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Selective Double-Hydrosilylation of Nitriles Catalyzed by an Iron Complex Containing Indium Trihalide

Masaki Ito, Masumi Itazaki, and Hiroshi Nakazawa*

Abstract: Selective double-hydrosilylation was achieved using tertiary and secondary silanes with an excess of organonitriles ($\text{RC}\equiv\text{N}$ (R = alkyl, aryl)), in the presence of a catalytic amount of triirondodecacarbonyl ($\text{Fe}_3(\text{CO})_{12}$) and indium trichloride (InCl_3). This reaction was also catalyzed by an iron complex containing indium trihalide $[\text{Fe}(\text{MeCN})_6][\text{Fe}(\text{CO})_4(\text{InX}_3)_2]$, prepared by the reaction of $\text{Fe}_3(\text{CO})_{12}$ with InX_3 (X = Cl, Br, I). This is a novel report of the combination of a transition metal complex and an indium source in organic synthesis.

Transformations of organonitriles into other organic compounds catalyzed by a transition metal complex have been reported, e.g., C–CN bond cleavage,^[1] hydrosilylation of $\text{C}\equiv\text{N}$ bond.^[2] We previously reported the synthesis of silyl cyanide through C–CN bond activation of organonitriles by an iron catalyst.^[3]

Among these reactions, hydrosilylation of a $\text{C}\equiv\text{N}$ triple bond is one of the most atom-efficient reactions because the reaction theoretically produces no by-products. In the reaction of $\text{RC}\equiv\text{N}$ with hydrosilane $\text{R}'_3\text{SiH}$, the expected products are the silylimine ($\text{RHC}=\text{N}(\text{SiR}'_3)$) and disilyl amine ($\text{RH}_2\text{C}-\text{N}(\text{SiR}'_3)_2$), which are formed by single^[4a–d] and double^[4e–k] hydrosilylation, respectively (Scheme 1). These *N*-silylated compounds are highly useful precursors of *N*-containing organic compounds^[5] and silicon-containing polymers.^[6] Moreover, hydrosilylation of a $\text{C}\equiv\text{N}$ triple bond is an effective method for the reduction of nitriles.^[7] Only a few examples of double hydrosilylation catalyzed by a transition metal complex have been reported.^[4e–k] In addition, catalytic hydrosilylations of nitriles without a transition metal catalyst have been reported; in 2015, Chang's group reported that $\text{B}(\text{C}_6\text{F}_5)_3$ exhibited catalytic activity for chemoselective hydrosilylation of conjugated nitriles.^[8] Unfortunately, the catalyst is moisture sensitive and expensive.

Scheme 1. Hydrosilylation of nitriles.

Most catalytic reactions for hydrosilylation of nitriles require an excess of hydrosilane in order to afford the disilyl-amine selectively. Here, we report a new catalytic system for the selective double-hydrosilylation of nitriles using an iron-based catalyst, without excess hydrosilane.

Acetonitrile (4.0 mmol), Me_2PhSiH (0.80 mmol), $\text{Fe}_3(\text{CO})_{12}$ (0.027 mmol), and InCl_3 (0.080 mmol) were charged into a sealed glass tube under a dry nitrogen atmosphere, and the solution was heated at 80 °C for 24 h (Scheme 2). After removal of volatile materials under reduced pressure, the disilyl amine $\text{MeCH}_2-\text{N}(\text{SiMe}_2\text{Ph})_2$ was obtained in 78% yield by extraction with *n*-hexane and drying in *vacuo* (Table 1, entry 1). Unexpectedly, double-hydrosilylation had occurred selectively, even if an excess of nitrile over hydrosilane was used. The ^1H NMR spectrum of the reaction mixture revealed that the silyl imine was not formed. A deuterium labeling experiment using CD_3CN in place of CH_3CN afforded $\text{CD}_3\text{CH}_2-\text{N}(\text{SiMe}_2\text{Ph})_2$ in 73% yield. To the best of our knowledge, there are no previous reports of an iron complex combined with an indium source used in organic synthesis.^[9]

Scheme 2. Double-hydrosilylation of acetonitrile promoted by $\text{Fe}_3(\text{CO})_{12}$ with InCl_3 .

$\text{Fe}_3(\text{CO})_{12}$ or InCl_3 when used separately for the double-hydrosilylation of acetonitrile with Me_2PhSiH showed no catalytic activity (Table 1, entries 2, 3). $[\text{Fe}(\text{MeCN})_6][\text{Fe}(\text{CO})_4(\text{InX}_3)_2]$ prepared from $\text{Fe}_3(\text{CO})_{12}$ and InX_3 ^[10,11] exhibited catalytic activity (entries 4–6), with $[\text{Fe}(\text{MeCN})_6][\text{Fe}(\text{CO})_4(\text{InCl}_3)_2]$ showing the highest activity among them. When the amount of $[\text{Fe}(\text{MeCN})_6][\text{Fe}(\text{CO})_4(\text{InCl}_3)_2]$ was reduced from 5 to 1 mol% or when THF was used as a solvent, the yield was greatly diminished (entries 7, 8). Further, the reaction did not proceed at room temperature (entry 9). When $[\text{Fe}(\text{MeCN})_6][\text{PF}_6]_2$ was used as a catalyst, hydrosilylation was not observed (entry 10), but the reaction proceeded when $[\text{PPN}]_2[\text{Fe}(\text{CO})_4(\text{InCl}_3)_2]$ was used (entry 11). It was therefore concluded that the anionic part of $[\text{Fe}(\text{MeCN})_6][(\text{CO})_4\text{Fe}(\text{InCl}_3)_2]$ acted as the catalyst in double-hydrosilylation. The different activities of the iron-indium complexes in entries 4 and 11 may result from the degree of stabilization by the cation.

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Supporting information for this article is given via a link at the end of the document.

Table 1. Catalytic double-hydrosilylation of acetonitrile with Me₂PhSiH.^[a]

$$2 \text{ Me}_2\text{PhSiH} \xrightarrow[80^\circ\text{C}, 24 \text{ h}]{\text{cat. 10 equiv MeC}\equiv\text{N}} \text{MeCH}_2\text{N} \begin{matrix} \text{SiMe}_2\text{Ph} \\ \text{SiMe}_2\text{Ph} \end{matrix}$$

entry	cat. [amount (mol%)] ^[b]	yield (%) ^[c]
1	Fe ₃ (CO) ₁₂ (3.3) + InCl ₃ (10)	78
2	Fe ₃ (CO) ₁₂ (3.3)	0
3	InCl ₃ (10)	0
4	[Fe(MeCN) ₆][Fe(CO) ₄ (InCl ₃) ₂] (5)	85
5	[Fe(MeCN) ₆][Fe(CO) ₄ (InBr ₃) ₂] (5)	56
6	[Fe(MeCN) ₆][Fe(CO) ₄ (InI ₃) ₂] (5)	21
7	[Fe(MeCN) ₆][Fe(CO) ₄ (InCl ₃) ₂] (1)	trace
8 ^[d]	[Fe(MeCN) ₆][Fe(CO) ₄ (InCl ₃) ₂] (5)	trace
9 ^[e]	[Fe(MeCN) ₆][Fe(CO) ₄ (InCl ₃) ₂] (5)	0
10	[Fe(MeCN) ₆][PF ₆] ₂ (5)	0
11	[PPN] ₂ [(CO) ₄ Fe(InCl ₃) ₂] (5)	35

[a] Me₂PhSiH/acetonitrile = 0.8:4.0 mmol. [b] Based on [Me₂PhSiH]. [c] Isolated yield. [d] In THF (0.5 mL). [e] At room temperature.

To explore the scope of double-hydrosilylation reactions catalyzed by [Fe(MeCN)₆][Fe(CO)₄(InCl₃)₂], several combinations of nitriles and hydrosilanes were examined (Table 2). Reactions were observed for the double-hydrosilylation of Me₂PhSiH with RC≡N, where R = Me, Et, *i*Bu, *i*Pr, Ph, *p*-Tol, *m*-Tol or *o*-Tol (entries 1–4, 6–9). In the case of propane nitrile (EtCN), the main product was EtCH₂N(SiMe₂Ph)₂, with MeCH₂N(SiMe₂Ph)₂ as a by-product (2% NMR yield). The by-product is believed to have formed from MeCN, due to EtCN/MeCN exchange on the cationic part of the catalyst (entry 2). The hydrosilylation was strongly influenced by steric effects of the substituent on the nitrile carbon; the yield decreased when using *i*PrCN (entry 4), and no reaction was observed when using *i*BuCN (entry 5). Yields from tolunitrile decreased in the order *p*->*m*->*o*-tolunitrile, presumably because of the increasing steric hindrance around the nitrile group (entries 7–9). Benzonitrile and *p*-tolunitrile gave the corresponding disilyl amines in similar yields (entries 6, 7). 4-PyCN was also converted into the corresponding disilyl amine, although the yield was low (entry 10). Nitriles containing electron-withdrawing substituents and NC(CH₂)₄CN did not undergo hydrosilylation (entries 11–13). Reactions were observed for the double-hydrosilylation of Me₂FcSiH with *p*-TolCN and MePhSiH₂ with MeCN, giving the corresponding disilyl amines in 43% and 76% yields, respectively (entries 14, 15). All disilyl amines obtained were characterized by ¹H, ¹³C{¹H}, ²⁹Si{¹H} NMR, GC/MS, and elemental analyses (see supporting information).

Table 2. Double-hydrosilylation of various nitriles with hydrosilanes catalyzed by an iron-indium complex.^[a]

$$2 \text{ R}'_3\text{SiH} \xrightarrow[80^\circ\text{C}, 24 \text{ h}]{\text{5 mol\% [Fe(MeCN)}_6\text{][Fe(CO)}_4\text{(InCl}_3\text{)}_2\text{] (vs. R}'_3\text{SiH) 10 equiv RC}\equiv\text{N}} \text{RCH}_2\text{N} \begin{matrix} \text{SiR}'_3 \\ \text{SiR}'_3 \end{matrix}$$

entry	RC≡N	R' ₃ SiH	RCH ₂ N(SiR' ₃) ₂	yield ^[b]
1	MeCN	Me ₂ PhSiH	MeCH ₂ N(SiMe ₂ Ph) ₂ (1)	85
2	EtCN	Me ₂ PhSiH	EtCH ₂ N(SiMe ₂ Ph) ₂ (2)	65 ^[c]
3	<i>i</i> BuCN	Me ₂ PhSiH	<i>i</i> BuCH ₂ N(SiMe ₂ Ph) ₂ (3)	75
4	<i>i</i> PrCN	Me ₂ PhSiH	<i>i</i> PrCH ₂ N(SiMe ₂ Ph) ₂ (4)	66
5	<i>t</i> BuCN	Me ₂ PhSiH	–	–
6	PhCN	Me ₂ PhSiH	PhCH ₂ N(SiMe ₂ Ph) ₂ (5)	54
7	(<i>p</i> -Tol)CN	Me ₂ PhSiH	(<i>p</i> -Tol)CH ₂ N(SiMe ₂ Ph) ₂ (6)	55
8	(<i>m</i> -Tol)CN	Me ₂ PhSiH	(<i>m</i> -Tol)CH ₂ N(SiMe ₂ Ph) ₂ (7)	49
9	(<i>o</i> -Tol)CN	Me ₂ PhSiH	(<i>o</i> -Tol)CH ₂ N(SiMe ₂ Ph) ₂ (8)	41
10	(4-Py)CN	Me ₂ PhSiH	(4-Py)CH ₂ N(SiMe ₂ Ph) ₂ (9)	21
11	CCl ₃ CN	Me ₂ PhSiH	–	–
12	(C ₆ F ₅)CN	Me ₂ PhSiH	–	–
13	NC(CH ₂) ₄ CN	Me ₂ PhSiH	–	–
14	(<i>p</i> -Tol)CN	Me ₂ FcSiH	(<i>p</i> -Tol)CH ₂ N(SiMe ₂ Fc) ₂ (10)	43
15	MeCN	MePhSiH ₂	MeCH ₂ N(SiMePhH) ₂ (11)	76

[a] See supporting information for details of reaction conditions. [b] Isolated yield. [c] The relatively low reaction yield of EtCH₂N(SiMe₂Ph)₂ is caused by the difficulty in the removal of MeCH₂N(SiMe₂Ph)₂ produced as a by-product in this reaction, by distillation because of the similar boiling points.

In order to obtain insight into the mechanism of the [Fe(MeCN)₆][Fe(CO)₄(InCl₃)₂] system, we examined two reactions. First, we carried out the reaction using InCl₃ as an additive in excess (eq. i) and found that no hydrosilylation occurred. We therefore concluded that the dissociation of InCl₃ is important in our system.

We suspected that InCl₃ eliminated from the catalyst precursor reacts with hydrosilane to give indium hydride HInCl₂, as reported by Baba and co-workers.^[12] Moreover, they reported that HInX₂ acts as a radical.^[13] We examined our reaction system in the presence of TEMPO as a radical scavenger and found that the formation of disilyl amine was suppressed (eq. ii).

We therefore concluded that HInCl_2 was involved in the reaction pathway.

Based on the observations mentioned above, we tentatively propose a catalytic cycle, as depicted in Scheme 3. First, one indium ligand in $[\text{Fe}(\text{CO})_4(\text{InCl}_3)_2]^{2-}$ dissociates and monoindium-iron species **A** is generated. Then, the released indium trichloride reacts with hydrosilane to give indium hydride and chlorosilane. One of CO ligands in **A** is replaced by the nitrile used to give **B**. Then, **B** reacts with indium hydride to form indylimine complex **C**. Intermediate **C** reacts with hydrosilane to give silylimine iron complex **D**, which reacts further to give indylsilylamine complex **E**. Finally, **E** reacts with hydrosilane then the nitrile used to produce disilylamine and HInCl_2 with regeneration of **B**. We think that the silylimine in **D** does not dissociate readily from the iron center and/or **D** is extremely reactive toward HInCl_2 ; therefore, selective disilyl amine formation is eventually achieved.

Scheme 3. Proposed catalytic cycle for the formation of a disilyl amine in the reaction of nitrile with hydrosilane promoted by $[\text{Fe}(\text{MeCN})_6][\text{Fe}(\text{CO})_4(\text{InCl}_3)_2]$.

In summary, we have described an unprecedented selective double-hydrosilylation of organonitriles promoted by a combination of triirondodecacarbonyl $\text{Fe}_3(\text{CO})_{12}$ with indium trichloride InCl_3 . Iron-indium complex $[\text{Fe}(\text{MeCN})_6][\text{Fe}(\text{CO})_4(\text{InX}_3)_2]$ also showed catalytic activity. In our reaction system, only the double hydrosilylation product was obtained and no single hydrosilylation product was produced. Our catalytic system was applicable to various nitriles and hydrosilanes.

Experimental Section

General procedure for synthesis of disilyl amine derivatives in Table 2: Nitrile (4.0 mmol) was treated with tertiary (or secondary) silane (0.80 mmol) in the presence of iron-indium catalyst $[\text{Fe}(\text{CH}_3\text{CN})_6][(\text{CO})_4\text{Fe}(\text{InCl}_3)_2]$ (36.5 mg, 0.040 mmol) at 80°C for 24 h under nitrogen atmosphere. After all volatile materials were removed under reduced pressure, the residue was extracted with *n*-hexane (2 mL $\times$ 3) and the filtrate was dried in *vacuo* to give the corresponding disilyl amine. Purified product was obtained by distillation using a Kugelrohr.

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Keywords: Double-hydrosilylation • Nitrile • Iron catalyst • Indium halide

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