# **ORGANOMETALLICS**

### Catalytic Hydrosilylation of Alkenes by Iron Complexes Containing Terpyridine Derivatives as Ancillary Ligands

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#### **Supporting Information**

**ABSTRACT:** Iron complexes formulated as  $Fe(terpy)X_2$ (terpy = 2,2':6',2"-terpyridine derivatives; X = Cl, Br) were prepared and their catalytic activities for hydrosilylation of olefin with hydrosilane were examined. Although  $Fe(terpy)X_2$ did not show catalytic activity, the treatment of  $Fe(terpy)X_2$ with NaHBEt<sub>3</sub> caused catalytic activity. The influence of substituents in terpy on the catalytic activity was examined, and it was found that some complexes with an unsymmetri-



cally disubstituted terpy selectively produced 1-silylalkane with quite high catalytic activity. In the reaction of 1-octene with  $PhSiH_3$ , the double-hydrosilylation product  $Ph(1-octyl)_2SiH$  was selectively obtained.

O rganosilicon compounds have now become indispensable to our daily life. As organosilicons consisting mainly of Si-C bonds do not exist naturally, these compounds have been synthesized artificially. One of the most convenient and widely used methods of forming Si-C bonds is the hydrosilylation reaction, which involves the addition of the Si-H bond in hydrosilane across an unsaturated hydrocarbon such as an alkene or alkyne. A transition-metal catalyst is required for hydrosilylation.<sup>1</sup>

Among the many transition-metal catalysts reported to date, platinum catalysts such as Speier's catalyst and Karstedt's catalyst are known to be very powerful and are often used commercially.<sup>2</sup> However, we now know that the use of precious metals in catalysis is not always required. The relatively high cost, environmental concerns, and uncertainty of the long-term supply of precious metals have inspired the search for equivalent or superior base-metal alternatives. Iron is an attractive precious metal surrogate because of its high natural abundance, low cost, and precedent in numerous biocatalytic reactions.

One of the most important issues with hydrosilylation of alkenes is selectivity; side reactions such as dehydrogenative silylation, giving a vinylsilane, and hydrogenation, providing an alkane, often accompany the desired reaction.<sup>1</sup> Therefore, creation of new catalysts with high selectivity as well as high activity is very important.

Several iron complexes have been reported for use in catalytic hydrosilylation of unsaturated hydrocarbons. To the best of our knowledge, the first such example was reported by Nesmeyanov et al. in 1962,<sup>3</sup> who achieved the thermal reaction of R<sub>3</sub>SiH with alkenes in the presence of a catalytic amount of Fe(CO)<sub>5</sub> to give a hydrosilylation product and a dehydrogenative silylation product. Photoreaction of R<sub>3</sub>SiH with alkenes using the Fe(CO)<sub>5</sub> catalyst was also reported.<sup>4</sup> A mechanism including insertion of a C==C double bond into an Fe–Si bond was proposed for Cp\*Fe(CO)<sub>2</sub>R (Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>, R = alkyl,

silyl).<sup>5</sup> CpFe(CO)<sub>2</sub>Me (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) was reported to catalyze the reaction of 1,3-divinyldisiloxane with hydrosilane to give the compound produced by dehydrogenative silvlation at one vinyl group and by hydrogenation at the other vinyl group.<sup>6</sup> A trinuclear iron carbonyl complex,  $Fe_3(CO)_{12}$ , showed catalytic activity in the reaction of styrene and its derivatives with Et<sub>3</sub>SiH to give dehydrogenative silvlation products, whereas the reaction of 1-hexene with Et<sub>3</sub>SiH produced both dehydrogenative silvlation and hydrogenation products.<sup>7</sup> In both cases,  $Fe_3(CO)_{12}$  did not produce the hydrosilylation product. A heterotrinuclear complex containing Fe and Pt, FePt<sub>2</sub>(CO)<sub>5</sub>(PPh<sub>3</sub>)<sub>2</sub>(PhC<sub>2</sub>Ph), also exhibited catalytic activity toward hydrosilylation of alkynes;<sup>8</sup> however, the role of Fe in the catalytic system was not clear. The reaction of CpFe- $(CO)_2(SiMe_3)$  (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) with CH<sub>2</sub>=CHR (R = SiMe\_3, Ph, H) stoichiometrically gave dehydrogenative silvlation products, and the  $Fe(CO)_5$  +  $Et_3SiH$  system catalyzed the reaction of  $(CH_2=CH)SiMe_2OSiMe_2(CH=CH_2)$  with Et<sub>3</sub>SiH to give both the dehydrogenative silvlation and hydrogenation products.9 Recently, iron bis(imino)pyridine complexes were reported by Chirik and co-workers to serve as excellent catalysts for alkene hydrosilylation.<sup>10</sup> Their impressive report prompted us to investigate the catalytic activity of iron complexes with terpyridine and its derivatives as a ligand, since an N3-type tridentate ligand such as bis(imino)pyridine seemed to endow iron complexes, which have been considered to have low selectivity and poor activity, with high selectivity and good catalytic activity. We herein report the synthesis of mononuclear iron complexes with a 2,2':6',2"-terpyridine ligand and its derivatives having two substituents, either symmetrically on the 6- and 6"-positions or unsymmetrically on the 6- and 6"-

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positions or on the 6- and 5"-positions (see Chart 1), and their catalytic activities for the hydrosilylation of olefins.<sup>11</sup>

#### Chart 1. Terpyridine and the Atom Numbering



6,6"-Symmetrically disubstituted terpyridines were prepared from 6,6"-dibromoterpyridine and the corresponding arylboronic acid using a Suzuki–Miyaura coupling reaction.<sup>12,13</sup> These terpyridine derivatives, together with nonsubstituted terpyridine, were treated with FeX<sub>2</sub> (X = Cl, Br) to give Fe(terpy)X<sub>2</sub> in good yields (eq 1) (terpy stands for terpyridine and its



derivatives). These complexes showed good stability in the solid state and in solution. The reaction of nonsubstituted terpy with FeCl<sub>2</sub> has already been reported to give  $[Fe(terpy)_2]$ - $[FeCl_4]_2$ .<sup>12</sup> Our results, on the basis of the elemental analysis data, showed that the reaction with FeBr<sub>2</sub> produced Fe(terpy)-Br<sub>2</sub> but not  $[Fe(terpy)_2][FeBr_4]_2$ .

The catalytic activity of these iron complexes was then examined. The reactions of PhSiH<sub>3</sub> with 1-hexene were examined in the presence of a catalytic amount of the iron complexes, but no reaction was observed at 50 °C. Adding NaBHEt<sub>2</sub> to the reaction system, however, led to the formation of the hydrosilylated product. Hydrosilane and 1-hexene in a 1:32 molar ratio and 0.3 mol % (based on the concentration of the hydrosilane) of the iron complex were placed in a Schlenk tube. To the suspension was added 1.1 mol % of NaBHEt<sub>3</sub> at room temperature, which resulted in the formation of a homogeneous solution that turned dark brown within several minutes. The solution was heated at 50 °C for 24 h. After the reaction mixture was cooled to room temperature, the hydrosilylated product was measured by HPLC.<sup>14</sup> The results are summarized in Table 1. Iron complexes with unsubstituted terpy showed no catalytic activity (entries 1 and 2), whereas those with 6,6" disubstituted terpy did show catalytic activity (entries 3-10). In all cases, the product was 1-silylhexane and no 2-silylhexane was formed, showing that selective anti-Markovnikov addition took place. These results are consistent with the fact that hydrosilylation to olefins with aliphatic substituent(s) occurs with anti-Markovnikov regioselectivity.<sup>15</sup> In addition, neither the corresponding dehydrogenative silvlation products nor hydrogenated products were formed. Comparisons of entries 3 and 4, entries 6 and 7, and entries 8 and 9 revealed that the dibromoiron complexes were better

$R'R^2SiH_2 + //$			$\sim\sim\sim$
entry	Fe cat.	$R^1R^2SiH_2$	TON
1	1-FeCl <sub>2</sub>	PhSiH <sub>3</sub>	0
2	1-FeBr <sub>2</sub>	PhSiH <sub>3</sub>	0
3	2-FeCl <sub>2</sub>	PhSiH <sub>3</sub>	4
4	2-FeBr <sub>2</sub>	PhSiH <sub>3</sub>	19
5	3-FeBr <sub>2</sub>	PhSiH <sub>3</sub>	4
6	4-FeCl <sub>2</sub>	PhSiH <sub>3</sub>	15
7	4-FeBr <sub>2</sub>	PhSiH <sub>3</sub>	70
8	4-FeCl <sub>2</sub>	$Ph_2SiH_2$	8
9	4-FeBr <sub>2</sub>	$Ph_2SiH_2$	71
10	4-FeBr <sub>2</sub>	MePhSiH <sub>2</sub>	90

precursors than the corresponding dichloroiron complexes. It has been reported that the bond energy of Fe–Cl in FeCl<sub>2</sub> (95.6 kcal/mol) is greater than that of Fe–Br in FeBr<sub>2</sub> (81.2 kcal/mol).<sup>16</sup> If this tendency is applied to Fe(terpy)X<sub>2</sub>, our observation that Fe(terpy)Br<sub>2</sub> is a better precursor than Fe(terpy)Cl<sub>2</sub> would indicate that Fe–X (X = Cl, Br) bond cleavage is involved in the formation of a catalytically active species. We expected the reaction of Fe(terpy)X<sub>2</sub> with NaBHEt<sub>3</sub> to give Fe(terpy)(H)<sub>2</sub>, and the reaction mixture was monitored by <sup>1</sup>H NMR. However, no species containing an Fe–H portion was observed. We tentatively think that Fe(terpy) is a real catalyst which is formed via Fe(terpy)(H)<sub>2</sub> being too reactive to be detected by <sup>1</sup>H NMR or by a concerted reaction of Fe(terpy)X<sub>2</sub> with NaBHEt<sub>3</sub> without Fe(terpy)(H)<sub>2</sub> formation.

Comparison of entries 4, 5, and 7 revealed that  $Fe(terpy)Br_2$  with mesityl substituents showed better catalytic activity than that with phenyl substituents, which showed better catalytic activity than that with *o*-tolyl substituents. Although this trend cannot be explained simply by steric factors, the mesityl groups in the terpy ligand seemed to be good substituents. **4-Br**<sub>2</sub> also showed good catalytic activity for secondary silanes (Ph<sub>2</sub>SiH<sub>2</sub> and MePhSiH<sub>2</sub>, entries 9 and 10). The iron complexes **1-** $FeX_2$ -**4-** $FeX_2$  did not show catalytic activity toward hydrosilylation of tertiary silanes or internal olefins, and the starting materials were recovered.

Next, we examined the effect of changing the olefin from 1hexene to 1-octene on the catalytic activity of 4-FeBr<sub>2</sub> (Table 2). Under the same reaction conditions (1/32 (mol) PhSiH<sub>3</sub>/ olefin, 50 °C, 24 h, 0.3 mol % 4-FeBr<sub>2</sub> based on PhSiH<sub>3</sub>), the TON (turnover number) decreased from 70 to 33 on going from 1-hexene to 1-octene. When 1-octene was used, a higher reaction temperature could be used (100 °C), which resulted in

#### Table 2. Hydrosilylation Reaction Catalyzed by 4-FeBr<sub>2</sub>

 $R^{1}R^{2}SiH_{2}$  + olefin  $\xrightarrow[cat. NaHBEt_{3}]{}$  hydrosilylated product

entry	Fe cat. (amt (mol %))	$R^1R^2SiH_2$	olefin	temp (°C)	TON
1	<b>4-FeBr</b> <sub>2</sub> $(0.3)$	PhSiH <sub>3</sub>	1-hexene	50	70
2	$4\text{-}\mathbf{FeBr}_{2}\left(0.3\right)$	PhSiH <sub>3</sub>	1 -octene	50	33
3	$4\text{-}\mathbf{FeBr}_{2}\left(0.3\right)$	PhSiH <sub>3</sub>	1 -octene	100	56
4	$4\text{-}\mathbf{FeBr}_{2}\left(0.1\right)$	PhSiH <sub>3</sub>	1 -octene	100	34
5	$4\text{-}\mathbf{FeBr}_{2}\left(0.3\right)$	$Ph_2SiH_2$	1-hexene	50	71
6	<b>4-FeBr</b> <sub>2</sub> $(0.1)$	Ph <sub>2</sub> SiH <sub>2</sub>	1 -octene	100	372

Scheme 1. Synthetic Routes of Iron Complexes with Unsymmetrically Disubstituted Terpyridine<sup>a</sup>



<sup>*a*</sup>Conditions: (i) anhydrous CuCl<sub>2</sub>, HCl, Et<sub>2</sub>O, at -80 °C (ca. 50% yield); (ii) n-BuLi, Bu<sub>3</sub>SnCl, in THF, at -78 °C (over 95% yield); (iii) Pd(PPh<sub>3</sub>)<sub>4</sub>, in toluene, at reflux temperature (ca. 45% yield); (iv) Pd(PPh<sub>3</sub>)<sub>4</sub>, arylboronic acid, Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O, H<sub>2</sub>O/DME, at reflux temperature (75–95% yield).

a better TON (56 at 100 °C versus 33 at 50 °C). Moreover, the amount of precatalyst **4-FeBr**<sub>2</sub> could be reduced to 0.1 mol %, although the TON did decrease slightly. When Ph<sub>2</sub>SiH<sub>2</sub> was used, the hydrosilylation of 1-octene at 100 °C resulted in a better TON (372) than that of 1-hexene at 50 °C (TON = 71).

The reaction of 6,6"-disubstituted terpy with FeCl<sub>2</sub> has been reported to give Fe(terpy)Cl<sub>2</sub>; in contrast, nonsubstituted terpy reacted with FeCl<sub>2</sub> to give [Fe(terpy)<sub>2</sub>][FeCl<sub>4</sub>]<sub>2</sub>.<sup>12</sup> This may provide insight as to why there was no catalytic activity of the iron complexes with nonsubstituted terpy. Bulky substituents at the 6- and 6"-positions in terpy presumably suppress the conversion of Fe(terpy) into the inactive  $Fe(terpy)_2$ . In order to improve the catalytic activity of Fe(terpy), we attempted to modify the terpy substituents. Having a substituent at the 6position seems to be required to prevent the formation of  $Fe(terpy)_2$  species. On the other hand, the central iron should require an appropriate space in its coordination sphere to conduct hydrosilylation of the olefin. Therefore, we attempted the preparation of unsymmetrically disubstituted terpy ligands and their complexation with FeBr<sub>2</sub> that satisfied both requirements.

As unsymmetrically disubstituted terpy species have not been reported, our synthetic routes are shown briefly in Scheme 1. 6,6'-Dibromo-2,2'-bipyridine (11) was prepared using an Ullmann coupling of 2,6-dibromopyridine. 14 (15) was synthesized from 11 and 12 (13) using Stille coupling. Finally, 14 and 15 were converted into 5-7 and 8-10, respectively, using Suzuki–Miyaura coupling. The unsymmetrical terpy compounds thus formed were treated with FeBr<sub>2</sub> to prepare the corresponding Fe complexes ( $5-FeBr_2-10-FeBr_2$ ). Those products were identified as Fe(terpy)Br<sub>2</sub> according to spectroscopic and elemental analysis data;  $9-FeBr_2$  was also characterized by X-ray diffraction analysis.

The hydrosilylation reactions of 1-octene with hydrosilanes in the presence of a catalytic amount of Fe(terpy)Br<sub>2</sub> bearing unsymmetrical terpy derivatives at 100 °C were examined. The results are summarized in Table 3, together with those for 4-FeBr<sub>2</sub> with a symmetric terpy. Complexes 5-FeBr<sub>2</sub>, 6-FeBr<sub>2</sub>, and 8-FeBr<sub>2</sub> showed no catalytic activities (entries 2, 3, and 5). In contrast, 7-FeBr<sub>2</sub>, 9-FeBr<sub>2</sub>, and 10-FeBr<sub>2</sub> exhibited much better catalytic activities (entries 4, 6, and 7) than 4-FeBr<sub>2</sub> (entry 1). Therefore, we surmised that catalytic activity is favored by the central iron atom containing a terpy derivative with a bulky aryl substituent at the 6-position and with a small

Table 3. Hydrosilylation of 1-Octene with  $R^1R^2SiH_2$ Catalyzed by 4-FeBr<sub>2</sub>-10-FeBr<sub>2</sub><sup>*a*</sup>

R <sup>1</sup>	R <sup>2</sup> SiH <sub>2</sub>	+ cat. Fe cat. NaHBEt <sub>3</sub>	→ R <sup>1</sup> R <sup>2</sup> HSi	$\sim\sim\sim$
	entry <sup>b</sup>	Fe cat. (amt (mol %))	$R^1R^2SiH_2$	TON
	1	<b>4-FeBr</b> <sub>2</sub> $(0.1)$	PhSiH <sub>3</sub>	34
	2	5-FeBr <sub>2</sub> (0.1)	PhSiH <sub>3</sub>	0
	3	<b>6-FeBr</b> <sub>2</sub> (0.1)	PhSiH <sub>3</sub>	0
	4	7-FeBr <sub>2</sub> (0.05)	PhSiH <sub>3</sub>	1458
	5	8-FeBr <sub>2</sub> (0.1)	PhSiH <sub>3</sub>	0
	6	9-FeBr <sub>2</sub> (0.05)	PhSiH <sub>3</sub>	1533
	7	<b>10-FeBr</b> <sub>2</sub> (0.05)	PhSiH <sub>3</sub>	898
	8	$4-FeBr_2$ (0.1)	Ph <sub>2</sub> SiH <sub>2</sub>	372
	9	7-FeBr <sub>2</sub> (0.1)	Ph <sub>2</sub> SiH <sub>2</sub>	377
	10	9-FeBr <sub>2</sub> (0.1)	Ph <sub>2</sub> SiH <sub>2</sub>	444
	11	$10-FeBr_2$ (0.1)	Ph <sub>2</sub> SiH <sub>2</sub>	300
	12	$4-FeBr_{2}(0.1)$	$MePhSiH_2$	66
	13	7-FeBr <sub>2</sub> (0.1)	$MePhSiH_2$	222
	14	<b>9-FeBr</b> <sub>2</sub> (0.1)	$MePhSiH_2$	153
	15	<b>10-FeBr</b> <sub>2</sub> (0.1)	$MePhSiH_2$	124

"At 100 °C for 24 h. <sup>b</sup>Molar ratios: entries 1–3 and 5, 32/1 1-octene/ $R^1R^2SiH_2$ ; entries 4, 6, and 7, 2/1 1-octene/ $R^1R^2SiH_2$ ; entries 8–15, 1/1 1-octene/ $R^1R^2SiH_2$ .

substituent (Me) at the 5"- or 6"-position. According to these criteria, **9-FeBr**<sub>2</sub> had the best combination of the two substituents. Complexes 7-FeBr<sub>2</sub>, 9-FeBr<sub>2</sub>, and 10-FeBr<sub>2</sub> showed good catalytic activity for Ph<sub>2</sub>SiH<sub>2</sub> and MePhSiH<sub>2</sub> as compared with 4-FeBr<sub>2</sub>. It should be noted that the catalytic activity of 4-FeBr<sub>2</sub> was relatively and unexpectedly higher for Ph<sub>2</sub>SiH<sub>2</sub> than for PhSiH<sub>3</sub> and for MePhSiH<sub>2</sub>; the reason for this is yet unclear.

Another interesting point in this work is that the product in the reaction of 1-octene with PhSiH<sub>3</sub> in 2:1 molar ratio depends on the amount used of 7-FeBr<sub>2</sub> and 9-FeBr as catalyst precursors (Scheme 2). When 0.05-0.3 mol % of the iron complex was used at 100 °C, the product was a mixture of Ph(octyl)SiH<sub>2</sub> and Ph(octyl)<sub>2</sub>SiH. When the amount was more than 0.3 mol %, PhSiH<sub>3</sub> was completely converted into Ph(octyl)<sub>2</sub>SiH. In contrast, when the amount was less than 0.05 mol %, the product was only Ph(octyl)SiH<sub>2</sub>. To the best of our knowledge, selective single/double alkylation of hydrosilane via hydrosilylation using a transition-metal catalyst has not been

## Scheme 2. Hydrosilylation Reaction of 1-Octene with PhSiH<sub>3</sub> Catalyzed by 0.3 and 0.05 mol % of an Fe Complex



reported to date. In contrast, the reaction of 1-hexene with  $PhSiH_3$  at 50 °C catalyzed by 7-FeBr<sub>2</sub> produced  $Ph(hexyl)SiH_2$  and that by 9-FeBr<sub>2</sub> produced a mixture of  $Ph(hexyl)SiH_2$  and  $Ph(hexyl)_2SiH$ , and no selectivity was observed even by changing the amount of 9-FeBr<sub>2</sub> (Table 4). Suitable selection of the kind and the amount of the catalyst precursor and high reaction temperature are required to achieve the selective single/double alkylation.

Table 4. Double-Alkylation Reaction of Olefins with  $PhSiH_3$  Catalyzed by 0.3 and 0.05 mol % of 7-FeBr\_2 and 9-FeBr\_2 for 24 h

				product (TON)	
entry	Fe cat. (amt (mol %))	olefin	temp (°C)		
1	7-FeBr <sub>2</sub> (0.3)	1-hexene	50	Ph(hexyl) SiH <sub>2</sub> (225)	Ph(hexyl) <sub>2</sub> SiH (0)
2	<b>9-FeBr</b> <sub>2</sub> (0.3)	1-hexene	50	Ph(hexyl) SiH <sub>2</sub> (179)	Ph(hexyl) <sub>2</sub> SiH (128)
3	7-FeBr <sub>2</sub> (0.05)	1-hexene	50	Ph(hexyl) SiH <sub>2</sub> (601)	Ph(hexyl) <sub>2</sub> SiH (0)
4	<b>9-FeBr</b> <sub>2</sub> (0.05)	1-hexene	50	Ph(hexyl) SiH <sub>2</sub> (1207)	Ph(hexyl) <sub>2</sub> SiH (139)
5	7-FeBr <sub>2</sub> (0.3)	1 -octene	100	Ph(octyl) SiH <sub>2</sub> (0)	Ph(octyl) <sub>2</sub> SiH (333)
6	<b>9-FeBr<sub>2</sub></b> (0.3)	1 -octene	100	Ph(octyl) SiH <sub>2</sub> (0)	Ph(octyl) <sub>2</sub> SiH (333)
7	7- <b>FeBr</b> <sub>2</sub> (0.05)	1 -octene	100	Ph(octyl) SiH <sub>2</sub> (1458)	Ph(octyl) <sub>2</sub> SiH (0)
8	<b>9-FeBr</b> <sub>2</sub> (0.05)	1 -octene	100	Ph(octyl) SiH <sub>2</sub> (1533)	Ph(octyl) <sub>2</sub> SiH (0)

In conclusion, we found that iron complexes bearing newly prepared 2,2':6',2"-terpy derivatives with substituents at the 6and 5"-/6"-positions, especially those bearing unsymmetrically disubstituted terpy, exhibit high catalytic activity for hydrosilylation of olefins with hydrosilanes. In the reaction of 1octene with PhSiH<sub>3</sub> at 100 °C selective single/double hydrosilylation was achieved by changing the amount of the iron catalyst.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Text, tables, and CIF files giving detailed experimental procedures, characterization data for the products, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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Examples listed in their patents are concerned with the catalytic activities of iron complexes with a nonsubstituted terpyridine ligand. As we found that iron complexes with terpyridine derivatives with substituents at the 6,6"- and 6,5"-positions exhibited noticeable catalytic activities, we report our results here.

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(14) The molar ratio of hydrosilane and 1-hexane was found to be important in this reaction system. The reaction with a ratio of 1:2 produced some unidentified byproducts. Changing the ratio from 1:2 to 1:8 and 1:16 caused a decrease in the amount of the byproduct, and when a ratio of 1:32 was used, no byproducts were observed.

(15) For example, see: (a) Takahashi, T.; Hasegawa, M.; Suzuki, N.;
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