

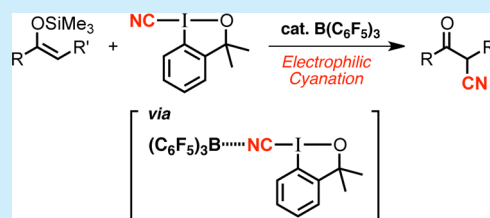
Catalytic Activation of 1-Cyano-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole with $B(C_6F_5)_3$ Enabling the Electrophilic Cyanation of Silyl Enol Ethers

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S Supporting Information

ABSTRACT: The Lewis acidic activation of a hypervalent iodine reagent containing a transferable cyano group, 1-cyano-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole (CDBX), with $B(C_6F_5)_3$, to achieve the catalytic electrophilic cyanation of silyl enol ethers is presented. Mechanistic studies indicate that CDBX is activated through coordination of its cyano group to $B(C_6F_5)_3$, thus enabling the electrophilic cyanation reaction to occur.



Nitriles are distributed across a wide range of molecules, from simple synthetic intermediates to biologically active molecules and functional materials.¹ Therefore, the development of efficient methods for introducing a cyano group into an organic molecule represents an important research topic in the field of organic chemistry. Conventional methods for preparing nitriles usually involve nucleophilic substitution and addition reactions using a cyanide (CN^-) source.² An alternative cyanation approach that employs an electrophilic cyanating reagent to produce a formal “ CN^+ ” species would offer a complementary synthetic strategy. Indeed, a variety of electrophilic cyanation reagents and synthetic applications utilizing them have been developed in recent decades. Electrophilic cyanating reagents generally contain a heteroatom–CN bond and include cyanates,³ cyanamides,⁴ *p*-toluenesulfonyl cyanide (TsCN),⁵ etc.⁶ Although cyanogen halides (XCN , X = Cl, Br, or I) may also be useful reagents for electrophilic cyanation reactions, the use of these reagents often suffers from several drawbacks including their high toxicity and competitive electrophilic halogenation reactions that occur, rather than cyanation.⁷ To address these issues, hypervalent iodine(III) reagents possessing a transferable cyano group has emerged as a promising electrophilic cyanating reagent. In the 1990s, noncyclic hypervalent iodine reagents, such as phenyl(cyano)iodonium triflate (**1a**) and (dicyanoiodo)benzene (**1b**), were synthesized by Zhdankin and Stang (Figure 1).⁸ However,

neither **1a** nor **1b** are frequently used in electrophilic cyanation reactions.⁹ A few years later, Zhdankin developed some relatively stable and easy-to-handle cyclic analogues, including 1-cyano-1,2-benziodoxol-3-(1*H*)-one (CBX, **1c**) and 1-cyano-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole (CDBX, **1d**), which were used in the $C(sp^3)$ –H cyanation of *N,N*-dialkylarylamines.¹⁰ Although several examples of electrophilic cyanation reactions employing **1c** and **1d**, including the cyanation of thiols¹¹ and β -ketoesters¹² under basic conditions, have been reported, these reagents continue to have limited applications in electrophilic cyanation reactions,¹³ probably because of their low reactivity. In this context, the development of a robust activation system would be highly desirable in terms of further expanding their synthetic utility. Herein, we report on the use of $B(C_6F_5)_3$ for efficiently activating the hypervalent iodine reagent **1d**, and the development of a system that can be applied to the catalytic electrophilic cyanation of silyl enol ethers to afford β -ketonitriles (Scheme 1). Although electrophilic cyanation of silyl enol ethers with *in situ* prepared hypervalent iodine(III) reagent from PhIO, Me_3SiCN , and BF_3

Scheme 1. $B(C_6F_5)_3$ -Catalyzed Electrophilic Cyanation of Silyl Enol Ethers with **1d**

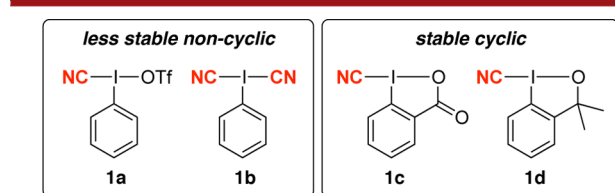
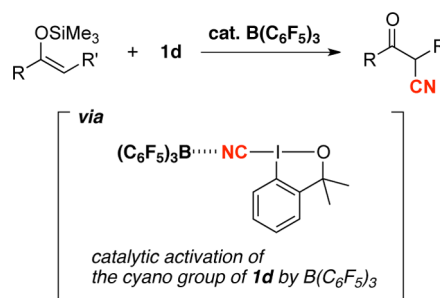


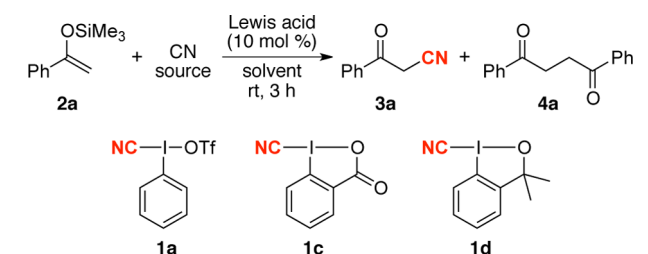
Figure 1. Hypervalent iodine reagents possessing a transferable cyano group.

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OEt₂ has recently been achieved,¹⁴ the use of **1c** and **1d** for the cyanation, which can simplify the experimental protocol and facilitate the synthetic application, has never been reported. To the best of our knowledge, the present work is the first examples of the catalytic activation of **1d** with a Lewis acid, enabling electrophilic cyanation.¹⁵

Boron Lewis acids have recently been found to efficiently promote electrophilic cyanation reactions.^{4g,h,16} Based on these findings, we hypothesized that boron Lewis acids could be used to activate the cyano group of hypervalent iodine reagents to generate a highly electrophilic species. To test this hypothesis, we examined the electrophilic cyanation of trimethyl(1-phenylvinyl)oxy)silane (**2a**) as the model reaction, and a series of Lewis acid catalysts were screened (Table 1). A brief

Table 1. Screening of Reaction Parameters for the Electrophilic Cyanation of **2a^a**



entry	CN source	Lewis acid	solvent	yield ^b (%)	
				3a	4a
1	1d	B(C ₆ F ₅) ₃	CH ₂ Cl ₂	84	6
2	1d	BF ₃ ·OEt ₂	CH ₂ Cl ₂	<5	31
3	1d	BEt ₃ ^c	CH ₂ Cl ₂	<5	<5
4	1a	B(C ₆ F ₅) ₃	CH ₂ Cl ₂	<5	38
5 ^d	1c	B(C ₆ F ₅) ₃	CH ₂ Cl ₂	7	<5
6	1d	none	CH ₂ Cl ₂	<5	<5
7 ^e	1d	B(C ₆ F ₅) ₃	CH ₂ Cl ₂	32	<5
8	1d	AlMe ₂ Cl ^f	CH ₂ Cl ₂	<5	<5
9	1d	AlMe ₃ ^c	CH ₂ Cl ₂	<5	<5
10	1d	InCl ₃	CH ₂ Cl ₂	<5	<5
11	1d	Me ₃ SiOTf	CH ₂ Cl ₂	<5	48
12	1d	Zn(OTf) ₂	CH ₂ Cl ₂	<5	52
13	1d	Cu(OTf) ₂	CH ₂ Cl ₂	<5	54
14	1d	Sc(OTf) ₃	CH ₂ Cl ₂	<5	63
15	1d	B(C ₆ F ₅) ₃	MeCN	69	8
16	1d	B(C ₆ F ₅) ₃	MeNO ₂	43	20
17	1d	B(C ₆ F ₅) ₃	toluene	<5	<5
18 ^f	ICN	B(C ₆ F ₅) ₃	CH ₂ Cl ₂	<5	<5
19 ^f	BrCN	B(C ₆ F ₅) ₃	CH ₂ Cl ₂	<5	<5

^aReaction conditions: **2a** (0.2 mmol), cyanating reagent (0.2 mmol), Lewis acid (10 mol %), solvent (2 mL), rt, 3 h. ^bDetermined by ¹H NMR analysis of the crude product using 1,1,2,2-tetrachloroethane as an internal standard. ^cLewis acid (1 M in hexane) was used. ^dReaction was run for 14 h. ^eB(C₆F₅)₃ (5 mol %) was used. ^fSee the Supporting Information for details.

screening of boron Lewis acids indicated that the cyanation proceeded effectively when 10 mol % of B(C₆F₅)₃ was added to the reaction using **1d** in CH₂Cl₂ at room temperature, thus affording the corresponding β-ketonitrile **3a** in 84% yield, along with a small amount of **4a** as a byproduct (entry 1).¹⁷ Meanwhile, both BF₃·OEt₂ and BEt₃ failed to promote the cyanation (entries 2 and 3), and when BF₃·OEt₂ was used in the reaction, **4a** was formed predominantly (31% yield).

Reactions using other hypervalent iodine reagents, such as **1a** and **1c**, resulted in quite low yields of **3a** (entries 4 and 5). Control experiments revealed that this reaction did not proceed in the absence of B(C₆F₅)₃, and decreasing the catalyst loading to 5 mol % resulted in a low yield of the product (entries 6 and 7). Furthermore, other group 13 Lewis acids, such as AlMe₂Cl, AlMe₃, and InCl₃, showed no catalytic activity (entries 8–10). We also tested some commonly used Lewis acids, such as Me₃SiOTf, Zn(OTf)₂, Cu(OTf)₂, and Sc(OTf)₃, but in all reactions, no cyanation products were detected, and the oxidative dimerization of **2a** proceeded exclusively to give **4a** (entries 11–14). Screening a series of solvents revealed that CH₂Cl₂ was the best medium for this transformation (entries 15–17). Only electrophilic halogenation, which leads to α-halogenated products, proceeded exclusively when cyanogen halides (ICN and BrCN) were used instead of hypervalent iodine reagents (entries 18 and 19). These results clearly demonstrate that the use of **1d** with B(C₆F₅)₃ is specifically effective in this electrophilic cyanation reaction.

To obtain additional insights into the activation mode of **1d** with B(C₆F₅)₃, spectroscopic analysis of a mixture of **1d** and 1 equiv of B(C₆F₅)₃ in dichloromethane were carried out. In a previous report,¹⁸ the coordination between the cyano group of ICN to B(C₆F₅)₃ was confirmed by IR spectroscopy. According to the literature, the CN stretching vibrational band of ICN was shifted significantly from 2169 to 2267 cm⁻¹ when the complex of ICN with B(C₆F₅)₃ was formed. Indeed, when 1 equiv of B(C₆F₅)₃ was added to a solution of **1d** in CH₂Cl₂, a significant shift in the CN stretching vibrational band of **1d**, from 2137 to 2216 cm⁻¹, was observed (Figure 2), strongly suggesting that

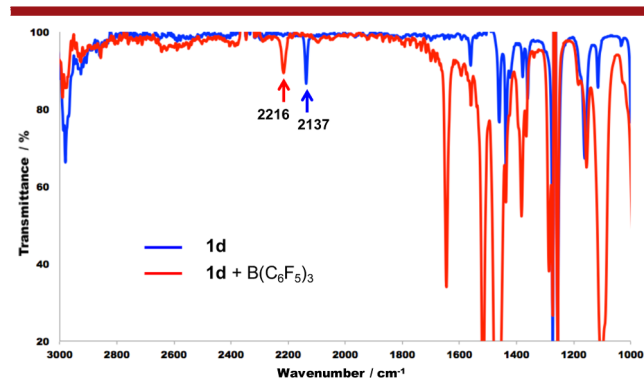


Figure 2. FTIR spectra of **1d** (blue line) and the mixture of **1d** and B(C₆F₅)₃ (red line) in CH₂Cl₂.

the cyano group of **1d** coordinates to B(C₆F₅)₃. Furthermore, control experiments using Lewis acids, which provided **4a** rather than **3a**, were carried out. The IR spectra of **1d** were essentially unchanged on the addition of BF₃·OEt₂, Me₃SiOTf, Zn(OTf)₂, and Sc(OTf)₃.¹⁹ These results clearly demonstrate that B(C₆F₅)₃ is specifically effective for activating **1d** through coordination, which results in the generation of a highly electrophilic species. To gain additional insights into the activation mode, a mixture of **1d** and B(C₆F₅)₃ was monitored by ¹³C NMR spectroscopy (Figure 2). When **1d** and 1 equiv of B(C₆F₅)₃ were mixed in CD₂Cl₂, the signal corresponding to the cyano group (98.4 ppm) was significantly shifted to a lower field (111.1 ppm) (Figure 3). In addition, the signal corresponding to the tertiary carbon adjacent to the oxygen atom (80.6 ppm) was also shifted to a lower field (86.8 ppm). These results also provide support for the Lewis acidic

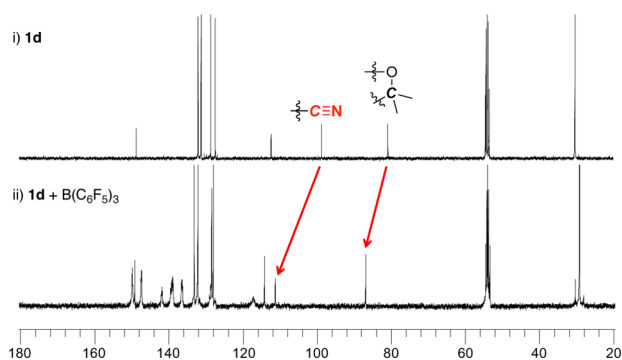
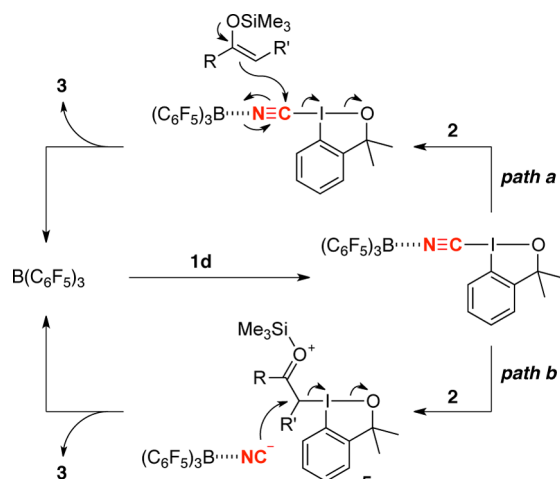


Figure 3. ^{13}C NMR spectra in CD_2Cl_2 : (i) **1d**; (ii) the mixture of **1d** and $\text{B}(\text{C}_6\text{F}_5)_3$.

activation of **1d**, which is different from the generally proposed activation mode of hypervalent iodine reagents by Lewis acids.^{15,20}

On the basis of the IR and NMR data, a plausible reaction pathway is depicted in **Scheme 2**. The reaction is initiated

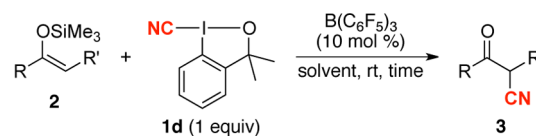
Scheme 2. Proposed Reaction Pathway



through the Lewis acidic activation of **1d** through the coordination of its cyano group to $\text{B}(\text{C}_6\text{F}_5)_3$. When the silyl enol ether **2** directly attacks the cyano group, the product **3** is obtained via an addition–elimination pathway (path a). Alternatively, the silyl enol ether could attack the electrophilic iodine center, to generate the intermediate **5** with the spontaneous dissociation of the cyanide from the iodine center (path b).²¹ A subsequent nucleophilic substitution by the cyanide at the α -carbon center affords the final product, along with the regeneration of $\text{B}(\text{C}_6\text{F}_5)_3$. In the latter pathway, substitution by the remaining silyl enol ether instead of the cyanide would afford **4**.¹⁷

Finally, we explored the scope of this electrophilic cyanation reaction (**Table 2**).²² In this cyanation, various silyl enol ethers derived from aromatic and aliphatic ketones were efficiently converted into the corresponding β -ketonitriles. Silyl enol ethers derived from acetophenone derivatives containing electron-donating groups in the *para* position on the phenyl ring, such as methoxy and methyl groups, participated in the reaction to give good product yields. (entries 2 and 3). The presence of a bromo substituent on the phenyl ring decreased the reactivity, and increasing the amount of $\text{B}(\text{C}_6\text{F}_5)_3$ from 10

Table 2. Scope of Silyl Enol Ethers for the Electrophilic Cyanation^a



entry	2	solvent	time (h)	product	yield ^b (%)
1	2a , X = H	CH_2Cl_2	3	3a	81
2	2b , X = 4-MeO	CH_2Cl_2	2	3b	74
3	2c , X = 4-Me	CH_2Cl_2	3	3c	75
4 ^c	2d , X = 4-Br	CH_2Cl_2	3	3d	80
5 ^c	2e , X = 4-CO ₂ Me	MeNO_2	3	3e	48
6	2f , X = 2-Me	MeCN	3	3f	64
7	2g , X = 3-Me	CH_2Cl_2	3	3g	89
8	2h	MeCN	3	3h	84
9	2i	CH_2Cl_2	6	3i	58
10 ^d	2j	MeCN	5	3j	37

^aReactions were conducted on a 0.5 mmol scale (0.1 M). ^bIsolated yield. ^c $\text{B}(\text{C}_6\text{F}_5)_3$ (20 mol %) was used. ^d MeCN (2 mL) was used.

to 20 mol % was effective, thus affording **3d** in a higher yield (entry 4). However, the reaction of the electron-deficient **2e** resulted in a low yield when the reaction was conducted in CH_2Cl_2 . A brief screening of solvents revealed that the use of MeNO_2 improved the efficiency to afford **3e** as the product (entry 5). This cyanation appears to be sensitive to steric effects by aryl substituents. For example, a methyl substituent at the *ortho* position resulted in a decreased reactivity to afford **3f** in 64% yield in MeCN (entry 6). A methyl substituent at the *meta* position had no effect on the cyanation reaction, giving high yields of **3g** (entry 7). In addition, silyl enol ethers containing vinyl and alkyl substituents were also applicable to this cyanation (entries 8 and 9). The silyl enol ether **2j** derived from propiophenone gave the corresponding β -ketonitrile, albeit in moderate yield (entry 10).

In conclusion, we report a novel catalytic activation of a hypervalent iodine reagent containing a transferable cyano group, 1-cyano-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole (CDBX), by $\text{B}(\text{C}_6\text{F}_5)_3$. The Lewis acidic activation of CDBX through the coordination of the cyano group to the boron center was confirmed by IR and NMR studies. In addition, the application of this activation system to the electrophilic cyanation of silyl enol ethers was demonstrated.²³ Further investigations to extend the scope and application of this method are currently ongoing in our laboratory.

■ ASSOCIATED CONTENT**● Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.orglett.7b02313](https://doi.org/10.1021/acs.orglett.7b02313).

Experimental procedures and characterization data for all new compounds; copies of ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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- (19) When 1 equiv of $\text{BF}_3\cdot\text{OEt}_2$ was added to a solution of **1d** in dichloromethane, the CN stretching vibrational band of **1d** was slightly shifted from 2137 to 2162 cm^{-1} . In addition, in the ^{13}C NMR spectrum, the signal corresponding to the cyano group was shifted upfield from 98.4 ppm to 78.1 ppm.
- (20) Although the Lewis acidic activation of a hypervalent fluoriodine(III) reagent through the coordination of its fluorine atom to a Lewis acid has recently been revealed (ref 15g–i), this type of activation mode for the related cyanoiodine(III) reagent has never been reported.
- (21) Path b cannot be ruled out at this stage even though there is no experimental evidence for the formation of the cyano- or isocyanoborate species.
- (22) When the cyanation of **2a** was carried out on a 1 mmol scale, the product **3a** was obtained in 85% yield. See the [Supporting Information](#) for details.
- (23) Attempts to use a silyl ketene acetal, 1-ethoxy-1-(trimethylsilyloxy)ethene, as a nucleophile resulted in low yield of the corresponding cyanated product (<10%).