DOI: 10.1002/adsc.201300007

Polystyrene-Supported N-Heterocyclic Carbene–Silver Complexes as Robust and Efficient Catalysts for the Reaction of Carbon Dioxide and Propargylic Alcohols

Xiaodong Tang,[a] Chaorong Qi,[a,]* Haitao He,[a] Huanfeng Jiang,[a,]* Yanwei Ren,[a] and Gaoqing Yuan[a]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China
Fax: (+86)-20-8711-2906; e-mail: crqi@scut.edu.cn or jianghf@scut.edu.cn

Received: January 10, 2013; Revised: May 10, 2013; Published online: July 12, 2013

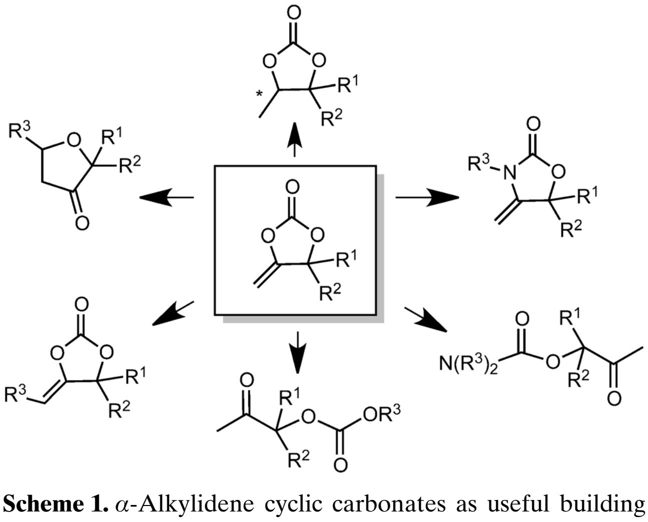
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201300007.

Abstract: Three polystyrene-supported N-heterocyclic carbene–silver complexes [PS-NHC-Ag(I)] and a polystyrene-supported N-heterocyclic carbene–copper complex [PS-NHC-Cu(I)] catalyst were synthesized and characterized by elemental analysis, Fourier transform infrared spectroscopy, inductively coupled plasma-atom emission spectrometer, thermogravimetric analysis and scanning electron micrographs. The catalytic activity of the supported catalysts was investigated for the reaction of propargylic alcohols and carbon dioxide. PS-NHC-Cu(I) showed no catalytic activity to the reaction, while PS-NHC-Ag(I) showed a considerable high activity and selectivity for the reaction, yielding the corresponding α-alkylidene cyclic carbonates in high to excellent yields under mild conditions. Most importantly, the supported catalysts could be separated easily from the products and reused up to 15 times without loss of their high catalytic activity, showing excellent stability. The effect of various reaction parameters such as carbon dioxide pressure, temperature, time, and catalyst loading on the reaction was also investigated.

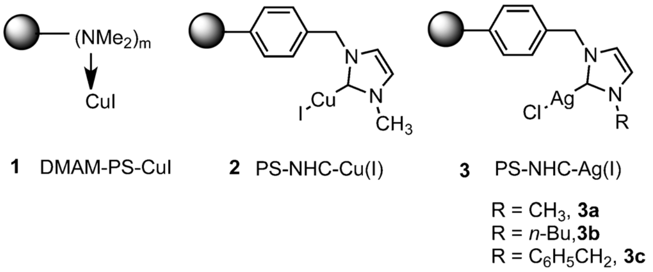
Keywords: carbon dioxide fixation; cyclic carbonates; N-heterocylic carbene complexes; propargylic alcohols; supported catalysts.

Introduction

Carbon dioxide (CO_2) is the chief greenhouse gas. Due to human activities, the amount of CO_2 released into the atmosphere has been rising extensively during and after the industrial revolution, which began in 1850. This has caused serious environmental problems such as global warming and climate change. Thus, the capture, utilization and storage of CO_2 have been attracting extensive attention in the whole world. Chemical fixation of CO_2 is regarded as an efficient route for the utilization of CO_2 because CO_2 can be used as a safe and cheap C_1 building block for the synthesis of many useful organic compounds.[1] One of the promising examples is the synthesis of α-alkylidene cyclic carbonates from the coupling of propargylic alcohols and CO_2, because α-alkylidene cyclic carbonates are useful building blocks in organic synthesis (Scheme 1).[2] Many transition metal salts and organic compounds have been found to be effective catalysts for the preparation of α-alkylidene cyclic carbonates, including copper,[3] silver,[4] cobalt,[5]



Scheme 1. α-Alkylidene cyclic carbonates as useful building blocks in organic synthesis.



Scheme 2. Heterogeneous catalysts for the reaction of propargylic alcohols with CO_2.

ruthenium,[6] palladium,[7] tri-*n*-butylphosphine,[8] N-heterocyclic carbenes,[9] and iodine of *tert*-butyl hypoiodite (*t*-BuOI).[10] And recently, an electrochemical method for the synthesis of α-alkylidene cyclic carbonates has also been developed by our group with a copper anode and a nickel cathode in an undivided cell containing $(n\text{-Bu})_4NBr$–MeCN electrolyte.[11]

Although the coupling of CO_2 with propargylic alcohols has been studied extensively, to date, only one heterogeneous catalyst, (dimethylamino)methyl-polystyrene-supported copper(I) iodide (DMAM-PS-CuI, **1**) (Scheme 2), has been used by our group for the production of the five-membered α-alkylidene cyclic carbonates.[12] Compared with the homogeneous catalytic systems mentioned above, catalyst **1** could work without organic solvent, be easily separated from the product and be reused. However, two problems associated with the catalyst **1** as a heterogeneous catalyst are: (i) the need for a high CO_2 pressure (14 MPa), and (ii) the instability of its catalytic capacity. These drawbacks limit the practical application of catalyst **1** in industrial process heavily. Therefore, there is continuing motivation for us to develop more robust and efficient heterogeneous catalysts for this transformation.

As a part of our program to develop more efficient and environmentally benign methods for the fixation of CO_2,[13] herein, we wish to report that polystyrene-supported N-heterocyclic carbene–silver complexes [PS-NHC-Ag(I), **3**] (Scheme 2) can be used as robust, efficient and environmentally friendly catalysts for the reaction of CO_2 and propargylic alcohols under mild conditions, offering the corresponding α-alkylidene cyclic carbonates in high to excellent yields.

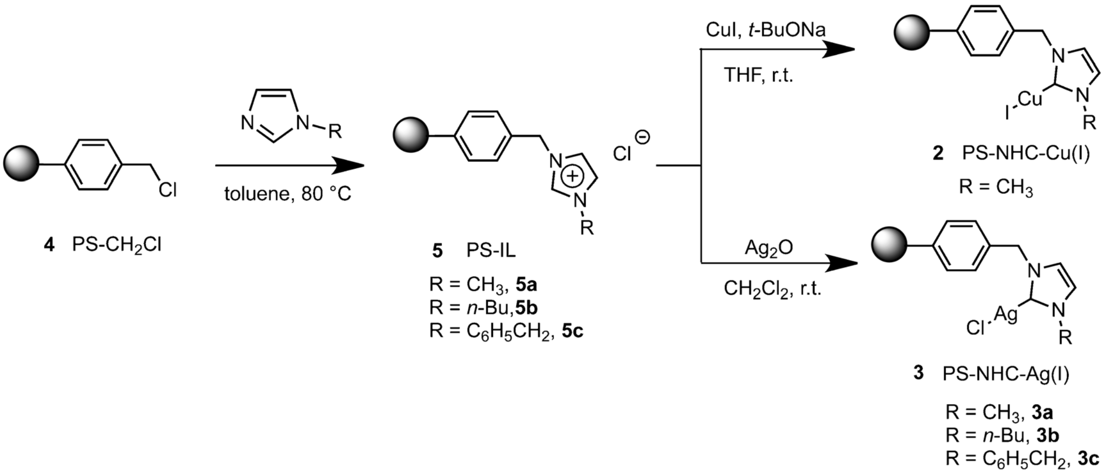
Results and Discussion

A PS-NHC-Cu(I) and three PS-NHC-Ag(I) catalysts were synthesized according to procedures reported in the literature,[14] and the preparation steps are shown in Scheme 3. The analytical data of the four polystyrene-supported catalysts are listed in Table 1. The copper content of catalyst **2** was 0.38 mmol g^{-1}, and the silver contents of catalyst **3a**, **3b** and **3c** were found to be 0.70, 0.65 and 0.49 mmol g^{-1}, respectively, based on inductively coupled plasma-atomic emission spectrometer (ICP-AES) analysis. In comparison with the nitrogen content in the catalysts, the data indicate that only a part of imidazolium groups anchored on

Table 1. Analytical data of the polymer-supported catalysts.

Catalyst	C [wt%][a]	H [wt%][a]	N [wt%][a]	Metal loading [mmol g^{-1}][b]
2	47.50	4.86	6.36	0.38
3a	58.63	6.26	7.85	0.70
3b	57.65	6.34	6.52	0.65
3c	64.66	5.78	6.33	0.49

[a] Determined by elemental analyses.
[b] Determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).



Scheme 3. Preparation of polystyrene-supported N-heterocyclic carbene Ag and Cu complexes.

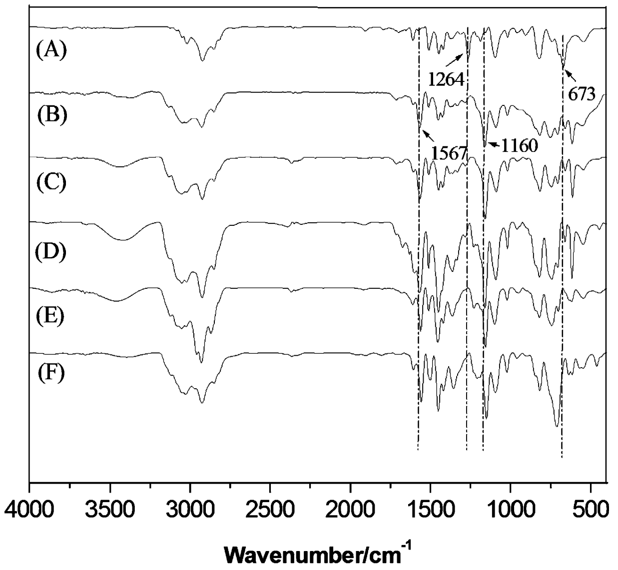


Figure 1. FT-IR spectra of (A) resin **4**, (B) resin **5a**, (C) catalyst **2**, (D) catalyst **3a**, (E) catalyst **3b**, and (F) catalyst **3c**.

the polymeric support **5** took part in the reactions with the metal Cu or Ag to form metal complexes.

Figure 1 shows the FT-IR spectra of resin **4**, polystyrene-supported ionic liquid **5a**, catalysts **2**, and catalyst **3**. In the spectrum of resin **4**, there are two characteristic absorption bands at 1264 cm^{-1} and 673 cm^{-1} which correspond to the C–Cl bond. However, they were absent and two strong absorption bands at 1567 cm^{-1} and 1160 cm^{-1} appeared in the spectrum of **5a**, which characterize the ring vibration and the position 2 C–H bond bending vibration of the imidazolium groups, respectively, providing clear evidence for the attachment of the ligands.[15] The presence of the two strong absorption bands in the spectra of the supported catalysts also suggests that not all the imidazolium group anchored on the polymeric support **5** reacted with the metal Cu or Ag to form metal carbene complexes, which is consistent with the data of elemental analyses. The IR spectra of 1-benzyl-3-methylimidazolium chloride and [1-benzyl-3-methylimidazol-2-ylidene]AgCl also confirm these results (see Supporting Information, Figure S1 and Figure S2).

The thermal stability of the four supported catalysts was estimated using TG analysis. TGA curves are shown in Figure 2, and TGA data are summarized in Table 2. The TGA curves of these four catalysts are similar and show three stages of distinct weight loss between 35 and 700 °C. A small decrease in weight was observed at less than 120 °C, which may correspond to the loss of the adsorbed and bound water in the polymer matrix.[16] The second stage of weight loss (25.8–35.8%) started at 190 °C and continued up to 393 °C, which occurred either may be due to the dissociation of the covalently bonded metal complexes or may be attributed to partial scission of the polymeric chain. The third stage of weight loss (30–35%) started immediately after completion of second stage, which may be due to the decomposition of the metal complexes.

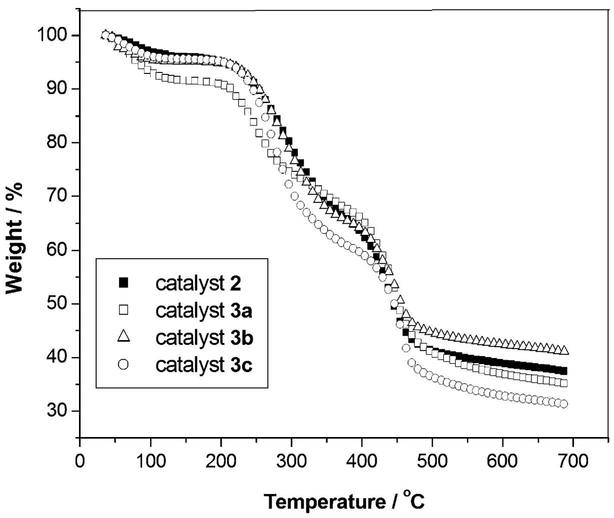


Figure 2. TGA curves of supported catalysts **2** and **3**.

Table 2. TG data of the polymer-supported catalysts.

Compound	Temperature [°C]	Weight loss [%]
Catalyst **2**	35–118	3.5
	190–393	31.5
	393–470	20.4
Catalyst **3a**	35–120	8.2
	190–390	25.8
	390–476	22.8
Catalyst **3b**	35–108	4.7
	204–390	31.3
	390–476	19.1
Catalyst **3c**	35–102	4.1
	200–390	35.8
	390–478	22.3

For a better understanding of the morphologies of the supported catalysts, SEM photographs were taken at different synthesis stages (Figure 3). It is clearly visible that the relative smooth surface of the starting polymer **4** changed after immobilization of the ligands and metals. Especially, as shown in Figure 3, D, the surface of the catalysts **3a** appeared to be covered with a large amount of small particles and thus became rougher. It should be noted that the sizes of the particles were on the nanometer scale although their shapes were irregular. The surface morphologies of catalysts **3b** and **3c** were similar and became looser in comparison with those of catalyst **2** and **3a**. Moreover, elemental mapping by energy dispersive X-ray absorption spectroscopy (EDS) confirmed a uniform distribution of Cu or Ag in the polymer supports.

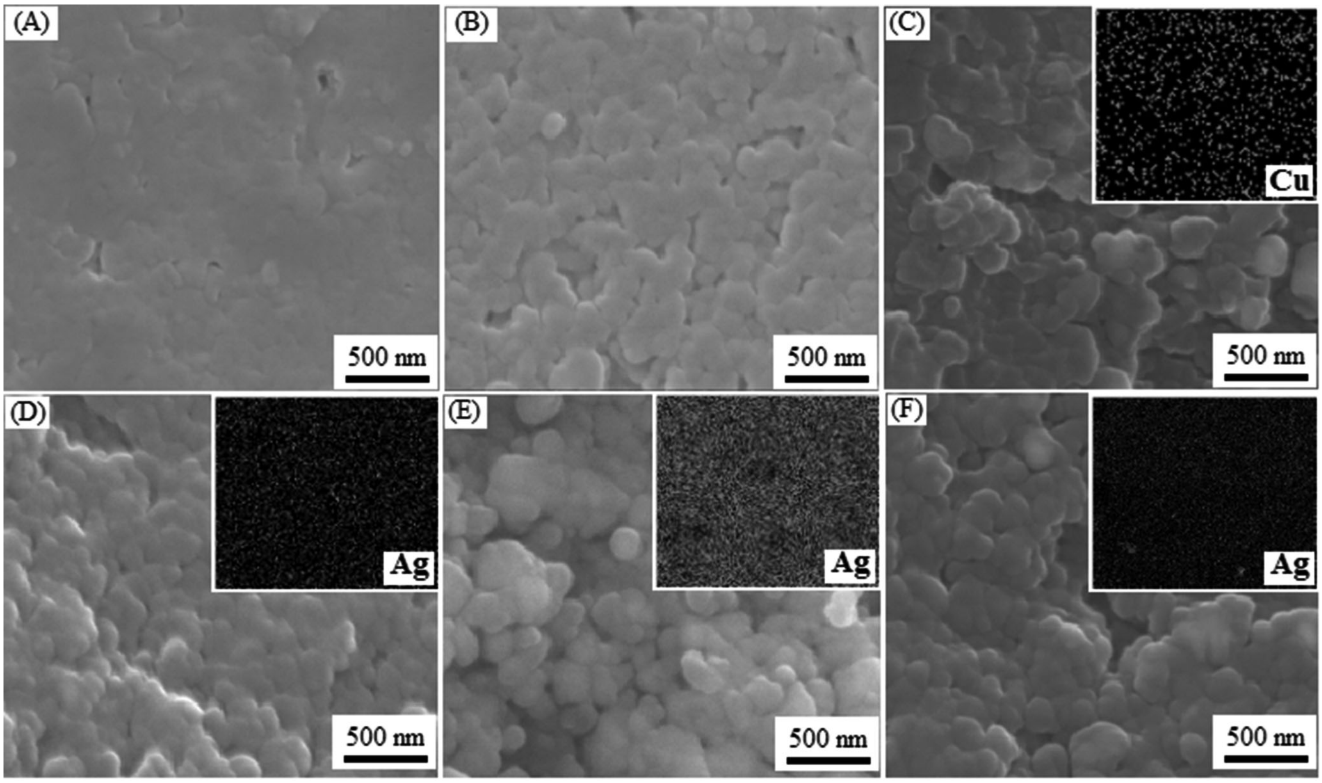
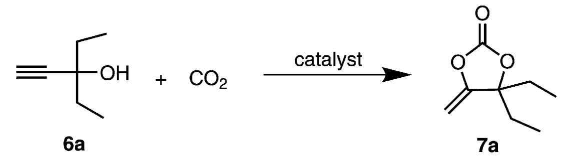


Figure 3. SEM and EDS elemental-mapping images of (A) resin **4**, (B) resin **5a**, (C) catalyst **2**, (D) catalyst **3a**, (E) catalyst **3b**, and (F) catalyst **3c**.

The catalytic activities of the four supported catalysts were first investigated using the coupling of 3-ethylpent-1-yn-3-ol with CO_2 as the model reaction under the same reaction conditions (Table 3). Control experiments showed that the coupling reaction did not occur without any catalyst (entry 1). Although it was reported that polymer-supported ionic liquids were very active catalysts for the cycloaddition of CO_2 to epoxides,[17] the reaction of 3-ethylpent-1-yn-3-ol with CO_2 could not occur in the presence of resin **5a** (entry 2). It should be noted that catalyst **1**, which could efficiently catalyze the reaction under supercritical conditions,[12] only gave 12% yield of the product with 82% selectivity, showing very low activity under present conditions (entry 3). No product was obtained when using compound **2** as catalyst, indicating that catalyst **2** is inactive for the reaction (entry 4). However, to our delight, in the presence of 2 mol% of **3a**, the reaction proceeded smoothly, producing cyclic carbonate **7a** almost quantitatively (entry 5). These results indicate the catalytic activity of catalyst **3a** is much higher than that of catalyst **1**. Catalysts **3b** and **3c** were less effective than catalysts **3a**, but they could still yield the desired product in 92% and 89% yields, respectively (entries 6 and 7).

Table 3. Catalytic activity of different catalysts in the reaction of 3-ethylpent-1-yn-3-ol with CO_2.[a]



Entry	Catalyst	Selectivity [%][b]	Yield [%][b]
1	–	0	0
2	**5a**	0	0
3	**1**	82	12
4	**2**	0	0
5	**3a**	>99	99 (93)
6	**3b**	>99	92
7	**3c**	97	89

[a] *Reaction condtions:* 0.5 mmol **6a**, 2 mol% catalyst, 5 MPa CO_2, 40 °C, 24 h.

[b] Determined by GC analysis; number in parenthesis is isolated yield.

With these good results at hand, we then examined the effect of CO_2 pressure, temperature, time, and catalyst loading on the reaction between **6a** and CO_2 with **3a** as catalyst. Figure 4 shows the influence of CO_2 pressure on the yield of **7a** at 40 °C with a reaction time of 24 h. It is noteworthy that a 71% yield of the product **7a** could be obtained at 1 MPa of CO_2, indicating the reaction could be performed under very low CO_2 pressure. As expected, an increase in CO_2

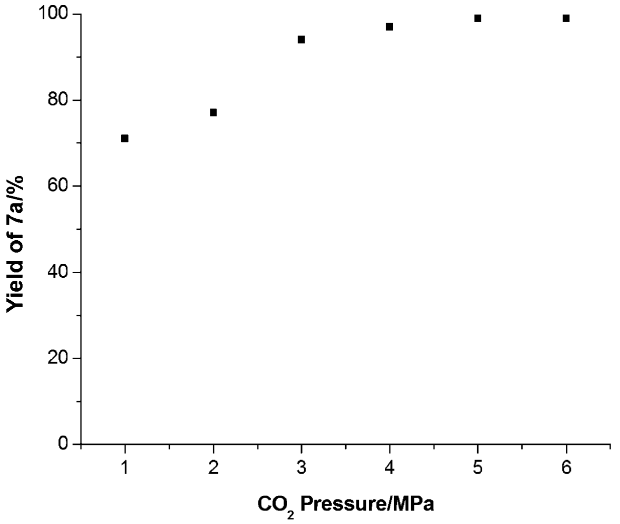


Figure 4. Effect of CO_2 pressure on the yield of **7a**. *Reaction conditions:* 0.5 mmol **6a**, 2 mol% **3a**, 40 °C, 24 h.

pressure resulted in an increase in the yield of **7a**, which reached a maximum value at 5 MPa. Further increase of pressure showed no effect on the yield.

The dependence of the yield of **7a** on the reaction temperature was investigated at a CO_2 pressure of 5 MPa with a reaction time of 24 h. As is easily seen from Figure 5, the catalytic activity of **3a** was strongly dependent on reaction temperature. In this respect, the yield of **7a** increased sharply with increasing temperature in the lower temperature region from 20 to 40 °C, while no significant change was observed from 40 to 100 °C.

The effect of reaction time on the yield of **7a** at 5 MPa CO_2 and 40 °C is shown in Figure 6. It shows that the yield of **7a** increased smoothly with the reaction time, and that **6a** could be quantitatively converted into cyclic carbonate **7a** within 24 h. Figure 7 shows the dependence of the yield of **7a** on the catalyst concentration. When the concentration of catalyst **3a** was increased from 0.5 mol% to 2 mol%, the rate of the reaction was obviously accelerated and the yield of **7a** was increased dramatically from 41 to 99%. Further increase of the amount of the catalyst showed no influence on the yield.

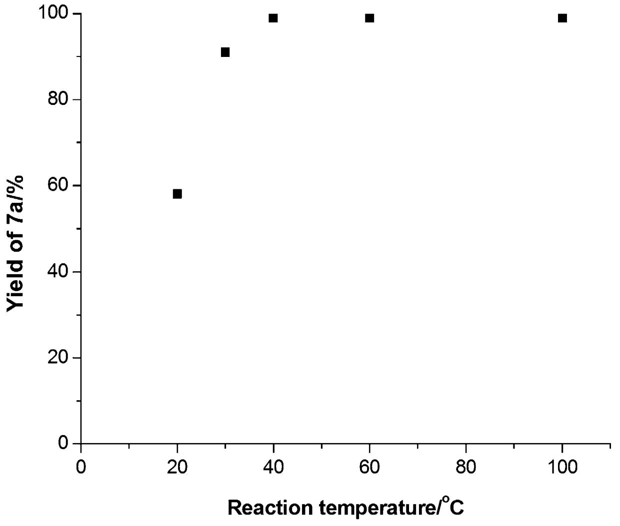


Figure 5. Effect of reaction temperature on the yield of **7a**. *Reaction conditions:* 0.5 mmol **6a**, 2 mol% **3a**, 5 MPa CO_2, 24 h.

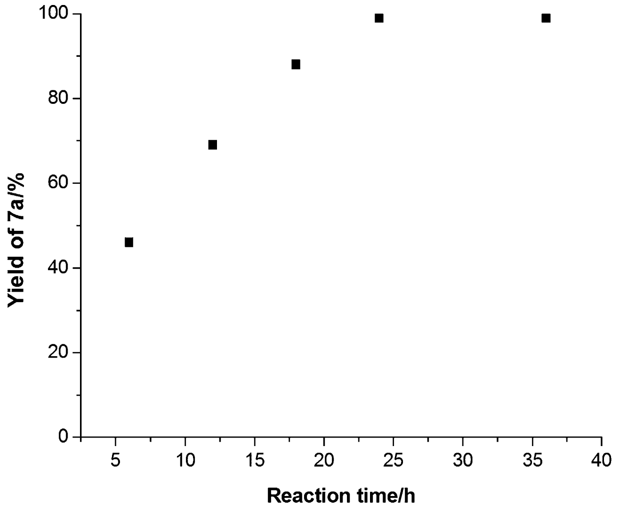


Figure 6. Effect of reaction time on the yield of **7a**. *Reaction conditions:* 0.5 mmol **6a**, 2 mol% **3a**, 5 MPa CO_2, 40 °C.

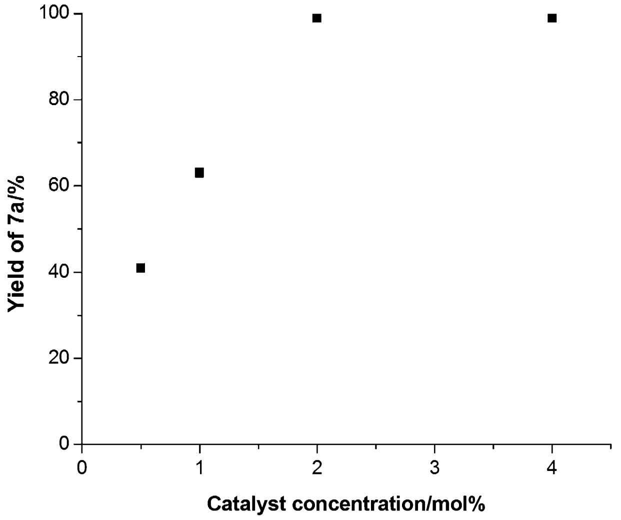
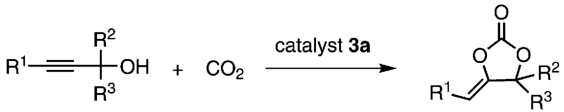
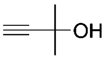
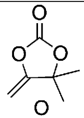
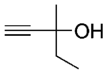
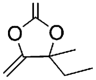
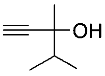
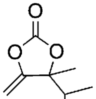
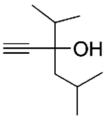
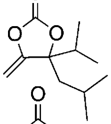
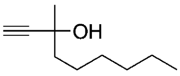
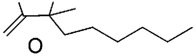
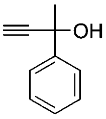
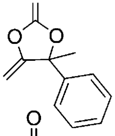
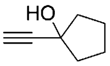
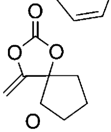
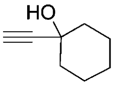
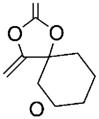
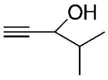
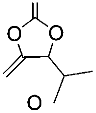
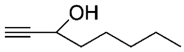
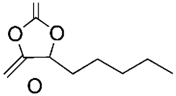
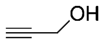
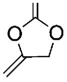
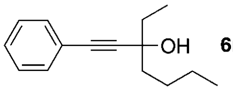
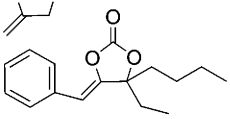


Figure 7. Effect of catalyst concentration on the yield of **7a**. *Reaction conditions:* catalyst **3a**, 0.5 mmol **6a**, 5 MPa CO_2, 40 °C, 24 h.

The scope of the reaction was further explored with various propargylic alcohols using **3a** as catalyst, and the results are summarized in Table 4. Under the optimized reaction conditions, other tertiary propargylic alcohols **6b**, **6c**, **6h** and **6i** could also undergo the car-

Table 4. Synthesis of various cyclic carbonates under the optimized conditions.[a]



Entry	Propargylic alcohol		Product		Selectivity[b]	Yield [%][c]
1		**6b**		**7b**	>99	96
2		**6c**		**7c**	>99	99
3		**6d**		**7d**	>99	68
4[d]					>99	99
5		**6e**		**7e**	>99	51
6[d]					>99	97
7		**6f**		**7f**	>99	65
8[d]					>99	99
9		**6g**		**7g**	84	81
10		**6h**		**7h**	95	93
11		**6i**		**7i**	>99	92
12		**6j**		**7j**	94	67
13[e]					90	89
14		**6k**		**7k**	>99	61
15[e]					>99	99
16[e]		**6l**		**7l**	0	0
17[d]		**6m**		**7m**	0	0

---

[a] *Reaction conditions:* 0.5 mmol propargylic alcohol, 2 mol% **3a**, 5 MPa CO_2, 40 °C, 24 h.

[b] Determined by GC analysis.

[c] Isolated yield.

[d] The reaction was carried out at 80 °C.

[e] The reaction was carried out at 60 °C.

boxylatic cyclization with CO_2 smoothly to give the corresponding products in high yields (entries 1, 2, 10 and 11). Sterically hindered substrates **6d–6f** could yield the desired products in excellent yields but at a higher temperature (80 °C); when the reactions were carried out at 40 °C, only moderate yields were obtained (entries 3–8). It is noteworthy that 2-phenylbut-3-yn-2-ol (**6g**), which showed no reactivity to the reaction when using DMAM-PS-CuI (**1**) as catalyst,[12] could smoothly react with CO_2 in the presence of **3a** (2 mol%) to give the expected product **7g** in 81% yield, along with 15% yield of 3-hydroxy-3-phenylbutan-2-one as the major by-product. Secondary propargylic alcohols **6j** and **6k** showed lower activity under standard conditions but could yield the corresponding products in high yields just by changing the reaction temperature to 60 °C (entries 12–15). But in the case of primary or internal propargylic alcohols as substrate, no α-alkylidene cyclic carbonates were obtained even at higher temperature such as 80 °C, and the starting materials were recovered (entries 16 and 17). These results also suggested that the present method seemed to be specific for terminal secondary and tertiary propargylic alcohols.

One of our most important goals in this work was to achieve more robust and recyclable catalysts for the synthesis of α-alkylidene cyclic carbonates from CO_2 and propargylic alcohols. In this experiment, the catalyst **3a** was reused 15 times in the reaction of **6a** and CO_2 to investigate the constancy of the catalyst activity and reusability. In each cycle, the heterogeneous catalyst **3a** could be easily recovered by filtration and washed with diethyl ether (3×5 mL). After drying, the catalyst was reused directly for the next run. The yields of **7a** for the fifteen repeated runs are shown in Figure 8. It is notable that the catalytic activity of the PS-NHC-Ag(I) catalyst remained unchanged even after being reused 15 times. The reactions at the 14th and 15th recycled runs gave **7a** in 98 and 97% yields, respectively. The leaching of Ag that occurred during the reaction was also examined. ICP-AES analysis of the filtrate obtained after filtration showed that the amount of Ag present in the filtrate was less than 0.01% of the initial amount. These results indicate that the catalyst exhibits excellent stability. This may be due to the specific coordination chemistry of the N-heterocyclic carbenes anchored on the polymers, which could effectively prevent the leakage of the catalytically active metal Ag from the supports to the solutions. The recovered catalyst **3a** after being reused 15 times was also characterized by IR, TGA and SEM-EDS (Figure 9, Figure 10 and Supporting Information, Figure S3), and no significant changes have been found in comparison with the fresh catalyst.

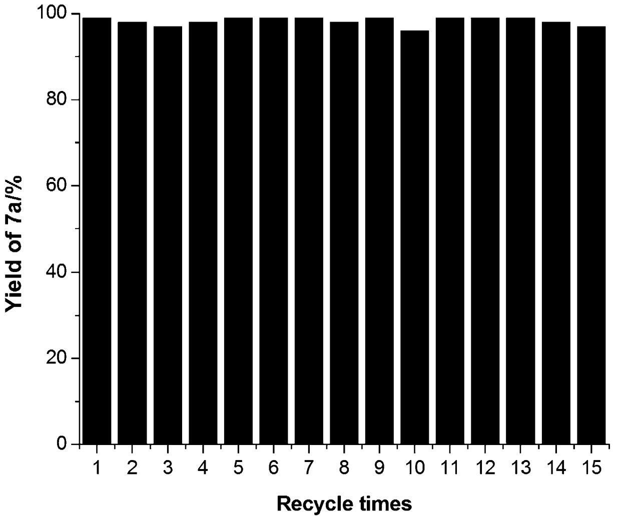


Figure 8. Reusability of **3a**. *Reaction conditions:* 0.5 mmol **6a**, 2 mol% **3a**, 5 MPa CO_2, 60 °C, 24 h.

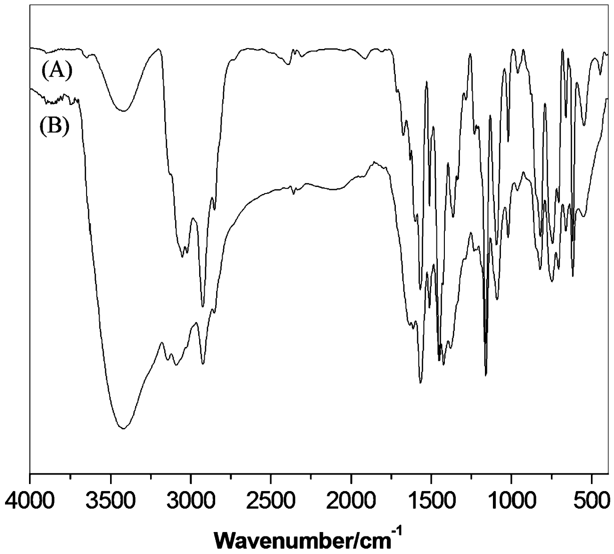


Figure 9. FT-IR spectra of catalyst **3a** before (A) and after being reused 15 times (B).

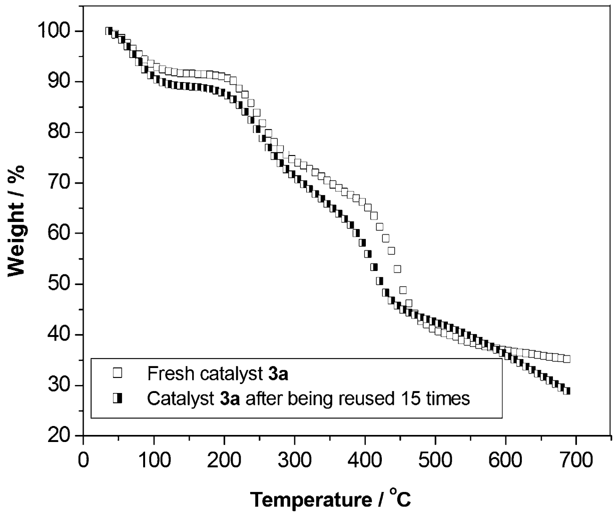


Figure 10. TGA curves of catalyst **3a** before and after being reused 15 times.

Conclusions

In conclusion, we have demonstrated that polystyrene-supported N-heterocylic carbene silver complexes can be used as robust and efficient catalysts for the reaction of various terminal tertiary and secondary propargylic alcohols with CO_2 under mild conditions, offering the corresponding α-alkylidene cyclic carbonates in high to excellent yields. The significant advantages of this methodology are mild reaction conditions, low catalyst loadings, high yields, and simple workup procedures. Most importantly, the supported catalysts showed excellent stability. They could be separated easily from the products and reused up to 15 times without loss of their high catalytic activity.

Experimental Section

General Information

NMR spectra were recorded with a Bruker DRX-400 spectrometer; $CDCl_3$ was used as solvent and TMS as an internal standard. GC analyses were performed on a GC-7900 chromatograph with an FID and equipped with an AT.SE-30 capillary column (internal diameter: 0.32 mm, length: 30 m). Mass spectra were recorded with a Shimadzu GCMS-QP5050A mass spectrometer at an ionization voltage of 70 eV and equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). IR spectra were recorded in KBr disks with a Bruker TENSOR 27 spectrometer. TGA was performed on TAINC-Q600SDT at a heating rate of 10 °C min^{-1}. Elemental analysis was performed on a Vario EL elemental analyzer. The amount of metal immobilized on the supports was determined by means of an inductively coupled plasma-atomic emission spectrometer (ICP-AES). Scanning electron microscope (SEM) and energy dispersive X-ray absorption spectroscopy (EDS) were was performed on a QUANTA400F. Carbon dioxide with a purity of 99.99% was supplied by Guangzhou Gases Factory Co., Ltd. All the other chemicals including propargylic alcohols and imidazoles were commercially available and used as received.

Representative Procedure for Preparation of Polystyrene-Supported Ionic Liquid (5a)

To a solution of 1-methylimidazole (2.57 g, 31.25 mmol) in 25 mL toluene, 2% DVB cross-linked chloromethylated polystyrene **4** (*ca.* 5.0 mmol Cl/g) (5 g) was added. Then the mixture was heated to 80 °C with stirring for 24 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered and the resin was washed with chloroform (10 mL × 3), methanol (10 mL × 3), and ethyl acetate (10 mL × 3), respectively, and dried under vacuum at 60 °C. A white resin was obtained; yield: 6.95 g. The composition of the polystyrene-supported ionic liquid (**5a**) was determined by elemental analysis (C 66.65, H 7.97, N 7.68%) and indicated that the loading capacity of imidazolium group was about 2.74 mmol g^{-1} based on nitrogen content.

General Procedure for Preparation of Polystyrene-Supported N-Heterocyclic Carbene–Copper Complex (2)

The synthesized resin **5a** (2 g), CuI (1.033 g, 5.44 mmol), NaO-*t*-Bu (0.52 g, 5.44 mmol) and dry THF (25 mL) were added in sequence to an oven-dried Schlenk flask. The resulting suspension was stirred at room temperature under a nitrogen atmosphere for 24 h. Then the solution was filtered and the resin was washed with H_2O (10 mL × 3), methanol (10 mL × 3) and acetone (10 mL × 3), respectively, and dried under vacuum at 60 °C overnight. The PS-NHC-Cu(I) catalyst was obtained as a gray-green resin; yield: 2.15 g. The copper amount of the PS-NHC-Cu(I) was found to be 0.38 mmol g^{-1} based on ICP-AES analysis.

Representative Procedure for Preparation of Polystyrene-Supported N-Heterocyclic Carbene–Silver Complex (3a)

The synthesized resin **5a** (2 g), Ag_2O (0.636 g, 2.74 mmol) and CH_2Cl_2 (25 mL) were added to an oven-dried Schlenk flask. The resulting suspension was stirred at room temperature for 24 h. Then the solution was filtered and the resin was washed with methanol (10 mL × 3) and acetone (10 mL × 3), respectively, and dried under vacuum at 60 °C overnight. The PS-NHC-Ag(I) catalyst was obtained as a light gray resin; yield: 2.17 g. The silver amount of the PS-NHC-Ag(I) was found to be 0.70 mmol g^{-1} based on ICP-AES analysis.

General Procedure for the Reaction of CO_2 and Propargylic Alcohols

Propargylic alcohol (0.5 mmol) and catalyst were added to a 15 mL stainless autoclave reactor with a magnetic stirrer. CO_2 was introduced from a cylinder and the reaction was carried out at the selected temperature under magnetic stirring for 24 h, and the pressure was kept constant during the reaction. When the reaction was completed, the vessel was cooled with an ice bath and the pressure was released slowly to atmospheric pressure. The residue was extracted with diethyl ether. The resin was filtrated, washed with diethyl ether (3 × 5 mL) and dried at 40 °C. The collected filtrate was condensed under reduced pressure. The crude product was purified by chromatography on a silica gel column using light petroleum ether/ethyl acetate as eluent and identified by IR, GC-MS and NMR.

4,4-Diethyl-5-methylene-1,3-dioxolan-2-one (7a):[5] ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.91$ (t, $J = 7.2$ Hz, 6H), 1.62–1.71 (m, 2H), 1.83–1.92 (m, 2H), 4.19 (d, $J = 3.2$ Hz, 1H), 4.80 (d, $J = 3.2$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 7.0$, 31.8, 85.7, 90.8, 151.8, 155.6; MS (70 eV): *m/z* (%) = 156 [M$^+$], 112, 97, 70, 55 (100).

4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one (7b):[11] ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.58$ (s, 6H), 4.28 (d, $J = 4.0$ Hz, 1H), 4.73 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 27.5$, 84.6, 85.2, 151.2, 158.7; MS (70 eV): *m/z* (%) = 128 [M$^+$], 84, 69, 56 (100).

4-Ethyl-4-methyl-5-methylene-1,3-dioxolan-2-one (7c):[11] ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.93$ (t, $J = 7.2$ Hz, 3H), 1.53 (s, 3H), 1.67–1.76 (m, 1H), 1.81–1.90 (m, 1H), 4.23 (d, $J = 3.2$ Hz, 1H), 4.75 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=7.2$, 25.8, 33.2, 85.5, 87.5, 151.4, 157.3; MS (70 eV): *m/z* (%) = 142 [M$^+$], 113, 70, 56 (100).

4-Isopropyl-4-methyl-5-methylene-1,3-dioxolan-2-one (7d):[12] ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=0.97$ (d, $J=6.8$ Hz, 3H), 0.99 (d, $J=7.2$ Hz, 3H), 1.54 (s, 3H), 1.87–1.94 (m, 1H), 4.24 (d, $J=3.2$ Hz, 1H), 4.78 (d, $J=3.6$ Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta=16.0$, 16.3, 24.0, 36.9, 86.1, 89.8, 151.6, 157.1; MS (70 eV): *m/z* (%) = 156 [M$^+$], 114, 97, 70 (100), 55.

4-Isobutyl-4-isopropyl-5-methylene-1,3-dioxolan-2-one (7e): Colorless liquid. IR (film): $\nu=1831$ (C=O), 1685 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=0.91$ (d, $J=5.2$ Hz, 6H), 0.93 (d, $J=5.2$ Hz, 6H), 1.54–1.58 (m, 2H), 1.78–1.83 (m, 2H), 4.20 (d, $J=2.8$ Hz, 1H), 4.81 (d, $J=2.8$ Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta=23.8$, 23.9, 24.1, 48.3, 86.0, 90.3, 151.6, 157.1; MS (70 eV): *m/z* (%) = 198 [M$^+$], 156, 112, 97 (100), 69, 55; anal. calcd for $C_{11}H_{18}O_3$: C 66.64, H 9.15; found: C 66.46, H 9.18.

4-Hexyl-4-methyl-5-methylene-1,3-dioxolan-2-one (7f):[11] ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=0.84$ (t, $J=6.0$ Hz, 3H), 1.24–1.37 (m, 8H), 1.54 (s, 3H), 1.62–1.69 (m, 1H), 1.79–1.86 (m, 1H), 4.23 (d, $J=3.6$ Hz, 1H), 4.75 (d, $J=3.2$ Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta=13.9$, 22.4, 22.8, 26.2, 28.8, 31.4, 40.4, 85.4, 87.2, 151.5, 157.7; MS (70 eV): *m/z* (%) = 198 [M$^+$], 139, 111, 97, 69, 55 (100).

4-Methyl-5-methylene-4-phenyl-1,3-dioxolan-2-one(7g):[11] ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=1.95$ (s, 3H), 4.45 (d, $J=3.2$ Hz, 1H), 4.93 (d, $J=3.2$ Hz, 1H), 7.38–7.47 (m, 5H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta=27.5$, 87.1, 88.1, 124.7, 128.9, 129.1, 139.2, 151.1, 157.5; MS (70 eV): *m/z* (%) = 190 [M$^+$], 145, 118 (100), 103, 77.

4-Methylene-1,3-dioxaspiro[4.4]nonan-2-one (7h):[12] ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=1.78$–1.87 (m, 6H), 2.12–2.15 (m, 2H), 4.29 (d, $J=3.6$ Hz, 1H), 4.69 (d, $J=3.2$ Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta=24.0$, 40.3, 85.1, 94.0, 151.2, 157.4; MS (70 eV): *m/z* (%) = 154 [M$^+$], 109, 95, 67-(100), 53.

4-Methylene-1,3-doxaspiro[4.5]decan-2-one (7i):[12] ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=1.54$–1.73 (m, 8H), 1.95–1.98 (m, 2H), 4.25 (d, $J=3.6$ Hz, 1H), 4.72 (d, $J=4.0$ Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta=21.6$, 24.4, 36.5, 85.5, 86.4, 151.5, 158.8; MS (70 eV): *m/z* (%) = 168 [M$^+$], 124, 109, 95, 82, 67 (100), 54.

4-Isopropyl-5-methylene-1,3-dioxolan-2-one (7j):[12] ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=0.96$ (d, $J=6.8$ Hz, 3H), 1.05 (d, $J=6.8$ Hz, 3H), 1.98–2.04 (m, 1H), 4.32 (d, $J=1.6$ Hz, 1H), 4.88 (s, 1H), 4.99 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta=15.0$, 17.6, 32.7, 84.2, 87.5, 152.1, 152.3; MS (70 eV): *m/z* (%) = 142 [M$^+$], 100, 83, 70, 56 (100).

4-Methylene-5-pentyl-1,3-dioxolan-2-one (7k):[11] ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=0.87$ (t, $J=5.6$ Hz, 3H), 1.29–1.45 (m, 6H), 1.73–1.83 (m, 2H), 4.31 (d, $J=1.6$ Hz, 1H), 4.82 (d, $J=1.6$ Hz, 1H), 5.10–5.15 m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta=13.8$, 22.3, 23.5, 31.1, 34.7, 79.8, 86.6, 152.1, 153.4; MS (70 eV): *m/z* (%) = 170 [M$^+$], 127, 97, 83, 69, 55 (100).

Acknowledgements

We thank the National Basic Research Program of China (973 Program) (2010CB732206), the National Natural Science Foundation of China (20932002, 21172078), the Guangdong Natural Science Foundation (10351064101000000), and the Fundamental Research Funds for the Central Universities (2011ZZ007) for financial support.

References

[1] a) E. J. Beckman, *Ind. Eng. Chem. Res.* **2003**, *42*, 1598–1602; b) M. Shi, Y. M. Shen, *Curr. Org. Chem.* **2003**, *7*, 737–745; c) G. W. Coates, D. R. Moore, *Angew. Chem.* **2004**, *116*, 6784–6806; *Angew. Chem. Int. Ed.* **2004**, *43*, 6618–6639; d) T. Sakakura, J. C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365–2387.

[2] a) Y. Inoue, K. Matsushita, I.-F. Ren, S. Imaizumi, *Chem. Lett.* **1991**, 1377–1378; b) K. Ohe, H. Matsuda, T. Ishihara, S. Ogoshi, N. Chatani, S. Murai, *J. Org. Chem.* **1993**, *58*, 1173–1178; c) K. Ohe, H. Matsuda, T. Morimoto, S. Ogoshi, N. Chatani, S. Murai, *J. Am. Chem. Soc.* **1994**, *116*, 4125–4126; d) P. Le Gendre, T. Braun, C. Bruneau, P. H. Dixneuf, *J. Org. Chem.* **1996**, *61*, 8453–8455; e) P. Le Gendre, P. Thominot, C. Bruneau, P. H. Dixneuf, *J. Org. Chem.* **1998**, *63*, 1806–1809; f) C. Toullec, A. Martin, M. Gio-Batta, C. Bruneau, P. H. Dixneuf, *Tetrahedron Lett.* **2000**, *41*, 5527–5531; g) M. Yoshida, M. Ihara, *Angew. Chem.* **2001**, *113*, 636–639; *Angew. Chem. Int. Ed.* **2001**, *40*, 616–619.

[3] a) H. Laas, A. Nissen, A. Nürrenbach, *Synthesis* **1981**, 958–959; b) H. S. Kim, J. W. Kim, S.-C. Shim, T. J. Kim, *J. Organomet. Chem.* **1997**, *545–546*, 337–344; c) Y. Gu, F. Shi, Y. Deng, *J. Org. Chem.* **2004**, *69*, 391–394.

[4] a) W. Yamada, Y. Sugawara, H. M. Cheng, T. Ikeno, T. Yamada, *Eur. J. Org. Chem.* **2007**, 2604–2607; b) S. Kikuchi, S. Yoshida, Y. Sugawara, W. Yamada, H. M. Cheng, K. Fukui, K. Sekine, I. Iwakura, T. Ikeno, T. Yamada, *Bull. Chem. Soc. Jpn.* **2011**, *84*, 698–717.

[5] Y. Inoue, J. Ishikawa, M. Taniguchi, H. Hashimoto, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1204–1206.

[6] Y. Sasaki, *Tetrahedron Lett.* **1986**, *27*, 1573–1574.

[7] K. Uemura, T. Kawaguchi, H. Takayama, A. Nakamura, Y. Inoue, *J. Mol. Catal. A: Chem.* **1999**, *139*, 1–9.

[8] a) J. Fournier, C. Bruneau, P. H. Dixneuf, *Tetrahedron Lett.* **1989**, *30*, 3981–3982; b) J. M. Joumier, J. Fournier, C. Bruneau, P. H. Dixneuf, *J. Chem. Soc. Perkin Trans. 1* **1991**, 3271–3274; c) J. M. Joumier, C. Bruneau, P. H. Dixneuf, *J. Chem. Soc. Perkin Trans. 1* **1993**, 1749–1751; d) C. Bruneau, P. H. Dixneuf, *J. Mol. Catal.* **1992**, *74*, 97–107; e) Y. Kayaki, M. Yamamoto, T. Ikariya, *J. Org. Chem.* **2007**, *72*, 647–649.

[9] Y. Kayaki, M. Yamamoto, T. Ikariya, *Angew. Chem.* **2009**, *121*, 4258–4261; *Angew. Chem. Int. Ed.* **2009**, *48*, 4194–4197.

[10] S. Minakata, I. Sasaki, T. Ide, *Angew. Chem.* **2010**, *122*, 1331–1333; *Angew. Chem. Int. Ed.* **2010**, *49*, 1309–1311.

[11] G. Q. Yuan, G. J. Zhu, X. Y. Chang, C. R. Qi, H. F. Jiang, *Tetrahedron* **2010**, *66*, 9981–9985.

[12] H. F. Jiang, A. Z. Wang, H. L. Liu, C. R. Qi, *Eur. J. Org. Chem.* **2008**, 2309–2312.

[13] a) C. R. Qi, H.-F. Jiang, *Green Chem.* **2007**, *9*, 1284–1286; b) H. Jiang, J. Zhao, A. Wang, *Synthesis* **2008**, 763–769; c) H.-F. Jiang, J.-W. Zhao, *Tetrahedron Lett.*

2009, *50*, 60–62; d) C. Qi, J. Ye, W Zeng, H. Jiang, *Adv. Synth. Catal.* **2010**, *352*, 1925–1933.

[14] a) P. Li, L. Wang, Y. Zhang, M. Wang, *Tetrahedron Lett.* **2008**, *49*, 6650–6654; b) M. Wang, P. Li, L. Wang, *Eur. J. Org. Chem.* **2008**, 2255–2261.

[15] K. Petrak, I. Degen, P. Beynon, *J. Polymer. Sci.* **1982**, *20*, 783–793.

[16] V. B. Valodkar, G. L. Tembe, M. Ravindranathan, H. S. Rama, *J. Mol. Catal. A: Chem.* **2004**, *223*, 31–38.

[17] Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu, K. Ding, *Angew. Chem.* **2007**, *119*, 7393–7396; *Angew. Chem. Int. Ed.* **2007**, *46*, 7255–7258.