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

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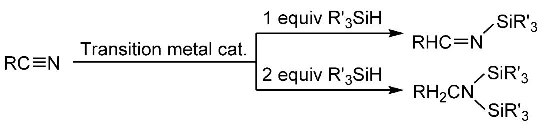
Selective double hydrosilylation was achieved by using tertiary and secondary silanes with an excess amount of an organonitrile (RC≡N; R = alkyl, aryl) in the presence of a catalytic amount of triirondodecacarbonyl [$Fe_3(CO)_{12}$] and indium trichloride ($InCl_3$). This reaction was also catalyzed by an iron complex containing indium trihalide [$Fe(MeCN)_6$][$Fe(CO)_4(InX_3)_2$], prepared by the reaction of $Fe_3(CO)_{12}$ 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.

The transformation of organonitriles into other organic compounds catalyzed by a transition-metal complex has been reported, including C–CN bond cleavage[1] and the hydrosilylation of C≡N bonds.[2] We previously reported the synthesis of silyl cyanides through C–CN bond activation of organonitriles by an iron catalyst.[3]

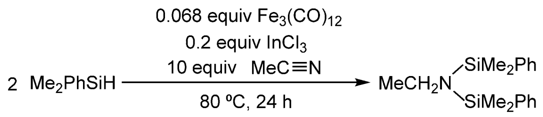
Among these reactions, the hydrosilylation of a C≡N bond is one of the most atom-efficient reactions, because the reaction theoretically produces no byproducts. In the reaction of RC≡N with hydrosilanes R'_3SiH, the expected products are silyl imines ($RHC{=}NSiR'_3$) and disilylamines [$RH_2C\text{-}N(SiR'_3)_2$], which are formed by single[4a–d] and double[4e–k] hydrosilylation, respectively (Scheme 1). These *N*-silylated compounds are highly useful precursors of nitrogen-containing organic compounds[5] and silicon-containing polymers.[6] Moreover, the hydrosilylation of a C≡N bond is an effective method to reduce nitriles.[7] Only a few examples of double hydrosilylation catalyzed by a transition-metal complex have been reported.[4e–k] In addition, the catalytic hydrosilylation of nitriles without a transition-metal catalyst has been reported; in 2015, Chang's group reported that $B(C_6F_5)_3$ exhibited catalytic activity for the chemoselective hydrosilylation of conjugated nitriles.[8] Unfortunately, the catalyst was moisture sensitive and expensive.



Scheme 1. Hydrosilylation of nitriles.

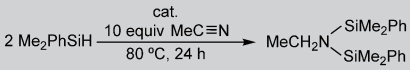
Most catalytic reactions for the hydrosilylation of nitriles require an excess amount of the hydrosilane to afford the disilylamine selectively. Herein, we report a new catalytic system for the selective double hydrosilylation of nitriles by using an iron-based catalyst without an excess amount of the hydrosilane.

Acetonitrile (4.0 mmol), Me_2PhSiH (0.80 mmol), $Fe_3(CO)_{12}$ (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 disilylamine $MeCH_2\text{-}N(SiMe_2Ph)_2$ 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 amount of the nitrile over the hydrosilane was used. The ^1H NMR spectrum of the reaction mixture revealed that the silyl imine was not formed. A deuterium-labeling experiment by using CD_3CN in place of CH_3CN afforded $CD_3CH_2\text{-}N(SiMe_2Ph)_2$ in 73 % yield. To the best of our knowledge, there



Scheme 2. Double hydrosilylation of acetonitrile promoted by $Fe_3(CO)_{12}$ with $InCl_3$.

Table 1. Catalytic double hydrosilylation of acetonitrile with Me_2PhSiH.[a]



Entry	Catalyst (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	[$Fe(MeCN)_6$][$(CO)_4Fe(InCl_3)_2$] (5)	85
5	[$Fe(MeCN)_6$][$(CO)_4Fe(InBr_3)_2$] (5)	56
6	[$Fe(MeCN)_6$][$(CO)_4Fe(InI_3)_2$] (5)	21
7	[$Fe(MeCN)_6$][$(CO)_4Fe(InCl_3)_2$] (1)	trace
8[d]	[$Fe(MeCN)_6$][$(CO)_4Fe(InCl_3)_2$] (5)	trace
9[e]	[$Fe(MeCN)_6$][$(CO)_4Fe(InCl_3)_2$] (5)	0
10	[$Fe(MeCN)_6$][PF_6]$_2$ (5)	0
11	[PPN]$_2$[$(CO)_4Fe(InCl_3)_2$] (5)	35

[a] Me_2PhSiH/acetonitrile = 0.8:4.0 mmol. [b] Based on [Me_2PhSiH]. [c] Yield of isolated product. [d] In THF (0.5 mL). [e] At room temperature.

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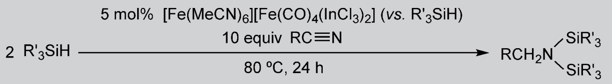
are no previous reports of an iron complex combined with an indium source used in organic synthesis.[9]

Upon using either $Fe_3(CO)_{12}$ or $InCl_3$ separately for the double hydrosilylation of acetonitrile with Me_2PhSiH, no catalytic activity was found (Table 1, entries 2 and 3). The $[Fe(MeCN)_6][Fe(CO)_4(InX_3)_2]$ complexes prepared from $Fe_3(CO)_{12}$ and InX_3[10,11] did, however, exhibit catalytic activity (Table 1, entries 4–6), and $[Fe(MeCN)_6][Fe(CO)_4(InCl_3)_2]$ showed the highest activity among them. If the amount of $[Fe(MeCN)_6][Fe(CO)_4(InCl_3)_2]$ was reduced from 5 to 1 mol% or if THF was used as the solvent, the yield was greatly diminished (Table 1, entries 7 and 8). Further, the reaction did not proceed at room temperature (Table 1, entry 9). Upon using $[Fe(MeCN)_6][PF_6]_2$ as the catalyst, hydrosilylation was not observed (Table 1, entry 10), but the reaction proceeded if $[PPN]_2[Fe(CO)_4(InCl_3)_2]$ was used (Table 1, entry 11). It was, therefore, concluded that the anionic part of $[Fe(MeCN)_6][(CO)_4Fe(InCl_3)_2]$ acted as the catalyst in the double hydrosilylation reaction. The different activities of the iron–indium complexes in entries 4 and 11 (Table 1) may result from the different degrees of stabilization by the cation.

To explore the scope of the double hydrosilylation reactions catalyzed by $[Fe(MeCN)_6][Fe(CO)_4(InCl_3)_2]$, several combinations of nitriles and hydrosilanes were examined (Table 2). Reactions were observed for the double hydrosilylation of Me_2PhSiH with $RC{\equiv}N$, for which R = Me, Et, *i*Bu, *i*Pr, Ph, *p*-Tol, *m*-Tol, or *o*-Tol (Table 2, entries 1–4, 6–9). In the case of propane nitrile (EtCN), the main product was $EtCH_2N(SiMe_2Ph)_2$, with $MeCH_2N(SiMe_2Ph)_2$ as a byproduct (2% yield, as determined by NMR spectroscopy). The byproduct is believed to have formed from MeCN, owing to EtCN/MeCN exchange on the cationic part of the catalyst (Table 2, entry 2). The hydrosilylation was strongly influenced by steric effects of the substituent on the nitrile carbon atom; the yield decreased upon using *i*PrCN (Table 2, entry 4), and no reaction was observed upon using *t*BuCN (Table 2, entry 5). Yields from tolunitrile decreased in the order *p*-tolunitrile > *m*-tolunitrile > *o*-tolunitrile, presumably because of the increasing steric hindrance around the nitrile group (Table 2, entries 7–9). Benzonitrile and *p*-tolunitrile gave the corresponding disilylamines in similar yields (Table 2, entries 6 and 7). 4-PyCN (py = pyridyl) was also converted into the corresponding disilylamine, although the yield was low (Table 2, entry 10). Nitriles containing electron-withdrawing substituents and $NC(CH_2)_4CN$ did not undergo hydrosilylation (Table 2, entries 11–13). Reactions were observed for the double hydrosilylation of Me_2FcSiH with *p*-TolCN and $MePhSiH_2$ with MeCN, which gave the corresponding disilylamines in yields of 43 and 76%, respectively (Table 2, entries 14 and 15). All disilylamines obtained were characterized by ^1H NMR, $^{13}C\{^1H\}$ NMR, $^{29}Si\{^1H\}$ NMR, GC–MS, and elemental analyses (see the Supporting Information).

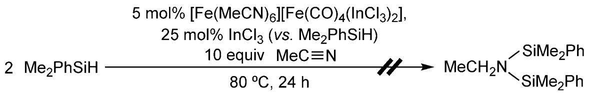
Table 2. Double hydrosilylation of various nitriles with hydrosilanes catalyzed by an iron–indium complex.[a]



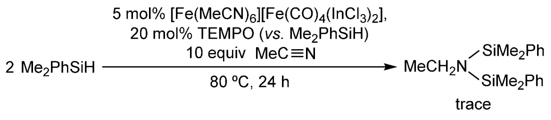
Entry	$RC{\equiv}N$	R'_3SiH	$RCH_2N(SiR'_3)_2$	Yield[b] [%]
1	MeCN	Me_2PhSiH	$MeCH_2N(SiMe_2Ph)_2$ (**1**)	85
2	EtCN	Me_2PhSiH	$EtCH_2N(SiMe_2Ph)_2$(**2**)	65[c]
3	*i*BuCN	Me_2PhSiH	*i*Bu$CH_2N(SiMe_2Ph)_2$(**3**)	75
4	*i*PrCN	Me_2PhSiH	*i*Pr$CH_2N(SiMe_2Ph)_2$(**4**)	66
5	*t*BuCN	Me_2PhSiH	–	–
6	PhCN	Me_2PhSiH	$PhCH_2N(SiMe_2Ph)_2$ (**5**)	54
7	(*p*-Tol)CN	Me_2PhSiH	(*p*-Tol)$CH_2N(SiMe_2Ph)_2$(**6**)	55
8	(*m*-Tol)CN	Me_2PhSiH	(*m*-Tol)$CH_2N(SiMe_2Ph)_2$(**7**)	49
9	(*o*-Tol)CN	Me_2PhSiH	(*o*-Tol)$CH_2N(SiMe_2Ph)_2$(**8**)	41
10	(4-Py)CN	Me_2PhSiH	(4-Py)$CH_2N(SiMe_2Ph)_2$(**9**)	21
11	CCl_3CN	Me_2PhSiH	–	–
12	$(C_6F_5)CN$	Me_2PhSiH	–	–
13	$NC(CH_2)_4CN$	Me_2PhSiH	–	–
14	(*p*-Tol)CN	Me_2FcSiH	(*p*-Tol)$CH_2N(SiMe_2Fc)_2$(**10**)	43
15	MeCN	$MePhSiH_2$	$MeCH_2N(SiMePhH)_2$(**11**)	76

[a] See the Supporting Information for details of the reaction conditions. [b] Yield of isolated product. [c] The relatively low reaction yield of $EtCH_2N(SiMe_2Ph)_2$ was caused by difficulties associated with removing the $MeCH_2N(SiMe_2Ph)_2$ byproduct produced in this reaction by distillation because of similar boiling points.

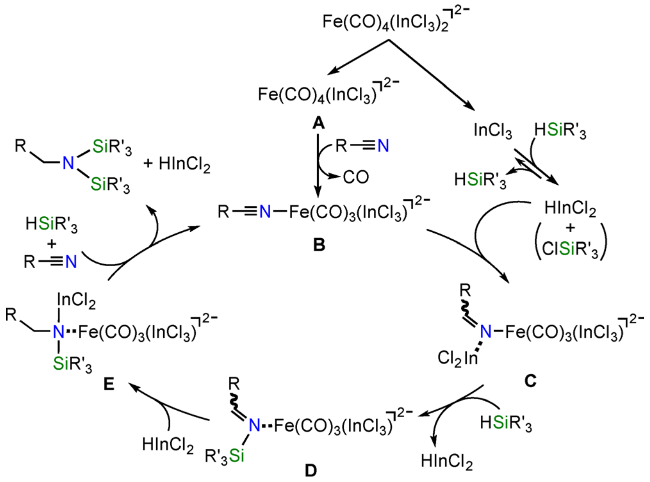
To obtain insight into the mechanism of the $[Fe(MeCN)_6][Fe(CO)_4(InCl_3)_2]$ system, we examined two reactions. First, we performed the reaction by using $InCl_3$ as an additive in excess amount [Eq. (1)] and found that no hydrosilylation occurred. We, therefore, concluded that the dissociation of $InCl_3$ was important in our system.



We suspected that $InCl_3$ eliminated from the catalyst precursor reacted with hydrosilane to give indium hydride $HInCl_2$, as reported by Baba and co-workers.[12] Moreover, they reported that $HInX_2$ acted as a radical.[13] We examined our reaction system in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a radical scavenger and found that the formation of the disilylamine was suppressed [Eq. (2)]. We, therefore, concluded that $HInCl_2$ was involved in the reaction pathway.



On the basis of the observations mentioned above, we tentatively propose a catalytic cycle, as depicted in Scheme 3. First, one indium ligand in $[Fe(CO)_4(InCl_3)_2]^{2-}$ dissociates and monoindium–iron species **A** is generated. Then, the released indium trichloride reacts with hydrosilane to give indium hydride and chlorosilane. One of the CO ligands in **A** is replaced by the nitrile used to give **B**. Then, **B** reacts with indium hydride to form indyl imine complex **C**. Intermediate **C** reacts with hydrosilane to give silyl imine iron complex **D**, which reacts further to give indylsilylamine complex **E**. Finally, **E**



Scheme 3. Proposed catalytic cycle for the formation of a disilylamine in the reaction of nitriles with hydrosilanes promoted by $[Fe(MeCN)_6][Fe(CO)_4(InCl_3)_2]$.

reacts with hydrosilane and then the nitrile used to produce disilylamine and $HInCl_2$ with regeneration of **B**. We think that the silyl imine in **D** does not dissociate readily from the iron center and/or that **D** is extremely reactive toward $HInCl_2$; therefore, selective disilylamine formation is eventually achieved.

In summary, we described an unprecedented selective double hydrosilylation of organonitriles promoted by a combination of triirondodecacarbonyl $[Fe_3(CO)_{12}]$ with indium trichloride ($InCl_3$). The iron–indium $[Fe(MeCN)_6][Fe(CO)_4(InX_3)_2]$ complex 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 disilylamine derivatives

The nitrile (4.0 mmol) was treated with a tertiary (or secondary) silane (0.80 mmol) in the presence of $[Fe(CH_3CN)_6][(CO)_4Fe(InCl_3)_2]$ (36.5 mg, 0.040 mmol) at 80 °C under a nitrogen atmosphere for 24 h. After all volatile materials were removed under reduced pressure, the residue was extracted with *n*-hexane (3×2 mL), and the filtrate was dried in vacuo to give the corresponding disilylamine. The purified product (see Table 2) was obtained by distillation by using a Kugelrohr.

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Keywords: hydrosilylation · indium · iron · nitriles · silanes

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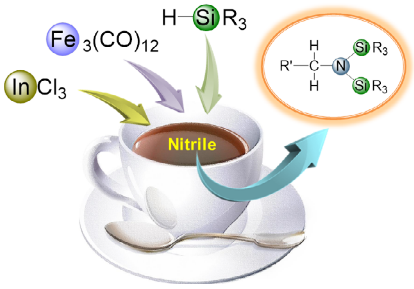
Selective Double Hydrosilylation of Nitriles Catalyzed by an Iron Complex Containing Indium Trihalide



My cup of tea! Selective double hydrosilylation is achieved by using tertiary and secondary silanes with an excess amount of an organonitrile ($RC \equiv N$; R = alkyl, aryl) in the presence of a catalytic amount of triirondodecacarbonyl [$Fe_3(CO)_{12}$] and indium trichloride ($InCl_3$). This reaction is also catalyzed by an iron complex containing indium trihalide [$Fe(MeCN)_6$][$Fe(CO)_4(InX_3)_2$], prepared by the reaction of $Fe_3(CO)_{12}$ with InX_3 (X = Cl, Br, I).