Utilization of *N,N*-Dialkylcarbamic Acid Derived from Secondary Amines and Supercritical Carbon Dioxide: Stereoselective Synthesis of *Z* Alkenyl Carbamates with a CO$_2$-Soluble Ruthenium–P(OC$_2$H$_5$)$_3$ Catalyst

Yoshihito Kayaki, Tomoyuki Suzuki, and Takao Ikariya*[a]

Abstract: Reversible transformation of diethylamine (**1**) and supercritical carbon dioxide (scCO$_2$) into *N,N*-diethylcarbamic acid (**2**) was confirmed by direct acquisition of ^{1}H and ^{13}C{^{1}H} NMR spectra. The equilibrium between **1**+CO$_2$ and **2** is strongly influenced by conditions of the supercritical state. Low temperature favors formation of carbamic acid, whereas high temperature causes decarboxylation. On the basis of the spectroscopic results of carbamic acid formation under scCO$_2$ conditions, the ruthenium-catalyzed formation of alkenyl carbamates from terminal alkynes, **1**, and carbon dioxide was investigated to demonstrate the useful transformation of elusive carbamic acids. Selectivity toward the CO$_2$-fixation products over enynes obtained by dimerization of the alkyne substrates was improved by the use of scCO$_2$ as a reaction medium. In particular, a CO$_2$-soluble ruthenium complex, *trans*-[RuCl$_2${P(OC$_2$H$_5$)$_3$}$_4$], was found to be effective in affording *Z* alkenyl carbamates with high stereoselectivity.

Keywords: alkynes · amines · carbon dioxide fixation · homogeneous catalysis · ruthenium

Introduction

The synthetic utilization of CO$_2$ has received much attention from the viewpoint of practical and environmental issues.[1] Acidic CO$_2$ can react readily with primary and secondary amines to form carbamic acids or their ammonium salts; these processes are valuable for CO$_2$ capture. However, reverse decarboxylation from these carbamate moieties takes place easily under certain conditions,[2,3,4] and further transformation of carbamic acids into fairly long-lived products such as urethanes and ureas is required for practical CO$_2$ fixation.

Supercritical CO$_2$ (scCO$_2$) has been recognized to offer advantages as a reaction medium and a reactant owing to its unique physical properties, such as high gaseous miscibility, effective mass transfer, and weakening of the solvation interactions around the reacting species.[5] In fact, it was suggested that scCO$_2$ is a promising reaction medium for efficient CO$_2$-fixation processes as opposed to conventional organic solvents.[6,7] We developed a high-pressure NMR cell assembly fitted for commercial probes without special modification of the spectrometer and investigated the solubility of the metal complexes, the chemical behavior of the reactant, and the solute–solvent interactions in scCO$_2$.[8] Direct spectroscopic observation of chemical species in scCO$_2$ can provide deep insight into its potential benefits as a reaction medium for CO$_2$-fixation processes. The present work investigates the dynamic behavior of diethylamine in scCO$_2$ by means of the high-pressure NMR system and to elucidate the influence of supercritical conditions on the equilibrium between amine+CO$_2$ and carbamic acid (Scheme 1). For

$$(C_2H_5)_2NH \;+\; CO_2 \;\rightleftharpoons\; (C_2H_5)_2NCOOH$$
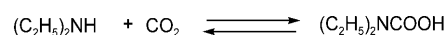
Scheme 1. Reversible formation of *N,N*-diethylcarbamic acid from diethylamine and CO$_2$.

the utilization of carbamic acids generated in scCO$_2$, we also investigated the synthesis of alkenyl carbamates from terminal alkynes, amines, and CO$_2$ in the presence of Ru catalysts. On the basis of the NMR spectroscopic study of the formation of *N,N*-diethylcarbamic acid in scCO$_2$, the effects of temperature and pressure on the outcome of the reaction as well as the reaction mechanism are discussed.

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FULL PAPERS

Results and Discussion

NMR Spectroscopic Investigation of the Reaction of Diethylamine and scCO$_2$

We first investigated the ^{1}H and ^{13}C NMR spectra of a mixture of CO$_2$ and diethylamine (**1**; 3.4×10^{-2} M) by using a high-pressure cell[8] under supercritical conditions with various pressures and temperatures. Figure 1 depicts the forma-
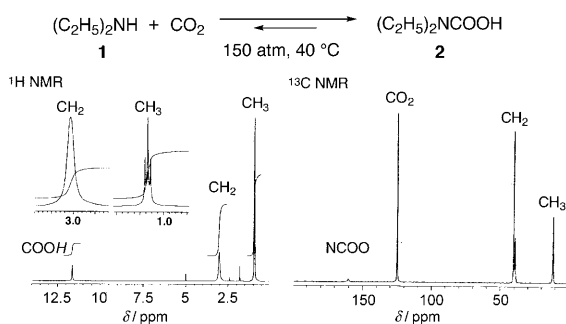

Figure 1. High-pressure ^{1}H and ^{13}C{^{1}H} NMR spectra of *N,N*-diethylcarbamic acid **2** derived from diethylamine **1** and 15.0 MPa of CO$_2$ at 40 °C.

tion of *N,N*-diethylcarbamic acid **2** from **1** in homogeneous scCO$_2$ solution at 15.0 MPa and 40 °C.[9] The characteristic ^{1}H NMR signal at 12.0 ppm associated with the carboxy proton is in accord with that in relevant reports.[10] The CH$_2$ signal of the ethyl group observed at 3.0 ppm was broad despite the sharpness of the CH$_3$ triplet signal, possibly because the protons of the CH$_2$ group are not fully averaged owing to hindered rotation around the amide C−N bond of **2**. The ^{13}C NMR spectrum displays a broad signal arising from the carbonyl carbon atom at around 160 ppm, which indicates that a CO$_2$ molecule had inserted into the N−H bond of diethylamine to form the urethane (NCOO) structure. Notably, **1** was not converted into **2** in CDCl$_3$ under otherwise identical conditions (15.0 MPa, 40 °C); therefore, formation of the carbamic acid was markedly promoted in scCO$_2$.

The equilibrium between **1**+CO$_2$ and **2** is strongly influenced by temperature. In an array of ^{1}H NMR spectra at various temperatures (Figure 2), the signal arising from the acidic proton of **2** shifted to higher frequency with increasing temperature and then appeared at 1.22 ppm, a chemical shift that approaches that of a free amine proton, at 140 °C. This suggests that the equilibrium shifts to **1** upon heating.[11] According to the Le Chatelier principle, this observation is consistent with the exothermic nature of the reaction between amines and CO$_2$, thus facilitating the reverse decarboxylation of **2** at higher temperature.

Ruthenium-Catalyzed Reaction of Terminal Alkynes and Diethylamine in scCO$_2$

On the basis of the fact that scCO$_2$ facilitates the formation of *N,N*-diethylcarbamic acid **2** from diethylamine **1**, we in-
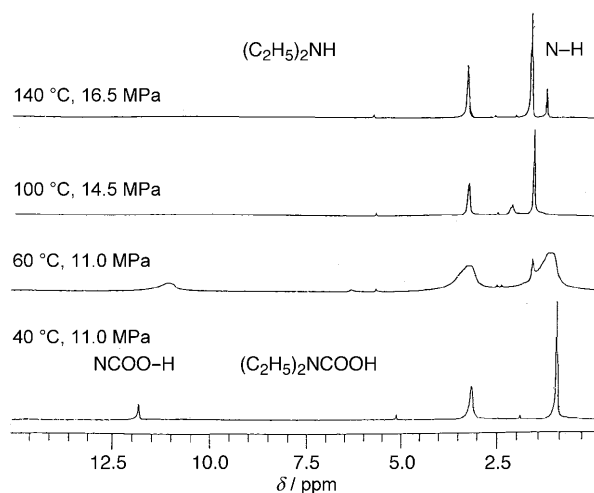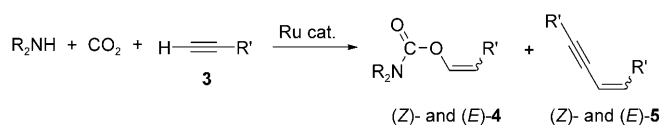

Figure 2. Observation of the dynamic behavior between **1** and **2** by high-pressure ^{1}H NMR spectroscopy at different temperatures.

vestigated the ruthenium-catalyzed transformation of amines into alkenyl carbamates **4** by addition of the carbamic acids generated in situ to terminal alkynes **3** (Scheme 2).

Scheme 2. Ru-catalyzed reaction of terminal alkynes, secondary amines, and CO$_2$.

Dixneuf and co-workers[12] originally studied the same reaction in organic solvents containing mono- or multinuclear Ru catalysts. The reaction with 1-hexyne catalyzed by [Ru-(cod)(cot)] (cod=1,5-cyclooctadiene, cot=cyclooctatetraene) and phosphines was also reported by Mitsudo et al.[13] Baiker and co-workers demonstrated the reaction of phenylacetylene (**3a**), **1**, and CO$_2$ in the presence of [RuCl$_2$(η^6-C$_6$H$_6$)(PMe$_3$)] or [RuCl$_2$(C$_5$H$_5$N)$_4$] under supercritical conditions.[14,15] However, these catalyst systems gave only modest selectivity toward the desired carbamate product, owing to simultaneous formation of conjugated enynes **5** arising from catalytic dimerization of the alkyne substrate.

As we revealed previously, alkyl phosphites are effective supporting ligands for the preparation of CO$_2$-soluble transition-metal complexes.[8a,16] Direct observation of the equilibrium between **1** and **2** in scCO$_2$ discussed above prompted us to study the details of the addition of carbamic acids to **3** with a CO$_2$-philic Ru–P(OC$_2$H$_5$)$_3$ catalyst.

When a 1:2 mixture of **3a** and **1** was treated with 8.0 MPa of CO$_2$ in the presence of [RuCl$_2${P(OC$_2$H$_5$)$_3$}$_4$] (8.0×10^{-2} mmol; S/C=50) at 80 °C, the alkyne substrate was almost completely consumed after 15 h reaction time (Table 1).[17] GC and NMR spectroscopic analyses of the product mixture revealed that an anti-Markovnikov adduct, the *Z* alkenyl carbamate, (*Z*)-**4a**, was preferentially formed

Table 1. Time course for the formation of **4a** and **5a**.[a]

Entry	t [h]	Conv. [%][b]	Yield [%][b]			
			(Z)-**4a**	(E)-**4a**	(Z)-**5a**	(E)-**5a**
1	2.5	46	27	<1	2	5
2	5	69	45	<1	2	8
3	10	89	63	<1	4	12
4	15	99	79	<1	4	12
5	20	99	83	<1	5	11

[a] Reaction conditions: *trans*-[RuCl₂{P(OC₂H₅)₃}₄] (8.0×10⁻² mmol), **3a** (4.0 mmol), **1** (8.0 mmol), CO₂ (8.0 MPa), 80 °C. [b] Determined by GC.

with the *E* alkenyl carbamate, (*E*)-**4a**, and enynes (*E*)-**5a** and (*Z*)-**5a** as minor products. A series of reactions of **3a** with **1** in scCO₂ catalyzed by Ru complexes are summarized in Table 2. The ratio of alkyne and amine substrates affected the outcome of the reaction; the yield of (*Z*)-**4a** improved with an increase in the molar ratio of **1** to **3a** from 1:1 to 1:4 (Table 2, entries 1–3).

Table 2. Ru-catalyzed reaction of phenylacetylene and diethylamine in scCO₂.[a]

Entry	Ru catalyst	1/3a	Yield [%][b]			
			(Z)-**4a**	(E)-**4a**	(Z)-**5a**	(E)-**5a**
1	*trans*-[RuCl₂{P(OC₂H₅)₃}₄]	4	85	<1	2	12
2	*trans*-[RuCl₂{P(OC₂H₅)₃}₄]	2	79	<1	4	12
3	*trans*-[RuCl₂{P(OC₂H₅)₃}₄]	1	63	<1	5	13
4	*trans*-[RuCl₂{P(OC₂H₅)₃}₄]	2	26	2	6	9
5	*trans*-[RuCl₂{P(CH₃)₃}₄]	2	3	0	11	36
6	*trans*-[RuCl₂{P(OCH₂CF₃)₃}₄]	2	40	2	17	20
7	*cis*-[RuH₂{P(OC₂H₅)₃}₄]	2	21	0	5	14
8	*trans*-[RuCl₂{P(OC₂H₅)₃}₄][c]	2	6	<1	4	5

[a] Reaction conditions: Ru catalyst (8.0×10⁻² mmol), **3a** (4.0 mmol), CO₂ (8 MPa), 80 °C, 15 h. [b] Determined by GC. [c] CH₃CN (10 mL) was added.

Dichlororuthenium(II) complexes with P(OC₆H₅)₃ and P-(CH₃)₃ ligands were less effective in terms of catalyst activity and selectivity toward the carbamate product (*E*)-**4a** (Table 2, entries 4 and 5). Optimal results obtained by use of *trans*-[RuCl₂{P(OC₂H₅)₃}₄] imply that the reaction may proceed preferably in the CO₂ phase in which the catalyst and substrate molecules are both dissolved.[18] Other CO₂-soluble Ru catalysts, such as the Ru–P(OCH₂CF₃)₃ complex and an isolable dihydrido complex, *cis*-[RuH₂{P(OC₂H₅)₃}₄], also worked under supercritical conditions; however, the selectivity toward carbamate formation with these complexes was lower than that with *trans*-[RuCl₂{P(OC₂H₅)₃}₄] (Table 2, entries 6 and 7). The positive effect of the scCO₂ medium for promoting CO₂ fixation was clearly demonstrated by comparison with the solution-phase reaction performed in 10 mL of CH₃CN (Table 2, entry 8).

Catalyst performance was markedly influenced by temperature and pressure. Figure 3 shows the effect of temperature on the yields of **4a** and **5a**. The yield of (*Z*)-**4a** increased significantly with an increase in temperature from 50 to 80 °C and then decreased toward 100 °C, whereas the total yields of enynes (*E*)- and (*Z*)-**5a** proportionally increased
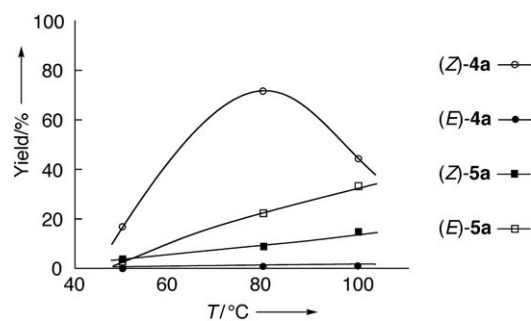

Figure 3. Effect of temperature on carbamate and enyne formation. Reaction conditions: *trans*-[RuCl₂{P(OC₂H₅)₃}₄] (8.0×10⁻² mmol), **3a** (4.0 mmol), **1** (8.0 mmol), CO₂ (8.0 MPa), 15 h.

with increasing the temperature. The loss of carbamate selectivity at elevated temperature is attributable to easy release of CO₂ from *N,N*-diethylcarbamic acid upon heating, as observed by the NMR experiments (see above).

A bell-shaped curve was also observed in the reaction pressure–yield plots (Figure 4). A positive pressure effect on
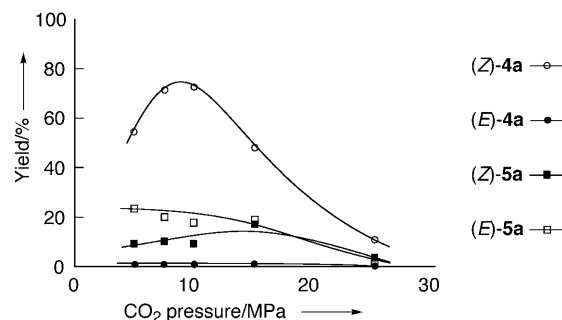

Figure 4. Effect of CO₂ pressure on carbamate and enyne formation. Reaction conditions: *trans*-[RuCl₂{P(OC₂H₅)₃}₄] (8.0×10⁻² mmol), **3a** (4.0 mmol), **1** (8.0 mmol), 80 °C, 15 h.

vinyl carbamate formation was observed in the CO₂ pressure range of 5–10 MPa, which might be explained by promotion of carbamic acid formation from amines and the dense CO₂. Further increase in pressure resulted in deactivation of the catalyst for carbamate formation and dimerization of **3a**, possibly arising from a high-dilution problem caused by high CO₂ density, as was often observed for homogeneous reactions in scCO₂.[4, 16]

The Ru–P(OC₂H₅)₃ catalyst system was found to be applicable to the production of alkenyl *N,N*-dialkyl carbamates[19] from a variety of terminal alkynes (Scheme 3 and Table 3). The addition of *N,N*-diethylcarbamic acid to phenylacetylene derivatives **3a–c** gave the *Z* alkenyl carbamates in 54–68% yields but with excellent regio- and stereoselectivities (Table 3, entries 1–3). Whereas the enyne substrate **3d** reacted under similar conditions, relatively harsh reaction conditions with prolonged reaction time were required for aliphatic terminal alkyne **3e** to yield the *Z* carbamate product (Table 3, entries 4 and 5). The selective reaction also oc-
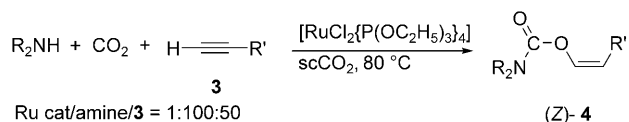
Scheme 3. Synthesis of enol carbamates catalyzed by *trans*-[RuCl$_2${P-(OC$_2$H$_5$)$_3$}$_4$].

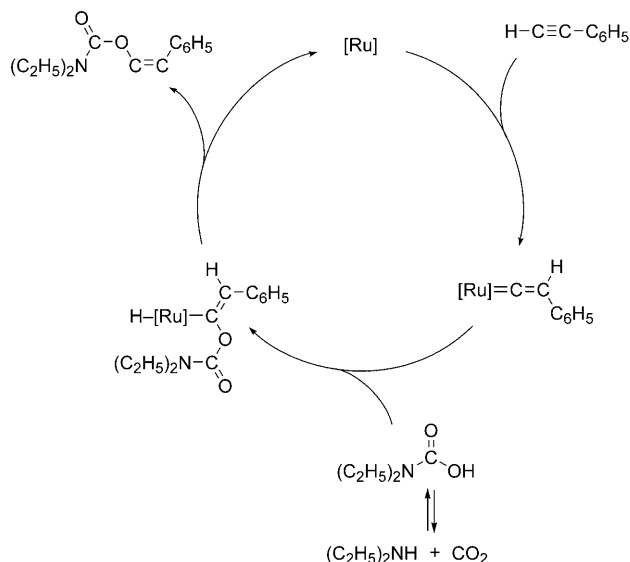Table 3. Ru-catalyzed reaction of terminal alkynes and secondary amines in scCO$_2$.[a]

Entry	Alkyne	R	Amine	Product	Yield [%][b]
1	3a	C$_6$H$_5$	(C$_2$H$_5$)$_2$NH	(Z)-4a	68
2	3b	*p*-CH$_3$-C$_6$H$_4$	(C$_2$H$_5$)$_2$NH	(Z)-4b	56
3	3c	*m*-Cl-C$_6$H$_4$	(C$_2$H$_5$)$_2$NH	(Z)-4c	54
4	3d	1-cyclohex-enyl	(C$_2$H$_5$)$_2$NH	(Z)-4d	35
5[c]	3e	C$_6$H$_5$(CH$_2$)$_2$	(C$_2$H$_5$)$_2$NH	(Z)-4e	39
6	3a	C$_6$H$_5$	[(CH$_3$)$_2$NH$_2$][(CH$_3$)$_2$NCO$_2$][d]	(Z)-4f	31
7	3a	C$_6$H$_5$	(C$_6$H$_5$CH$_2$)$_2$NH	(Z)-4g	45

[a] Reaction conditions: 3 (4.0 mmol), amine (8.0 mmol), [RuCl$_2${P(OC$_2$H$_5$)$_3$}$_4$] (8.0×10^{-2} mmol), 8.0 MPa, 80°C, 15 h. [b] Yield of isolated product. [c] The reaction was performed at 9.0 MPa and 100°C for 60 h. [d] The ammonium carbamate [(CH$_3$)$_2$NH$_2$][(CH$_3$)$_2$NCO$_2$] (4.0 mmol) was used as a source of the dimethylamine moiety.

curred with other secondary amine derivatives. When dimethylammonium *N,N*-dimethylcarbamate, [(CH$_3$)$_2$NH$_2$][(CH$_3$)$_2$NCO$_2$], was employed as an alternative to dimethylamine under the optimized conditions, the corresponding *Z* carbamate was obtained in 31% yield (Table 3, entry 6). Dibenzylamine, which is more amenable to the formation of *N,N*-dibenzylcarbamic acid,[3b] also afforded the desired product in a similar manner (Table 3, entry 7).

Mechanism of Formation of *Z* Alkenyl Carbamates and Enynes

Previous work on the Ru-catalyzed hydrooxycarbonylation of terminal alkynes implied that the catalytic cycle involves a vinylidene–ruthenium intermediate (Scheme 4).[20] Carbamate formation is explicable by the generation of carbamic acids from secondary amines and CO$_2$ and subsequent attack on the α-carbon atom of vinylidene intermediate 6 generated from the Ru precursor and the terminal alkyne[21] (Scheme 4, cycle A). The formation of 4 as anti-Markovnikov adducts can be clearly explained by the present 1,1-insertion mechanism. Moreover, the trend in *Z* carbamate selectivity is also consistent with that reported in the addition of carboxylic acids to terminal alkynes.[22] Thus, the reaction proceeds stereoselectively through a *trans* addition of carbamic acids to C–C triple bonds. The possible vinylidene species 6 can react competitively with another alkyne molecule to afford 5 as undesired enyne products (Scheme 4, cycle B). Owing to the pivotal role of the vinylidene–ruthenium(II) complex in the reaction of carbamic acids with terminal alkynes as well as in alkyne dimerization, the equilib-

Scheme 4. Possible reaction pathway for the Ru-catalyzed reaction of terminal alkynes and secondary amines in scCO$_2$.

rium between amines and carbamic acids is crucial for the control of the selectivity in the catalytic system. Indeed, the reaction with scCO$_2$ offers remarkable enhancement of carbamate selectivity on the basis of the facile formation of carbamic acids.

Conclusions

By using the high-pressure NMR system, we confirmed that the scCO$_2$ medium facilitates the formation of *N,N*-diethylcarbamic acid from diethylamine. On the basis of the spectroscopic results of carbamic acid formation under supercritical conditions, Ru-catalyzed reaction of terminal alkynes and carbamic acids generated from secondary amines and CO$_2$ was demonstrated as a promising CO$_2$-fixation process. In fact, efficient synthesis of *Z* alkenyl carbamates was achieved in scCO$_2$ containing *trans*-[RuCl$_2${P(OC$_2$H$_5$)$_3$}$_4$] complex as the CO$_2$-soluble catalyst. Furthermore, we also revealed that the competitive dimerization of alkynes can be suppressed by tuning the operating conditions and with proper catalyst design. These findings provide a promising avenue to utilize scCO$_2$ as both the reactant and the reaction medium.

Experimental Section

General Considerations

Catalyst preparation was conducted under argon atmosphere with Schlenk techniques. Solvents and amines were used after drying and distillation and stored under argon. Terminal alkynes were freshly distilled under argon before use. Special-grade liquefied CO$_2$ (99.999% purity) was used as received from commercial suppliers. Ru complexes *trans*-[RuCl$_2${P(OC$_2$H$_5$)$_3$}$_4$],[23] *cis*-[RuH$_2${P(OC$_2$H$_5$)$_3$}$_4$],[24] *trans*-[RuCl$_2${P(OCH$_2$CF$_3$)$_3$}$_4$],[8a] and *trans*-[RuCl$_2${P(OC$_6$H$_5$)$_3$}$_4$][25] were synthesized ac-

cording to the reported preparative methods. NMR spectra of the carbamate products were recorded on a JEOL Lambda 300 spectrometer for ^1H (referenced to $Si(CH_3)_4$ by residual solvent protons) and $^{13}C\{^1H\}$ (referenced to $Si(CH_3)_4$ by the solvent resonance). Coupling constants (J) are given in hertz (Hz), and spin multiplicities are indicated as follows: d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Gas chromatography was carried out on a GL Science GC-353 chromatograph equipped with a G-100 column (1.2-mm I.D.×40 m) and N_2 as carrier gas. IR spectra were recorded on a Jasco FTIR-610 spectrometer. Mass spectra were measured by using a JEOL JMS-T100LC mass spectrometer. Elemental analysis was carried out using a PE2400 Series II CHNS/O Analyzer (Perkin Elmer).

High-Pressure NMR Experiments

High-pressure ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a 300-MHz NMR spectrometer (JEOL LA-300) operating at a proton frequency of 300.5 MHz and a carbon frequency of 75.6 MHz, respectively. C_6D_6 was used as the external standard for measuring the ^1H and ^{13}C NMR chemical shifts. The experimental setup is presented in our previous report.[8a] The high-pressure cell assembly consisted of a nonmagnetic Ti–Al alloy valve and a zirconia tube with a inner volume of 3.4 mL. The valves were attached to the top of the zirconia tube and fixed with Kalrez perfluoroelastomer O rings. CO_2 solvent was provided through stainless-steel capillaries to the cell controlled by a syringe pump (ISCO model 260D). The pressure of the system was maintained with a back-pressure regulator (JASCO model 880–81). The assembly was operated at a pressure of up to 25 MPa in a nonspinning mode, and the temperature of the probe can be controlled with heated air up to 423 K.

Before the NMR spectra were recorded, **1** (12.1 μL, 0.117 mmol) was placed in the high-pressure cell and degassed by freeze–pump–thaw cycles at −78 °C. After the introduction of CO_2 at 35 °C, the pressure of the system and the temperature in the NMR probe were set to the desired value. The system was allowed to equilibrate until the pressure reading was stable for at least 15 min.

Syntheses

Typical experimental procedure for the catalytic reaction of terminal alkynes with amines and CO_2: A 50-mL reactor equipped with a magnetic stirrer bar and a small vial was charged with argon gas in a desiccator. *trans*-[RuCl$_2$(P(OC$_2$H$_5$)$_3$)$_4$] (67 mg, 8.0×10^{-2} mmol) was placed in this vial, and **1** (585 mg, 8.0 mmol) and **3a** (410 mg, 4.0 mmol) were added to the reactor (outside the vial) with a syringe. Subsequently, the reactor was placed in an oven at 80 °C, and the reactor was then filled with CO_2 (8.0 MPa) through a cooling apparatus with an HPLC pump (Jasco PU-2080). After the mixture was stirred for 15 h, the reactor was cooled in a bath of methanol with dry ice, and the CO_2 was vented. The reaction mixture was collected and analyzed by GC with n-C$_{12}$H$_{26}$ as internal standard. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate=40:1→20:1) to afford (*Z*)-**4a** (593 mg, 68%) as a pale-yellow liquid. Effects of the catalyst and substrates, CO_2 pressure, and reaction temperature were examined in a similar manner with variation of the reaction conditions.

(*Z*)-**4a**: (*Z*)-2-Phenylethenyl *N,N*-diethylcarbamate: IR (CHCl$_3$): $\tilde{v}$=2980 (m), 1714 (vs), 1661 (m), 1475 (m), 1423 (s), 1382 (m), 1272 cm^{-1}(s); ^1H NMR (300.5 MHz, CDCl$_3$): δ=1.18 (t, $^3J_{H,H}$=7.1 Hz, 3H, NCH$_2$CH_3), 1.23 (t, $^3J_{H,H}$=7.1 Hz, 3H, NCH$_2$CH_3), 3.37 (q, $^3J_{H,H}$=7.1 Hz, 2H, NCH_2CH$_3$), 3.42 (q, $^3J_{H,H}$=7.1 Hz, 2H, NCH_2CH$_3$), 5.61 (d, $^3J_{H,H}$=7.3 Hz, 1H, C=CH), 7.1–7.4 (m, 4H, C=CH and C$_6$H$_5$), 7.53 ppm (d, $^3J_{H,H}$=7.3 Hz, 2H, C$_6$H$_5$); ^{13}C NMR (75.6 MHz, CDCl$_3$): δ=13.2, 14.0, 41.6, 42.2, 109.3, 126.6, 128.2, 128.5, 134.5, 135.4, 152.7 ppm; HRMS (ESI): m/z calcd for C$_{13}$H$_{17}$NNaO$_2$: 242.1157 [M+Na]$^+$; found: 242.1190; elemental analysis: calcd for C$_{13}$H$_{17}$NO$_2$: C 71.21, H 7.81, N 6.39; found: C 71.13, H 7.92, N 6.42.

(*Z*)-**4b**: According to the procedure for the preparation of (*Z*)-**4a**, (*Z*)-2-(4′-methylphenyl)ethenyl *N,N*-diethylcarbamate ((*Z*)-**4b**; 519 mg, 56%) was obtained as a pale-yellow liquid after purification by column chromatography. IR (CHCl$_3$): $\tilde{v}$=2980 (m), 1713 (vs), 1663 (m), 1513 (m), 1475 (s), 1430 (s), 1381 (m), 1272 cm^{-1}(s); ^1H NMR (300.5 MHz, CDCl$_3$): δ=

1.18 (t, $^3J_{H,H}$=7.1 Hz, 3H, NCH$_2$CH_3), 1.24 (t, $^3J_{H,H}$=7.1 Hz, 3H, NCH$_2$CH_3), 2.33 (s, 3H, C$_6$H$_4$CH_3), 3.38 (q, $^3J_{H,H}$=7.1 Hz, 2H, NCH_2CH$_3$), 3.43 (q, $^3J_{H,H}$=7.1 Hz, 2H, NCH_2CH$_3$), 5.58 (d, $^3J_{H,H}$=7.3 Hz, 1H, C=CH), 7.13 (d, $^3J_{H,H}$=8.1 Hz, 2H, C$_6$H$_4$), 7.24 (d, $^3J_{H,H}$=7.3 Hz, 1H, C=CH), 7.43 ppm (d, $^3J_{H,H}$=8.1 Hz, 2H, C$_6$H$_4$); ^{13}C NMR (75.6 MHz, CDCl$_3$): δ=13.2, 14.0, 21.1, 41.6, 42.2, 109.3, 128.4, 128.9, 131.7, 134.8, 136.4, 152.8 ppm; elemental analysis: calcd for C$_{14}$H$_{19}$NO$_2$: C 72.07, H 8.21, N 6.00; found: C 72.09, H 8.41, N 5.91.

(*Z*)-**4c**: According to the procedure for the preparation of (*Z*)-**4a**, (*Z*)-2-(3′-chlorophenyl)ethenyl *N,N*-diethylcarbamate ((*Z*)-**4c**; 546 mg, 2.15 mmol, 54%) was obtained as a pale-yellow liquid after purification by column chromatography. IR (CHCl$_3$): $\tilde{v}$=2980 (m), 1718 (vs), 1659 (m), 1475 (s), 1430 (s), 1382 (m), 1271 cm^{-1} (s); ^1H NMR (300.5 MHz, CDCl$_3$): δ=1.17 (t, $^3J_{H,H}$=7.1 Hz, 3H, NCH$_2$CH_3), 1.26 (t, $^3J_{H,H}$=7.1 Hz, 3H, NCH$_2$CH_3), 3.37 (q, $^3J_{H,H}$=7.1 Hz, 2H, NCH_2CH$_3$), 3.43 (q, $^3J_{H,H}$=7.1 Hz, 2H, NCH_2CH$_3$), 5.54 (d, $^3J_{H,H}$=7.1 Hz, 1H, C=CH), 7.1–7.4 (m, 4H, C$_6$H$_4$ and C=CH), 7.24 ppm (s, 1H, C$_6$H$_4$); ^{13}C NMR (75.6 MHz, CDCl$_3$): δ=13.2, 14.1, 41.8, 42.5, 108.0, 126.6, 126.7, 128.4, 129.4, 134.1, 136.3, 136.5, 152.4 ppm; HRMS (ESI): m/z calcd for C$_{13}$H$_{16}$ClNNaO$_2$: 276.07673 [M+Na]$^+$; found: 276.07593.

(*Z*)-**4d**: According to the procedure for the preparation of (*Z*)-**4a**, (*Z*)-2-(1′-cyclohexenyl)ethenyl *N,N*-diethylcarbamate ((*Z*)-**4d**; 310 mg, 1.38 mmol, 35%) was obtained as a pale-yellow liquid after purification by column chromatography. IR (CHCl$_3$): $\tilde{v}$=2935 (m), 1705 (vs), 1475 (s), 1433 (s), 1381 (m), 1274 cm^{-1}(s); ^1H NMR (300.5 MHz, CDCl$_3$): δ=1.13 (t, $^3J_{H,H}$=7.1 Hz, 6H, NCH$_2$CH_3), 1.50–1.68 (m, 4H, CH$_2$), 2.08 (br, 2H, CH$_2$), 2.37 (br, 2H, CH$_2$), 3.31 (q, $^3J_{H,H}$=7.1 Hz, 4H, NCH_2CH$_3$), 5.08 (d, $^3J_{H,H}$=7.3 Hz, 1H, C=CH), 5.74 (s, 1H, C=CH), 6.86 ppm (d, $^3J_{H,H}$=7.3 Hz, 1H, C=CH); ^{13}C NMR (75.6 MHz, CDCl$_3$): δ=13.3, 14.1, 21.9, 22.9, 25.8, 28.1, 41.4, 42.0, 112.8, 128.2, 132.4, 133.0, 153.0 ppm; HRMS (ESI) m/z calcd for C$_{13}$H$_{21}$NNaO$_2$: 246.1470 [M+Na]$^+$; found: 246.1469.

(*Z*)-**4e**: According to the procedure for the preparation of (*Z*)-**4a**, (*Z*)-4-phenylbut-1-en-1-yl *N,N*-diethylcarbamate ((*Z*)-**4e**; 386 mg, 1.56 mmol, 39%) was obtained as a pale-yellow liquid after purification by column chromatography. IR (CHCl$_3$): $\tilde{v}$=2935 (m), 1703 (vs), 1429 (s), 1274 cm^{-1}(s); ^1H NMR (300.5 MHz, CDCl$_3$): δ=1.14 (t, $^3J_{H,H}$=7.1 Hz, 6H, NCH$_2$CH_3), 2.43 (dt, $^3J_{H,H}$=8.0, 7.3 Hz, 2H, CH$_2$), 2.43 (t, $^3J_{H,H}$=7.3 Hz, 2H, CH$_2$), 3.25–3.33 (m, 4H, NCH_2CH$_3$), 4.77 (dt, $^3J_{H,H}$=6.4, 7.3 Hz, 1H, C=CH), 6.98 (d, $^3J_{H,H}$=6.4 Hz, 1H, C=CH), 7.1–7.3 ppm (m, 5H, C$_6$H$_5$); ^{13}C NMR (75.6 MHz, CDCl$_3$): δ=13.2, 14.0, 21.1, 41.6, 42.2, 109.3, 128.4, 128.9, 131.7, 134.8, 136.4, 152.8 ppm; HRMS (ESI): m/z calcd for C$_{15}$H$_{21}$NNaO$_2$: 270.1470 [M+Na]$^+$; found: 270.1465.

(*Z*)-**4f**: According to the procedure for the preparation of (*Z*)-**4a**, (*Z*)-2-phenylethenyl *N,N*-dimethylcarbamate ((*Z*)-**4f**; 240 mg, 1.25 mmol, 31%) was obtained as a pale-yellow liquid after purification by column chromatography. IR (CHCl$_3$): $\tilde{v}$=2938 (w), 1720 (vs), 1661 (m), 1493 (m), 1446 (m), 1371 (s), 1241 cm^{-1}(m); ^1H NMR (300.5 MHz, CDCl$_3$): δ=1.18 (t, $^3J_{H,H}$=7.1 Hz, 3H, NCH$_2$CH_3), 1.23 (t, $^3J_{H,H}$=7.1 Hz, 3H, NCH$_2$CH_3), 3.37 (q, $^3J_{H,H}$=7.1 Hz, 2H, NCH_2CH$_3$), 3.42 (q, $^3J_{H,H}$=7.1 Hz, 2H, NCH_2CH$_3$), 5.61 (d, $^3J_{H,H}$=7.3 Hz, 1H, C=CH), 7.1–7.4 (m, 4H, C=CH and C$_6$H$_5$), 7.53 ppm (d, $^3J_{H,H}$=7.3 Hz, 2H, C$_6$H$_5$); ^{13}C NMR (75.6 MHz, CDCl$_3$): δ=13.2, 14.0, 41.6, 42.2, 109.3, 126.6, 128.2, 128.5, 134.5, 135.4, 152.7 ppm; elemental analysis: calcd for C$_{11}$H$_{13}$NO$_2$: C 69.09, H 6.85, N 7.32; found: C 68.75, H 6.94, N 7.36.

(*Z*)-**4g**: According to the procedure for the preparation of (*Z*)-**4a**, (*Z*)-2-phenylethenyl *N,N*-dibenzylcarbamate ((*Z*)-**4g**; 620 mg, 45%) was obtained as a white powder after purification by column chromatography. IR (KBr): $\tilde{v}$=3056 (w), 3029 (w), 1715 (s), 1661 (m), 1494 (m), 1464 (m), 1449 (m), 1432 (m), 1382 (m), 1222 (s), 1098 cm^{-1} (s); ^1H NMR (300.5 MHz, CDCl$_3$): δ=4.60 (s, 4H, NCH_2C$_6$H$_5$), 5.69 (d, $^3J_{H,H}$=7.3 Hz, 1H, C=CH), 7.1–7.5 ppm (m, 16H, C=CH and C$_6$H$_5$); ^{13}C NMR (75.6 MHz, CDCl$_3$): δ=49.2, 50.1, 110.2, 126.8, 126.9, 127.6, 127.7, 128.17, 128.20, 128.6, 128.7, 128.8, 134.1, 135.4, 136.5, 136.6, 153.9 ppm; elemental analysis: calcd for C$_{23}$H$_{21}$NO$_2$: C 80.44, H 6.16, N 4.08; found: C 80.65, H 6.00, N 3.80.

FULL PAPERS

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