APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 767–775
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.497

Transition-metal-catalyzed reactions of 5-methylene-2-oxazolidinone and 5-methylene-1,3-thiazolidine-2-thione with isocyanates

Yu-Mei Shen and Min Shi*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, People's Republic of China

Received 23 January 2003; Accepted 25 April 2003

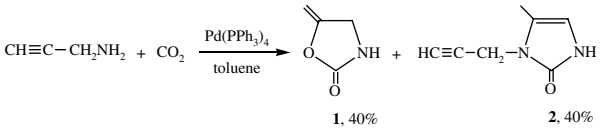
5-Methylene-2-oxazolidinone (1) and 5-methylene-1,3-thiazolidine-2-thione (4) react with various isocyanates to give the corresponding urethanes 3 and 5 in high yields in the presence of palladium(0) or palladium(II) catalyst under mild reaction conditions. A mechanism is proposed. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: transition metal; catalyst; 5-methylene-2-oxazolidinone; 5-methylene-1,3-thiazolidine-2-thione; isocyanates; urethanes

INTRODUCTION

Advantage has been taken of the coordination of transition metals to stabilize reactive intermediates, such as carbene, cyclobutadiene, trimethylenemethane (TMM; Fig. 1), etc. There is also much that can be learned by the preparation of new transition-metal complexes of otherwise unstable and highly reactive chemical species.[1] Carbene complexes have shown widespread utility for organic synthesis,[2] and the introduction of the TMM–palladium complex by Trost and coworkers, amongst others, has provided fruitful chemistry in cycloaddition constructing cyclopentane skeletons.[3–6] Transition-metal complexes of heterotrimethylenemethane,[7–12] silatrimethylenemethane,[13,14] and thiatrimethylenemethane[15,16] have been investigated from the point of view of their structural interest and synthetic utility. Especially, the reaction of 5-methylene-1,3-dioxolan-2-one with aromatic isocyanates to give the corresponding oxazolidinones as a result of [3 + 2] cycloaddition is very attractive.[17,18] During our own investigation on the fixation of carbon dioxide using propargylamine in the presence of palladium(0) catalyst, we found that cyclic enol carbamate **1** and cyclic urethane **2** could be obtained in moderate yields (Scheme 1). (Mitsudo *et al*.[19] have reported ruthenium-catalyzed selective synthesis of enol carbamates (5-methylene-2-oxazolidinines).) Thus, we examined the reaction of enol carbamate (5-methylene-2-oxazolidinone) (**1**) or cyclic urethane **2** with isocyanates in the presence of metal catalysts because we expected that [3 + 2] cycloadditions in the fashion of Murai would take place. Herein, we wish to report the full details of the reactions of **1**,**2** and 5-methylene-1,3-thiazolidine-2-thione (**4**) with isocyanates in the presence of transition-metal catalysts, along with a proposed reaction mechanism.

*Correspondence to: Min Shi, State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, People's Republic of China.
E-mail: mshi@pub.sioc.ac.cn
Contract/grant sponsor: State Key Project of Basic Research; Contract/grant number: G2000048007.
Contract/grant sponsor: Shanghai Municipal Committee of Science and Technology.
Contract/grant sponsor: National Natural Science Foundation of China; Contract/grant numbers: 20025206, 20272069.



Scheme 1.

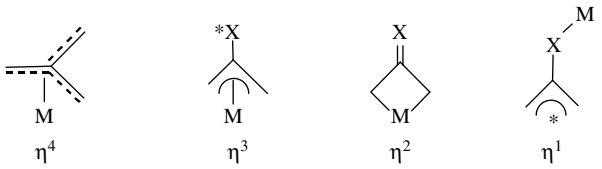


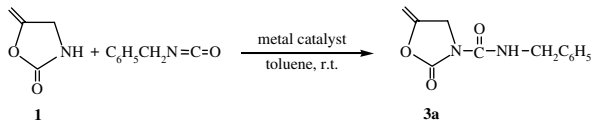
Figure 1. TMM–PdL_2 complexes.

RESULTS AND DISCUSSION

We found that 5-methylene-2-oxazolidinone (**1**) can react with benzylisocyanate in the presence of $Pd(PPh_3)_4$, $Pd_2(dba)_3$, or $Pd(OAc)_2$ catalyst to give the condensed product **3a** in excellent yields under mild reaction conditions rather than a [3 + 2] cycloaddition product (Scheme 2; Table 1, entries 1–3). However, the other transition-metal catalysts, such as $RuH_4(PPh_3)_2$, CuBr, $Ni(acac)_2$, gave low yields of **3a** under the same reaction conditions (Table 1, entries 4–9). No reactions occurred in the absence of metal catalysts. The aliphatic isocyanate can also react with 1 to give the condensed product **3b** at room temperature (Scheme 3; Table 2, entry 1). As can be seen from Table 2, aromatic isocyanates needed higher temperature to complete the reaction and 73–95% of the condensed products could be obtained at 60 °C (Scheme 3; Table 2, entries 2–9).

In fact, the reactivities of isocyanates have been well documented,[20] and it is known that tertiaryl amines,[20] organolithium,[21] lead[22] and tin[23–26] compounds have good to excellent catalytic activities for the reaction of alcohols and amines with isocyanates. However, the reactions of amides or carbamates with isocyanates are, in general, very difficult to carry out. Only some very special amides and carbamates can react with isocyanate under basic conditions.[27–31] Moreover, the palladium-catalyzed reactions of carbamates with isocyanate have been seldom reported so far. The crystal structure of **3a** was found by X-ray analysis (Fig. 2).

On the other hand, we also found that the reaction of propargylamine with carbon disulfide in the presence



Scheme 2.

Table 1. Transition-metal-catalyzed reactions of 5-methylene-2-oxazolidinone (**1**) with benzylisocyanate

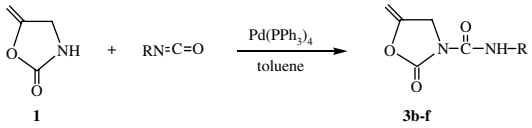
Entry	Transition-metal catalyst	Yield[a] (%)
1	$Pd(PPh_3)_4$	99
2	$Pd(OAc)_2$	99
3	$Pd_2(dba)_3$	99
4	$RuH_4(PPh_3)_2$	5
5	$Ir(CO)Cl(PPh_3)_2$	5
6	$NiBr_2(PPh_3)_2$	3
7	CuBr	30[b]
8	$Ni(acac)_2$	20[c]
9	$V(acac)_2$	5[d]

[a] Isolated yield.
[b] 99% at 60 °C.
[c] 60% at 60 °C.
[d] 7% at 60 °C.

Table 2. Palladium-catalyzed reactions of 5-methylene-2-oxazolidinone (**1**) with isocyanate

Entry	Isocyanate RN=C=O	Temperature (°C)	Product	Yield[a] (%)
1	$CH_3(CH_2)_{17}$	20	**3b**	99
2	*p*-$MeOC_6H_4$	20	**3c**	79
3	*p*-$MeOC_6H_4$	60	**3c**	95
4	*m*-$MeOC_6H_4$	20	**3d**	38
5	*m*-$MeOC_6H_4$	60	**3d**	71
6	*o*-$EtOC_6H_4$	20	**3e**	47
7	*o*-$EtOC_6H_4$	60	**3e**	95
8	*p*-ClC_6H_4	20	**3f**	34
9	*p*-ClC_6H_4	60	**3f**	90

[a] Isolated yield.



Scheme 3.

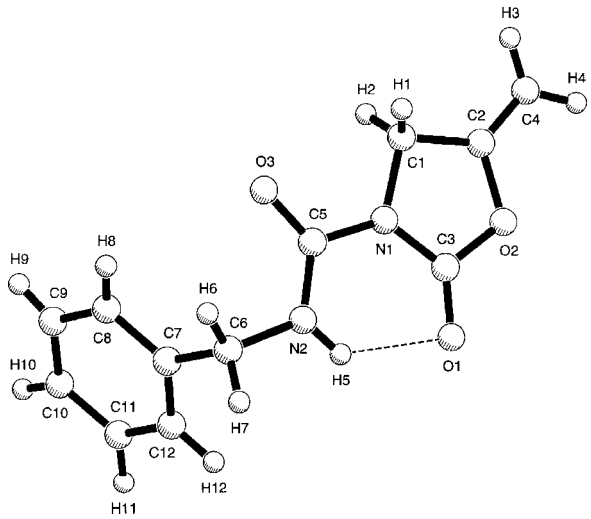
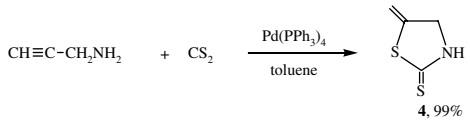


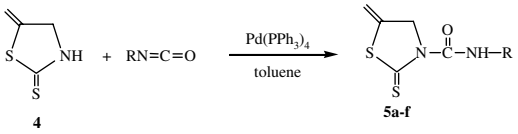
Figure 2. ORTEP drawing of **3a**.

of $Pd(PPh_3)_4$ can give the corresponding 5-methylene-1,3-thiazolidine-2-thione (**4**) in excellent yield (99%; Scheme 4). (Hanefild and Bercin[32] have reported the synthesis of 5-methylene-1,3-thiazolidine-2-thione from the direct reaction of propargylamine with carbon disulfide in 45% yield.) Thus, we also examined the reactions of 5-methylene-1,3-thiazolidine-2-thione (**4**) with isocyanates in the presence of $Pd(PPd_3)_4$ (10 mol%; Scheme 5). Among these isocyanates, the aliphatic isocyanates, such as benzylisocyanate or octadecylisocyanate, gave the corresponding products **5** in 50% yield at room temperature, but almost quantitatively gave the final products in 99% yield at 60 °C. By contrast, the aromatic isocyanates gave the products in high yields only at 60 °C. The results are summarized in Table 3. The crystal structure of **5a** was found by X-ray analysis (Fig. 3).

Furthermore, we also found that 1*H*-imidazole-2-one, 1,2-dihydro-4-methyl-3-(2-propynyl) (**2**) can react with benzylisocyanate in toluene in the presence of palladium catalyst at 60 °C to give the corresponding condensed compound **6** in moderate yield (Scheme 6). In comparison, compound **1** is the most reactive substrate with isocyanates. Compound **4** is more reactive than **2** with isocyanates.



Scheme 4.



Scheme 5.

Table 3. Palladium-catalyzed reactions of 5-methylene-1,3-thiazolidine-2-thione (**4**) with isocyanate

Entry	Isocyanates RN=C=O	Temperature (°C)	Product	Yield[a] (%)
1	$C_6H_5CH_2$	20	**5a**	50
2	$C_6H_5CH_2$	60	**5a**	99
3	$C_6H_5CH_2$	60	**5a**	99[b]
4	$CH_3(CH_2)_{17}$	60	**5b**	97[c]
5	*p*-$MeOC_6H_4$	60	**5c**	80
6	*m*-$MeOC_6H_4$	60	**5d**	70
7	*o*-$EtOC_6H_4$	60	**5e**	78
8	*p*-ClC_6H_4	60	**5f**	60

[a] Isolated yield.
[b] $Pd(OAc)_2$ was used as a catalyst.
[c] 50% isolated yield at room temperature.

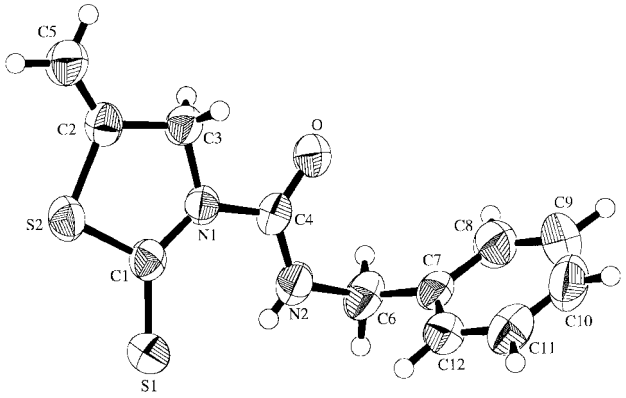
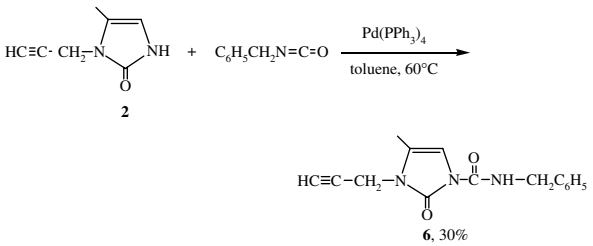


Figure 3. ORTEP drawing of **5a**.



Scheme 6.

It should be emphasized here that two isomers (the *endo* and *exo* forms) of **3a**–**g** and **5a**–**f** may be produced at the same time, owing to the C—N bond of carbamate having double bond character, but during the above reactions only one isomer of **3a**–**g** and **5a**–**f**, which has been determined as the *syn* form by X-ray analysis, was formed exclusively. From the crystal structures of **3a** and **5a** (Figs 2 and 3 and Tables 4 and 5; data deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 160760 and 160761 respectively.), it is very clear that the intramolecular hydrogen bond between the carbonyl oxygen atom or the thiocarbonyl sulfur atom and the hydrogen atom of amide to form a six-membered ring is the driving force to give the *endo* form configurations of **3** and **5** ($O1\cdots H5 = 2.064$ Å, $S1\cdots H5 = 2.417$ Å; Fig. 4). We believe that the *endo* form is more stable than the *exo* one because of the intramolecular hydrogen bonding. Selected bond lengths and angles for **3a** and **5a** are listed in Tables 6 and 7 respectively.

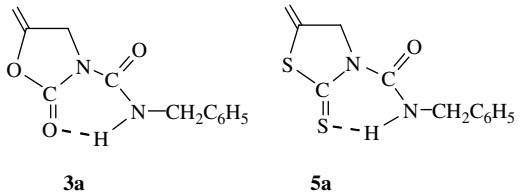


Figure 4. The intramolecular hydrogen bonds of **3a** and **5a**.

Table 4. Crystal data, data collection and structure refinement parameters for **3a**

Crystal data	
Empirical formula	$C_{12}H_{12}N_2O_3$
Formula weight	232.24
Crystal size (mm^3)	$0.20 \times 0.20 \times 0.30$
Crystal color, habit	Colorless, primitive
Temperature (°C)	20
Radiation, wavelength (Å)	Mo Kα, 0.71069
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	10.621(2)
b (Å)	12.393(3)
c (Å)	4.4400(9)
α(°)	92.721(10)
β(°)	95.086(10)
γ(°)	96.772(10)
V(Å^3)	577.1(2)
Z	2
D_{calc}(g cm^{-3})	1.337
Absorption coefficient μ(cm^{-1})	0.98
Crystallization solvent	Ethyl acetate–hexane
Data collection	
Instrument	Rigaku AFC7R
Scan	ω–2θ, 16° min^{-1} (in ω)—up to 3 scans
Measured reflections	2161
Independent reflections	2040
Reflections with $I > 2\sigma(I)$	5667
Intensity check	3 representative reflections every 200 reflections
Corrections	Lorentz and polarization
Secondary extinction coefficient	1.59956×10^{-5}
R_{int}	0.017
θ_{max}(°)	25
Refinement	
Refinement on F^2	
H atoms constrained	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0388$, $wR_2 = 0.0983$
R indices (all data)	$R_1 = 0.0663$, $wR_2 = 0.1109$
Goodness-of-fit indicator	1.012
Parameters	203
Extinction coefficient	0.097(10)
Largest difference peak and hole (e$^-$ Å^{-3})	0.143 and −0.156

Table 5. Crystal data, data collection and structure refinement parameters for **5a**

Crystal data	
Empirical formula	$C_{12}H_{12}N_2O_3S_2$
Formula weight	264.36
Crystal size (mm^3)	$0.20 \times 0.20 \times 0.30$
Crystal color, habit	Colorless, primitive
Temperature (°C)	20
Radiation, wavelength (Å)	Mo Kα, 0.710 69
Crystal system	Triclinic
Space group	$P\,\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	10.769(1)
b (Å)	12.311(2)
c (Å)	4.7820(7)
α(°)	97.058(10)
β(°)	97.173(10)
γ(°)	88.613(10)
V(Å^3)	642.2(2)
Z	2
D_{calc}(g cm^{-3})	1.406
Absorption coefficient μ(cm^{-1})	4.10
Crystallization solvent	Ethyl acetate–hexane
Data collection	
Instrument	Rigaku AFC7R
Scan	$\omega - 2\theta$, 16° min^{-1}(inω)—up to 4 scans
Measured reflections	3009
Independent reflections	2858
Reflections with $I > 3\sigma(I)$	1951
Intensity check	3 representative reflections every 200 reflections
Corrections	Lorentz and polarization
Secondary extinction coefficient	2.34193×10^{-6}
R_{int}	0.018
θ_{max}(°)	27.5
Refinement	
Refinement on F^2	
H atoms constrained	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0527$, $wR_2 = 0.1389$
R indices (all data)	$R_1 = 0.0733$, $wR_2 = 0.1539$
Goodness-of-fit indicator	1.052
Parameters	203
Extinction coefficient	0.022(8)
Largest difference peak and hole (e$^-$ Å^{-3})	0.463 and −0.382

In order to clarify the scope and limitations of this novel palladium-catalyzed reaction, we carried out the reaction of linear amides with isocyanate but found that no reaction could take place under the same reaction conditions (Scheme 7).

Table 6. Selected bond lengths (Å) and angles (°) for **3a**

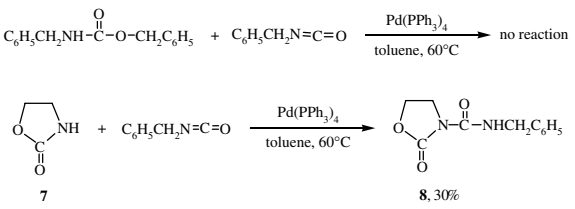
O(1)–C(3)	1.192(2)
O(2)–C(2)	1.394(2)
O(2)–C(3)	1.356(2)
O(3)–C(5)	1.222(2)
N(1)–C(1)	1.454(2)
N(1)–C(3)	1.364(2)
N(1)–C(5)	1.407(2)
N(2)–C(5)	1.330(2)
N(2)–C(6)	1.463(3)
C(1)–C(2)	1.495(3)
C(2)–C(4)	1.299(3)
C(6)–C(7)	1.498(3)
C(7)–C(8)	1.371(3)
C(7)–C(12)	1.378(3)
C(8)–C(9)	1.395(4)
C(9)–C(10)	1.358(4)
C(10)–C(11)	1.352(4)
C(11)–C(12)	1.366(3)
C(2)–O(2)–C(3)	110.1(1)
C(1)–N(1)–C(3)	111.6(2)
C(1)–N(1)–C(5)	120.3(1)
C(3)–N(1)–C(5)	128.0(2)
C(5)–N(2)–C(6)	120.6(2)
N(1)–C(1)–C(2)	101.2(1)
O(2)–C(2)–C(1)	108.1(2)
O(2)–C(2)–C(4)	120.9(2)
C(1)–C(2)–C(4)	131.0(2)
O(1)–C(3)–O(2)	122.4(2)
O(1)–C(3)–N(1)	128.7(2)
O(2)–C(3)–N(1)	108.9(2)
O(3)–C(5)–N(1)	118.2(2)
O(3)–C(5)–N(2)	125.2(2)
N(1)–C(5)–N(2)	116.5(2)
N(2)–C(6)–C(7)	113.2(2)
C(6)–C(7)–C(8)	121.8(2)
C(6)–C(7)–C(12)	120.2(2)
C(8)–C(7)–C(12)	118.0(2)
C(7)–C(8)–C(9)	120.3(2)
C(8)–C(9)–C(10)	120.3(2)
C(9)–C(10)–C(11)	119.4(3)
C(10)–C(11)–C(12)	120.9(3)
C(7)–C(12)–C(11)	121.0(2)

Table 7. Selected bond lengths (Å) and angles (°) for **5a**

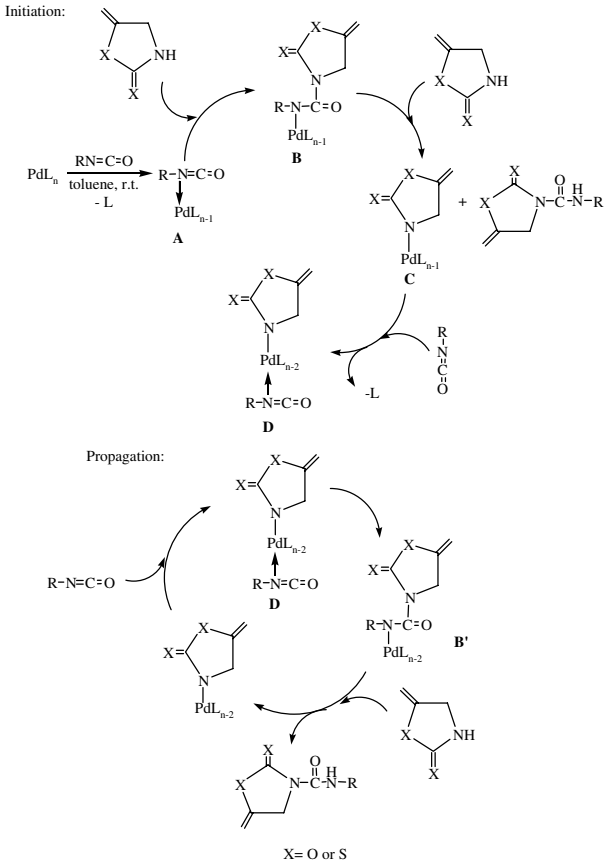
S(1)–C(1)	1.641(3)
S(2)–C(1)	1.741(3)
S(2)–C(2)	1.755(3)
O–C(4)	1.221(3)
N(1)–C(1)	1.369(4)
N(1)–C(3)	1.468(4)
N(1)–C(4)	1.440(3)
N(2)–C(4)	1.312(4)
N(2)–C(6)	1.471(4)
C(2)–C(3)	1.506(4)
C(2)–C(5)	1.305(4)
C(6)–C(7)	1.513(4)
C(7)–C(8)	1.378(4)
C(7)–C(12)	1.380(4)
C(8)–C(9)	1.374(6)
C(9)–C(10)	1.375(6)
C(10)–C(11)	1.363(6)
C(11)–C(12)	1.384(5)
C(1)–S(2)–C(2)	94.5(1)
C(1)–N(1)–C(3)	117.1(2)
C(1)–N(1)–C(4)	128.4(3)
C(3)–N(1)–C(4)	114.4(2)
C(4)–N(2)–C(6)	120.7(3)
S(1)–C(1)–S(2)	118.8(2)
S(1)–C(1)–N(1)	130.6(2)
S(2)–C(1)–N(1)	110.6(2)
S(2)–C(2)–C(3)	109.7(2)
S(2)–C(2)–C(5)	124.9(2)
C(3)–C(2)–C(5)	125.4(3)
N(1)–C(3)–C(2)	108.0(2)
O–C(4)–N(1)	117.0(3)
O–C(4)–N(2)	125.2(3)
N(1)–C(4)–N(2)	117.8(3)
N(2)–C(6)–C(7)	113.5(3)
C(6)–C(7)–C(8)	120.3(3)
C(6)–C(7)–C(12)	121.3(3)
C(8)–C(7)–C(12)	118.4(3)
C(7)–C(8)–C(9)	121.1(4)
C(8)–C(9)–C(10)	119.9(4)
C(9)–C(10)–C(11)	119.9(4)
C(10)–C(11)–C(12)	120.1(4)
C(7)–C(12)–C(11)	120.6(3)

For the cyclic carbamate **7**, the reaction could take place, but the condensed product **8** was obtained in only 30% yield (Scheme 7). At present, we do not understand why **1** and **4** can react with isocyanates to give the coupling products in such high yields.

Concerning the reaction mechanism, three fundamental mechanisms of base-catalyzed reactions of isocyanates with hydrogen-acidic compounds have been discovered,[32] but the transition-metal-catalyzed reaction remains uncertain. Recently, Roy and coworkers[33] reported efficient organotin catalysts for the formation of urethanes and carried out kinetic and mechanistic investigations by spectroscopic analysis. Based on their findings, we believe that the reaction of **1**,**2** or **4** with isocyanates proceeded via a similar mechanism. A mechanism is proposed in Scheme 8, which consists of two stages: an initiation step and a propagation step. In the first stage, pre-coordination of isocyanates to palladium occurred to produce intermediate **A**, which underwent further attack



Scheme 7.



Scheme 8.

by **1**,**2** or **4** at the carbonyl group to give the intermediate **B**. Elimination took place to afford intermediate **C**. The active catalyst **D** was generated through the coordination of isocyanates to **C**. The propagation step involved the generation of intermediate **B'**, which is similar to intermediate **B**, from the isocyanate activation of **D**. The final product was afforded via a similar process, as shown in the initiation step (Scheme 8).

CONCLUSION

We have discovered a new reaction of cyclic carbamates with isocyanate in the presence of a transition-metal catalyst under mild reaction conditions. This new reaction using transition-metal catalysts will create new opportunities in this field. Efforts are under way to elucidate the more mechanistic details of this reaction and to identify systems enabling other carbamates or amides to react with isocyanates, and the subsequent transformations thereof.

EXPERIMENTAL

General

Melting points were obtained with a Yanagimoto micro-melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J values are in hertz;. δ is in parts per million. IR: KBr; ν is given in wavenumbers. Mass spectra were recorded with an HP-5989 instrument and high-resolution mass spectrometry (HRMS) was undertaken using a Finnigan MA+ mass spectrometer. Organic solvents were dried by standard methods when necessary. Some of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by thin-layer chromatography with Huanghai GF_{254} silica-gel-coated plates. Flash column chromatography was carried out using 200–300 mesh silica gel.

*General procedure for the formation of oxazolidinone **1***

To a solution of propargylamine (550 mg, 10 mmol) in anhydrous toluene (20 ml) was added a catalytic amount of $Pd(PPh_3)_4$ (45 mg, 0.05 mmol) and the reaction mixture was stirred at room temperature under carbon dioxide atmosphere (40 kg cm^{-2}) for 24 h. The solvent was removed under reduced pressure, and the residue was purified by silica-gel column chromatography (eluent: petroleum ether/EtOAc = 1/4) to give **1** as a white solid. This solid was further recrystallized from dichloromethane/petroleum ether (1/4) to afford a crystal: 350 mg, 35% yield; m.p. 50–52 °C. IR ($CHCl_3$) cm^{-1}: ν 1780 (C═O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 4.20 (2H, dd, J = 2.1, 1.0, CH_2), 4.31 (1H, dd, J = 2.9, 2.1, CH_2), 4.78 (1H, dd, J = 2.1, 2.1, CH_2), 5.77 (1H, *s*, NH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 44.35, 86.86, 151.34, 157.64 (C═O). EI-MS: m/z 100 (100) $(MH)^+$, 71 (24.71) $(M^+ - 28)$, 43 (66.17) $(M^+ - 56)$; EI-HRMS: m/z 99.0321, $C_4H_5NO_2$ requires M, 99.0320. Anal. Found: C, 48.39; H, 5.03; N, 14.15. Calc. for $C_4H_5NO_2$: C, 48.48; H, 5.05; N, 14.14%.

*General procedure for the palladium-catalyzed reactions of cyclic carbamate **1** with isocyanates*

5-Methylene-2-oxazolidinone (**1**; 40 mg, 0.40 mmol) in toluene (10 ml), benzyl isocyanate (60 mg, 0.44 mmol), and $Pd(PPh_3)_4$ (5.0 mg, 0.040 mmol) was added into a 50 ml round-bottom flask with a magnetic stir bar. The reaction

mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was purified by a silica-gel column chromatograph (eluent: petroleum ether/EtOAc = 5/1) to give **3a** as a white solid: 93 mg, 99% yield; m.p. 83–85 °C. IR ($CHCl_3$) cm^{-1}: ν 1780 and 1702 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 4.49 (2H, d, $J = 5.7$, CH_2), 4.49 (1H, dd, $J = 4.1$, 2.2, CH_2), 4.63 (2H, t, $J = 2.4$, CH_2), 4.88 (1H, dd, $J = 6.3$, 2.7, CH_2), 7.26–7.38 (5H, m, Ar), 7.98 (1H, s, NH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 44.19, 46.23, 88.91, 127.63, 127.69, 128.77, 137.63, 147.30, 150.63 (C═O), 153.23 (C═O). EI-MS: m/z 232 (M^+). Anal. Found: C, 61.90; H, 5.23; N, 11.97. Calc. for $C_{12}H_{12}N_2O_3$ (232.2354): C, 62.06; H, 5.21; N, 12.06%.

*The formation of compound **3b***

This compound was prepared in the same manner as that described above. A white solid, 158 mg, 99% yield; m.p. 80–82 °C. IR ($CHCl_3$) cm^{-1}: ν 1780 and 1704 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 0.85 (3H, t, $J = 7.0$, CH_3), 1.16–1.27 (30H, m, CH_2), 1.32–1.60 (2H, m, CH_2), 3.27 (2H, q, $J = 7.0$, CH_2), 4.32 (1H, dd, $J = 4.3$, 1.6, CH_2), 4.57 (2H, t, $J = 2.3$, CH_2), 4.84 (1H, dd, $J = 5.6$, 2.9, CH_2). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 14.13, 22.71, 26.83, 29.26, 29.38, 29.53, 29.58, 29.60, 29.66, 29.72, 31.95, 40.34, 46.22, 88.67, 147.41, 150.52 (C═O), 153.27 (C═O). EI-MS: m/z 395 (MH^+); EI-HRMS: calc. for $C_{23}H_{42}N_2O_3$ (394.5913), requires M, 394.3195; found: M^+ 394.3190. Anal. Found: C, 70.10; H, 10.63; N, 7.07. calc. for $C_{23}H_{42}N_2O_3$ (394.5913): C, 70.01; H, 10.73; N, 7.10%.

*The formation of compound **3c***

This compound was prepared in the same manner as that described above. A white solid, 95 mg, 95% yield; m.p. 116–118 °C. IR ($CHCl_3$) cm^{-1}: ν 1778 and 1704 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 3.81 (3H, s, OCH_3), 4.54 (1H, dd, $J = 4.0$, 2.2, CH_2), 4.69 (2H, t, $J = 2.3$, CH_2), 4.94 (1H, dd, $J = 6.3$, 2.7, CH_2), 6.88–6.92 (2H, m, Ar), 7.39–7.42 (2H, m, Ar), 9.48 (1H, s, NH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 46.17, 55.51, 89.23, 114.34, 122.03, 129.65, 147.05, 148.51, 153.02 (C═O), 156.79 (C═O). EI-MS: m/z 248 (M^+); EI-HRMS: calc. for $C_{12}H_{12}N_2O_4$ (248.2348), requires M, 248.0797; found: M^+ 248.0796. Anal. Found: C, 58.04; H, 4.73; N, 11.27. Calc. for $C_{12}H_{12}N_2O_4$ (248.2348): C, 58.06; H, 4.87; N, 11.29%.

*The formation of compound **3d***

A white solid, 71 mg, 71% yield; m.p. 116–118 °C. IR ($CHCl_3$) cm^{-1}: ν 1770 and 1713 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 3.80 (3H, s, OCH_3), 4.52 (1H, dd, $J = 3.9$, 2.2, CH_2), 4.66 (2H, t, $J = 2.4$, CH_2), 4.92 (1H, dd, $J = 5.8$, 3.0, CH_2), 6.68 (1H, dt, $J = 8.1$, 0.8, Ar), 7.0 (1H, dd, $J = 8.1$, 1.3, Ar), 7.10–7.30 (2H, m, Ar), 9.62 (1H, s, NH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 46.07, 55.31, 89.26, 105.61, 110.46, 112.15, 129.80, 137.90, 146.93, 147.77, 153.28 (C═O), 160.24 (C═O). EI-MS: m/z 248 (M^+); EI-HRMS: calc. for $C_{12}H_{12}N_2O_4$ (248.2348), requires M, 248.0797; found: M^+ 248.0779. Anal. Found: C, 57.94; H, 4.78; N, 11.33. Calc. for $C_{12}H_{12}N_2O_4$ (248.2348): C, 58.06; H, 4.87; N, 11.29%.

*The formation of compound **3e***

A white solid, 101 mg, 95% yield; m.p. 117–119 °C. IR ($CHCl_3$) cm^{-1}: ν 1780 and 1704 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.48 (3H, t, $J = 7.0$, CH_3), 4.08 (2H, q, $J = 7.0$, CH_2), 4.49 (1H, dd, $J = 4.1$, 2.3, CH_2), 4.66 (2H, t, $J = 2.3$, CH_2), 4.89 (1H, dd, $J = 6.1$, 2.8, CH_2), 6.90 (1H, dt, $J = 6.5$, 1.3, Ar), 6.93 (1H, dd, $J = 7.9$, 1.4, Ar), 7.02 (1H, dt, $J = 6.1$, 1.6, Ar), 8.15 (1H, dd, $J = 8.0$, 1.6, Ar). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 14.75, 46.14, 64.54, 88.98, 111.35, 119.35, 120.92, 123.99, 127.10, 147.19, 147.73, 147.94 (C═O), 153.01 (C═O). EI-MS: m/z 262 (M^+). Anal. Found: C, 59.46; H, 5.51; N, 10.73. Calc. for $C_{13}H_{14}N_2O_4$: C, 59.54; H, 5.34; N, 10.68.

*The formation of compound **3f***

A white solid, 93 mg, 90% yield; m.p. 162–164 °C. IR ($CHCl_3$) cm^{-1}: ν 1778 and 1700 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 4.54 (1H, dd, $J = 4.1$, 2.2, CH_2), 4.67 (2H, t, $J = 2.4$, CH_2), 4.94 (1H, dd, $J = 6.3$, 2.8, CH_2), 7.26–7.32 (2H, m, Ar), 7.42–7.47 (2H, m, Ar), 9.65 (1H, s, NH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 46.06, 89.49, 121.20, 129.16, 129.69, 135.31, 146.80, 147.82 (C═O), 153.31 (C═O). EI-MS: m/z 252 (M^+); EI-HRMS: calc. for $C_{11}H_9N_2O_3Cl$ (252.6535), requires M, 252.0302; found: M^+ 252.0299. Anal. Found: C, 52.35; H, 3.62; N, 11.13. Calc. for $C_{11}H_9ClN_2O_3$: C, 52.29; H, 3.59; N, 11.09%.

*The formation of compound **4***

A white solid, 472 mg, 99% yield; m.p. 120–121 °C. IR ($CHCl_3$) cm^{-1}: ν 1626, 1490, 902. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 4.67 (2H, t, $J = 2.7$, CH_2), 5.14 (1H, dd, $J = 5.4$, 2.7, CH_2), 5.24 (1H, dd, $J = 4.8$, 2.4, CH_2), 7.96 (1H, s, NH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 57.05, 105.67, 141.13, 199.11 (C═S). EI-MS: m/z 131 (M^+); EI-HRMS: calc. for $C_4H_6NS_2$ (132.2292) $(M + 1)^+$, requires M, 131.9942; found: M^+ 131.9954. Anal. Found: C, 36.55; H, 3.72; N, 10.81. Calc. for $C_4H_5NS_2$: C, 36.61; H, 3.84; N, 10.67%.

*The formation of compound **5a***

A white solid, 103 mg, 99% yield; m.p. 40–42 °C; IR ($CHCl_3$) cm^{-1}: ν 1731 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 4.53 (2H, d, $J = 5.6$, CH_2), 5.07 (1H, dd, $J = 5.1$, 2.7, CH), 5.25 (3H, d, $J = 2.4$, CH), 7.26–7.36 (5H, m, Ar). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) : δ 44.53, 62.00, 105.22, 127.49, 127.51, 128.66, 134.03, 137.27, 151.81 (C═O), 197.49 (C═S). EI-MS: m/z 264 (M^+); HR-EIMS: calc. for $C_{12}H_{12}N_2OS_2$ (264.3686), requires M, 264.0391; found: M^+ 264.0386. Anal. Found: C, 54.66; H, 4.63; N, 10.77. Calc. for $C_{12}H_{12}N_2OS_2$: C, 54.52; H, 4.58; N, 10.60%.

*The formation of compound **5b***

A white solid, 95 mg, 97% yield; m.p. 76–78 °C. IR ($CHCl_3$) cm^{-1}: ν 1705 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 0.88 (3H, t, $J = 6.3$, CH_3), 1.19–1.31 (30H, m, CH_2), 1.52–1.59 (2H, m, CH_2), 3.32 (2H, q, $J = 6.8$, CH), 5.07 (1H, dd, $J = 5.1$, 2.6, CH_2), 5.25 (3H, d, $J = 2.5$, CH). ^{13}C

NMR ($CDCl_3$, TMS, 75 MHz): δ 14.11, 22.69, 26.97, 29.10, 29.18, 29.37, 29.49, 29.57, 29.64, 29.70, 31.93, 40.74, 62.10, 105.08, 134.26, 151.76 (C═O), 197.33 (C═S). EI-MS: m/z 426 (M^+); EI-HRMS: calc. for $C_{23}H_{42}N_2OS_2$ (426.7245), requires M, 426.2739; found: M^+ 426.2713. Anal. Found: C, 64.63; H, 9.87; N, 5.63. Calc. for $C_{23}H_{42}N_2OS_2$: C, 64.74; H, 9.92; N, 5.56%.

*The formation of compound **5c***

A white solid, 89 mg, 80% yield; m.p. 104–106 °C. IR ($CHCl_3$) cm^{-1}: ν 1705 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 3.79 (3H, s, OCH_3), 5.11 (1H, dd, $J = 5.0$, 2.6, CH), 5.30 (3H, d, $J = 4.3$, CH), 6.85–6.89 (2H, m, Ar), 7.39–7.42 (2H, m, Ar). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 55.51, 62.03, 105.52, 114.37, 122.29, 129.62, 133.61, 149.26, 156.92 (C═O), 197.13 (C═S). EI-MS: m/z 280 (M^+); EI-HRMS: calc. for $C_{12}H_{12}N_2O_2S_2$ (280.3680), requires M, 280.0340; found: M^+ 280.0351. Anal. Found: C, 51.36; H, 4.26; N, 9.85. Calc. for $C_{12}H_{12}N_2O_2S_2$: C, 51.41; H, 4.31; N, 9.99%.

*The formation of compound **5d***

A white solid, 78 mg, 70% yield; m.p. 106–108 °C. IR ($CHCl_3$) cm^{-1}: ν 1704 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 3.82 (3H, s, OCH_3), 5.13 (1H, dd, $J = 5.2$, 2.6, CH), 5.33 (3H, d, $J = 2.6$, CH), 6.70 (1H, dd, $J = 8.2$, 1.9, Ar), 7.04 (1H, dd, $J = 6.7$, 1.3, Ar), 7.20 (1H, dd, $J = 4.4$, 2.2, Ar), 7.26 (1H, d, $J = 7.8$, Ar). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 55.31, 61.91, 105.58, 106.17, 110.67, 112.72, 129.77, 133.41, 137.82, 146.89, 160.20 (C═O), 197.79 (C═S). EI-MS: m/z 280 (M^+); EI-HRMS: calc. for $C_{12}H_{12}N_2O_2S_2$ (280.3680), requires M, 280.0340; found: M^+ 280.0338. Anal. Found: C, 51.53; H, 4.23; N, 10.03. Calc. for $C_{12}H_{12}N_2O_2S_2$: C, 51.41; H, 4.31; N, 9.99%.

*The formation of compound **5e***

A white solid, 92 mg, 78% yield; m.p. 117–119 °C. IR ($CHCl_3$) cm^{-1}: ν 1704 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.45 (3H, t, $J = 7.0$, CH_3), 4.09 (2H, q, $J = 7.0$, CH_2), 5.10 (1H, dd, $J = 5.0$, 2.6, CH), 5.29 (1H, dd, $J = 4.8$, 2.4, CH), 5.33 (2H, dd, $J = 5.0$, 2.4, CH), 6.89 (1H, td, $J = 8.1$, 1.3, Ar), 6.95 (1H, td, $J = 7.7$, 1.3, Ar), 7.08–7.25 (1H, m, Ar), 8.22 (1H, ddd, $J = 8.1$, 6.6, 1.6, Ar). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 15.05, 29.72, 62.11, 64.52, 105.24, 111.29, 120.42, 120.78, 125.04, 126.68, 134.15, 148.50 (C═O), 197.22 (C═S). EI-MS: m/z 294 (M^+); EI-HRMS: calc. for $C_{13}H_{14}N_2O_2S_2$ (294.3945), requires M, 294.0497; found: M^+ 294.0483. Anal. Found: C, 53.16; H, 4.83; N, 9.55. Calc. for $C_{13}H_{14}N_2O_2S_2$: C, 53.04; H, 4.79; N, 9.52%.

*The formation of compound **5f***

A white solid, 68 mg, 60% yield; m.p. 152–154 °C. IR ($CHCl_3$) cm^{-1}: ν 1724 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 5.13 (1H, dd, $J = 5.0$, 2.5, CH), 5.31 (3H, d, $J = 2.4$, CH), 7.25–7.32 (2H, m, Ar), 7.42–7.51 (2H, m, Ar). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 61.88, 105.80, 121.67, 128.59, 129.19, 132.21, 133.29, 135.32, 148.98 (C═O), 198.03 (C═S). EI-MS: m/z 285 (MH^+); EI-HRMS: calc. for $C_{11}H_9ClN_2OS_2$ (284.7867), requires M, 283.9845; found: M^+ 283.9839. Anal. Found: C, 46.33; H, 3.12; N, 9.76. Calc. for $C_{11}H_9ClN_2OS_2$: C, 46.39; H, 3.19; N, 9.84%.

*The formation of compound **6***

A white solid, 32 mg, 30% yield; m.p. 123–125 °C. IR ($CHCl_3$) cm^{-1}: ν 1713 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.17 (3H, s, CH_3), 2.30 (1H, t, $J = 2.1$, CH), 4.41 (2H, d, $J = 2.3$, CH_2), 4.45 (2H, d, $J = 5.8$, CH_2), 6.74 (1H, s, CH), 6.91–7.37 (5H, m, Ar), 8.92 (1H, s, NH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 10.0, 30.18, 43.90, 72.61, 104.07, 119.77, 127.43, 127.55, 128.64, 137.88, 150.09 (C═O), 151.60 (C═O). EI-MS: m/z 269 (MH^+). EI-HRMS: calc. for $C_{15}H_{15}N_3O_2$ (269.2986), requires M, 269.1164; found: M^+ 269.1165. Anal. Found: C, 66.87; H, 5.77; N, 15.56. Calc. for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61; N, 15.60%.

*The formation of compound **8***

A white solid, 30 mg, 30% yield; m.p. 66–68 °C. IR ($CHCl_3$) cm^{-1}: ν 1691 and 1749 (C═O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 3.91 (2H, dd, $J = 8.6$, 7.2, CH_2), 4.25 (2H, dd, $J = 8.6$, 7.2, CH_2), 4.42 (2H, d, $J = 5.9$, CH_2), 7.19–7.32 (5H, m, Ar), 8.14 (1H, s, NH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 42.10, 43.57, 62.09, 127.12, 127.17, 128.31, 137.84, 151.41 (C═O), 155.43 (C═O). EI-MS: m/z 220 (M^+); EI-HRMS: calc. for $C_{11}H_{12}N_2O_3$ (220.2247), requires M, 220.0848; found: M^+ 220.1165. Anal. Found: C, 59.76; H, 5.42; N, 12.79. Calc. for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72%.

Acknowledgements

We thank the State Key Project of Basic Research (project 973) (no. G2000048007), Shanghai Municipal Committee of Science and Technology, and the National Natural Science Foundation of China for financial support (20025206 and 20272069).

REFERENCES

1. McQuillin FJ, Parker DG, Stephenson GR. *Transition Metal Organometallics for Organic Synthesis*. Cambridge University Press: Cambridge, 1991.
2. Wulff WD. In *Advances in Metal–Organic Chemistry*, Liebeskind LS (ed.). JAI: Greenwich, CT, 1989.
3. Trost BM. *Angew. Chem. Int. Ed. Engl.* 1986; **25**: 1.
4. Trost BM, Grese TA, Chan DMT. *J. Am. Chem. Soc.* 1991; **113**: 7350.
5. Shimizu I, Ohashi Y, Tsuji J. *Tetrahedron Lett.* 1984; **24**: 5183.
6. Jones MD, Kemmitt RDW. *Chem. Commun.* 1986; 1201.
7. Fawcett J, Henderson W, Jones MD, Kemmitt RDW, Russell DR, Lam B, Kang SK, Albright TA. *Organometallics* 1989; **8**: 1991.
8. Jones MD, Kemmitt RDW, Fawcett J, Russell DR. *Chem. Commun.* 1986; 427.
9. Imran A, Kemmitt RDW, Markwick AJW, Mckenna P, Russell DR, Scherry LJS. *J. Chem. Soc. Dalton Trans.* 1985; 549.
10. Kemmitt RDW, Mckenna P, Russell DR, Scherry LJS. *J. Chem. Soc. Dalton Trans.* 1985; **259**.
11. Holmgren JS, Shapley JR, Wilson SR, Pennington WT. *J. Am. Chem. Soc.* 1986; **108**: 508.
12. Tulip TH, Thron DL. *J. Am. Chem. Soc.* 1981; **103**: 2448.
13. Ando W, Yamamoto T, Saso H, Kabe Y. *J. Am. Chem. Soc.* 1991; **113**: 2791.
14. Saso H, Ando W. *Chem. Lett.* 1988; 1567.

15. Choi N, Kabe Y, Ando W. *Tetrahedron Lett.* 1991; **32**: 4573.
16. Choi N, Kabe Y, Ando W. *Organometallics* 1992; **11**: 1506.
17. Ohe K, Matsuda H, Ishihara T, Ogoshi S, Chatani N, Murai S. *J. Org. Chem.* 1993; **58**: 1173.
18. Ohe K, Ishihara T, Chatani N, Murai S. *J. Am. Chem. Soc.* 1990; **112**: 9646.
19. Mitsudo T, Hore Y, Yamakawa Y, Watanabe Y. *Tetrahedron Lett.* 1987; **28**: 4417.
20. Ozaki S. *Chem. Rev.* 1972; 474.
21. Bailey WJ, Griffith L. *J. Org. Chem.* 1978; **43**: 2690.
22. Davies AG, Puddephatt RJ. *J. Chem. Soc. C* 1968; 1479.
23. Karpel S. *Tin Uses* 1980; **125**: 1.
24. Hostettler F, Cox EF. *Ind. Eng. Chem.* 1960; **52**: 609.
25. Bloodworth AJ, Davies AG. *J. Chem. Soc.* 1965; 5238.
26. Ratier M, Khatmi D, Duboudin JG. *Appl. Organometal. Chem.* 1992; **6**: 293.
27. Ravindranathan T, Hiremath SV, Rajgopal Reddy D, Tejwani RB. *Synth. Commun.* 1988; **18**: 1855.
28. Nabeya A, Endo T, Saito J, Mitsuishi T, Inahara M. *J. Heterocyclic Chem.* 1990; **27**: 903.
29. Ozaki S, Ike Y, Mizuno H, Ishikawa K, Mori H. *Bull. Chem. Soc. Jpn.* 1977; **50**: 2406.
30. Ulrich H, Tucker B, Sayigh AA. *J. Org. Chem.* 1967; **32**: 3938.
31. Whitehead CW, Traverso J. *J. Am. Chem. Soc.* 1958; **80**: 962.
32. Hanefild W, Bercin E. *Liebigs Ann. Chem.* 1985; 58.
33. Schwetlick K, Noack R, Stebner F. *J. Chem. Soc. Perkin Trans. 1* 1994; 599.
34. Majumdar KK, Kundu A, Das I, Roy S. *Appl. Organometal. Chem.* 2000; **14**: 79.

