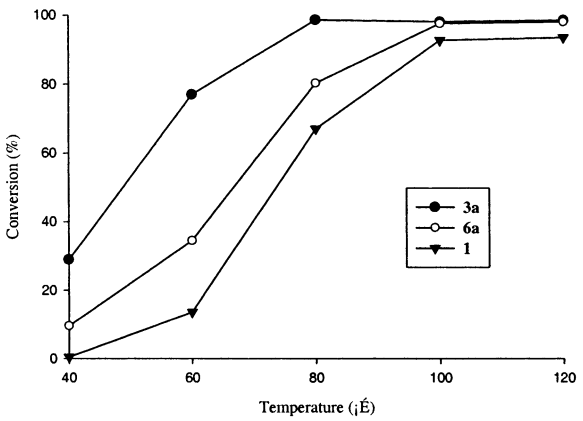


Figure 4. Effect of temperature on the oxidative carbonylation of aniline performed with catalysts **3a**, **6a**, and **1**. Conditions: aniline 40 mmol, catalyst 0.16 mmol, methanol 25 mL, P = 1.4 MPa (O_2/CO = 20/80 v/v), t = 1 h.

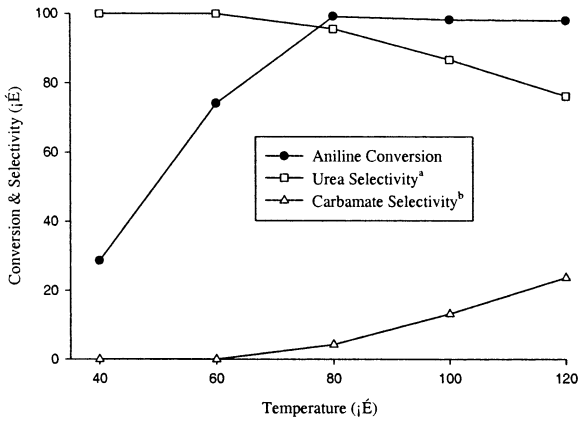


Figure 5. Effect of temperature on the oxidative carbonylation of aniline catalyzed by **3a**. Conditions: aniline 40 mmol, **3a** 0.16 mmol, methanol 25 mL, P = 1.4 MPa (O_2/CO = 20/80, v/v), t = 1 h. Legend: (a) urea = *N*,*N*′-diphenylurea; (b) carbamate = methyl *N*-phenylcarbamate.

Effect of Solvent. The effect of solvent on the oxidative carbonylation of aniline was studied using **3a** at 60 °C, 1.4 MPa (O_2/CO = 20/80 v/v), for 2 h, and the results are listed in Table 4.

In alcoholic solvents such as methanol, ethanol, and *n*-propyl alcohol, high conversions of aniline were obtained. Unlike the catalytic system SeO_2−K_2CO_3,[6]

Table 4. Effect of Solvents on the Oxidative Carbonylation of Aniline[a]

solvent	conversn (%)	selectivity[b] (%)	TOF[c] (h^{-1})
MeOH	98.3	99.9	121
EtOH	99.6	99.2	125
n-PrOH	88.7	99.3	111
acetone	10.3	100	13
acetone[d]	96.6	100	121
MC	2.1	72.1	3
MC[d]	95.7	100	120
e	1.0	90.2	9
d,*e*	53	99.6	445

[a] Conditions: aniline 40 mmol, **3a** 0.16 mmol, $T = 60$ °C, $P =$ 1.4 MPa (O_2/CO = 20/80 v/v), $t = 2$ h. [b] *N*,*N*′-Diphenylurea. [c] TOF = (mol of aniline consumed) (mol of catalyst)$^{-1}$ h^{-1}. [d] Methanol 0.5 g. [e] Aniline 25 g without solvent.

immobilized catalyst **3a** showed poor activity in polar solvents such as acetone, methylene chloride (MC), and DMF, though the catalysts are highly soluble in these solvents. However, it is worth noting that high conversions of aniline (>95%) were achieved in the carbonylation of aniline when small amounts of methanol (0.5 g) were added to these solvents, implying that the presence of an alcohol is required for the oxidative carbonylation to proceed at 60 °C. The oxidative carbonylation reaction of aniline also did not proceed well in the absence of a solvent. When the reaction was performed at 60 °C in the presence of **3a** (0.04 g) using aniline (25 g) as a solvent and a substrate, only 0.3 g of diphenylurea was produced (conversion 1.0%, TOF 9 h^{-1}) with the coproduction of trace amounts of methanol and dimethyl carbonate. In contrast, when 0.5 g of methanol was provided in the carbonylation reaction, 14.9 g of diphenylurea was obtained (conversion 53%, TOF 445 h^{-1}). From these results, it is likely that the presence of an alcohol is essential in regenerating an active species during the catalytic cycle.

^{13}C Labeling NMR Study. To have a better understanding of the active species and the mechanistic pathways to the formation of N,N′-disubstituted urea, a series of ^{1}H and ^{13}C NMR experiments were carried out using [emim][SeO_2($O^{13}CH_3$)] (**3a′**). Due to the overlap of ^{1}H NMR resonances arising from the imidazolium and aniline moieties in the range 6.8−7.4 ppm, cyclohexylamine was used instead as a substrate.

Figure 6A represents the ^{1}H NMR spectrum of **3a′** (▼: Se−O$^{13}C\mathit{H}_3$, $^1J_{^{13}C-H} = 122$ Hz) in $CDCl_3$ at 60 °C. As shown in Figure 6B, the addition of 1.5 equiv of $C_6H_{11}NH_2$ (●: $-C_6\mathit{H}_{11}$) to the NMR tube containing **3a′** did not give any spectral change, possibly due to the fast exchange between **3a′** and selenium amido species **3e** (see Scheme 5). However, when the NMR tube was pressurized with ^{13}CO (0.14 MPa) at 60 °C, a set of resonances newly appeared (■, ★, ○ in Figure 6C) which is believed to be associated with an intermediate, carbamoyl species, [emim][SeO_2(^{13}CONHC_6H_{11})] (**3f**). The doublet of doublets (■) at 6.1 ppm can be ascribed to N*H* in ^{13}CON*H*C_6H_{11}. The peaks (★) at 3.62 and 3.18 ppm can be assigned to $^{13}C\mathit{H}_3$ in free $^{13}C\mathit{H}_3$OH. This can be more clearly seen in ^{13}C NMR spectra in Figure 7.

As can be seen in Figure 7B, no spectral change was observed by adding $C_6H_{11}NH_2$ (●: $-C_6\mathit{H}_{11}$) to a **3a′**-containing NMR tube. The introduction of ^{13}CO (0.14 MPa) into the NMR tube containing **3a′** and $C_6H_{11}NH_2$ in $CDCl_3$ at 60 °C results in the formation of **3f**, [emim]-

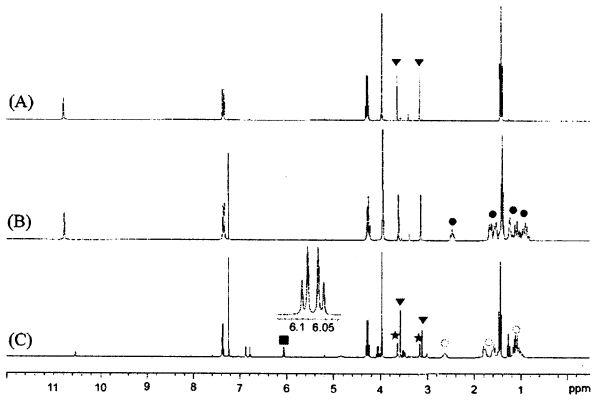


Figure 6. ^{1}H NMR spectra: (A) **3a′** in $CDCl_3$; (B) solution in (A) after addition of 1.5 equiv of $C_6H_{11}NH_2$; (C) solution in (B) after introduction of 0.14 MPa of ^{13}CO and heating to 60 °C for 1 h. Legend: (▼) SeO$^{13}C\mathit{H}_3$; (●) $C_6\mathit{H}_{11}NH_2$; (■) Se^{13}CON*H*C_6H_{11}; (★) free $^{13}C\mathit{H}_3$OH.

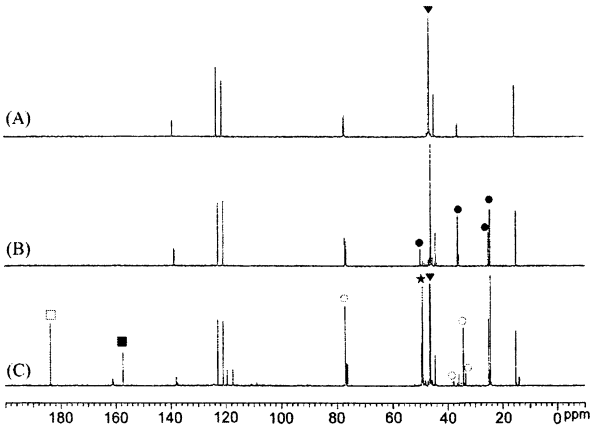
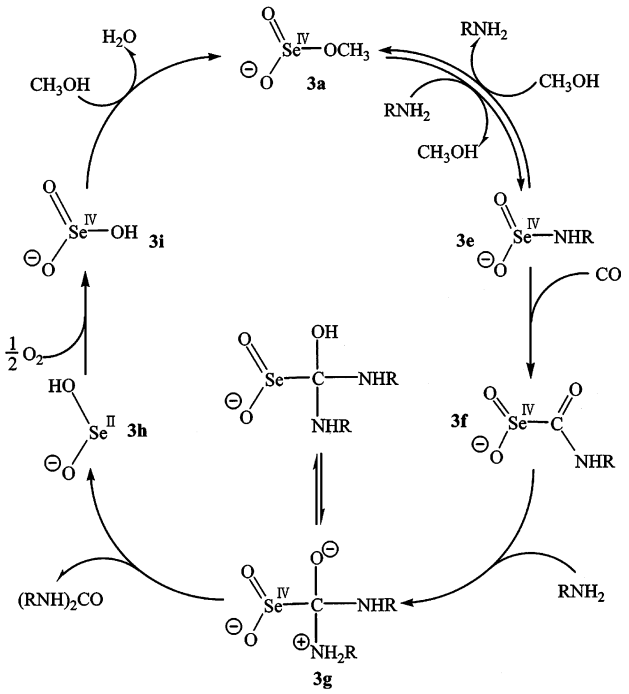


Figure 7. ^{13}C NMR spectra: (A) **3a′** in $CDCl_3$; (B) after addition of 1.5 equiv of $C_6H_{11}NH_2$ into (A); (C) solution in (B) after introduction of 0.14 MPa of ^{13}CO and heating to 60 °C for 1 h. Legend: (▼) SeO$^{13}C\mathit{H}_3$; (●) $\mathit{C}_6H_{11}NH_2$; (■) Se$^{13}\mathit{C}$ONHC_6H_{11}; (□) free ^{13}CO; (★) free $^{13}\mathit{C}H_3$OH.

[SeO_2(^{13}CONHC_6H_{11})] (Figure 7C). The peaks at 157 ppm (■) and 49 ppm (★) can be attributed tothe ^{13}C-labeled carbonyl carbon in **3f** and $^{13}\mathit{C}H_3$ in free methanol, respectively. The introduction of oxygen into the sample C resulted in the precipitation of solid dicyclohexylurea, which is insoluble in $CDCl_3$, suggesting that the carbamoyl species **3f** is an important intermediate in the oxidative carbonylation of amines.

Plausible Mechanism. On the basis of the experimental results, the mechanism for the oxidative carbonylation of an amine catalyzed by [emim][SeO_2(OCH_3)] (**3a**) is proposed as shown in Scheme 5. In the first step, the methoxy group of **3a** is likely to be replaced by an amido group to give **3e**. Amido species could take up one molecule of CO to generate selenium carbonyl species, and the subsequent insertion of CO into the Se−N bond would produce the selenium carbamoyl complex **3f**, suggested from ^{13}C labeling NMR studies. Subsequently, an additional amine could attack at the carbonyl carbon of **3f**, leading to the elimination of a molecule of urea to produce **3h**, which, in turn, reacts with oxygen and methanol to regenerate **3a**. The imidazolium-based alkylselenite compound may facilitate the redox mechanism (**3g**^{IV} → **3h**^{II} → **3i**^{IV}) by electronically communicating with imidazolium cation,[8] which

Scheme 5. Plausible Reaction Mechanism of Oxidative Carbonylation of Amine Catalyzed by 3a



gives a plausible explanation why ionic liquid methylselenite shows high catalytic activity in the oxidative carbonylation of amine.

Conclusions

Imidazolium- and phosphonium-based ionic liquids containing methylselenite anions were synthesized by the reaction of imidazolium or phosphonium halides with potassium methylselenite. The methoxy group in [Rmim][$SeO_2(OCH_3)$] was easily replaced by another alkoxy group to give [Rmim][$SeO_2(OR')$] upon interaction with R′OH (R′ = CH_3CH_2, CF_3CH_2, C_6H_5). In the absence of methanol, 1,3-dimethylimidazolium methylselenite (**4a**) is slowly transformed into the dimeric selenium species **5a**, which has been characterized by X-ray crystallographic analysis. Interestingly, upon addition of methanol to **5a**, the monomeric species **4a** is regenerated. All the imidazolium- and phosphonium-based ionic liquids containing alkylselenite anions exhibit surprisingly high activities for the oxidative carbonylation of aniline at temperatures as low as 40 °C. The maximum turnover frequency was found to be 545 h^{-1} at the aniline/catalyst molar ratio of 2025 at 60 °C. The presence of methanol in the oxidative carbonylation of aniline catalyzed by **3a** is essential in regenerating **3a** in the catalytic cycle. From the ^{13}C labeling NMR study, the carbamoyl species **3f** was found to be an important intermediate in the oxidative carbonylation of aniline.

Experimental Section

General Considerations. Amines, alkali-metal carbonates, 1-methylimidazole, 1-chlorobutane, chloroethane, chloromethane, tetra-*n*-butylphosphonium bromide, and tetraethylphosphonium bromide were purchased from Aldrich Chemical Co. Selenium dioxide and 2,2,2-trifluoroethanol were purchased from Strem Chemicals Inc. and Lancaster Synthesis Ltd., respectively, and used as received. Solvents were all reagent grade and were distilled from appropriate drying agents under a nitrogen atmosphere prior to use. Carbon monoxide and oxygen were obtained from Samsung Fine Chemical Co. and Daesung Oxygen Co., respectively. The imidazolium salts [bmim]Cl, [emim]Cl, and [dmim]Cl were prepared according to the literature procedure.[9] Gas chromatographic analyses of gaseous and liquid samples of the oxidative carbonylation experiments were made with a Gow-Mac gas chromatograph equipped with a thermal conductivity detector and a Carbosphere column (6 ft) and a Hewlett-Packard 6890 gas chromatograph equipped with a thermal conductivity detector and an HP-5 capillary column (0.32 μm × 50 m), respectively. The identities of reaction products were confirmed with a Hewlett-Packard 6890-5973 MSD GC-mass spectrometer. Urea analysis was carried out on a Waters HPLC using a 4.6 × 150 mm Hyersil ODS column and UV detector (254 nm). ^1H and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer. Elemental analysis was carried out by the Advanced Analytical Center at KIST using a Perkin-Elmer 2400 CHNS analyzer. LC-MS spectra were recorded using a Finnigan LCQ spectrometer.

Synthesis. Potassium Methylselenite (1).[8] 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 two-necked flask at room temperature for 1 h with vigorous stirring. As soon as K_2CO_3 was added, CO_2 started to evolve. Addition of THF into the resulting colorless solution produced $KSeO_2(OCH_3)$ (**1**) as a white solid. Yield: 92%. Anal. 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. ^1H NMR (300 MHz, CD_3OD, 25 °C): δ 3.35 (s).

1-*n*-Butyl-3-methylimidazolium Methylselenite (2a). A solution of [bmim]Cl (bmim = 1-*n*-butyl-3-methylimidazolium; 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 it was stirred for 6 h, the solution was filtered to remove KCl and the solvent was evaporated under reduced pressure to give **2a** as a yellow liquid. The resulting liquid was further purified by adding CH_2Cl_2 and filtered to remove excess **1** and KCl, followed by drying under high vacuum for 12 h. Yield: 85%. Anal. 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. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 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, $SeOCH_3$); 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 (s, 1H, $C_3H_3N_2$). LC-MS (CH_3OH): positive ion, 139 $[bmim]^+$; negative ion, 143 $[SeO_2(OCH_3)]^-$.

1-Ethyl-3-methylimidazolium Methylselenite (3a) and 1,3-Dimethylimidazolium Methylselenite (4a). 3a and **4a** were prepared in a manner similar to that for **2a**, by replacing [bmim]Cl with [emim]Cl (emim = 1-ethyl-3-methylimidazolium) and [dmim]Cl (dmim = 1,3-dimethylimidazolium), respectively.

3a: yield 86%. Anal. 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. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.51 (t, $^3J(H,H)$ = 7.8 Hz, 3H, CH_3); 3.47 (s, 3H, $SeOCH_3$); 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 (s, 1H, $C_3H_3N_2$). LC-MS (CH_3OH): positive ion, 111 $[emim]^+$; negative ion, 143 $[SeO_2(OCH_3)]^-$.

4a: yield 87%. Anal. 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. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.25 (s, 3H, $SeOCH_3$); 3.98 (s, 6H, 2(NCH_3)); 7.31 (s, 2H, $C_3H_3N_2$); 10.83 (s, 1H, $C_3H_3N_2$). LC-MS (CH_3OH): positive ion, 97 $[dmim]^+$; negative ion, 143 $[SeO_2(OCH_3)]^-$.

Bis(1,3-Dimethylimidazolium) Diselenite (5a). 4a was slowly transformed into **5a** upon storing under argon in the

(9) (a) Hasan, M.; Kozhevnikov, I. V.; Siddiqui, M. R. H.; Steiner, A.; Winterton, N. *Inorg. Chem.* **1999**, *38*, 5637. (b) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263.

absence of methanol for several days to give a white crystalline solid, which was recrystallized in propylene carbonate for X-ray crystallographic analysis. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.92 (s, br, 6H, 2(NCH_3)); 4.05 (s, 6H, 2(NCH_3)); 7.36 (s, 2H, $C_3H_3N_2$); 7.63 (s, br, 2H, $C_3H_3N_2$); 10.18 (s, br, 1H, $C_3H_3N_2$); 10.79 (s, 1H, $C_3H_3N_2$).

Tetra-*n*-butylphosphonium Methylselenite (6a) and Tetraethylphosphonium Methylselenite (7a). 6a and **7a** were prepared in a manner similar to that of **2a** by reacting **1** with (*n*-butyl)$_4$PBr and (ethyl)$_4$PBr.

6a: yield 92%. Anal. Calcd for $C_{17}H_{39}PSe$: C, 50.89; H, 9.73; P, 7.73; Se, 19.68. Found: C, 50.62; H, 9.69; P, 7.83; Se, 19.70. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.9 (t, 12H, 4($PC_3H_6CH_3$)); 1.49 (m, 16H, 4($PCH_2C_2H_4CH_3$)); 2.48 (m, 8H, 4($PCH_2C_3H_7$)); 3.35 (s, 3H, $SeOCH_3$).

7a: yield 80%. Anal. Calcd for $C_9H_{23}PSe$: C, 37.39; H, 7.96; P, 10.72; Se, 27.31. Found: C, 37.32; H, 7.90; P, 10.21; Se, 27.01. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.01 (t, 12H, 4(PCH_2CH_3)); 2.55 (q, 8H, 4(PCH_2CH_3)); 3.34 (s, 3H, $SeOCH_3$).

1-Ethyl-3-methylimidazolium Ethylselenite (3b) and 1-Ethyl-3-methylimidazolium 1,1,1-Trifluoroethylselenite (3c). 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 2 h to give **3b** or **3c** as a yellow liquid.

3b: yield 99%. Anal. Calcd for $C_8H_{16}N_2Se$: C, 35.97; H, 5.99; N, 10.49; Se, 29.56. Found: C, 36.01; H, 5.90; N, 10.30; Se, 28.97. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.18 (t, ^3J(H,H) = 7.2 Hz, 3H, OCH_2CH_3); 1.54 (t, ^3J(H,H) = 7.5 Hz, 3H, CH_3); 3.89 (s, br, 2H, $SeOCH_2CH_3$); 4.03 (s, 3H, NCH_3); 4.38 (q, ^3J(H,H) = 7.2 Hz, 2H, NCH_2); 7.27 (s, 1H, $C_3H_3N_2$); 7.28 (s, 1H, $C_3H_3N_2$); 10.95 (s, 1H, $C_3H_3N_2$).

3c: yield 99%. Anal. Calcd for $C_8H_{13}N_2Se$: C, 29.92; H, 4.05; N, 8.73; Se, 24.59. Found: C, 29.82; H, 4.07; N, 8.63; Se, 23.88. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.52 (t, ^3J(H,H) = 7.5 Hz, 3H, CH_3); 4.02 (s, 5H, NCH_3 + $SeOCH_2CF_3$); 4.34 (q, ^3J(H,H) = 7.2 Hz, 2H, NCH_2); 7.25 (s, 1H, $C_3H_3N_2$); 7.26 (s, 1H, $C_3H_3N_2$); 10.57 (s, 1H, $C_3H_3N_2$).

1-Ethyl-3-methylimidazolium Phenylselenite (3d). 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 2 h gave **3d** as a yellow liquid. Yield: 99%. Anal. Calcd for $C_{12}H_{16}N_2Se$: C, 45.73; H, 5.08; N, 8.89; Se, 25.06. Found: C, 45.91; H, 5.01; N, 8.81; Se, 24.97. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.45 (t, ^3J(H,H) = 7.2 Hz, 3H, CH_3); 3.95 (s, 3H, NCH_3); 4.26 (q, ^3J(H,H) = 7.2 Hz, 2H, NCH_2); 6.74 (t, ^3J(H,H) = 7.8 Hz, 1H, $SeOC_6H_5$); 6.88 (d, ^3J(H,H) = 7.8 Hz, 2H, $SeOC_6H_5$); 7.09 (t, ^3J(H,H) = 6.3 Hz, 2H, $SeOC_6H_5$); 7.02 (s, 1H, $C_3H_3N_2$); 7.01 (s, 1H, $C_3H_3N_2$); 10.18 (s, 1H, $C_3H_3N_2$).

Tetra-*n*-butylphosphonium Ethylselenite (6b) and Tetra-*n*-butylphosphonium 1,1,1-Trifluoroethylselenite (6c). A solution of **6a** (0.1 g, 0.25 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 2 h to give **6b** and **6c**.

6b: yield 99%. Anal. Calcd for $C_{18}H_{41}PSe$: C, 52.06; H, 9.88; P, 7.46; Se, 19.02. Found: C, 50.02; H, 9.83; P, 7.52; Se, 19.00. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.92 (t, 12H, 4($PC_3H_6CH_3$)); 1.10 (t, ^3J(H,H) = 6.8 Hz, 3H, $SeOCH_2CH_3$); 1.43 (m, 16H, 4($PCH_2C_2H_4CH_3$)); 2.44 (m, 8H, 4($PCH_2C_3H_7$)); 3.70 (s, br, 2H, $SeOCH_2CH_3$).

6c: yield 99%. Anal. Calcd for $C_{17}H_{38}PSe$: C, 51.02; H, 9.50; P, 7.75; Se, 19.73. Found: C, 51.00; H, 9.43; P, 7.68; Se, 19.70. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.90 (t, 12H, 4($PC_3H_6CH_3$)); 1.45 (m, 16H, 4($PCH_2C_2H_4CH_3$)); 2.47 (m, 8H, 4($PCH_2C_3H_7$)); 3.89 (s, br, 2H, $SeOCH_2CF_3$).

Tetra-*n*-butylphosphonium Phenylselenite (6d). A solution of **6a** (0.1 g, 0.25 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 2 h gave **6d**. Yield: 99%. Anal. Calcd for $C_{22}H_{41}PSe$: C, 57.04; H, 8.86; P, 6.69; Se, 17.05. Found: C, 57.12; H, 8.80; P, 6.52; Se, 16.97. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.92 (t, 12H, 4($PC_3H_6CH_3$)); 1.52 (m, 16H, 4($PCH_2C_2H_4CH_3$)); 2.50 (m, 8H, 4($PCH_2C_3H_7$)); 6.70 (t, ^3J(H,H) = 7.6 Hz, 1H, $SeOC_6H_5$); 6.81 (d, ^3J(H,H) = 7.5 Hz, 2H, $SeOC_6H_5$); 6.98 (t, ^3J(H,H) = 6.0 Hz, 2H, $SeOC_6H_5$).

[1-Ethyl-3-methylimidazolium][$SeO_2(O^{13}CH_3)$] (3a′). A solution of **3a** (0.2 g, 0.8 mmol) in $^{13}CH_3OH$ (2 mL) was stirred at room temperature for 6 h, followed by removal of the solvent under high vacuum for 4 h to give **3a′** as a yellow liquid. Yield: 99%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.41 (t, ^3J(H,H) = 7.8 Hz, 3H, CH_3); 3.40 (d, $^1J(^{13}C,H)$ = 122 Hz, 3H, $SeOCH_3$); 3.98 (s, 3H, NCH_3); 4.25 (q, ^3J(H,H) = 7.5 Hz, 2H, NCH_2); 7.36 (s, 1H, $C_3H_3N_2$); 7.38 (s, 1H, $C_3H_3N_2$); 10.79 (s, 1H, $C_3H_3N_2$).

In Situ ^{13}CO Labeling NMR Study. Inside a drybox, **3a′** (30 mg, 0.12 mmol) and cyclohexylamine (18 mg, 0.18 mmol) dissolved in $CDCl_3$ (0.5 mL) was placed into a thick-walled NMR tube (o.d. 5 mm) equipped with a Teflon valve. The NMR tube was pressurized with 0.14 MPa of ^{13}CO and then heated to 60 °C.

X-ray Crystallographic Study. Single crystals suitable for X-ray structural analysis were obtained by dissolving **5a** (0.1 g) in propylene carbonate (5 mL) and storing at 0 °C in a refrigerator for several days. A crystal with appropriate dimensions was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed at 173 K using a Siemens SMART CCD detector single-crystal X-ray diffractometer. Structure solution and refinement were carried out using the SHELXTL-PLUS (5.1) software package (G. M. Sheldrick, Siemens Analytical X-ray Division, Madison, WI, 1997). The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were treated using an appropriate fixed model. The final residual values for the observed reflections ($I > 2\sigma(I)$) and for all reflections and relevant structure refinement parameters are listed in Table 1.

Catalytic Reactions. Oxidative carbonylation reactions were conducted in a 100 mL Parr reactor equipped with a magnetic drive stirrer and an electrical heater. The reactor was charged with known amounts of an 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 gas reservoir equipped with a high-pressure regulator and a pressure transducer. The drop in pressure in the gas reservoir was recorded as a function of time to observe the progress of the reaction. After the reaction was completed, the reactor was cooled to room temperature and the reaction mixture was filtered off to remove solid urea. The resulting solution and the isolated urea were analyzed by GC, HPLC, and GC-MS.

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Supporting Information Available: Tables of crystallographic data (excluding structure factors) for compound **5a**. This material is available free of charge via the Internet at http://pubs.acs.org. These data have also been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-200274. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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