Chloroesterification of Enynes Catalyzed by NHC Rhodium Compounds

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Abstract: An efficient rhodium N-heterocyclic carbene (NHC)-catalyzed chloroesterification of terminal alkynes and enynes has been developed. The reaction was highly regio- and stereospecific: the *Z*-isomer was obtained as the sole product.

Key words: N-heterocyclic carbene, rhodium, catalysis, chloroesterification, enyne

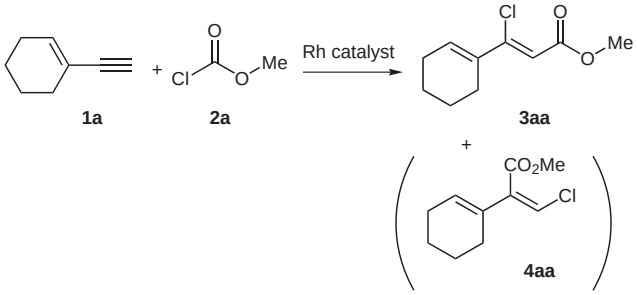
The use of chloroformate in organic synthesis can be traced back to a century ago,[1] although the extent of its use was quite limited.[2] Chloroformate has been utilized in reactions such as Curtius rearrangement, syntheses of *N*-alkyl carbamic acid alkyl esters and *N*-alkylcarbamates, and the dealkylation of amines.[3] Chloroformates may be used in the chloroesterification of alkynes to produce 3-chloroacrylate esters which are valuable intermediates in organic synthesis.[4] Thus we expected that a lot of attention would have been given to this chloroesterification process. However, on the contrary, only a few studies have been reported.[5] For example, Tanaka et al. reported a rhodium-catalyzed chloroesterification of terminal alkynes and 1,2-dienes (allenes).[5a,b]

Recently, N-heterocyclic carbenes (NHCs) have emerged as a group of promising ligands for the design of new homogeneous catalysts.[6] They are normally stable toward air, heat, and moisture, and are very powerful σ-donors. Some of them are commercially available. Metal complexes of NHCs were shown to be alternatives for the widely used phosphine complexes in homogeneous catalysis. In some cases, replacement of phosphines by NHCs can provide complexes with enhanced catalytic performances.[7] Despite the intense interest in the catalytic properties of NHC complexes,[8] reports on the use of rhodium–NHC complexes are still restricted in hydroformylation,[9] hydrogenation,[10] arylation,[11] hydrosilylation,[12] and cycloaddition[13] reactions. As a further step in our program toward the use of Rh–NHC complexes as catalysts,[12,13b] we initiated a study on the use of Rh–NHC complexes in chloroesterification of unsaturated hydrocarbons because the unsaturated hydrocarbons having chlorine and olefinic functionalities were envisioned to be useful in synthetic applications. Thus, we investigated the rhodium–NHC-catalyzed chloroesterification of alkynes and enynes. To the best of our knowledge, this is the first example of transition-metal–NHC-complex-catalyzed chloroesterification of enynes and alkynes.

Chloroesterification was studied using enyne **1a** as a model substrate and Rh(IPr)(cod)Cl [IPr = bis(2,6-diisopropylphenyl)imidazol-2-ylidene (Figure 1); cod = 1,5-cyclooctadiene] as a catalyst (Table 1).

Treatment of **1a** (0.5 mmol, 53 mg) with methyl chloroformate (1.0 mmol, 95 mg) in the presence of a catalytic amount of Rh(IPr)(cod)Cl (1 mol%, 3.2 mg) in toluene

Table 1 Rh–NHC-Catalyzed Chloroesterification of Enyne[a]



Entry	Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%) of **3aa**[b,c]
1	Rh(IPr)(cod)Cl	toluene	100	18	80
2	Rh(IPr)(cod)Cl	toluene	100	18	83[d]
3	Rh(IPr)(cod)Cl	toluene	70	18	61
4	Rh(IPr)(cod)Cl	toluene	100	12	83
5	Rh(IPr)(cod)Cl	toluene	100	6	65
6	Rh(IPr)(cod)Cl	TCE[e]	100	12	53 (11)[f]
7	Rh(IPr)(cod)Cl	DME[g]	100	12	8 (5)[f]
8	Rh(IPr)(CO)Cl	toluene	100	18	38
9	Rh(IMes)(cod)Cl	toluene	100	18	70
10	$Rh(PPh_3)$(cod)Cl	toluene	100	18	18 (4)[f]

[a] Reaction was run using **1a** (1.0 equiv), methyl chloroformate (2.0 equiv), Rh catalyst (1 mol%), and solvent (0.3 M).
[b] Isolated yield.
[c] In all cases, the ratio of product **3aa**/**4aa** was >19:1, as determined by ^{1}H NMR (300 MHz).
[d] A higher amount of methyl chloroformate (3 equiv) was used.
[e] TCE = tetrachloroethane.
[f] Yields in parentheses are for the trimerized product [1,3,5-tri(cyclohexenyl)benzene].
[g] DME = 1,2-dimethoxyethane.

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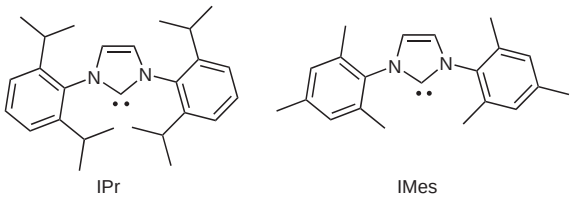


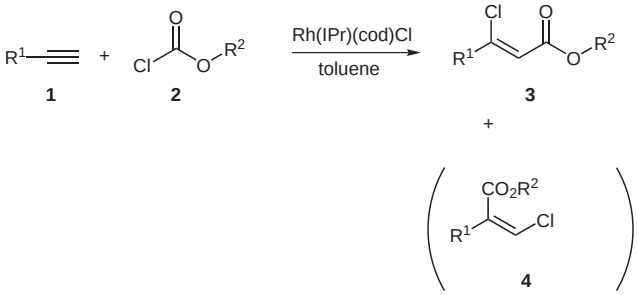
Figure 1 Structure of IPr and IMes, two N-heterocyclic carbenes

(1.5 mL) at 100 °C for 18 hours gave the chloroesterificated product **3aa** in 80% yield along with 0.2% yield of a cyclotrimerized product, 1,3,5-tri(cyclohexenyl)benzene. By comparing with the known ^{1}H NMR data of the *E*- and *Z*-isomer reported by Tanaka,[5a] we determined that the formation of the *E*-isomer was not observed. Thus, we could confirm that the *Z*-isomer was obtained as the sole product by ^{1}H NMR. Thus, the chloroesterification was highly regio- and stereospecific. Formation of **3aa** was confirmed by ^{1}H NMR and high resolution mass spectrometry. Encouraged by this result, we screened various reaction conditions, including the solvent, the reaction temperature, the reaction time, and rhodium catalysts for the esterification of **1a**. The effect of an increase in the amount of methyl chloroformate used on the yield of the reaction was negligible (entry 2). Thus, we used two equivalents of methyl chloroformate for all cases.

The yield of the reaction in toluene solution was dependent upon the reaction time and the reaction temperature (entries 1–5). The best result (83%) was obtained when the reaction was carried out at 100 °C for 12 hours. Changing the solvent from toluene to tetrachloroethane or 1,2-dimethoxyethane did not help the reaction (entries 5 and 6). In these cases, a trimerized product was also obtained in 11% and 5% yields, respectively. Replacement of the cod moiety in Rh(IPr)(cod)Cl by carbon monoxide led to a noticeable decrease in the yield (38%) of the reaction (entry 8). Substitution of IPr in Rh(IPr)(cod)Cl by 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) resulted in a decrease in the yield to 70%. When the phosphine rhodium complex [Rh(PPh_3)(cod)Cl] was used as a reference, only 18% of the reaction product was obtained, with the concomitant formation of a trimerized product (4%). Thus, among the rhodium catalysts examined, [Rh(cod)(IPr)Cl] was the best catalyst for the chloroesterification of **1a**. The optimized reaction conditions were established to be as follows: Rh(IPr)(cod)Cl (1 mol%), enyne (or alkyne; 0.5 mmol), chloroformate (2 equiv), toluene (0.3 M), 100 °C, and 12 hours.

We next investigated the chloroesterification of various alkynes and enynes under these optimized reaction conditions (Table 2). Treatment of **1a** with ethyl and phenyl chloroformates, instead of methyl chloroformate, led to isolation of the expected chloroesterified products in 66% and 77% yields, respectively (entries 2 and 3). Recently, Tanaka et al. reported[15] the addition reaction of ethyl chlorooxoacetate (ClCOCOOEt) to alkynes. Thus, when ethyl chlorooxoacetate was used instead of chloroformate under our reaction conditions, only 17% of the expected product was obtained. However, when the amount of the catalyst used was increased to 5 mol%, the yield of the reaction increased to 85% (entry 4). Several (functionalized) conjugated enynes (entries 5–10) were tested for the chloroesterification. Conjugated enynes **1b**–**d** with a terminal alkyne (entries 5–7) were good substrates, but for the conjugated enyne **1e** with a terminal alkyne (entry 8) a rather poor yield (38%) was obtained, presumably due to the volatility of the enyne. Treatment of an enyne with a hydroxyl group (**1f**, entry 9) gave no isolable products, but an enyne with a protected alcohol (**1g**, entry 10) produced the expected product in 77% yield. Thus, the protection of the alcohol group was necessary. Phenylacetylene (**1h**; entry 11) was a good substrate and the expected product was obtained in 82% yield. However, modest yields (32% and 48%) were obtained for terminal alkyl acetylenes **1i** and **1j** (entries 12 and 13). Unfortunately, our catalytic system proved ineffective for internal alkynes.[16] This observation was similar to Tanaka's result. According to their paper, all attempts to chloroesterify internal alkynes were unsuccessful and the starting material was recovered.

Table 2 Rh(IPr)(cod)Cl-Catalyzed Chloroesterification of Conjugated Enyne[a,14]



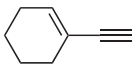
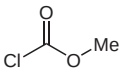
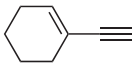
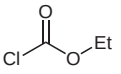
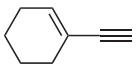
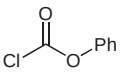
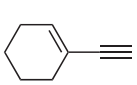
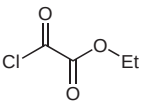
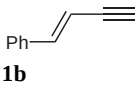
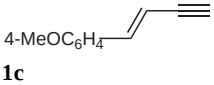
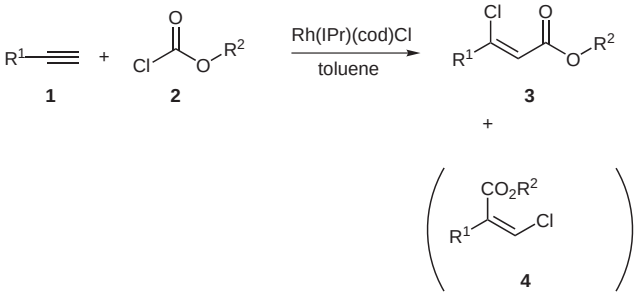
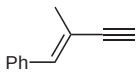
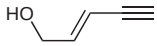
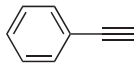
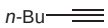
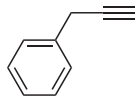
Entry	Reactant	Ester	Product	Yield[b] (%)
1	 **1a**	 **2a**	**3aa**	83
2	 **1a**	 **2b**	**3ab**	66
3	 **1a**	 **2c**	**3ac**	77
4	 **1a**	 **2d**	**3ad**	17 85[c]
5	 **1b**	**2a**	**3ba**	54
6	 **1c**	**2a**	**3ca**	56

Table 2 Rh(IPr)(cod)Cl-Catalyzed Chloroesterification of Conjugated Enyne[a,14] (continued)



1 2 3 4

Entry	Reactant	Ester	Product	Yield[b] (%)
7	 **1d**	**2a**	**3da**	71
8	 **1e**	**2a**	**3ea**	38
9	 **1f**	**2a**	**3fa**	–
10	 **1g**	**2a**	**3ga**	77
11	 **1h**	**2a**	**3ha**	82
12	 **1i**	**2a**	**3ia**	32
13	 **1j**	**2a**	**3ja**	48

[a] Reaction was run using Rh(IPr)(cod)Cl (1 mol%), enyne (or alkyne; 1.0 equiv), ester (2.0 equiv), toluene (0.3 M), 100 °C, 18 h.
[b] Isolated yield. In all cases, the ratio of product **3**/**4** was >19:1.
[c] A higher amount of the catalyst (5 mol%) was used, and the reaction was conducted at 60 °C for 20 h.

In conclusion, we have developed a highly efficient rhodium–NHC-catalyzed chloroesterification of terminal alkynes and enynes. The catalytic system is a highly versatile tool for obtaining products that cannot be easily attained with other metals. We are currently investigating other useful transformations using Rh–NHC catalysts.

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(14) **General Procedure for Rh–NHC-Catalyzed Chloroesterification of Alkyne**: To an oven-dried 10-mL tube containing toluene (5 mL), Rh–NHC (14 mg, 1 mol%) and alkyne (0.7 mmol) were added sequentially. After sealing the tube, the reaction temperature was elevated to 100 °C. The reaction was carried out in a test tube capped with a rubber septum. The rubber septum was tied with an aluminum binder. Thus, the reaction could be monitored by taking a small amount of the reaction mixture using a syringe. After the reactant was consumed, the solvent was removed under reduced pressure. Flash column chromatography gave the product.
3ab: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.1 Hz, 3 H), 1.61 (m, 2 H), 1.71 (dd, *J* = 5.4, 9.2 Hz, 2 H), 2.25 (d, *J* = 4.1 Hz, 4 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 6.11 (s, 1 H), 6.76 (t, *J* = 3.6 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 21.7, 22.6, 26.4, 60.5, 112.9, 133.6, 136.0, 148.9, 165.0. HRMS (EI): *m*/*z* calcd for $C_{11}H_{15}ClO_2$: 214.0761; found: 214.0764. IR: 1414 (w), 1433 (w), 1539 (w), 1601 (s), 1720 (s), 2120 (w), 2240 (w), 2296 (s), 2400 (w), 2504 (w), 2672 (m), 2920 (s), 2984 (m), 3048 (s), 3408 (br), 3680 (w), 3736 (w), 3936 (w) cm^{-1}.
3ac: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.58 (m, 2 H), 1.68 (m, 2 H), 2.22 (d, *J* = 6.0 Hz, 4 H), 6.15 (s, 1 H), 6.77 (s, 1 H), 7.35 (m, 5 H) ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 22.5, 26.3, 66.3, 112.4, 128.3, 128.5, 128.7, 133.6, 136.0, 136.4, 147.6, 164.1. HRMS (EI): *m*/*z* calcd for $C_{15}H_{15}ClO_2$: 262.0761; found: 262.0755. IR: 1416 (w), 1454 (w), 1486 (w), 1595 (s), 1723 (s), 1764 (w), 2128 (w), 2304 (s), 2408 (w), 2512 (w), 2672 (w), 2864 (w), 2928 (m), 2976 (w), 3048 (s), 3400(br), 3680 (w), 3744 (w), 3936 (m) cm^{-1}.
3ba: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 3 H), 6.20 (s, 1 H), 6.82 (d, *J* = 15.3 Hz, 1 H), 7.25–7.38 (m, 4 H), 7.47–7.50 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.8, 117.8, 125.9, 127.8, 129.1, 129.7, 135.4, 138.9, 144.6, 164.9. HRMS (EI): *m*/*z* calcd for $C_{12}H_{11}ClO_2$: 222.0447; found: 222.0445. IR: 1416 (w), 1596 (w), 1723 (s), 2296 (m), 2968 (s), 3048 (s) cm^{-1}.
3da: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.77 (s, 3 H), 3.83 (s, 3 H), 6.70 (d, *J* = 15.2 Hz, 2 H), 6.90 (d, *J* = 7.0 Hz, 2 H), 7.32 (d, *J* = 15.2 Hz, 1 H), 7.42 (d, *J* = 7.0 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.7, 55.6, 114.6, 116.6, 123.8, 128.2, 129.4, 138.6, 145.1, 161.0, 165.1. HRMS (EI): *m*/*z* calcd for $C_{13}H_{13}ClO_3$: 252.0553; found: 252.0555. IR: 1539 (w), 1584 (w), 1721 (s), 2296 (m), 2968 (s), 3048 (s) cm^{-1}.
3ea: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02 (s, 3 H), 3.78 (s, 3 H), 5.43 (s, 1 H), 5.92 (s, 1 H), 6.24 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 51.9, 115.7, 122.9, 139.7, 146.1, 165.1. HRMS (EI): *m*/*z* calcd for $C_7H_9Cl_1O_2$: 160.0291; found: 160.0294. IR: 1417 (w), 1435 (w), 1596 (m), 1729 (s), 2296 (s), 2400 (w), 2572 (w), 2672 (w), 2976 (m), 3048 (s), 3416 (br), 3672 (w), 3736 (w), 3928 (m) cm^{-1}.
3ga: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 6 H), 0.84 (s, 9 H), 3.67 (s, 3 H), 4.28 (m, 2 H), 6.01 (s, 1 H), 6.34 (m, 1 H), 6.54 (td, *J* = 3.7, 14.7 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.2, 18.6, 26.0, 26.1, 51.7, 62.6, 117.1, 126.4, 140.8, 144.3, 165.1. HRMS (FAB): *m*/*z* calcd for $C_{12}H_{23}ClO_3Si$: 290.1105; found: 291.1185. IR: 1420 (br), 1460 (w), 1603 (s), 1640 (w), 1728 (s), 2304 (m), 2400 (w), 2512 (w), 2672 (w), 2848 (w), 2944 (s), 3056 (m), 3360 (br), 3672 (w), 3736 (w), 3936 (w) cm^{-1}.

(15) Hua, R.; Onozawa, S.-Y.; Tanaka, M. *Chem. Eur. J.* **2005**, *11*, 3621.

(16) One of the referees suggested the possibility of the formation of an alkynic ester in the cases where low activities for the chloroesterification were observed (entries 4, 8, and 12 in Table 2): Nozaki, K.; Sato, N.; Takaya, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1629; however, no other by-products, except the trimerized product, were found.