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$FeCl_3$-Assisted Niobium-Catalyzed Cycloaddition of Nitriles and Alkynes: Synthesis of Alkyl- and Arylpyrimidines Based on Independent Functions of $NbCl_5$ and $FeCl_3$ Lewis Acids

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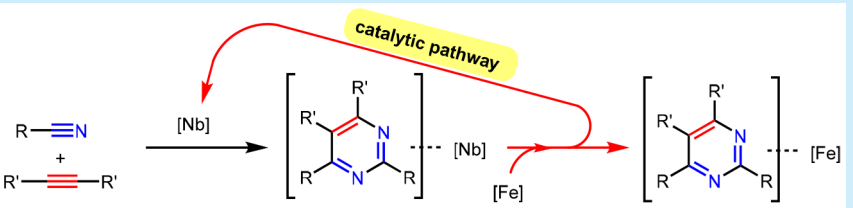
Supporting Information



ABSTRACT: $NbCl_5$-catalyzed [2 + 2 + 2] cycloaddition of nitriles with alkynes was used to synthesize pyrimidine derivatives. In this reaction, the use of individual Lewis acids, namely $NbCl_5$ and $FeCl_3$, is a key strategy for achieving the reaction using a catalytic amount of $NbCl_5$. The roles of the two Lewis acids were investigated using FT-IR spectroscopy. The results showed that $NbCl_5$ served as an efficient Lewis acid catalyst for nitrile activation, whereas $FeCl_3$ showed stronger Lewis acidity toward pyrimidines, releasing $NbCl_5$ into the catalytic cycle.

Pyrimidine derivatives are present as scaffolds in numerous natural products and bioactive products.[1a−f] Some pyrimidine-containing polymers or π-conjugated pyrimidines[1g] have been used as semiconductors,[1h,i] fluorescent molecules,[1j] liquid crystalline materials,[1k] and photovoltaic materials,[1l,m] while alkylpyrimidines are important synthetic intermediates.[2] Various methods for the formation of pyrimidine rings have been reported,[1−4] e.g., the well-known Pinner[3a] and Bredereck[3b] syntheses, involving cyclocondensations of 1,3-dicarbonyl compounds with amidines and formamide, respectively. However, preparation of the starting materials is not always easy. In addition, few methods for alkylpyrimidine synthesis have been reported, despite their simple structures.

Ramsey (in 1876) and Reppe (in 1949) reported metal-catalyzed [2 + 2 + 2] cycloaddition reactions for the production of pyridine[5a] or benzene.[5b] Since then, [2 + 2 + 2] cycloaddition reactions have become widely used because of their economy and efficiency in constructing three bonds in a single step from various unsaturated substrates, without byproduct formation. Transition-metal-catalyzed [2 + 2 + 2] cycloaddition reactions are powerful tools for forming various six-membered carbocycles such as benzenes and cyclohexadienes, or heterocycles such as pyridines and pyrimidines. Many transition-metal catalysts have been studied.[5]

In 1991, Plessis et al. reported that a low-valent niobium species generated from $NbCl_5/C_2H_6AlCl_2$ catalyzed the [2 + 2 + 2] cycloaddition of three alkyne molecules to form benzene derivatives.[6a] Niobium species are thermally stable and have high reductive abilities and Lewis acidities, therefore their use in many organic reactions has been reported.[6] Recently, we have contributed to the development of niobium-catalyzed [2 + 2 + 2] cycloadditions.[7] We reported the cycloaddition of two alkynes with one alkene to give 1,3-cyclohexadiene derivatives using the following systems: $NbCl_3$(DME),[7b−d] $NbCl_5$/hydrosilane,[7e] and an external-additive-free $NbCl_5$/alkene−solvent.[7f] In addition, a $Nb(OEt)_5$/Grignard reagent system catalyzed isocyanate cyclotrimerization.[7g] We have also reported cycloadditions involving nitriles; a $NbCl_5$/Zn/alkoxysilane system gives pyridine derivatives via cycloaddition of two alkynes with one nitrile molecule.[7h]

The [2 + 2 + 2] cycloaddition of two nitrile moieties with one alkyne moiety is one of the most efficient methods in terms of atom and step economy for preparing tetra- or trisubstituted pyrimidine derivatives.[8] This reaction traditionally required use of an alkali metal[8a] or a large amount of a strong protonic acid (TfOH or H_3PO_4/BF_3).[8b−e] Transition-metal-mediated/catalyzed reactions have been developed in recent years (Scheme 1). Liu et al. reported pyrimidine synthesis using a zirconium-mediated cycloaddition of aryl- or silyl-nitriles.[8f] However, an excess of the zirconium reagent was required. Rosenthal et al. reported the catalytic synthesis of pyrimidines using a seven-membered zirconium complex (eq 1).[8g] Louie et al. reported the synthesis of bicyclic pyrimidines using alkynenitriles and cyanamides in an FeI_2/Zn system (eq 2).[8h] Liu et al. reported the synthesis of aminopyrimidines from ynamides and nitriles (eq 3).[8i] However, the method cannot be used with simple monoalkynes such as diphenylacetylene and phenylacetylene.

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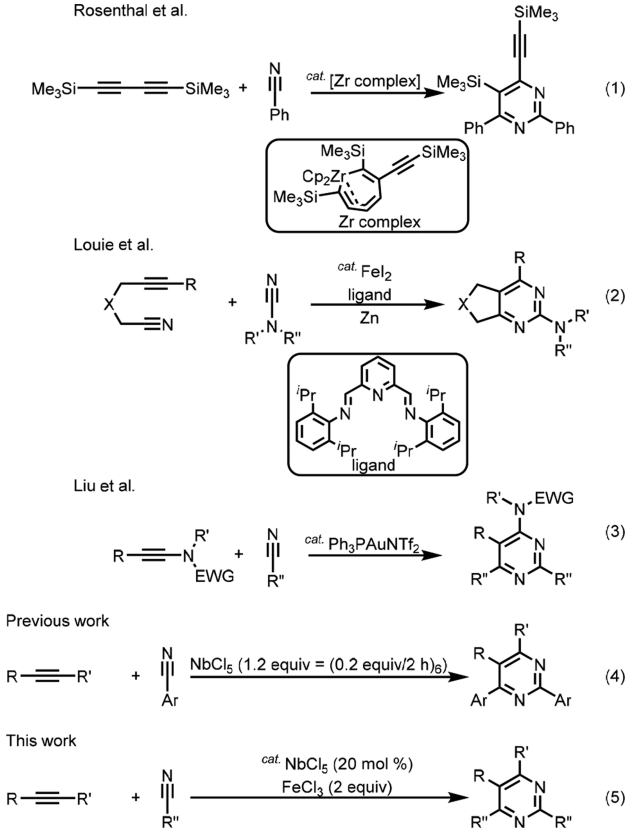
Scheme 1. Transition-Metal-Mediated/Catalyzed Synthesis of Pyrimidine Derivatives



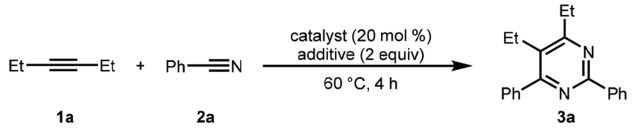
We reported the synthesis of pyrimidine derivatives via [2 + 2 + 2] cycloaddition of readily available alkynes and arylnitriles using $NbCl_5$ as a Lewis acid.[7i] However, a greater than stoichiometric amount of $NbCl_5$ had to be added several times to the reaction system.

In a previous study of pyrimidine synthesis, we found that the cycloaddition of nitriles and alkynes could be achieved by addition of $NbCl_5$ (1.2 equiv) in six batches to the reaction system (eq 4). The reason is as follows. The Lewis acidic niobium species was poisoned by the pyrimidine product, which is a Lewis base. We hypothesized that this problem could be solved by addition of another Lewis acid to capture the product, enabling regeneration of the active niobium species (eq 5).

Initially, we selected 3-hexyne (**1a**) and benzonitrile (**2a**) as model substrates to test our hypothesis. Table 1 shows the effects of various Lewis acid combinations in the cycloaddition. When **1a** (0.5 mmol) was reacted with **2a** (1 mL) in the presence of a catalytic amount of $NbCl_5$ (20 mol %), the pyrimidine derivative **3a** was obtained in 13% yield (entry 1). This reaction was promoted by addition of $FeCl_3$ and **3a** was obtained in 86% yield (entries 2–4). The product was obtained in an acceptable yield even when $NbCl_5$ (10 mol %) was used (entries 5 and 6). $AlCl_3$ also promoted the reaction (entry 7). However, other additives such as $FeBr_3$, CuCl, and TMSCl were not suitable for this reaction (entries 8–10).

In the absence of a catalyst, the reaction gave only 22% yield (entry 11). When $AlCl_3$ and $TaCl_5$ were used instead of $NbCl_5$, the yields were significantly lower (entries 12 and 13). $ZrCl_4$ had no catalytic activity (entry 14). $Nb(OEt)_5$ inhibited the reaction (entry 15). The use of TfOH[8d,e] instead of $FeCl_3$ led to decrease the yield of **3a** under these conditions (entry 16).

Table 1. Cycloaddition of 3-Hexyne and Benzonitrile under Various Conditions[a]



entry	catalyst	additive	conv (%)[b]	yield (%)
1	$NbCl_5$	none	42	13
2[c]	$NbCl_5$	$FeCl_3$	81	19
3[d]	$NbCl_5$	$FeCl_3$	78	47
4	$NbCl_5$	$FeCl_3$	91	86 [83[e], 65[f]]
5[g]	$NbCl_5$	$FeCl_3$	87	63
6[c,g]	$NbCl_5$	$FeCl_3$	91	60
7	$NbCl_5$	$AlCl_3$	90	60
8	$NbCl_5$	$FeBr_3$	80	28
9	$NbCl_5$	CuCl	11	n.d.
10	$NbCl_5$	TMSCl	99	11
11	none	$FeCl_3$	54	22
12	$AlCl_3$	$FeCl_3$	79	44
13	$TaCl_5$	$FeCl_3$	85	47
14	$ZrCl_4$	$FeCl_3$	54	21
15	$Nb(OEt)_5$	$FeCl_3$	47	trace
16	$NbCl_5$	TfOH	>99	75

[a]Reaction conditions: **1a** (0.50 mmol), **2a** (1.0 mL), catalyst (0.10 mmol), and additive (1.0 mmol) were stirred at 60 °C for 4 h under Ar. [b]Conversions and yields were determined by GC based on **1a** used. [c]$FeCl_3$ (0.50 mmol) was used. [d]$FeCl_3$ (0.75 mmol) was used. [e]Isolated yield. [f]Isolated yield from larger scale reaction (**1a**: 1.0 mmol). [g]$NbCl_5$ (0.05 mmol) was used.

We investigated the scopes and limitations of various substrates under the optimized conditions (Table 2). Symmetrical internal alkynes such as 3-hexyne (**1a**), 4-octyne (**1b**), and 5-decyne (**1c**) gave the corresponding pyrimidine derivatives **3a–c** with excellent selectivities. The unsymmetrical alkynes **1d** and **1e** gave the corresponding products in good yields as a mixture of regioisomers, i.e., **3d**,**3e** and **3d′**,**3e′**. The product regioselectivities were affected by steric hindrance. Methylphenylacetylene (**1f**) gave **3f** as the sole product. The terminal alkyne phenylacetylene (**1g**) and 1-hexyne (**1h**) gave excellent selectivities and yields.

Next, we investigated the reaction of **1a** with various nitriles. The reaction with an electron-rich nitrile, *p*-tolylnitrile (**2b**), gave the product **3i** in 43% yield. An electron-deficient nitrile, *p*-fluorobenzonitrile (**2c**), also reacted and gave the product **3j** in 57% yield.

Aliphatic nitriles such as acetonitrile (**2d**) and octanonitrile (**2e**) reacted with **1a** and gave the corresponding alkylpyrimidines, i.e., **3k** and **3l**, in moderate yields. Acrylonitrile (**2f**) was a good substrate and the vinyl group remained intact throughout the reaction; the divinylpyrimidine **3m** was obtained in good yield.

We used FT-IR analysis to clarify the roles of the two Lewis acids. A weak Lewis base such as acetonitrile or pyridine can be used to evaluate the Lewis acidities of ionic liquids and metal chlorides by FT-IR analysis.[9] The shifts to higher wavenumbers of the CN stretching or ring vibrations are related to the acidity. This is because the lone pair of the nitrogen in acetonitrile or pyridine interacts with Lewis acid sites. We used this method to support our hypothesis. First, we monitored the CN stretching vibrations of PhCN (Figure 1A). Pure PhCN gave a band at 2228 cm^{-1} arising from CN stretching.[10a] $FeCl_3$/PhCN caused only a

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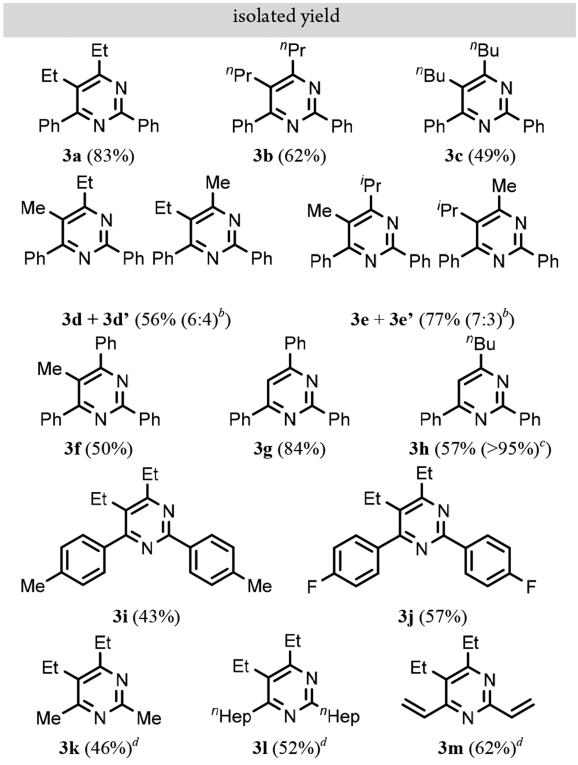
Table 2. Cycloadditions of Various Alkynes and Nitriles[a]



[a]Reaction conditions: **1** (0.50 mmol), **2** (1.0 mL), $NbCl_5$ (0.10 mmol), and $FeCl_3$ (1.0 mmol) were stirred at 60 °C for 4 h under Ar. [b]Selectivity of regioisomers. [c]The values in parentheses show the selectivity. [d]Reaction time was 6 h.

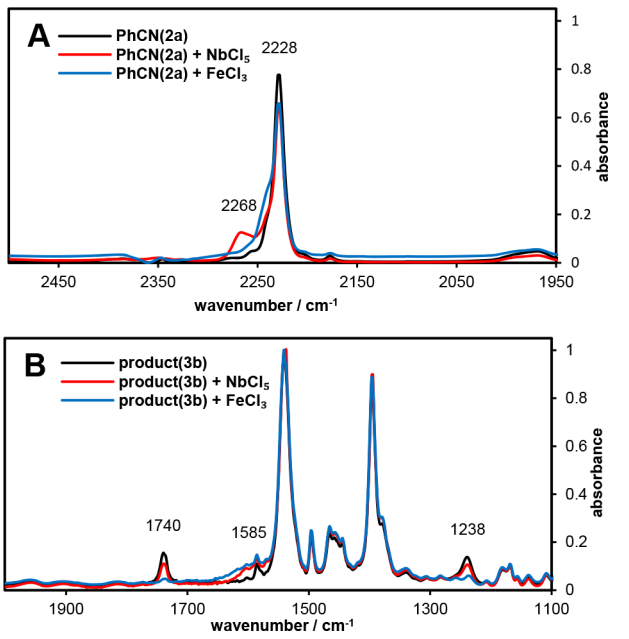


Figure 1. FT-IR spectra of (A) pure PhCN, PhCN + $NbCl_5$ (0.5 M), and PhCN + $FeCl_3$ (0.5 M) and (B) pure **3b**, **3b** + $NbCl_5$ (2:1 by weight) and **3b** + $FeCl_3$ (2:1 by weight).

slight change. However, $NbCl_5$/PhCN significantly shifted the peak to 2268 cm^{-1}. The shift to higher wavenumber of the CN bond vibration indicates the nitrile acidity. $NbCl_5$ has a higher affinity for the nitrile than $FeCl_3$. Next, we monitored the pyrimidine ring vibration mode of **3b** using the same method (Figure 1B). The vibration peak for pure **3b** appeared at 1585 cm^{-1}.[1f,10b] Mixtures of $FeCl_3$/**3b** and $NbCl_5$/**3b** were examined. The peak for $FeCl_3$/**3b** was at a higher wavenumber than that for $NbCl_5$/**3b**. This shows that $FeCl_3$ interacted more strongly than $NbCl_5$ with the pyrimidine ring. These outcomes are consistent with a reaction mechanism in which the two Lewis acids have different roles. The use of a mixture of $NbCl_5$/$FeCl_3$/PhCN was also investigated. FT-IR analysis showed negligible interactions between $NbCl_5$ and $FeCl_3$ (Figure S2), i.e., $NbCl_5$ (which activated the nitriles) and $FeCl_3$ (which coordinated with the pyrimidine and led to release of $NbCl_5$ into the catalytic cycle) performed independent Lewis acid functions in the catalytic cycle.

Figure 2 shows a plausible reaction mechanism based on our hypothesis and these experiments. Initially, a nitrile reacts with another nitrile activated by $NbCl_5$ to form a 1,3-diaza-1,3-butadiene scaffold (**B**). Subsequently, **B** undergoes cycloaddition with an alkyne to form a pyrimidine scaffold (**C**).[4i] The pyrimidine scaffold migrates from niobium to $FeCl_3$, regenerating the niobium catalyst. After the reaction, **D** is decomposed by quenching and pyrimidines are obtained.

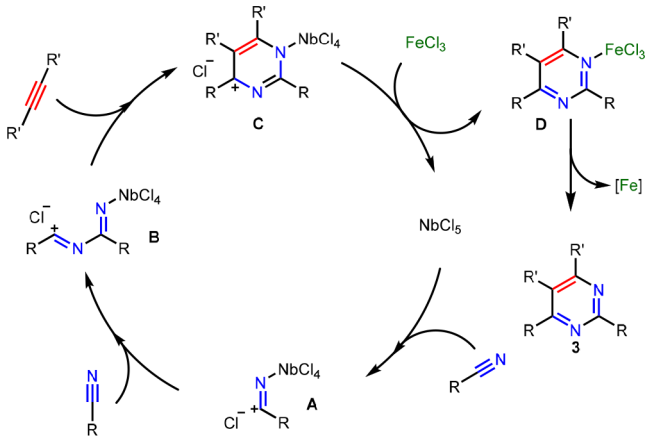


Figure 2. Plausible reaction mechanism for cycloaddition of nitriles with alkynes.

In conclusion, we developed a niobium-catalyzed [2 + 2 + 2] cycloaddition of one alkyne with two nitrile molecules, leading to pyrimidine derivatives. In this reaction, independent Lewis acid functions of $NbCl_5$ and $FeCl_3$ achieved a "catalytic version" of the $NbCl_5$-catalyzed cycloaddition of alkynes with nitriles to give pyrimidines, which had previously only been achieved using stoichiometric amounts of $NbCl_5$.

Further investigations with regard to the scrutiny the detailed functions of $NbCl_5$ and $FeCl_3$ are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02708.

Figures S1−S3, experimental procedures, and compound characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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