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N-Heterocyclic carbenes as ligands in palladium-catalyzed Tsuji–Trost allylic substitution

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Abstract

A Pd(0)-catalyzed allylic substitution (i.e., Tsuji–Trost reaction) using N-heterocyclic carbene as a ligand was investigated. It has been proven that an imidazolium salt **2d** having bulky aromatic rings attached to the nitrogens in its imidazol-2-ylidene skeleton is suitable as a ligand precursor and that a Pd_2dba_3–imidazolium salt **2d**–Cs_2CO_3 system is highly efficient for producing a Pd–NHC catalyst in this reaction. Allylic substitution using a Pd–NHC complex differed from that using a Pd–phosphine complex as follows: (1) the reaction using a Pd–NHC complex required elevated temperature (50 °C or reflux in THF), (2) allylic carbonates were inert to a Pd–NHC complex, and (3) nitrogen nucleophiles such as sulfonamide and amine did not react with allylic acetate. It was also found that allylic substitution with a soft nucleophile using a Pd–NHC catalyst proceeds via overall retention of configuration to give the product in a stereospecific manner, the stereochemical reaction course obviously being the same as that of the reaction using a Pd–phosphine complex.

Keywords: N-Heterocyclic carbene; Palladium; Allylation; Tsuji–Trost reaction

1. Introduction

After the first isolation and X-ray crystallographic characterization of nucleophilic N-heterocyclic carbenes (NHCs) [1], the chemistry of the NHC has rapidly developed, since NHCs are attractive not only as a stable isolable carbene species but also as molecules able to coordinate to various transition metals [2]. NHCs are regarded as strong σ-donor ligands and have reactivities similar to those of sterically bulky tertiary phosphines. Recently, high catalytic efficiency has been found in a variety of reactions, especially those catalyzed by a palladium complex, by virtue of using NHCs as ligands (e.g., Suzuki–Miyaura coupling [3], Kumada–Tamao–Corriu-type coupling [4], Mizoroki–Heck reaction [5], amination of aryl halide [6], Sonogashira coupling [7]).

The reaction of a π-allylpalladium complex with soft carbon nucleophiles to give an allylated product was reported for the first time by Tsuji in 1965 [8]. The reaction was expanded to a catalytic process by Hata and Atkins [9], and its synthetic utility was greatly enhanced by Trost [10]. Pd(0)-catalyzed allylic substitution is now called "Tsuji–Trost reaction" and has been recognized as one of the most synthetically useful C–C bond forming reactions. However, Pd(0)-catalyzed allylic substitution using NHCs as ligands has not been investigated in detail [11,12]. We describe herein results of our continuing studies on Pd(0)-catalyzed allylic substitution using NHCs as ligands.

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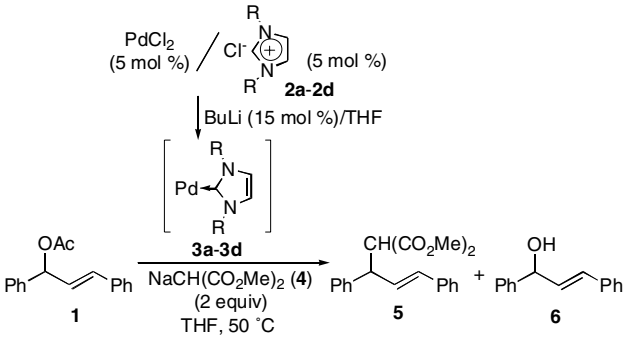
2. Results and discussion

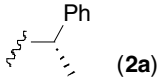
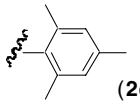
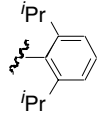
2.1. Reaction of allylic acetates with dimethyl malonate using NHCs as ligands

Initially, reactions of acetate **1** with sodium dimethylmalonate (**4**) were investigated using various Pd–NHC catalysts (**3a**)–(**3d**) formed by treatment of $PdCl_2$ with BuLi in the presence of imidazolium salts (**2a**)–(**2d**) (Table 1) [13].

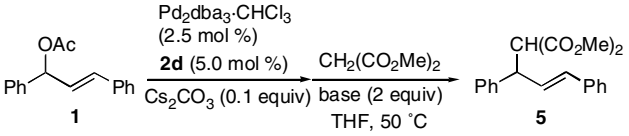


To a THF suspension of $PdCl_2$ (5 mol%) and imidazolium salt **2a** (5 mol%) was added a solution of BuLi–hexane (15 mol%) at 0 °C, and the mixture was stirred for about 1 h at this temperature. To the mixture of a Pd–NHC catalyst (**3a**) was added a THF solution of **1** followed by addition of a solution of **4** at 0 °C, and the mixture was heated at 50 °C for 24 h. As a result, the desired substitution product **5** was afforded in only 6% yield, and the starting material **1** was recovered in 76% yield along with alcohol **6**, which would be derived from **1** although the mechanism was not clear, in 13% yield (Table 1, run 1). It was found that the reaction of **1** and **4** with Pd–NHC catalyst **3c** or **3d**, having aromatic rings on nitrogens in the imidazol-2-ylidene skeleton, improved the yield of the desired product. The use of **3d**, having a sterically bulky substituent on the aromatic ring, showed the best reactivity in this reaction, giving **5** in 77% yield (run 4).

Table 1
Allylic substitution of **1** with **4** using a Pd–NHC complex

Run	Imidazolium salt (–R)	Time (h)	Yield (%)		Recover of **1** (%)
			5	**6**	
1	 (**2a**)	24	6	13	76
2	 (**2b**)	15	–	11	79
3	 (**2c**)	18	25	16	30
4	 (**2d**)	37	77	–	16

It has been reported that Pd–NHC species can be formed in situ from a palladium complex and imidazolium salts in the presence of Cs_2CO_3 as a base, and this Pd–NHC catalyst has been used in various C–C coupling reactions [3c]. Thus, reactions of **1** with dimethyl malonate were again investigated using a Pd–NHC catalyst formed from $Pd_2dba_3 \cdot CHCl_3$ and imidazolium salt **2d** in the presence of Cs_2CO_3 (Table 2).

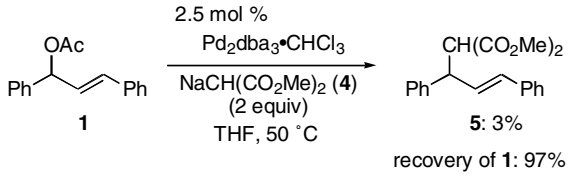


Surprisingly, when a THF solution of acetate **1** and sodium dimethylmalonate (**4**) was treated with a Pd–NHC catalyst formed from $Pd_2dba_3 \cdot CHCl_3$ (2.5 mol%), imidazolium salt **2d** (5.0 mol%), and Cs_2CO_3 (10 mol%), the reaction was completed in 2 h to give the desired product **5** in excellent yield (98%) (Table 2, run 1). In addition, the reaction of **1** and dimethyl malonate using $Pd_2dba_3 \cdot CHCl_3$ and imidazolium salt **2d** in the presence of an excess amount of Cs_2CO_3 at 50 °C gave the desired product **5** in quantitative yield, although the reaction was slightly prolonged (run 2). These results indicate that the Pd–NHC species generated from $Pd_2dba_3 \cdot CHCl_3$, **2d**, and Cs_2CO_3 is more reactive than the above-mentioned Pd–NHC catalyst prepared from $PdCl_2$, **2d**, and BuLi and that a prior preparation of sodium dimethylmalonate (**4**) from dimethyl malonate and NaH is unnecessary in this catalyst system.

A control experiment without imidazolium salt **2d** was carried out in order to confirm that a NHC, generated from imidazolium salt **2d** and Cs_2CO_3, operates as a ligand in this reaction (Scheme 1).

Table 2
Reaction of **1** with dimethyl malonate using Pd_2dba_3 and imidazolium salt **2d**

Run	Base	Time (h)	Yield (%)
1	NaH	2	98
2	Cs_2CO_3	10	100



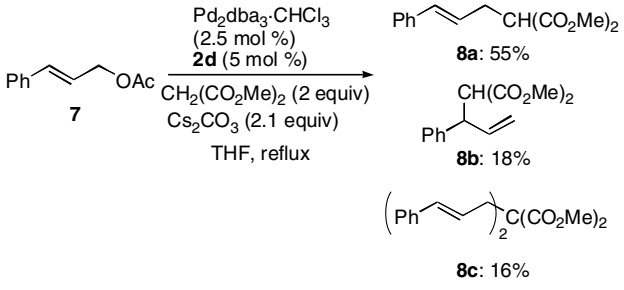
Scheme 1.

The reaction of **1** and sodium dimethylmalonate (**4**) with $Pd_2dba_3 \cdot CHCl_3$ (2.5 mol%) in the absence of imidazolium salt **2d** in THF at 50 °C produced a trace amount of desired product **5** in 3%, and the starting material **1** was recovered in 97% yield. This result indicates that the NHC formed from **2d** actually operates as a ligand in this reaction.

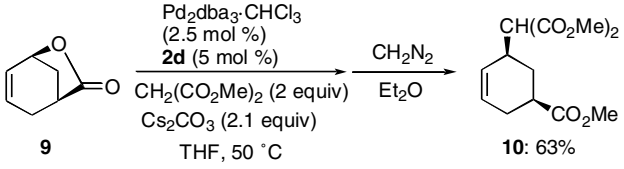
2.2. Scope and limitations of allylic substitution by Pd–NHC complex

To evaluate the scope of this reaction, allylic substitution of various substrates using a Pd–NHC complex, generated in situ from Pd_2dba_3 and imidazolium salt **2d** in the presence of Cs_2CO_3, was investigated. The reaction of unsymmetrically substituted allylic actetate **7** and dimethyl malonate required heating to reflux, and allylation products were produced in a total 89% yield (linear-allylation product **8a**, 55%; branched-allylation product **8b**, 18%; double-allylation product **8c**, 16%) (Scheme 2).

In the case of cyclic lactone **9**, the reaction with dimethyl malonate proceeded at 50 °C to give the product **10** in 63% yield as a single diastereomer (Scheme 3).



Scheme 2.



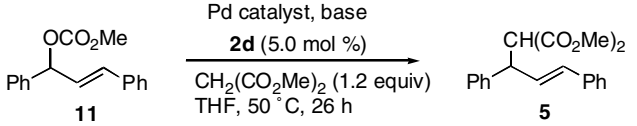
Scheme 3.

It is well known that Pd(0)-catalyzed allylic substitution of the allylic carbonate proceeds without addition of bases bacause an alkoxide is formed via oxidative addition of the carbonate to the Pd(0) complex followed by decarbonylation [14]. Thus, allylic substitution of carbonate **11** using a Pd–NHC complex was investigated (Table 3).

Unexpectedly, reaction of **11** with dimethyl malonate using Pd–NHC complex generated in situ from Pd_2dba_3 and imidazolium salt **2d** in the presence of Cs_2CO_3 gave allylation product **5** in a very low yield (5%) and unchanged **11** was recovered in 90% (run 1). The use of a Pd–NHC catalyst generated by treatment of $PdCl_2$–imidazolium salt **2d** with BuLi showed the same tendency and only a trace amount of the desired product was obtained along with unchanged **11** in 85% (run 2). At present, the reason why a Pd–NHC catalyst system is ineffective for the allylic substitution of carbonates is not clear.

Next, the reaction of allylic acetate with other nuclephiles instead of malonate was investigated. The reaction of allylic acetate **1** with β-ketoester **12** using the above-mentioned Pd–NHC complex, generated from Pd_2dba_3 and **2d**, in the presence of Cs_2CO_3, gave allylation product **13** in 38% yield as a mixture of diastereomers (ratio of 1:1) along with **13′** in 48% yield (Scheme 4). The product **13′**, which would be formed via isomerization from **13**, was obtained as a sole

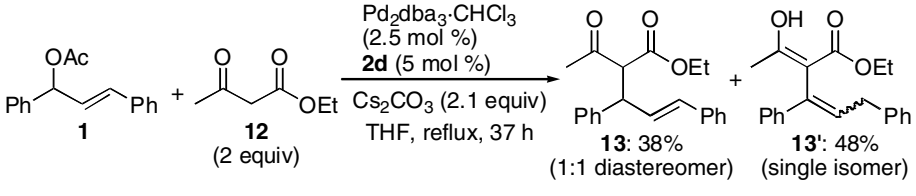
Table 3
Allylic substitution of carbonate **11** with dimethyl malonate using Pd–NHC complex



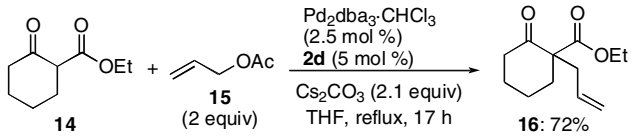
Run	Pd catalyst (mol%)	Base (mol%)	Yield	Recovery of **11** (%)
1	$Pd_2dba_3 \cdot CHCl_3$ (2.5)	Cs_2CO_3 (10)[a]	5%	90
2	$PdCl_2$ (5)	BuLi (15)[b]	Trace	85

[a] 10 mol% of Cs_2CO_3 was used for preparation in situ of a Pd–NHC complex from Pd_2dba_3 and imidazolium salt **2d**.

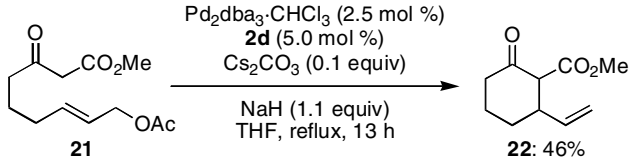
[b] Pd–NHC complex was prepared by treatment of $PdCl_2$ and **2d** with BuLi and then carbonate **11** and dimethyl malonate were added to the catalyst mixture.



Scheme 4.



Scheme 5.



Scheme 8.

product, although the geometry of the alkene fragment of **13′** was not determined.

Allylic substitution of allyl acetate **15** with cyclic β-ketoester **14** under similar conditions also proceed smoothly to afford the product **16**, having a quaternary carbon center, in good yield (Scheme 5).

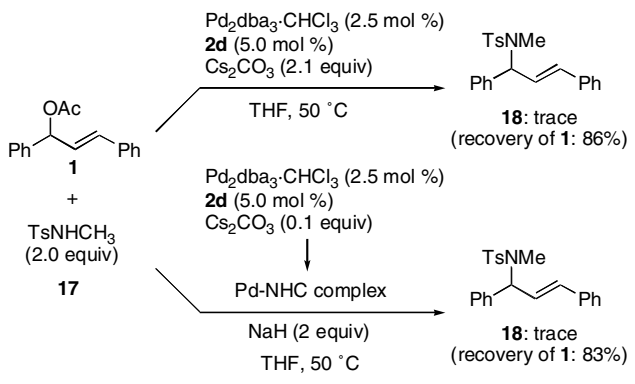
On the other hand, the reaction of **1** with a nitrogen nucleophile, *N*-methyltosylamide (**17**), under similar conditions and under conditions using NaH as a base did not afford the product **18**, and the starting material **1** was recovered in 86% and 83% yields, respectively (Scheme 6). Similarly, the reaction of **1** with benzylamine did not afford the coupling product **19**, only producing deacetylation product **20** in 41% yield (*E*/*Z* = 2.7:1) along with the starting material **1** in 43% yield. Although the reason is not clear, allylic substitution using a Pd–NHC complex seems to be inapplicable to nitrogen nucleophiles (Scheme 7).

Intramolecular allylic substitution of **21** was also carried out under similar conditions, and the cyclized product **22** was obtained in a moderate yield [15] (Scheme 8).

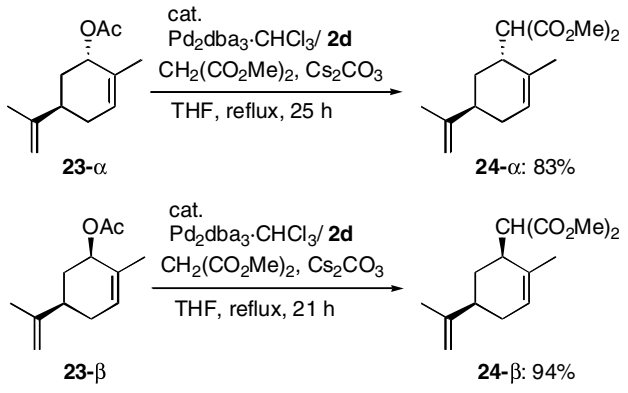
2.3. Stereochemistry in the allylic substitution using a Pd–NHC catalyst

In order to examine the stereochemical reaction course in the allylic substitution using a Pd–NHC catalyst, reactions of **23**-α and **23**-β were investigated (Scheme 9).

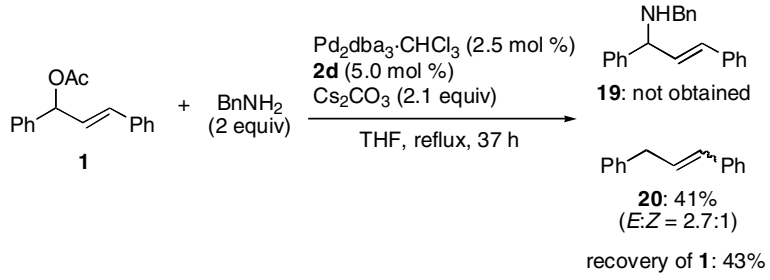
In the reactions of **23**-α and **23**-β under similar conditions, **24**-α and **24**-β were stereospecifically produced in 83% and 94% yields, respectively. These results indicate that allylic substitution using a Pd–NHC catalyst proceeds via an overall retention of configuration in a manner similar to when Pd–phosphine complexes are used.



Scheme 6.



Scheme 9.



Scheme 7.

2.4. Conclusions

A Pd(0)-catalyzed allylic substitution using N-heterocyclic carbene (NHC) as a ligand was investigated, and it was found that an imidazolium salt **2d** having bulky aromatic rings attached to the nitrogens in its imidazol-2-ylidene skeleton is suitable as a ligand precursor. It has also been proven that a Pd_2dba_3–imidazolium salt **2d**–Cs_2CO_3 system is highly efficient for producing a Pd–NHC catalyst in this reaction. Allylic substitution using a Pd–NHC complex is different from that using a Pd–phosphine complex as follows: (1) the reaction using a Pd–NHC complex requires elevated temperature (50 °C or reflux in THF), (2) allylic carbonates are inert to a Pd–NHC complex, and (3) nitrogen nucleophiles such as sulfonamide or amine do not react with allylic acetate in the Pd–NHC catalyst system. It was also found that allylic substitution with a soft nucleophile such as a malonate using a Pd–NHC catalyst proceeds via overall retention of configuration to give the product in a stereospecific manner, the stereochemical reaction course obviously being the same as that of the reaction using a Pd–phosphine complex.

3. Experimental

All manipulations were performed under an argon atmosphere unless otherwise stated. All solvents and reagents were purified when necessary using standard procedures. Imidazolium salts were dried in vacuo at 80 °C just before its use. Column chromatography was performed on silica gel 60 (Merck, 70–230 mesh), and flash chromatography was performed on silica gel 60 (Merck, 230–400 mesh).

3.1. Typical procedure for allylic substitution of *1* with *4* using a Pd–NHC catalyst generated from $PdCl_2$, imidazolium salt *2d*, and BuLi (Table 1, run 4)

To a suspension of $PdCl_2$ (12.6 mg, 0.07 mmol) and imidazolium salt **2d** (29.6 mg, 0.07 mmol) in THF was added BuLi (1.52 M in hexane, 0.14 mL, 0.21 mmol) at 0 °C, and the mixture was stirred at the same temperature for 45 min. To the reddish-brown mixture were added a solution of acetate **1** (353.2 mg, 1.4 mmol) in THF (7 mL) and a solution of sodium dimethylmalonate in THF (21 mL), which was prepared from dimethyl malonate (0.32 mL, 2.8 mmol) and NaH (60% oil suspension, 112.2 mg, 2.8 mmol), at room temperature, and the mixture was heated at 50 °C for 37 h. To the mixture was added sat. NH_4Cl aqueous solution at 0 °C, and the organic layer was extracted with Et_2O. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane–EtOAc, 8/1) to give **5** in 77% yield.

3.2. Typical procedure for allylic substitution of *1* with *4* using a Pd–NHC catalyst generated from $Pd_2dba_3 \cdot CHCl_3$ and imidazolium salt *2d* in the presence of Cs_2CO_3 (Table 2, run 2)

To a reddish-brown suspension of $Pd_2dba_3 \cdot CHCl_3$ (10.4 mg, 0.01 mmol), imidazolium salt **2 d** (8.5 mg, 0.02 mmol) and Cs_2CO_3 (273.7 mg, 0.84 mmol) in THF (0.4 mL) were added a solution of acetate **1** (100.9 mg, 0.4 mmol) in THF (2 mL) and a solution of dimethyl malonate (0.09 mL, 0.8 mmol) in THF (2 mL) at 0 °C, and the mixture was heated at 50 °C for 10 h. To the mixture was added sat. NH_4Cl aqueous solution at 0 °C, and the organic layer was extracted with Et_2O. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane–EtOAc, 4/1) to give **5** in 100% yield.

3.3. Spectral data

3.3.1. (*E*)-Methyl-9-acetoxy-3-oxonon-7-enoate (*21*)

The compound **21** was synthesized by acetylation of (*E*)-methyl-9-hydroxy-3-oxonon-7-enoate [15b]. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.71 (tt, $J = 7.3$, 7.3 Hz, 2H), 2.05–2.11 (m, 2H), 2.06 (s, 3 H), 2.55 (t, $J = 7.3$ Hz, 2H), 3.45 (s, 2H), 3.74 (s, 3H), 4.51 (d, $J = 6.4$ Hz, 2H), 5.54–5.61 (m, 1H), 5.72 (dt, $J = 15.7$, 6.4 Hz, 1 H); IR (neat) 2952, 1740, 1717, 1235 cm^{-1}; EI LRMS *m/z* 242 (M^+), 211 ($M^+ - OCH_3$), 182 ($M^+ - AcOH$), 150, 122. EI HRMS Calc. for $C_{11}H_{15}O_4$ ($M^+ - OCH_3$) 211.0970, found 211.0980.

3.3.2. rel-4S-Isopropenyl-6R-(1,1-bis(methoxycarbony)-methyl)-1-methyl-cyclohexene (*24*-α)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62–1.92 (m, 9H), 2.10–2.20 (m, 2H), 2.92 (m, 1H), 3.61 (d, $J = 7.6$ Hz, 1H), 3.73 (s, 3 H), 3.74 (s, 3H), 4.69 (s, 1H), 4.72 (s, 1H), 5.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) d 20.7, 22.5, 30.5, 31.2, 36.2, 38.9, 52.3, 52.4, 54.8, 108.9, 125.1, 132.5, 148.6, 168.8, 169.3; IR (neat) 2952, 1738, 1645, 1435, 1251 cm^{-1}; EI LRMS *m/z* 266, 234, 207, 203, 191, 149, 134, 119, 105. Anal. Calc. for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found C, 67.40; H, 8.26.

3.3.3. CAS registry numbers of other compounds known in the literature

1, 96482-68-7; **5**, 95071-02-6; **6**, 62668-02-4; **7**, 1566-65-0; **8a**, 119793-72-5; **8b**, 129047-20-7; **8c**, 119784-73-5; **9**, 68217-48-1; **10**, 79644-04-5; **11**, 121440-72-0; **13**, 191542-57-1; **16**, 61771-75-3; **20**-(*E*), 65149-83-9; **20**-(*Z*),

65149-82-8; **22**, 75351-30-3; **23**-α, 5258-01-5; **23**-β, 76704-27-3; **24**-β, 77517-64-7.

Acknowledgments

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