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Design and Synthesis of Isocyanide Ligands for Catalysis: Application to Rh-Catalyzed Hydrosilylation of Ketones

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Abstract: New isocyanide ligands with *meta*-terphenyl backbones were synthesized. 2,6-Bis[3,5-bis(trimethylsilyl)-phenyl]-4-methylphenyl isocyanide exhibited the highest rate acceleration in rhodium-catalyzed hydrosilylation among other isocyanide and phosphine ligands tested in this study. ^{1}H NMR spectroscopic studies on the coordination behavior of the new ligands to $[Rh(cod)_2]BF_4$ indicated that 2,6-bis-[3,5-bis(trimethylsilyl)phenyl]-4-methylphenyl isocyanide exclusively forms the biscoordinated rhodium–isocyanide complex, whereas less sterically demanding isocyanide ligands predominantly form tetracoordinated rhodium–isocyanide complexes. FTIR and ^{13}C NMR spectroscopic studies on the hydrosilylation reaction mixture with the rhodium–isocyanide catalyst showed that the major catalytic species responsible for the hydrosilylation activity is the Rh complex coordinated with the isocyanide ligand. DFT calculations of model compounds revealed the higher affinity of isocyanides for rhodium relative to phosphines. The combined effect of high ligand affinity for the rhodium atom and the bulkiness of the ligand, which facilitates the formation of a catalytically active, monoisocyanide–rhodium species, is proposed to account for the catalytic efficiency of the rhodium–bulky isocyanide system in hydrosilylation.

Keywords: hydrosilylation · isocyanide ligands · ketones · ligand design · rhodium

Introduction

Isocyanides are isoelectronic with carbon monoxide and coordinate to various transition metals at the terminal isocyano carbon atom.[1] In general, both isocyanides and carbon monoxide are extremely compact ligands. Unlike CO, however, the electronic and steric properties of isocyanides are tunable through substituents at the nitrogen atom. There are, in fact, many different isocyanide compounds that have been used as ligands in transition-metal complexes, with interesting and diverse properties,[2,3] and their diverse reactivities can be taken advantage of in both organic and organometallic chemical applications.[4–6]

Although isocyanides have significant potential as ligands, only a limited number have been used as supporting ligands in transition-metal catalysis.[7–10] For example, Nile and Yamazaki and their co-workers used 2,6-disubstituted phenyl isocyanides in rhodium- and platinum-catalyzed hydrosilylations.[7] Ito and co-workers developed the bissilylation of carbon–carbon unsaturated bonds and related reactions by the use of *tert*-alkyl isocyanide–palladium complexes as catalyst precursors.[8] Recently, Nagashima and co-workers reported that a nickel complex of 2-biphenyl isocyanide is highly active in ethylene polymerization.[9]

One reason for the scarcity of metal catalysts with isocyanides as supporting ligands arises from their stability constraints. Indeed, little is understood about the chemical stability of coordinating isocyanides in catalytic reactions, although these ligands are susceptible to degradation through insertion into metal–carbon and metal–hydrogen bonds in the catalytic intermediates.

We report herein the synthesis and coordination properties of new isocyanide ligands (**1a**–**d**; Scheme 1) with a *meta*-terphenyl backbone, and their use in the Rh-catalyzed hydrosilylation of ketones.[11] The isocyanide ligand **1c**, with its appropriate steric demand, markedly accelerates the reaction relative to the new terphenyl isocyanide ligands **1a**, **1b**, and **1d**, as well as other conventional isocyanide and phosphine ligands, thus demonstrating its usefulness as a supporting ligand in transition-metal catalysis. FTIR and ^{13}C NMR spectroscopic studies reveal that the bulky isocya-

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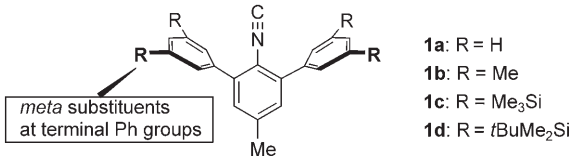


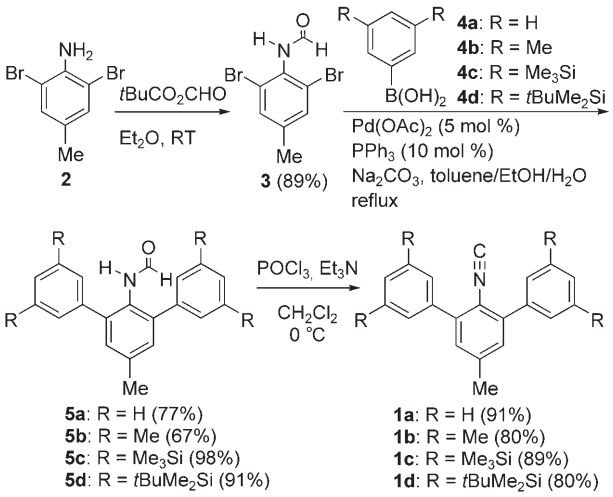
Scheme 1. New isocyanide ligands for catalysis.

nide **1c** has reasonable stability in the Rh-catalyzed hydrosilylation of ketones. A plausible mechanism of action of the Rh–isocyanide catalyst is also proposed.

Results and Discussion

Synthesis of Isocyanides

The synthesis of the terphenyl isocyanides **1a–d** is straightforward (Scheme 2). First, N-formylation of 2,6-dibromotoluidine (**2**) gave *N*-formyl-2,6-dibromotoluidine (**3**; 89%). Suzuki–Miyaura coupling of dibromoarene **3** with 3,5-disubstituted phenylboronic acid **4a–d** in the presence of 5 mol% of $Pd(OAc)_2$ and 10 mol% of PPh_3 gave *N*-terphenyl formamides **5a–d** in 67–91% yield. Treatment of **5a–d** with $POCl_3/Et_3N$ resulted in clear conversion into the desired isocyanides **1a–d** in high yields (80–91%). The new isocyanides are odorless and colorless crystals, and are stable against oxidation and hydrolytic decomposition in air, thus making



Scheme 2. Synthesis of substituted *m*-terphenyl isocyanides.

them easy to handle. The space-filling representation of the optimized structures (MMFF94, MacSpartan Pro 1.0.4.) of **1a** and **1c** (Figure 1) shows that the *meta*-terphenyl backbone is an ideal platform for creating a concave steric environment around the isocyano carbon atom.

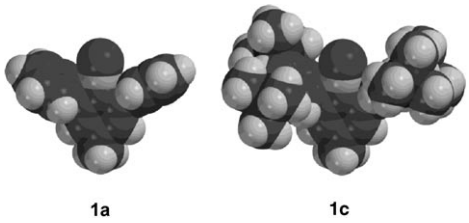


Figure 1. Space-filling models of isocyanide ligands **1a** and **1c**.

Coordination Behavior of Isocyanides

To compare the bulkiness of the terphenyl isocyanides, we carried out complexation experiments of neutral and cationic Rh complexes with the terphenyl isocyanides **1a–c**. ^{1}H NMR spectroscopic observations of the interaction of terphenyl isocyanides **1** with cationic complex $[Rh(cod)_2]BF_4$ (**6**; cod = 1,5-cyclooctadiene) and neutral complex $[RhCl(cod)]_2$ (**9**) indicate that the Me_3Si-substituted terphenyl isocyanide **1c** is much more sterically demanding than the corresponding nonsubstituted (**1a**) and Me-substituted (**1b**) analogues. Thus, **6** was mixed with the terphenyl isocyanide ligands **1a–c** at three different molar ratios (1:1, 1:2, and 1:4) in $CDCl_3$ at room temperature, and the mixture was subjected to ^{1}H NMR spectroscopy. The results are shown in Table 1 (see also the Supporting Information). For the nonsubstituted (**1a**) and Me-substituted (**1b**) terphenyl isocyanides, all the isocyanides in the mixture were associated with the formation of a single rhodium–isocyanide complex assignable to the tetracoordinated complex $[Rh(L)_4]BF_4$ (**7a**: L = **1a**; **7b**: L = **1b**), irrespective of the Rh/ligand molar ratio (Table 1, entries 1–6). This is an indication of

Abstract in Japanese:
m-ターフェニルを基本骨格とする立体障害の大きなイソシアニド配位子を開発した。ロジウム触媒によるケトンのヒドロシリル化反応においてこの配位子の支持配位子としての有用性が明確になった。$[Rh(cod)_2]BF_4$ に対する配位挙動を ^{1}H NMR で調べたところ、2,6-ビス[3,5-ビス(トリメチルシリル)フェニル]-4-メチルフェニルイソシアニドでは、ロジウム-イソシアニド 1:2 錯体が選択的に生成したのに対し、より立体障害の小さな配位子では、ロジウム-イソシアニド 1:4 錯体が生成した。この 2,6-ビス[3,5-ビス(トリメチルシリル)フェニル]-4-メチルフェニルイソシアニドは、ケトンのロジウム触媒によるヒドロシリル化において、今回検討したイソシアニドおよびリン配位子の中で最も大きな加速効果を示した。FTIR および ^{13}C NMR を用いて、ヒドロシリル化後の反応混合物を調べたところ、この触媒系のヒドロシリル化活性は、主にロジウム- イソシアニド錯体に由来することが明らかになった。また、DFT 計算により、イソシアニドのロジウム原子に対する親和性は、リン配位子よりも大きいことが示された。イソシアニド配位子がもつロジウムへの高い親和性と立体障害の効果は、高活性なロジウム-イソシニド 1:1 錯体の形成を促進し、ヒドロシリル化反応の高い効率の要因となっていると考えられる。

Table 1. ^{1}H NMR spectroscopy of the in situ complexation of Rh complexes and isocyanide ligands.[a]

$[Rh(L)_4]BF_4$	*cis*-$[Rh(L)_2(cod)]BF_4$	$[Rh(L)_4]Cl$	[RhCl(L)(cod)]
7a (L = **1a**) **7b** (L = **1b**)	**8** (L = **1c**)	**10a** (L = **1a**)	**11a** (L = **1a**) **11c** (L = **1c**)

Entry	Rh complex	Ligand	Rh/L Ratio	Product
1	**6**	**1a**	1:1	**7a+6**
2	**6**	**1a**	1:2	**7a+6**
3	**6**	**1a**	1:4	**7a** (79%)[b]
4	**6**	**1b**	1:1	**7b+6**
5	**6**	**1b**	1:2	**7b+6**
6	**6**	**1b**	1:4	**7b** (97%)[b]
7	**6**	**1c**	1:1	**8+6**
8	**6**	**1c**	1:2	**8** (71%)[b]
9	**6**	**1c**	1:4	**8** + **1c**
10	**9**	**1a**	1:1	**11a**
11	**9**	**1a**	1:2	**11a+10a**[c]
12	**9**	**1a**	1:4	**10a** (99%)[b]
13	**9**	**1c**	1:1	**11c** (78%)[b]
14	**9**	**1c**	1:2	**11c+1c**
15	**9**	**1c**	1:4	**11c+1c**

[a] Conditions: Rh complex ($[Rh(cod)_2]BF_4$ (**6**; 2.0 μmol) or $[RhCl(cod)]_2$ (**9**; 1.0 μmol)) and ligand **1** (2.0–8.0 μmol) at room temperature in $CDCl_3$ (0.7 mL). [b] Yield of isolated product in parentheses. The complex was prepared by the reaction of the Rh complex (**6** or **9**, 0.006–0.04 mmol with respect to Rh) and ligand **1** at room temperature in CH_2Cl_2. [c] The reaction was accompanied by formation of some uncharacterized complexes.

the compactness of the isocyanide ligands. In contrast, studies with the Me_3Si-substituted terphenyl isocyanide **1c** under the same conditions resulted in the exclusive formation of biscoordinated Rh–isocyanide complex *cis*-$[Rh(\mathbf{1c})_2(cod)]BF_4$ (**8**), again irrespective of the Rh/ligand molar ratio (Table 1, entries 7–9). When Rh was in excess (Rh/**1c** = 1:1), half of **6** remained unreacted (Table 1, entry 7). When the isocyanide was in excess (Rh/**1c** = 1:4), **1c** remained (Table 1, entry 9).

Reaction of neutral $[RhCl(cod)]_2$ (**9**) and the small isocyanide **1a** at an Rh/ligand ratio of 1:1 resulted in the formation of monocoordinated isocyanide–Rh complex [RhCl(**1a**)(cod)] (**11a**; Table 1, entry 10), whereas tetracoordinated complex $[Rh(\mathbf{1a})_4]Cl$ (**10a**) was mainly formed when **1a** was in excess (Rh/**1a** = 1:4; Table 1, entry 12). Reaction at an Rh/ligand ratio of 1:2 produced a mixture of **10a** and **11a** (Table 1, entry 11). Reaction of **9** with **1c** resulted in the formation of monocoordinated complex [RhCl(**1c**)(cod)] (**11c**), irrespective of the Rh/ligand molar ratio (Table 1, entries 13–15).

These results demonstrate that the steric demand of the isocyanide ligand **1c** is quite different from those of **1a** and **1b**. The complexes **7a**, **7b**, **8**, **10a**, and **11c** were isolated and characterized by ^{1}H and $^{13}C\{^1H\}$ NMR and IR spectroscopy, mass spectrometry, and elemental analysis (Table 1, entries 3, 6, 8, 12, 13). It is clear that the bulkiness of **1c** hampers further coordination of the isocyanide ligand to the bisisocyanide (**8**) and monoisocyanide (**11c**) complexes.

Rh-Catalyzed Hydrosilylation of Ketones with Various Ligands

Next, the Rh–isocyanide complexes were examined for catalytic activity in the hydrosilylation of cyclohexanone (**12**) with Me_2PhSiH (**13**). Results of the hydrosilylation experiments carried out in benzene at room temperature in the presence of 1 mol% each of $[Rh(cod)_2]BF_4$ and the isocyanide ligand (**1a–h**; see Figure 2 for the structures of **1e–h**)

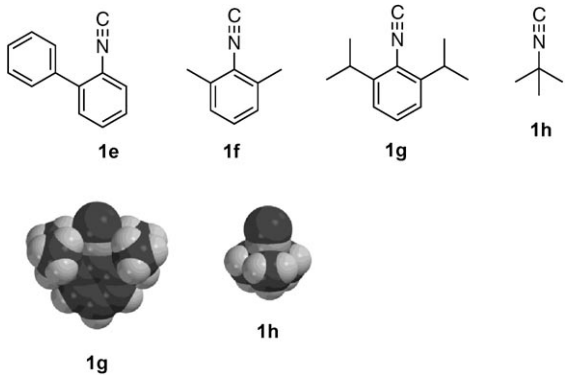
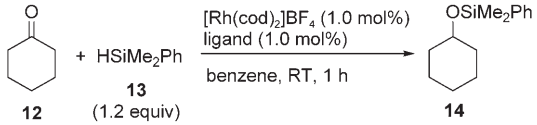


Figure 2. Schematic and space-filling structures of isocyanide ligands.

are summarized in Table 2. Results with conventional phosphine ligands (PPh_3 and dppp) are also shown for comparison. The acceleration effect with each ligand was evaluated by the yield of the corresponding silyl ether determined by GC after 1 h.

The acceleration with isocyanides varied considerably depending on the bulkiness of the ligand. In particular, the Me_3Si-substituted terphenyl isocyanide **1c** exhibited the most significant effect: it gave the silyl ether product **14** in

Table 2. Hydrosilylation in the presence of cationic Rh complex with various isocyanide and phosphine ligands.[a]



Entry	Ligand	Yield [%][b]
1	–	13
2	**1a**	36 (85, 4 h)
3	**1b**	22 (89, 4 h)
4	**1c**	97
5	**1d**	79
6	**1e**	7
7	**1f**	14 (32, 4 h)
8	**1g**	39 (61, 4 h)
9	**1h**	36
10	PPh_3	34–71 (46–81, 3 h)
11	dppp	trace

[a] Conditions: ligand (0.015 mmol), $[Rh(cod)_2]BF_4$ (0.015 mmol), **12** (1.5 mmol), and **13** (1.8 mmol) in benzene (1.5 mL) at room temperature (21–24 °C). [b] Yield of the silyl ether determined by GC. dppp = 1,3-bis(diphenylphosphanyl)propane.

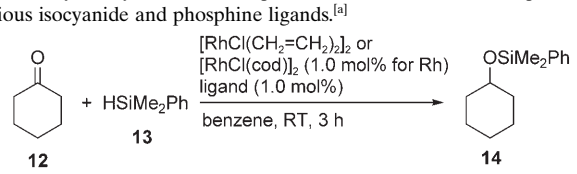
97% yield (Table 2, entry 4). The *t*BuMe$_2$Si-substituted isocyanide **1d** showed a slightly decreased acceleration effect (79% yield; Table 2, entry 5), which suggests that this ligand is overly bulky.

The terphenyl isocyanides **1a** and **1b** with smaller steric demands than **1c** are much less effective (Table 2, entries 2 and 3). 2-Biphenyl isocyanide (**1e**)[9] and 2,6-xylyl isocyanide (**1f**)[7] showed no acceleration effect relative to the rate without added ligand (Table 2, entries 6 and 7). On the other hand, acceleration with 2,6-diisopropylphenyl isocyanide (**1g**) was comparable to that of the nonsubstituted terphenyl isocyanide **1a** (Table 2, entry 8),[7] which suggests that the steric effect of the *i*Pr substituents at positions *ortho* to the isocyano group is comparable only to the Ph substituents in simple terphenyl isocyanide **1a**. *tert*-Butyl isocyanide (**1h**)[8,10] gave a similar result (Table 2, entry 9). The yields with the small isocyanides (**1a**, **1b**, **1f**, and **1g**) increased slightly on prolonging the reaction time to 4 h (Table 2, entries 2, 3, 7, and 8), which indicates that the low yields are due to low catalytic activity rather than catalyst deactivation. Although the reaction with PPh_3 gave a good yield after 1 h, it suffered from poor reproducibility and substantial catalyst deactivation over time (Table 2, entry 10). The bidentate phosphine ligand dppp inhibited the reaction almost completely (Table 2, entry 11). These results strongly suggest that the accelerating effect with **1c** and **1d** is due to their concave steric features.

The **1c**/[Rh(cod)$_2$]BF$_4$ catalyst was also effective in the hydrosilylation of other ketones. The reaction of **13** with acetophenone (4 h), benzophenone (4 h), 4-phenyl-2-butanone (26 h), and β-tetralone (2 h) afforded the corresponding alcohols after the given reaction times in high yields (84–88% after acidic hydrolysis).

Similar rate-acceleration effects were observed when neutral [RhCl(CH$_2$=CH$_2$)$_2$]$_2$ or [RhCl(cod)]$_2$ were used as catalyst precursor (Table 3). The Me$_3$Si-substituted terphenyl isocyanide **1c** (3 h, 97%; Table 3, entry 3) exhibited the most significant effect. Sterically less demanding isocyanides **1a** and **1g** as well as PPh_3 exhibited smaller acceleration effects (Table 3, entries 2, 4, and 5). When [RhCl(cod)]$_2$ was used as a precursor for **1c**, the activity was lower than that of the [RhCl(CH$_2$=CH$_2$)$_2$]$_2$/**1c** catalyst (63% after 4 h; Table 3, entry 6).

Table 3. Hydrosilylation in the presence of neutral Rh complex with various isocyanide and phosphine ligands.[a]



Entry	Rh precursor	Ligand	Yield [%][b]
1	[RhCl(CH$_2$=CH$_2$)$_2$]$_2$	–	15
2	[RhCl(CH$_2$=CH$_2$)$_2$]$_2$	**1a**	48
3	[RhCl(CH$_2$=CH$_2$)$_2$]$_2$	**1c**	97
4	[RhCl(CH$_2$=CH$_2$)$_2$]$_2$	**1g**	15
5	[RhCl(CH$_2$=CH$_2$)$_2$]$_2$	PPh_3	24
6	[RhCl(cod)]$_2$	**1c**	63 (4 h)[c]

[a] Conditions: ligand (0.015 mmol), Rh precursor (0.015 mmol with respect to Rh), **12** (1.5 mmol), and **13** (1.8 mmol) in benzene (1.5 mL) at room temperature (21–24 °C). [b] Yield of the silyl ether determined by GC. [c] Conditions: ligand (0.015 mmol), Rh precursor (0.015 mmol with respect to Rh), **12** (1.5 mmol), and **13** (1.95 mmol) in benzene (1.5 mL) at room temperature (25 °C).

Rh/Ligand Stoichiometry in Catalysis

The correlations between catalytic activity and Rh/**1c** ratio are shown in Figure 3. Hydrosilylation with [Rh(cod)$_2$]BF$_4$ and **1c** at a 1:1 ratio proceeded with the highest rate among reactions carried out with five different Rh/**1c** ratios ranging from 1:0 to 1:3 (Figure 3a).[12] When neutral Rh complexes ([RhCl(CH$_2$=CH$_2$)$_2$]$_2$ or [RhCl(cod)]$_2$) were used as catalyst precursors, the highest reaction rate was also observed at a Rh/**1c** ratio of 1:1 (Figure 3b). Accordingly, we postulate that the active species is a 1:1 Rh/**1c** complex, and that the coordination of a second molecule of **1c** (Rh/**1c** = 1:2) causes a slight decrease in catalytic activity.[13,14]

Bulky phosphine ligands, such as the bowl-shaped phosphine **15** and triethynylphosphine **16**, were also reported to

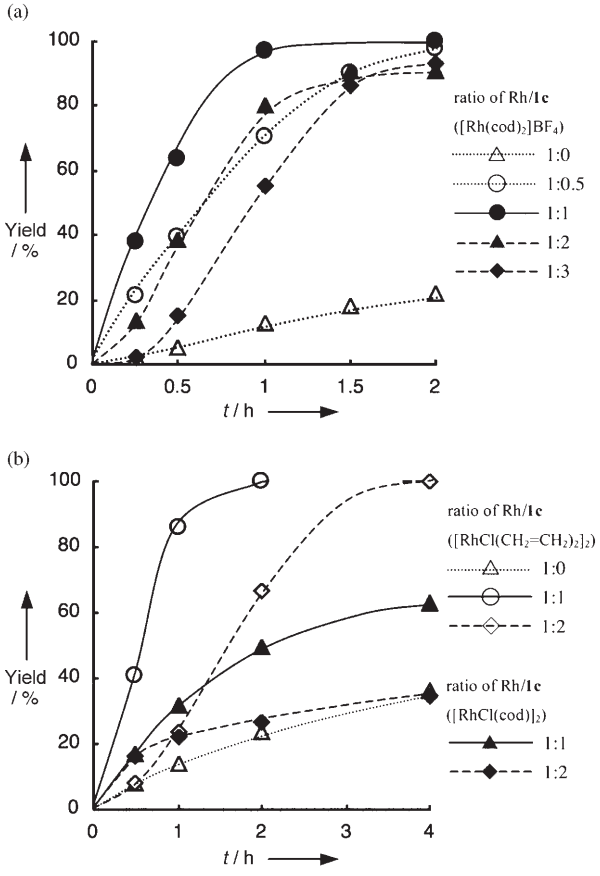
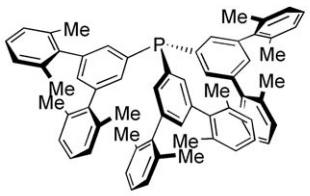


Figure 3. Time–conversion curves for the hydrosilylation of **12** with **13** at room temperature (20–25 °C) in benzene. a) Ligand **1c** (0.015 mmol), [Rh(cod)$_2$]BF$_4$ (0.015 mmol), **12** (1.5 mmol), and **13** (1.8 mmol) in benzene (1.5 mL). b) Ligand **1c** (0.015 mmol), [RhCl(CH$_2$=CH$_2$)$_2$]$_2$ or [RhCl(cod)]$_2$ (0.0075 mmol), **12** (1.5 mmol), and **13** (1.95 mmol) in benzene (1.5 mL).

have marked rate-acceleration effects in the Rh-catalyzed hydrosilylation of ketones (Scheme 3).[14–16] As in the case of the Rh/**1c** system, the Rh/**16** catalyst exerted the highest activity with an Rh/ligand ratio of 1:1, and a slight decrease in the activity was observed with a 1:2 ratio. The acceleration effect of **16** is explained by assuming the 1:1 Rh/**16** complex as the active species.[16] The highest activities reported for these Rh/phosphine catalyst systems ($[RhCl(cod)]_2$/**15** and $[RhCl(cod)]_2$/**16**) are comparable with that of the Rh/**1c** catalyst.



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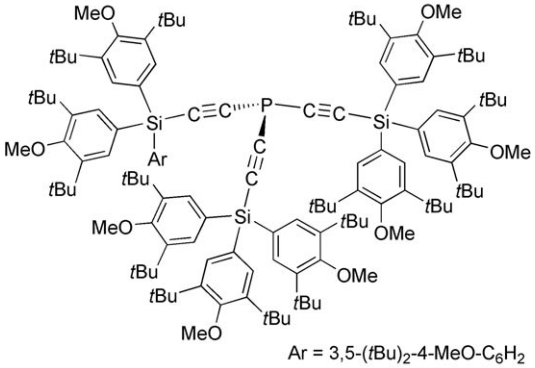

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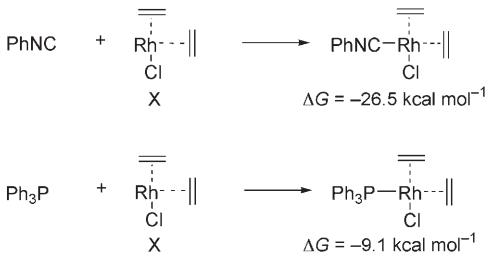
[silica]-SMAP (**17**)

Scheme 3. Structures of bowl-shaped phosphine **15**, triethynylphosphine **16** with bulky end caps, and silica-supported compact trialkylphosphine [silica]-SMAP (**17**; SMAP = silicon-constrained monodentate alkylphosphine).

Affinity of Isocyanide for Rh: DFT Calculations

DFT calculations show the high affinity of isocyanide ligands for Rh atoms.[18] The affinity of phenyl isocyanide for Rh was evaluated by calculating the changes in the Gibbs free energy of formation of *cis*-$[RhCl(CH_2{=}CH_2)_2(CNPh)]$ from phenyl isocyanide and a Rh complex **X** (B3LYP/SDD) at 298 K ($\Delta G = -26.5$ kcal mol^{-1}; Scheme 4). The free-energy change for PPh_3 in *cis*-$[RhCl(H_2C{=}CH_2)_2(PPh_3)]$ was also calculated ($\Delta G = -9.1$ kcal mol^{-1} at 298 K). A comparison of these free-energy changes ($\Delta\Delta G = -17.4$ kcal mol^{-1}) shows clearly that phenyl isocyanide has higher affinity for Rh than PPh_3. In the light of this result, it would be reasonable to assume that the isocyanide ligand **1c** has a high affinity for Rh atoms. This high affinity leads to suppressed dissociation of the isocyanide ligand from the Rh/**1c** complex and contributes to the large population of the 1:1 Rh/**1c** complex in the catalytic reaction.



Scheme 4. Calculated coordination energies for Rh/isocyanide and Rh/phosphine complexes (B3LYP/SDD).

Stability of the Isocyanide Ligand in Catalytic Reactions: FTIR and ^{13}C NMR Spectroscopic Studies

In general, a metal-coordinated isocyanide moiety is susceptible to insertion into metal–carbon and metal–hydride bonds. These reactions cause the conversion of the metal–isocyanide complex into the iminoacyl and carbene species.[1,19] Therefore, to obtain insight into the chemical stability of isocyanide ligands, FTIR and ^{13}C NMR spectroscopic measurements were conducted under various conditions related to Rh-catalyzed hydrosilylation (Figures 4 and 5).

FTIR Spectroscopic Studies

The FTIR spectrum of a mixture of isocyanide ligand **1c** and $[Rh(cod)_2]BF_4$ (1:1, 0.01 mmol) in benzene (1.0 mL) shows an intense absorption of the isocyanide N≡C stretch in *cis*-$[Rh(\mathbf{1c})_2(cod)]BF_4$ (**8**) at higher frequency (2127 cm^{-1}) than that of free **1c** (2115 cm^{-1}) (Figure 4b and c).[20,21] A mixture of **1c** and $[Rh(cod)_2]BF_4$ (1:1, 0.01 mmol) in benzene (1.0 mL) was then treated with ketone **12** (10 equiv, 0.10 mmol) and hydrosilane **13** (9 equiv, 0.09 mmol). After the hydrosilylation was complete, the resultant orange solution was subjected to FTIR spectroscopy (Figure 4d). A broad absorption at 2108 cm^{-1}, which corresponds to the isocyanide group in the Rh complex, was observed, but the absorption of neither **1c** nor **8** was detected. In a similar experiment with isocyanide ligand **1c′**, which was isotopically labeled with ^{13}C (99 atom %) at the isocyano carbon, a shift

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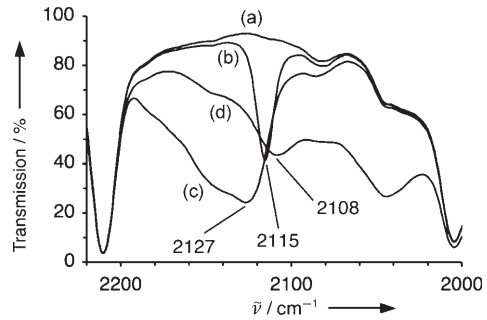

Figure 4. FTIR spectra of a) benzene as a reference, b) a solution of the free isocyanide **1c** (10 mM) in benzene, c) a mixture of **1c** (10 mM) and $[Rh(cod)_2]BF_4$ (10 mM) in benzene, and d) the crude hydrosilylation mixture of **12** (100 mM) with **13** (90 mM) in the presence of **1c** (10 mM) and $[Rh(cod)_2]BF_4$ (10 mM) in benzene. All spectra were obtained in a sealed NaCl cell (1.0 mm thickness). The absorptions at 2115 cm^{-1} (b), 2127 cm^{-1} (c), and 2108 cm^{-1} (d) are due to stretching of the isocyanide N≡C bonds.

of the absorption band in the isocyanide region to lower frequency ($\Delta\tilde{\nu} = -38$ cm^{-1}) was observed, thus confirming the assignments of the isocyano band ($\tilde{\nu}(N^{13}C) = 2070$ cm^{-1}; data not shown in Figure 4). In the above IR spectroscopic experiments, use of a small excess of ketone **12** (0.10 mmol) over hydrosilane **13** (0.09 mmol) was required to observe the N≡C stretch for the Rh–isocyanide complex. When an excess of **13** was used, the absorption band of the Rh–isocyanide complex was not detected in the crude mixture.

^{13}C NMR Spectroscopic Studies

Next, to examine the structure of the Rh–isocyanide complex observed in the crude hydrosilylation mixture above, $^{13}C\{^1H\}$ NMR spectroscopy was performed under five different conditions (Figure 5 A–E) by using either isotopically labeled isocyanide ligand **1c′** or unlabeled **1c**. In the $^{13}C\{^1H\}$ NMR spectrum of a mixture of **1c′** and $[Rh(cod)_2]BF_4$ (1:1, 0.01 mmol) in C_6D_6, the signal for the isocyano carbon atom appeared as a ^{103}Rh-coupled doublet a at $\delta = 147.5$ ppm ($^1J_{Rh,C} = 66.4$ Hz), which is shifted upfield from that of free isocyanide ligand **1c** ($\delta = 173.2$ ppm in C_6D_6) (Figure 5 A).[22] This doublet is assignable to the Rh-coordinated isocyano carbon atom of the catalyst precursor, *cis*-$[Rh(\mathbf{1c'})_2(cod)]BF_4$. This resonance did not change upon addition of excess cyclohexanone (**12**) (Figure 5 B).

When a mixture of **1c′**, $[Rh(cod)_2]BF_4$ (1:1, 0.01 mmol), ketone **12** (10 equiv, 0.10 mmol), and C_6D_6 (1.0 mL) was treated with hydrosilane **13** (9 equiv, 0.09 mmol), hydrosilylation proceeded rapidly (<30 min). Hydrosilane **13** was completely consumed, while a reasonable amount of cyclohexanone **12** remained. The resultant orange solution was subjected to $^{13}C\{^1H\}$ NMR spectroscopy (Figure 5 C). The initial doublet a ($\delta = 147.5$ ppm) of the catalyst precursor disappeared, and a new doublet b ($\delta = 171.6$ ppm, $^1J_{Rh,C} = 81.3$ Hz) appeared. This new signal should be ascribed to the coordinated isocyano carbon atom in the Rh complex, and the simple doublet without ^{13}C–^{13}C coupling is assignable to either the monoisocyanide complex **18** or a biscoordinated complex with two equivalent isocyanide ligands (Scheme 5). On the basis of its chemical shift, the small doublet c ($\delta = 198.7$ ppm, $^1J_{Rh,C} = 42.4$ Hz) may be assigned to

18 19

Scheme 5. Expected structures of Rh complexes in reaction mixture C.

Rh–carbene complex **19**, which is formed through reaction of the isocyanide.[19] Two small unidentified resonances at $\delta = 160.9$ (d) and 158.0 ppm (e) were also observed. By taking into account the fact that intensities of the $^{13}C\{^1H\}$ NMR signals of isocyano carbon atoms are significantly smaller than those of other signals, the intensity of signal b in spectrum C indicates that a reasonable amount of the Rh–isocyanide complex exists.

To identify the signals for the decomposition products originating from the corresponding isocyanide ligand in the high-field region, spectrum C was compared with the spectrum obtained with unlabeled ligand **1c** (Figure 5 D). Comparison of the spectra led to the identification of three signals, f, g, and h, which are missing in spectrum D. Signal f is in the imine region ($\delta = 124.8$ ppm), and signals g and h are in the amine region ($\delta = 39.4$, 36.0 ppm). These three signals should be due to the decomposition products of the ^{13}C-labeled isocyanide ligand **1c′**. As is the case for the IR spectroscopic experiments, ketone **12** must exist in the reaction mixture for the isocyanide signal to be observed. When a mixture of **1c′** and $[Rh(cod)_2]BF_4$ was treated with hydrosilane **13** in the absence of ketone **12**, the Rh–isocyanide complex decomposed immediately to give the signals (g, h, and i) for the decomposition products in the ^{13}C NMR spectrum (Figure 5 E). This resultant solution showed very low hydrosilylation activity. Thus, the reaction that occurred upon addition of **12** (10 equiv with respect to Rh) and **13** (9 equiv with respect to Rh) to solution E required 7 h for 70% conversion of **12**. These results clearly indicate that the catalytic activity is not attributable to the decomposed complexes but to the Rh–isocyanide complex itself.

Summary of FTIR and ^{13}C NMR Spectroscopic Studies

To summarize the results of the FTIR and NMR spectroscopic experiments, the major catalytic species bears the isocyanide ligand **1c** as a supporting ligand. As long as ketone **12** is in excess, a reasonable amount of the isocyanide ligand of the complex remains in the reaction mixture during hydrosilylation. Furthermore, NMR spectroscopy shows that catalyst-decomposition processes, which involve the reaction of the coordinated isocyanide with hydrosilane, compete with the hydrosilylation of the ketone.

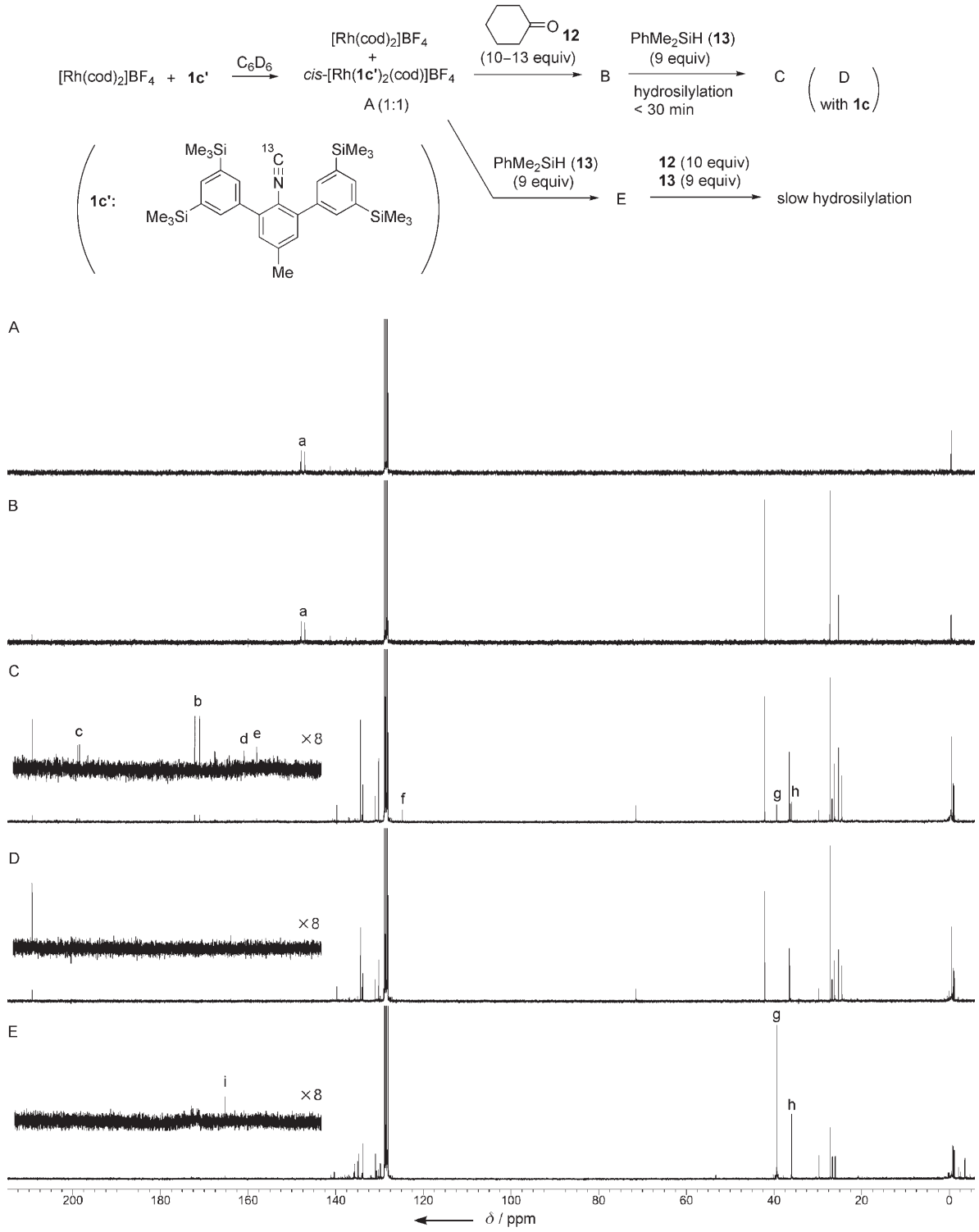

Figure 5. ^{13}C NMR spectra of the reaction mixtures of Rh complexes in C_6D_6. A: **1c′** (10 mM) and $[Rh(cod)_2]BF_4$ (10 mM). B: **1c′** (10 mM), $[Rh(cod)_2]BF_4$ (10 mM), and ketone **12** (126 mM). C: The crude mixture after hydrosilylation of **12** (100 mM) with hydrosilane **13** (90 mM) in the presence of **1c′** (10 mM) and $[Rh(cod)_2]BF_4$ (10 mM). D: The crude mixture after hydrosilylation of **12** (100 mM) with **13** (90 mM) in the presence of **1c** (10 mM) and $[Rh(cod)_2]BF_4$ (10 mM). E: **1c′** (10 mM), $[Rh(cod)_2]BF_4$ (10 mM), and **13** (90 mM).

Active Species

The reaction of an equimolar amount of $[Rh(cod)_2]BF_4$ (**6**) and **1c** first gives a mixture of bisisocyanide complex *cis*-$[Rh(\mathbf{1c})_2(cod)]BF_4$ (**11c**) and $[Rh(cod)_2]BF_4$ (**6**). The mixture of catalyst precursors should release the cod ligand upon rapid hydrosilylation prior to entering the catalytic cycle. Although the molar ratio of Rh/**1c** for the active species was not determined by NMR spectroscopy alone, the

active species in the Rh/**1c** catalysis is highly likely to be the monoisocyanide–rhodium complex as a result of the catalytic reaction.

Conclusions

We have developed new bulky isocyanide ligands with *meta*-terphenyl backbones. Their usefulness as supporting ligands in catalysis was illustrated by application to the rhodium-catalyzed hydrosilylation of ketones, in which we proposed that the combined effect of the high affinity of the ligand for the rhodium atom and the bulkiness of the ligand would facilitate the formation of a catalytically active monoisocyanide–rhodium species. Efforts aimed at further exploiting the efficient transition-metal-catalyzed reactions influenced by the isocyanide ligands and developing chiral derivatives of the isocyanides are ongoing in our laboratory.

Experimental Section

General

NMR spectra were recorded on a Varian Gemini 2000 (^{1}H: 300 MHz; ^{13}C: 75.4 MHz) spectrometer. Tetramethylsilane (TMS; ^{1}H, internal) and $CDCl_3$ and [D_6]dimethyl sulfoxide ([D_6]DMSO) (^{13}C, external) were employed as standards. GLC analysis was conducted on a Shimadzu GC-14B instrument equipped with a flame ionization detector. IR spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer. Elemental analysis was performed at the Center for Instrumental Analysis, Hokkaido University. Low- and high-resolution mass spectra were recorded on a JEOL JMS-T50LC mass spectrometer. Melting points were measured with a Yanaco MP500D apparatus.

All reactions were carried out under argon atmosphere. Materials were obtained from commercial suppliers and were purified by using standard procedures, unless otherwise noted. Dry benzene for Rh-catalyzed hydrosilylation was degassed by three freeze–pump–thaw cycles and was further dried on 4-Å molecular sieves. Dimethylphenylsilane and cyclohexanone were distilled under argon from CaH_2. [Rh(cod)$_2$]BF_4 and 3,5-bis(trimethylsilyl)bromobenzene were prepared according to the procedure in the literature.[23,24] Sodium [^{13}C]formate was purchased from Aldrich Chemical Co., Inc.

Computational Calculations

All calculations were performed with the Gaussian 03 program. Geometry optimizations for the compounds in Scheme 4 were performed at the B3LYP level with the SDD basis set, which included a double-zeta valence basis set with the Stuttgart quasirelativistic effective core potential. Values of Gibbs free energy were obtained on the basis of the frequency calculations of the model molecules.

Preparation of Isocyanide Ligands

3: Sodium formate (8.16 g, 120 mmol) was dried under reduced pressure for 1 h at 50 °C. Pivaloyl chloride (7.24 mL, 60 mmol) was slowly added to a suspension of dry sodium formate in Et_2O (60 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 2 days. 2,6-Dibromo-4-methylaniline (7.95 g, 30 mmol) was added to the resulting white suspension, and the reaction mixture was stirred for another 2 days. The resulting white solid was filtered and washed with water and diethyl ether. Recrystallization from toluene gave *N*-(2,6-dibromo-4-methylphenyl)formamide (**3**) as a white solid (7.9 g, 89 %). M.p.: 75 °C; IR (neat): $\tilde{\nu}$ = 3240, 2928, 1652 cm^{-1} (C=O); ^{1}H NMR (300 MHz, [D_6]DMSO, 20 °C, TMS): 2:8 mixture of isomers: δ = 10.00 (s, 0.8 H, CHO), 9.76 (d, $^3J_{H,H}$ = 10.2 Hz, 0.2 H, CHO), 8.28 (s, 0.8 H, NH), 8.02 (d, $^3J_{H,H}$ = 10.7 Hz, 0.2 H, NH), 7.61 (s, 0.4 H, ArH), 7.56 (s, 1.6 H, ArH), 2.29 ppm (s, 3 H, CH_3); ^{13}C NMR (75 MHz, [D_6]DMSO, 20 °C): δ = 164.7, 159.8, 141.1, 140.9, 133.2, 132.8, 132.1, 132.0, 123.42, 123.41, 19.8, 19.7 ppm; HRMS (atmospheric pressure chemical ionization; APCI): *m*/*z* calcd for $C_8H_8Br_2NO$: 291.89726 [*M*+H]$^+$; found: 291.89781.

4c: *n*-Butyllithium (9.2 mL, 1.60 M in hexane, 14.8 mmol) was added to a stirred solution of 3,5-bis(trimethylsilyl)bromobenzene[24] (4.1 g, 13.4 mmol) in THF (50 mL) at −78 °C. After 1.5 h, triisopropyl borate (9.3 mL, 40.3 mmol) was added. The resulting mixture was allowed to warm to room temperature, and the reaction was quenched with aqueous HCl (2.0 M). The mixture was extracted three times with ethyl acetate. The combined organic layer was washed with water and saturated aqueous NaCl and dried over $MgSO_4$. The solution was concentrated in vacuo and subjected to silica-gel chromatography (EtOAc/hexane = 3:7) to afford 3,5-bis(trimethylsilyl)phenylboronic acid (**4c**) as a white powder (2.4 g, 67 %). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): δ = 8.42 (s, 2 H, PhH), 7.91 (s, 1 H, PhH), 0.36 ppm (s, 18 H, Si(CH$_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 142.5, 141.3, 139.0, 138.9, 128.2 (br), −1.29 ppm.

4d: 3,5-Bis(*tert*-butyldimethylsilyl)phenylboronic acid (**4d**) was prepared from 3,5-bis(*tert*-butyldimethylsilyl)bromobenzene[25] (0.39 g, 1.02 mmol), *n*-butyllithium (0.65 mL, 1.60 M in hexane, 1.04 mmol), and triisopropyl borate (1.17 mL, 5.07 mmol) according to a procedure similar to that for the synthesis of **4c**. The crude product was purified by silica-gel chromatography (EtOAc/hexane = 2:8) to afford **4d** as a white solid (0.14 g, 38 %). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): δ = 8.34 (s, 2 H, PhH), 7.90 (s, 1 H, PhH), 0.92 (s, 18 H, SiC(CH$_3$)$_3$), 0.35 ppm (s, 12 H, SiC(CH$_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 144.8, 142.2, 135.9, 135.8, 26.4, 16.8, −6.43, −6.47 ppm.

5c: Compound **3** (0.65 g, 2.2 mmol), **4c** (1.24 g, 4.7 mmol), Na_2CO_3 (1.17 g, 11.1 mmol), $Pd(OAc)_2$ (25 mg, 0.11 mmol), and PPh_3 (58 mg, 0.22 mmol) were placed in a two-necked round-bottomed flask. After the flask was evacuated and backfilled with argon, toluene (12 mL), ethanol (12 mL), and H_2O (7 mL) were added. The mixture was heated to reflux and stirred for 14 h. After cooling to room temperature, the reaction mixture was extracted three times with ethyl acetate. The combined organic layer was washed with H_2O and saturated aqueous NaCl. The resulting solution was dried over $MgSO_4$ and concentrated in vacuo. The crude product was subjected to silica-gel chromatography (EtOAc/hexane = 2:98–5:95) to afford *N*-{2,6-bis[3,5-bis(trimethylsilyl)phenyl]-4-methylphenyl}formamide (**5c**) as a white powder (1.25 g, 98 %). M.p.: 90 °C; IR (neat): $\tilde{\nu}$ = 3399, 3019, 2955, 1702, 1670 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): 3:7 mixture of isomers: δ = 7.87 (br s, 0.3 H, CHO), 7.75 (d, $^3J_{H,H}$ = 11.4 Hz, 0.7 H, CHO), 7.66–7.62 (m, 2 H, ArH), 7.57–7.53 (m, 1.2 H, ArH), 7.53–7.47 (m, 2.8 H, ArH) 7.25–7.15 (m, 2 H, ArH), 6.58 (d, $^3J_{H,H}$ = 11.4 Hz, 0.7 H, NH), 6.45 (br s, 0.3 H, NH), 0.29 ppm (s, 36 H); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 165.7, 161.9, 142.9, 141.7, 140.7, 139.4, 138.7, 138.6, 138.44, 138.40, 137.6, 136.1, 135.6, 132.4, 132.1, 129.8, 128.5, 22.3, 22.1, 0.07 ppm; HRMS (APCI): *m*/*z* calcd for $C_{32}H_{49}NOSi_4Na$: 598.27889 [*M*+Na]$^+$; found: 598.27827.

5a: *N*-(2,6-Diphenyl-4-methylphenyl)formamide (**5a**) was prepared from **3** (1.16 g, 3.95 mmol) and **4a** (1.20 g, 9.87 mmol) by a procedure similar to that for the synthesis of **5c**. The crude product was subjected to silica-gel chromatography (EtOAc/hexane = 3:97–10:90) to afford **5a** as a white powder (0.77 g, 77 %). M.p.: 156 °C; IR (neat): $\tilde{\nu}$ = 3269, 3031, 1652 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): 3:7 mixture of isomers: δ = 7.82 (s, 0.3 H, CHO) , 7.73 (d, $^3J_{H,H}$ = 11.7 Hz 0.7 H, CHO), 7.48–7.33 (m, 10 H, PhH), 7.19 (s, 2 H, ArH), 6.71 (d, $^3J_{H,H}$ = 11.7 Hz, 0.7 H, NH), 6.61 (s, 0.3 H, NH), 2.42 ppm (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 164.8, 160.4, 140.8, 139.8, 138.7, 137.9, 137.2, 136.6, 131.3, 130.8, 129.4, 129.0, 128.9, 128.3, 128.2, 127.8, 127.5, 20.9, 20.8 ppm; HRMS (APCI): *m*/*z* calcd for $C_{20}H_{17}NONa$: 310.12078 [*M*+Na]$^+$; found: 310.12190.

5b: *N*-[2,6-Bis(3,5-dimethylphenyl)-4-methylphenyl]formamide (**5b**) was prepared from **3** (0.68 g, 2.33 mmol) and **4b**[26] (0.73 g, 4.85 mmol) by a procedure similar to that for the synthesis of **5c**. The crude product was purified by silica-gel chromatography (EtOAc/hexane = 3:97–10:90) to afford **5b** as a white powder (0.54 g, 67 %). M.p.: 180 °C; IR (neat): $\tilde{\nu}$ =

3188, 2860, 1682 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): 2:8 mixture of isomers: $\delta = 7.84$ (s, 0.2 H, CHO) 7.74 (d, $^3J_{H,H} = 11.4$ Hz, 0.8 H, CHO), 7.13 (s, 2 H, ArH), 7.00–6.97 (m, 6 H, ArH), 6.80 (br d, $^3J_{H,H} = 11.4$ Hz, 0.8 H, NH), 6.62 (br s, 0.2 H), 2.39 (s, 3 H, CH_3), 2.34 ppm (s, 12 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 164.8$, 160.1, 140.8, 139.8, 138.8, 138.6, 137.7, 137.5, 136.9, 135.9, 131.0, 130.6, 129.4, 129.0, 128.2, 127.1, 126.6, 21.2, 20.7 ppm; HRMS (APCI): *m/z* calcd for $C_{24}H_{25}NONa$: 366.18338 $[M+Na]^+$; found: 366.18213.

5d: *N*-{2,6-Bis[3,5-bis(*tert*-butyldimethylsilyl)phenyl]-4-methylphenyl}-formamide **(5d)** was prepared from **3** (0.040 g, 0.136 mmol) and **4d** (0.105 g, 0.30 mmol) according to a procedure similar to that for the synthesis of **5c**. The crude product was purified by silica-gel chromatography (EtOAc/hexane = 3:97–10:90) to afford **5d** as a white powder (0.093 g, 91 %). ^1H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): 3:7 mixture of isomers: $\delta = 7.78$ (s, 0.3 H, CHO), 7.73 (d, $^3J_{H,H} = 11.5$ Hz, 0.7 H, CHO), 7.63 (s, 2 H, ArH), 7.53 (s, 1.2 H, ArH), 7.49 (s, 2.8 H, ArH), 7.19 (s, 2 H, ArH), 6.55 (d, $^3J_{H,H} = 11.1$ Hz, 0.7 H, NH), 6.48 (s, 0.3 H, NH), 2.45 (s, 3 H, CH_3), 0.90 (s, 36 H, $SiCCH_3$), 0.30 ppm (s, 24 H, $SiCH_3$).

1c: Triethylamine (1.88 mL, 13.5 mmol) was added to a solution of **5c** (0.78 g, 1.35 mmol) in THF (15 mL) under argon atmosphere at 0 °C. Phosphorus oxychloride (0.38 mL, 4.05 mmol) was then added dropwise to the mixture. After the mixture was stirred for 1 h at 0 °C, the reaction was quenched with aqueous Na_2CO_3, and the mixture was extracted three times with EtOAc. The combined organic layer was washed with H_2O and aqueous NaCl, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by silica-gel chromatography (EtOAc/hexane = 1:99) to afford 2,6-bis[3,5-bis(trimethylsilyl)phenyl]-4-methylphenyl isocyanide **(1c)** as a white powder (0.67 g, 89 %). M.p.: 167.5 °C; IR (neat): $\tilde{\nu} = 3017$, 2953, 2112, 1247 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.64$–7.71 (m, 6 H, ArH), 7.22 (s, 2 H, ArH), 2.48 (s, 3 H, CH_3), 0.32 ppm (s, 36 H, $Si(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 169.0$ (C−N≡*C*), 140.5, 139.7, 139.4, 138.0, 136.2, 134.6, 130.1, 120.7 (br, *C*−N≡C), 21.3, −1.2 ppm; MS (APCI): *m/z* calcd for $C_{32}H_{47}NSi_4Na$: 580.3 $[M+Na]^+$; found: 580.3; elemental analysis: calcd (%) for $C_{32}H_{47}NSi_4$ (558.06): C 68.87, H 8.49, N 2.51; found: C 68.63, H 8.49, N 2.54.

1a: 2,6-Diphenyl-4-methylphenyl isocyanide (**1a**) was prepared from **5a** (0.24 g, 0.95 mmol) by a procedure similar to that for the synthesis of **1c**. The crude product was purified by silica-gel chromatography (EtOAc/hexane = 10:90) to afford **1a** as a white powder (0.20 g, 91 %). M.p.: 104 °C; IR (neat): $\tilde{\nu} = 3056$, 3032, 2118 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.55$–7.42 (m, 10 H, PhH), 7.21 (s, 2 H, ArH), 2.45 ppm (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 168.6$ (C−N≡*C*), 139.9, 139.5, 137.8, 130.2, 129.2, 128.5, 128.3, 120.4 (br, *C*−N≡C), 21.2 ppm; HRMS (APCI): *m/z* calcd for $C_{20}H_{15}NNa$: 292.11022 $[M+Na]^+$; found: 292.11066.

1b: 2,6-Bis(3,5-dimethylphenyl)-4-methylphenyl isocyanide **(1b)** was prepared from **5b** (0.4 g, 1.17 mmol) according to a procedure similar to that for the synthesis of **1c**. The crude product was purified by silica-gel chromatography (EtOAc/hexane = 1:99) to afford **1b** as a white powder (0.30 g, 80 %). M.p.: 138 °C; IR (neat): $\tilde{\nu} = 3000$, 2914, 2126 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.16$ (s, 2 H, ArH), 7.14 (s, 4 H, ArH), 7.05 (s, 2 H, ArH), 2.42 (s, 3 H, CH_3), 2.39 ppm (s, 12 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 168.2$ (C−N≡*C*), 140.1, 139.2, 138.0, 137.8, 129.95, 129.85, 126.9, 120.4 (br, *C*−N≡C), 21.2, 21.2 ppm; HRMS (APCI): *m/z* calcd for $C_{24}H_{23}NNa$: 348.17282 $[M+Na]^+$; found: 348.17155.

1d: 2,6-Bis[3,5-bis(*tert*-butyldimethylsilyl)phenyl]-4-methylphenyl isocyanide (**1d**) was prepared from **5d** (91 mg, 0.12 mmol) by a procedure similar to that for the synthesis of **1c**. The crude product was purified by silica-gel chromatography (EtOAc/hexane = 1:99) to afford **1d** as a white powder (71 mg, 80 %). M.p.: 157 °C; IR (neat): $\tilde{\nu} = 2953$, 2928, 2856, 2113, 1248 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.69$ (s, 2 H, ArH), 7.62 (s, 4 H, ArH), 7.19 (s, 2 H, ArH), 2.47 (s, 3 H, CH_3), 0.90 (s, 36 H, $SiC(CH_3)_3$), 0.30 ppm (s, 24 H, $Si(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 168.7$ (C−N≡*C*), 140.7, 140.5, 139.2, 136.6, 135.9, 135.5, 130.2, 26.4, 21.3, 16.8, −6.3 ppm; MS (APCI): *m/z* calcd for $C_{44}H_{71}NSi_4Na$: 748.45612 $[M+Na]^+$; found: 748.45696.

1c′: *N*-(2,6-Dibromo-4-methylphenyl)[^{13}C]formamide was prepared according to a procedure similar to that for the synthesis of **3**, by using sodium [^{13}C]formate (99 atom %) instead of sodium formate. 2,6-Bis[3,5-bis(trimethylsilyl)phenyl]-4-methylphenyl [^{13}C]isocyanide (**1c′**) was synthesized from *N*-(2,6-dibromo-4-methylphenyl)[^{13}C]formamide along the same synthetic pathway as **1c** (Suzuki–Miyaura coupling and dehydration).

General Procedure for ^1H NMR Spectroscopy of In Situ Complexation of Rh Cation Complex and Isocyanide Ligands

In a glove box, a solution of $[Rh(cod)_2]BF_4$ in $CDCl_3$ (10 mM, 200 μL) was mixed with a solution of **1** in $CDCl_3$ (20 mM, 50–300 μL) and $CDCl_3$ (350–200 μL) in an NMR sample tube equipped with a screw cap containing a teflon-coated rubber septum to give 600 μL of mixed solution. The sample tube was sealed and subjected to NMR spectroscopy.

Preparation of Rh/Isocyanide Complexes

7a: $[Rh(cod)_2]BF_4$ (4.1 mg, 0.01 mmol) and **1a** (10.8 mg, 0.04 mmol) were placed in a reaction tube equipped with a gas inlet and a septum. The tube was evacuated and backfilled with argon. Anhydrous, degassed CH_2Cl_2 (3 mL) was then added, and the mixture was stirred at room temperature for 1 h. After the solvent was evaporated, the residual yellow solid was washed with hexane and recrystallized from methanol to give **7a** as yellow crystals (10 mg, 79 %). IR (neat): $\tilde{\nu} = 3034$, 2134 (C≡N) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.29$ (s, 8 H), 6.95–7.18 (m, 40 H), 2.54 ppm (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 148.2$ (d, $J_{C,Rh} = 55.0$ Hz, C−N≡*C*), 141.5, 139.8, 136.4, 130.4, 129.1, 128.5, 128.4, 119.4, 21.5 ppm; MS (ESI): *m/z* calcd for $C_{80}H_{60}N_4Rh$: 1179.3873 $[M-BF_4]^+$; found: 1179.3850; elemental analysis: calcd (%) for $C_{80}H_{60}N_4RhBF_4$: C 75.83, H 4.77, N 4.42; found: C 75.36, H 4.88, N 4.40.

7b: This compound was prepared form $[Rh(cod)_2]BF_4$ (2.4 mg, 5.9 μmol) and **1b** (8.0 mg, 0.024 mmol) according to the procedure described above. Complex **7b** was obtained as a yellow solid (8.7 mg, 5.7 μmol, 97 %). IR (neat): $\tilde{\nu} = 2965$, 2916, 2142 (C≡N), 1592 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.22$ (s, 8 H), 6.75 (s, 16 H), 6.66 (s, 8 H), 2.50 (s, 12 H), 1.95 ppm (s, 48 H); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 148.7$ (d, $J_{C,Rh} = 55.0$ Hz, C−N≡*C*), 141.0, 140.1, 137.9, 136.5, 130.1, 129.9, 126.8, 119.8, 21.4, 20.8 ppm; HRMS (ESI): *m/z* calcd for $C_{96}H_{92}N_4Rh$: 1404.6410 $[M-BF_4]^+$; found: 1404.6370.

8: A solution of **1c** (25 mg, 0.045 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of $[Rh(cod)_2]BF_4$ (7.7 mg, 0.0189 mmol) in CH_2Cl_2 (0.5 mL). After the mixture was stirred for 1 h, hexane (5 mL) was added, and the solvent was then evaporated slowly. At the early stage of the evaporation, an orange solid first precipitated. After the orange solid was removed by filtration, the filtrate was further evaporated to afford a yellow solid. This solid was washed with hexane and dried under reduced pressure to give **8** as a yellow powder (19 mg, 0.013 mmol, 71 %). IR (neat): $\tilde{\nu} = 2954$, 2160 (C≡N), 2131 (C≡N), 1246 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.70$ (s, 4 H), 7.51 (s, 8 H), 7.20 (s, 4 H), 3.98–3.90 (m, 4 H), 2.51 (s, 6 H), 2.12–1.95 (m, 4 H), 1.95–1.71 (m, 4 H), 0.21 ppm (s, 72 H); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 145.6$ (d, $J_{C,Rh} = 65.9$ Hz, C−N≡*C*), 141.6, 140.8, 140.6, 138.4, 136.2, 134.3, 131.3, 120.1, 101.6 (d, $J_{C,Rh} = 6.9$ Hz), 30.3, 21.4, −1.0 ppm; MS (ESI): *m/z* calcd for $C_{72}H_{106}N_2RhSi_8$: 1326.5 $[M-BF_4]^+$; found: 1326.4; elemental analysis: calcd (%) for $C_{72}H_{106}N_4RhSi_8BF_4$: C 61.16, H 7.56, N 1.98; found: C 61.31, H 7.63, N 1.91.

10a: $[RhCl(cod)]_2$ (2.47 mg, 0.005 mmol) and **1a** (10.8 mg, 0.04 mmol) were placed in a reaction tube equipped with a gas inlet and a septum. The tube was evacuated and backfilled with argon. After addition of anhydrous, degassed CH_2Cl_2 (1 mL), the mixture was stirred at room temperature for 20 min. The solvent was evaporated to give a yellow solid. The resulting solid was recrystallized from CH_2Cl_2/hexane to afford **10a** (12 mg, 9.9 mmol, 99 %). IR (neat): $\tilde{\nu} = 3033$, 2138 (C≡N) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.29$ (s, 8 H), 6.98–7.21 (m, 40 H), 2.55 ppm (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 148.3$ (d, $J_{C,Rh} = 51.0$ Hz, C−N≡*C*), 141.5, 139.8, 136.4 130.4, 129.0, 128.4, 128.4, 119.4, 21.6 ppm; HRMS (ESI): *m/z* calcd for $C_{80}H_{60}N_4Rh$: 1179.38730 $[M-Cl]^+$; found: 1179.39092.

11c: $[RhCl(cod)]_2$ (9.8 mg, 0.02 mmol) and **1c** (22.4 mg, 0.04 mmol) were placed in a reaction tube equipped with a gas inlet and a septum. The tube was evacuated and backfilled with argon. After addition of anhydrous, degassed CH_2Cl_2 (2 mL), the mixture was stirred at room temperature for 2 h. After the solvent was removed under reduced pressure, the residual oil was subjected to recycle GPC to give **11c** as a yellow oil (25 mg, 0.031 mmol, 78%). The yellow crystalline **11c** was obtained by recrystallization from methanol. IR (neat): $\tilde{\nu}=2951$, 2138 (C≡N), 1244 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 20°C, TMS): $\delta=7.75$–7.71 (m, 2H), 7.54 (d, $J=1.1$ Hz, 4H), 7.16 (s, 2H), 5.23–5.28 (m, 2H), 2.91–2.95 (m, 2H), 2.44 (s, 3H), 2.02–2.32 (m, 4H), 1.77–1.99 (m, 4H), 0.36 ppm (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$, 20°C): $\delta=149.3$ (d, $J_{C,Rh}=68.7$ Hz, C–N≡*C*), 140.8, 140.1, 139.4, 138.3, 136.2, 134.2, 130.3, 121.6, 108.2 (d, $J_{C,Rh}=6.3$ Hz, RH*C*=*C*HR), 70.6 (d, $J_{C,Rh}=12.6$ Hz, RH*C*=*C*HR), 32.5, 28.5, 21.3, −1.0 ppm; HRMS (ESI): *m/z* calcd for $C_{40}H_{59}ClNNaRhSi_4$: 826.2366 $[M+Na]^+$; found: 826.2371; elemental analysis: calcd (%) for $C_{40}H_{59}ClNRhSi_4$: C 59.71, H 7.39, N 1.74; found: C 59.53, H 7.32, N 1.72.

General Procedure for Rh-Catalyzed Hydrosilylation of Ketones (Tables 2 and 3 and Figure 3)

The Rh complex (0.015 mmol with respect to Rh) and the isocyanide (0.015–0.045 mmol) were placed in a reaction tube equipped with a gas inlet and a septum. The tube was evacuated and backfilled with argon. After addition of anhydrous, degassed benzene (1.5 mL), the mixture was stirred at room temperature for 1 h. Cyclohexanone (**12**; 147 mg, 1.5 mmol), 1,4-diisopropylbenzene (66.9 mg, 0.412 mmol, as an internal standard for GC analysis), and dimethylphenylsilane (**13**; 245 mg, 1.8 mmol) were then added by syringe. The yield of product **14** was determined by gas chromatography.

FTIR and NMR Spectroscopy of the Rh/Isocyanide Complex in the Reaction Mixture During Hydrosilylation (Scheme 4 and Figures 4 and 5)

$[Rh(cod)_2]BF_4$ (4.1 mg, 0.01 mmol) and the isocyanide (0.01 mmol) were placed in a reaction tube equipped with a gas inlet and a septum. The tube was evacuated and backfilled with argon. After addition of anhydrous, degassed benzene (for FTIR) or C_6D_6 (for NMR) (1.0 mL), the mixture was stirred at room temperature for 1 h. Cyclohexanone (**12**; 10.4 μL, 0.10 mmol) and dimethylphenylsilane (**13**; 13.8 μL, 0.09 mmol) were then added by syringe. After the mixture was stirred for 1 h, it was transferred into a sealed NaCl cell for IR spectroscopy or an NMR sample tube under argon atmosphere.

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