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Hemilabile *N*-Xylyl-*N*′-methylperimidine Carbene Iridium Complexes as Catalysts for C−H Activation and Dehydrogenative Silylation: Dual Role of *N*-Xylyl Moiety for ortho-C−H Bond Activation and Reductive Bond Cleavage

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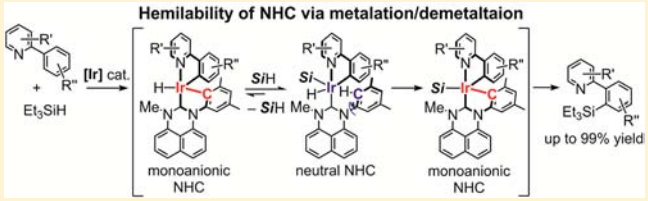
Supporting Information

ABSTRACT: Direct dehydrogenative silylation of pyridyl and iminyl substrates with triethylsilane was achieved using (L)Ir(cod)(X) (**1**) (L = a perimidine-based carbene ligand, X = OAc and OCOPh) complexes as catalysts under toluene refluxing conditions in the presence of norbornene as a hydrogen scavenger, and the silylated products were obtained in good yields. The isolated bis(cyclometalated)iridium complexes, (C^C:)(C^N)IrOAc (**2**) (C^C: = a cyclometalated perimidine-carbene ligand and C^N = a cyclometalated pyridyl- and iminyl-ligated aromatic substrate), were key intermediates, where cyclometalated five-membered metallacycles of substrates such as phenylpyridine were selectively formed before yielding mono-ortho-silylation products. The bis(cyclometalated)iridium complex (^{Xy}C^C:)(C^N)IrOAc (**2d**) (^{Xy}C^C: = a cyclometalated *N*-xylyl-*N*′-methylperimidine-carbene ligand and C^N = a 2-pyridylphenyl ligand), reacted with 2 equiv of Et_3SiH to give an iridium hydride complex, (L^4)(C^N)Ir(H)($SiEt_3$) (**8d**) (L^4 = *N*-CH_3, *N*-3,5-$(CH_3)_2C_6H_3$ perimidine), via demetalation of a *N*-3,5-xylyl ring of the carbene ligand of **2d**. The formation of **8d** was confirmed by isolating the corresponding chloro complex (L^4)(C^N)Ir(Cl)($SiEt_3$) (**8d-Cl**) by treatment with CCl_4. The *N*-methyl moiety of the carbene ligand coordinated to **8d** was cyclometalated in the presence of norbornene at room temperature to afford (^{Me}C^C:)(C^N)Ir($SiEt_3$) (**10d**) (^{Me}C^C: = a cyclometalated *N*-xylyl-*N*′-methylperimidine-carbene), while at high temperature **8d** reacted with norbornene and Et_3SiH to afford the silylated product, 2-(2-triethylsilyl)phenylpyridine (**3a**) and norbornane. A deuterium labeling experiment using **2d** and Et_3SiD (excess) revealed the incorporation of deuterium atoms at two ortho-positions of the *N*-xylyl group (>90%) and at the 3-position of 2-pyridylphenyl ligand (ca. 40%) within 3 h at room temperature, indicating that the cyclometalation/demetalation of the *N*-xylylperimidine carbene and 2-phenylpyridine ligands were reversible processes. Isolation of these cyclometalated iridium complexes under controlled conditions and D-labeling experiments thus revealed a dual function of the *N*-aryl group bound to the perimidine-carbene ligand, which acted as both a neutral carbene ligand and a monoanionic ortho-metalated aryl-carbene ligand through reversible C−H bond activation and Ir−C bond cleavage of the *N*-aryl group during the catalytic cycle.



INTRODUCTION

Transition metals supported by chelating ligands are versatile scaffolds for mediating various catalytic organic transformations. Among the chelating ligands, hemilabile ligands in which two or more different heteroatoms coordinate to a metal center[1] have attracted increased attention due to their ability to change their coordination mode from a rigid multidentate chelation to a coordinatively unsaturated monodentate ligation for approaching substrates, as well as to occupy the coordinatively unsaturated sites by chelation to stabilize the unstable intermediate species. In such a context, suitable selection of heteroatoms and the rational design of hemilabile ligands lead to high activity and selectivity of their transition metal complexes in various catalytic reactions. A large number of hemilabile ligands with a phosphine atom combined with N, O, or S donor atom(s) have been developed (Chart 1a).[2]

The advantages of *N*-heterocyclic carbene (NHC) ligands are their strong coordination ability and their easily sterically and electronically tunable nature.[3,4] Some hemilabile ligands of NHCs connected with a N or O donor atom have been reported.[5] The recent development of NHCs and their hemilabile ligand system prompted us to design and prepare a new type of hemilabile ligand comprising NHCs and carbanions as a more labile site in which the M−C bond formation is kinetically labile due to facile C−H bond activation and reversible C−H bond formation of the *N*-aromatic unit of the carbene ligands by late transition metals (Chart 1b). The hemilabile nature of the *N*-arylated heterocyclic carbene ligand of Cp*Ir(NHC) is a notable example reported by Peris et al.,[6] in which the carbene

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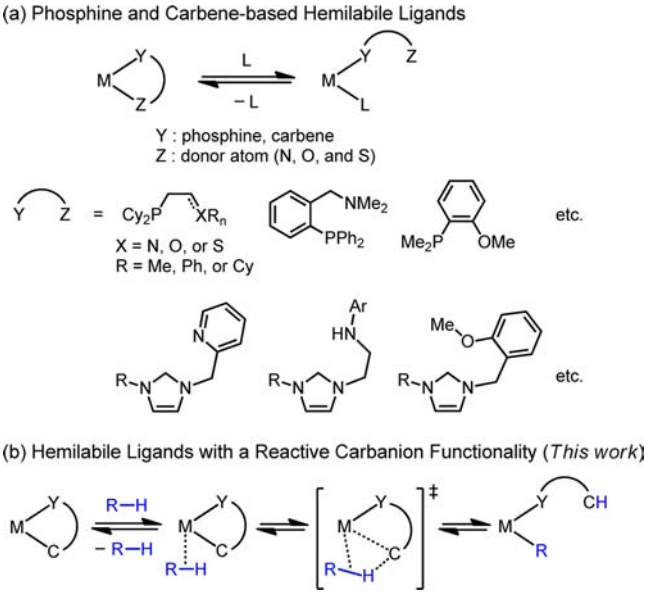
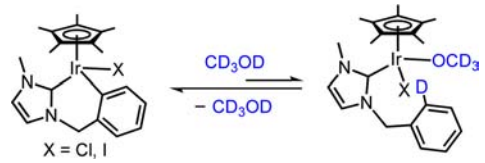
Chart 1. Hemilabile Ligation to Transition Metal Centers

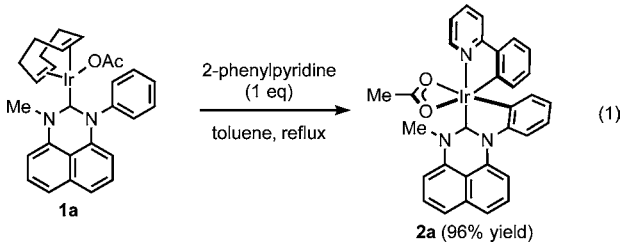


ligand showed hemilability via metalation/demetalation of a phenyl group attached to one N atom of the carbene ligand (Chart 2), although many heterometallacycles are very stable and can act as a supporting ligand under catalytic conditions.[7−9]

Chart 2. Reversible Metalation/Demetalation Behavior of a Carbene-Based Hemilabile Ligand



We[10] and Richeson's group[11] reported the synthesis of rhodium and iridium complexes having a series of six-membered perimidine carbene ligands with different functional groups on two nitrogen atoms. Recently, we found that the *N*-phenyl group of perimidine ligands bound to the iridium atom of (L^1)Ir(cod)(OAc) (L^1 = *N*-CH_3, *N*-C_6H_5 perimidine carbene ligand) (**1a**) in the presence of 2-phenylpyridine underwent smooth C−H bond activation of not only the *N*-phenyl group of the ligand but also the phenyl group of the coordinating 2-phenylpyridine to give a distinctive bis(cyclometalated)iridium complex **2a** (eq 1). In association with

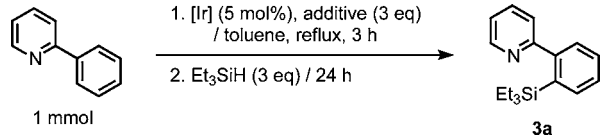


the unique double C−H bond activation at the iridium center, we report here that iridium complexes with an *N*-arylperimidine carbene ligand are catalysts for the C−H activation/dehydrogenative silylation reaction of pyridyl- and iminyl substrates.[12,13] Mechanistic studies, including the isolation of key intermediates, revealed that the *N*-aryl group of perimidine carbene ligands act as a hemilabile ligand through the formation and cleavage of an Ir−C bond, which directly controls the catalytic reaction, as the first example of a carbanion site acting as a labile coordination site of hemilabile ligation during the catalytic cycle.

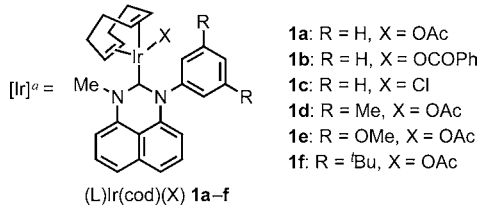
RESULTS AND DISCUSSION

Direct Dehydrogenative Silylation Reaction. We began a direct dehydrogenative silylation of 2-phenylpyridine with triethylsilane by screening for the best iridium catalyst precursor among **1a** and its derivatives (L)Ir(cod)(X) (**1b—f**) with different *N*-substituted perimidine-based carbene ligands (L) and monoanionic ligands (X). A toluene solution of **1a—f** (5 mol%) and 2-phenylpyridine was heated at refluxing temperature for 3 h prior to the addition of triethylsilane (3 equiv), and the results of the catalytic dehydrogenative silylation are summarized in Table 1.[14] Iridium complexes **1a** and **1b**, having an acetate and a

Table 1. Screening of Ligands and Additive Effect[19]



entry	[Ir][a]	R	X	additive	yield (%)[b]
1	**1a**	H	OAc		22
2	**1b**	H	OCOPh		21
3	**1c**	H	Cl		*c*
4	**1d**	Me	OAc		68[d]
5	**1e**	OMe	OAc		18
6	**1f**	*t*Bu	OAc		*c*
7	**1d**	Me	OAc	1,5-cyclooctadiene	74
8	**1d**	Me	OAc	norbornadiene	43
9	**1d**	Me	OAc	cyclooctene	57
10	**1d**	Me	OAc	2-norbornene	99
11	**1d**	Me	OAc	3,3-dimethylbutene	46



[b]Determined by GC analysis by using dodecane as an internal standard. [c]Trace. [d]Isolated yield.

benzoate ligand attached to the metal center, showed almost the same reactivity, giving 2-(2-(triethylsilyl)phenyl)pyridine (**3a**) in 22% and 21% yield, respectively (entries 1 and 2 in Table 1), while a chloride derivative **1c** did not give any silylated product (entry 3), indicating that carboxylate ligands were necessary to activate C−H bonds of 2-phenylpyridine and the *N*-phenyl group of the carbene ligand.[10,15,16] Substituents at the 3,5-positions of the phenyl group attached to the nitrogen atom of the perimidine-based carbene ligand sensitively affected the catalytic activity; complex **1d** with a 3,5-xylyl group produced **3a** in 68% yield (entry 4), whereas both **1e** with a 3,5-dimethoxyphenyl group and **1f** with a 3,5-di-*tert*-butylphenyl group were inferior catalyst precursors (entries 5 and 6), suggesting that bulkiness on the carbene ligands was a critical predetermining factor.[17] Thus, we presumed that the *N*-3,5-xylyl group was more effective for the

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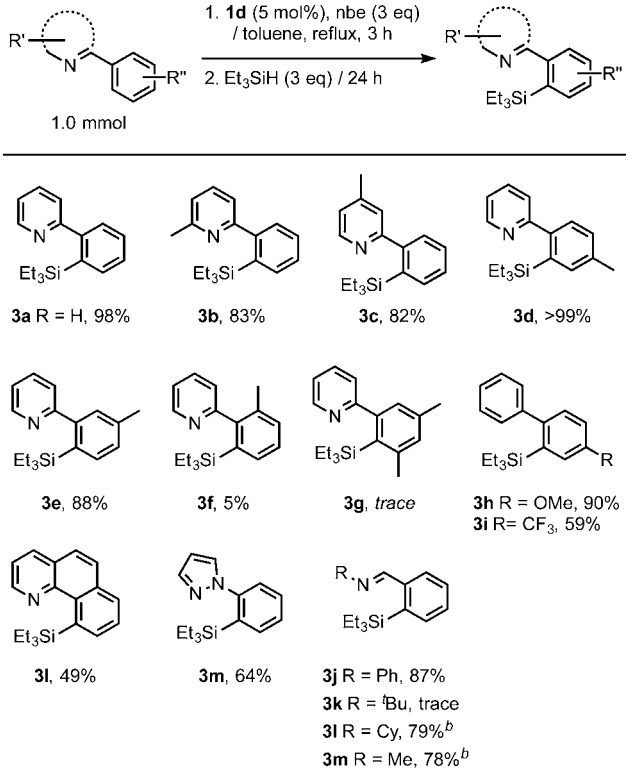
product elimination step compared with *N*-Ph and *N*-3,5-dimethoxyphenyl groups (vide infra).

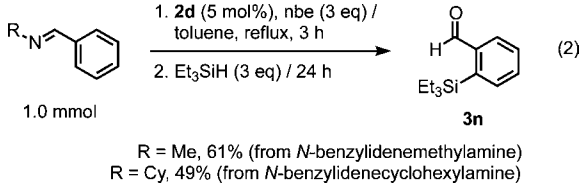
Using the best catalyst precursor **1d**, we examined the additive effects of olefins and cyclic dienes, because the cyclooctadiene ligand of **1d** was liberated in the reaction course to give 1,3-cyclooctadiene and cyclooctene (vide infra).[10] The combination of **1d** with cyclooctadiene afforded **3a** in a slightly increased yield (74%, entry 7), while the addition of norbornadiene, another chelating diene, suppressed the yield of **3a** (43%, entry 8), indicating that cyclic dienes have somewhat negative additive effects due to the strong affinity to the coordinatively unsaturated metal center. On the other hand, to our surprise, the addition of 2-norbornene improved the catalytic activity to afford **3a** in quantitative yield (entry 10) because of the high reactivity ascribed to the ring strain, although the addition of cyclooctene (3 equiv) and 3,3-dimethylbutene gave **3a** in 57% (entry 9) and 46% yield (entry 11), respectively.[18] GC-MS analysis of the reaction mixture in entry 10 revealed the formation of more than 1 equiv of norbornane, clearly indicating that norbornene acted as a hydrogen scavenger for the coupling reaction. Such alkene additive effects have been noted for the C−H functionalization/silylation of arenes with hydrosilanes catalyzed by ruthenium and iridium complexes.[13,18]

Substrate Scope Using Pyridyl and Iminyl as Directing Groups. Under the best catalyst conditions of **1d** and norbornene (3 equiv), we explored the scope of direct silylation of some *N*-functionalized substrates such as pyridyl- and iminyl-arenes, and the results are summarized in Table 2. The methyl substituent at the para and ortho positions of the pyridine ring of phenylpyridine afforded the corresponding products in good yields (**3b**: 83% yield and **3c**: 82% yield). In sharp contrast, substituents at the phenyl ring of 2-phenylpyridiene sensitively affected the yield of the silylated products: a monomethyl substituent at the para and meta positions of the phenyl ring afforded excellent yields, quantitative for **3d** and 88% for **3e**, whereas ortho-monomethyl and 3,5-dimethyl derivatives of the phenyl ring suppressed the silylation reaction, 5% for **3f** and trace for **3g**. 2-(4′-Anisyl)pyridine afforded the product **3h** in 90% yield, which was comparable to that of **3d** (98%), while a withdrawing substituent, a trifluoromethyl group, at the para-position resulted in a low yield of **3i** (59%). These observations clearly indicated that steric congestion at the phenyl ring of the substrates was an important factor. Benzo[*h*]quinoline and *N*-phenylpyrazole were silylated under the same conditions (**3l**: 49% yield and **3m**: 64% yield, respectively). The low yields of **3l** and **3m** might be due to the formation of relatively stable five-membered iridacycles compared with that of 2-phenylpyridine. Furthermore, several aromatic imines bearing a Ph, ^{t}Bu, Cy, or Me substituent at the nitrogen atom were examined for direct dehydrogenative silylation. The reaction of *N*-benzylideneaniline with Et_3SiH under the optimized reaction conditions gave the ortho silylation product **3j** in 87% yield without any C═N bond reduction of the imine moiety of the substrates.[20] *N*-Benzylidenemethylamine and *N*-benzylidenecyclohexylamine smoothly reacted with Et_3SiH to give the corresponding silylated products in moderately high yields; however, these compounds were moisture-sensitive and readily hydrolyzed upon purification through silica gel chromatography to give the same aldehyde, 2-(triethylsilyl)benzaldehyde (**3n**) (eq 2). In contrast, a bulky substrate such as *N*-benzylidene-*tert*-butylamine, which could not form a bis(cyclometalated)iridium complex via C−H bond activation due to steric hindrance around the nitrogen atom of the substrate (vide infra), resulted in a trace amount of a silylated product.

Table 2. Direct Dehydrogenative *ortho*-C−H Silylation of Arenes[a]

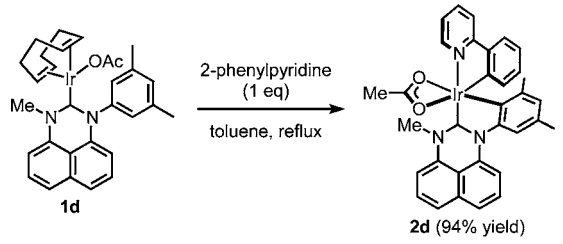


[a]Reaction conditions: substrate (1.0 mmol), nbe (norbornene, 3 equiv), and 5 mol% of **1d** in 5 mL of toluene. Reactions were run at 115 °C (oil-bath temperature) and Et_3SiH (3 equiv) was added to the reaction mixture after 3 h. Products were isolated by silica gel chromatogaraphy. [b]Determined by ^{1}H NMR using ferrocene as an internal standard.



(2)

Isolation and Characterization of Bis(cyclometalated) iridium Complex 2d. Pretreatment to heat the reaction mixture of **1d** and 2-phenylpyridine in refluxing toluene for 3 h before the addition of triethylsilane was essential; otherwise the yield of the desired silylated product was significantly decreased. These observations prompted us to conduct the reaction by heating the toluene solution of **1d** in the presence of 1 equiv of 2-phenylpyridene to afford a bis(cyclometalated)iridium complex **2d**, in which the carbene ligand and 2-phenylpyridine were cyclometalated to give a spiro-type skeleton of two five-membered iridacycles (eq 3).[11] The ^{1}H NMR spectrum of **2d** showed one set of the perimidine-based carbene ligand, cyclometalated 2-phenylpyridine, and the acetate group, whereas



(3)

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the resonances due to cyclooctadiene of **1d** were not observed. The most notable resonance in the $^{13}C\{^1H\}$ NMR spectra of **2d** was that of the $C_{carbenes}$, which appeared at δ_C 193.7. We tested the catalytic activity of the isolated complex **2d** under the optimized reaction conditions heated at 115 °C with 3 equiv of norbornene, the silylation reaction of 2-phenylpyridine with Et_3SiH using 5 mol% of **2d** without any preheating treatment gave the corresponding silylated product **3a** in quantitative yield, consistent with the catalytic activity observed when using **1d** as the catalyst precursor under the preheating conditions.[21]

The cyclometalated structure of **2d** was determined by X-ray crystallographic analysis (Figure 1), and selected bond distances

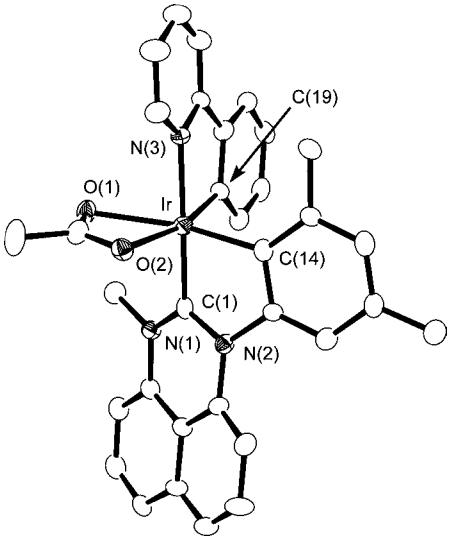
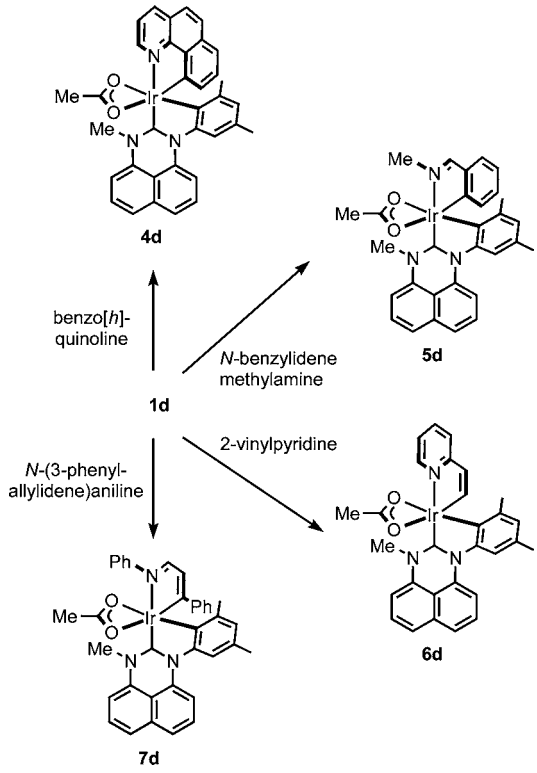


Figure 1. ORTEP drawings of the molecular structure of **2d**. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir−C(1), 1.986(8); Ir−C(14), 2.202(6); Ir−C(19), 2.003(8); Ir−N(3), 2.116(6); Ir−O(1), 2.222(5); Ir−O(2), 2.249(4); C(1)−Ir−C(14), 80.1(3); C(19)−Ir−N(3), 80.3(3); C(14)−Ir−N(3), 101.7(3); O(1)−Ir−O(2), 58.84(19); C(14)−Ir−C(19), 90.2(3).

and angles were compared with its analog **2a**.[10] The coordination environments around the iridium metal are essentially the same: each iridium atom possesses both the cyclometalated 2-phenylpyridine and the cyclometalated perimidine ligand. An acetate coordinates to the iridium atom in a κ^2-coordination mode. The C(1)−Ir distances for **2a** and **2d** are 1.979(8) and 1.987(7) Å, respectively. The distance of Ir−C(14) for **2d** is 2.021(6) Å, noticeably longer than that of **2a** (1.979(7) Å). The bond angles of C(14)−Ir−N(3) and C(14)−Ir−C(27) for **2d** are 101.8(3)° and 90.3(3)°, slightly larger than those of **2a** (98.5(2)° and 87.8(3)°) due to the steric congestion around the metal center of **2d**, which accelerated the C−Si bond formation in the catalytic cycle.

Isolation and Characterization of Cyclometalated Iridium Complexes bearing Cyclometalated Perimidine-based Carbene Ligand. As outlined in Scheme 1, reactions of **1d** with benzo[*h*]quinoline and *N*-benzylidenemethylamine, respectively, afforded the bis(cyclometalated)iridium complexes **4d** and **5d** via activation of the aromatic $C(sp^2)$−H bond, corresponding to the catalytic silylation of benzo[*h*]quinoline and *N*-benzylidenemethylamine.[16d,e,22] Similarly, reactions of **1d** with 2-vinylpyridine and *N*-(3-phenylallylidene)aniline yielded the corresponding complexes **6d** and **7d** by the activation of olefinic $C(sp^2)$−H bonds.[23] These complexes were characterized

Scheme 1. Preparation of Bis(cyclometalated)iridium Complexes



by spectroscopic methods and combustion analyses, together with crystallographic studies for **4d**, **5d**, **6d**, and **7d**.[24] Thus, such experimental results suggested that pyridyl and iminyl moieties worked as directing groups for C−H bond activation, and stability of the resulting metallacycle played a key role in the catalytic silylation reaction (vide supra).

Mechanistic Study for Dehydrogenative Silylation. *NMR Measurements of the Controlled Reaction Mixture.* To investigate catalytically active species for the dehydrogenative silylation reaction, we conducted controlled experiments using the isolated complex **2d**. At first, the reaction mixture of complex **2d** and Et_3SiH (3 equiv) in C_6D_6 at room temperature was monitored by NMR spectroscopy, and several resonances in the region of metal hydride were detected, but not all of them could be assigned (Figure 2a).[25] In this reaction, the formation of triethylsilyl acetate, Et_3SiOAc, was confirmed by its ^1H NMR spectrum along with GC-MS. In sharp contrast to the formation

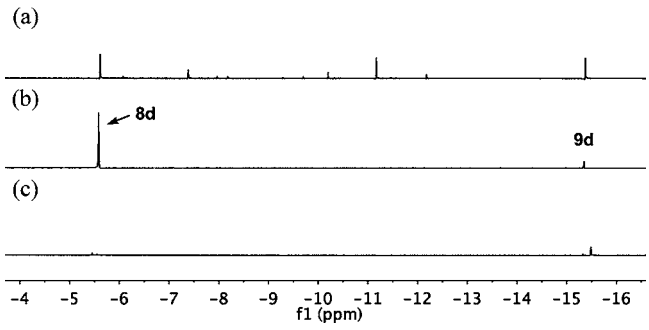


Figure 2. The ^1H NMR spectra in the region of Ir-hydride for reactions of **2d** with (a) Et_3SiH (3 equiv), (b) Et_3SiH (3 equiv) and 2-phenylpyridine (1.5 equiv), (c) Et_3SiH (3 equiv), 2-phenylpyridine (1.5 equiv), and norbornene (3 equiv) at room temperature.

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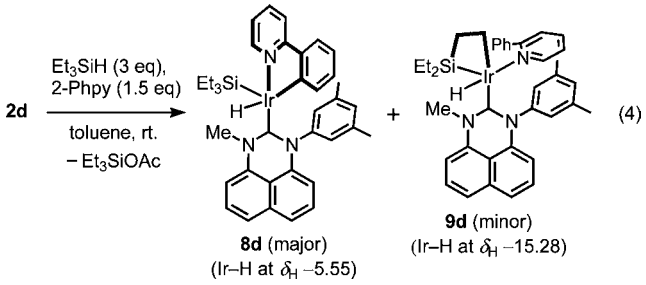
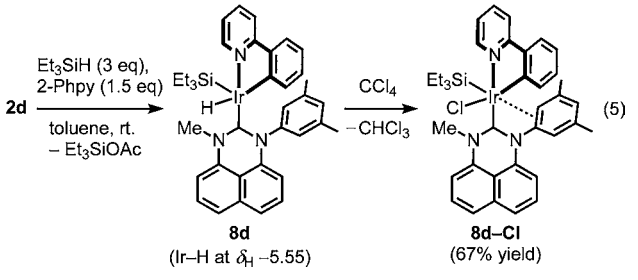
of several complicated species without 2-phenylpyridine, the reaction of **2d** and Et_3SiH (3 equiv) in the presence of 1.5 equiv of 2-phenylpyridine afforded only two singlet peaks assignable to Ir−H at δ_H −5.55 (major product) and −15.28 (minor product) in a 7:1 ratio (Figure 2b). The major product was determined spectroscopically to be a hydride complex **8d**, while the minor product was assigned to be the other hydride complex **9d**, which was a cyclometalated product of the Et_3Si moiety (eq 4)



(vide infra). Such cyclometalation reaction of the Ir−SiR_3 (R = alkyl, aryl) moiety to form iridasilacycle structures was independently reported by Milstein[26] and Tilley et al.[27] Upon heating of this reaction mixture at 100 °C, no silylated product **3a** was obtained, but these complexes decomposed to give unidentified species.

We already confirmed the additive effects of norbornene in the catalytic reaction. Thus, 3 equiv of norbornene was added to the C_6D_6 solution containing **2d**, Et_3SiH (3 equiv), and 2-phenylpyridine (1.5 equiv) at room temperature to induce a decrease in the intensity of the major Ir−H resonance at δ_H −5.55, suggesting that norbornene inserted into Ir−H presumably gives a norbornyliridium species, though this could not be detected. Meanwhile, the signal of the minor Ir−H species appearing at δ_H −15.28 remained intact (Figure 2c), suggesting that the minor product **9d** was a decomposed product outside of the catalytic cycle. At room temperature, no silylated product **3a** was obtained; however, heating the reaction mixture at 100 °C for 6 h produced **3a** (quant.) and norbornane (3 equiv), in good accordance with the catalytic reaction.

*Major Product **8d** and its Decomposed Product **10d**.* We first focused on isolating and characterizing the major hydride species **8d**. Although isolation of **8d** was difficult due to facial decomposition during the purification process, we could characterize the complex **8d** by ^1H NMR measurement even when minor species were contained in the reaction mixture. The ^1H NMR spectrum displays two ortho C−H bonds and two CH_3 resonances of the *N*-xylyl moiety at δ_H 7.28, 6.88, 2.16, and 1.22 inequivalently, indicating the difficulty of the *N*-xylyl ring to freely rotate at ambient temperature.[28] According to the general method of converting Ir−H to Ir−Cl species by CCl_4, we added CCl_4 to in situ-generated **8d** in toluene at room temperature, followed by silica-gel column chromatography, thus isolating the corresponding Ir complex **8d-Cl** (eq 5). The spectral features of



8d-Cl were superimposed on those of **8d** except for the absence of a hydride signal and one singlet for one of two ortho-*N*-xylyl moieties: two singlet resonances assignable to ortho-hydrogen atoms of the *N*-xylyl moiety were observed at δ_H 8.13 and 6.23, and one signal was shifted to a lower magnetic field due to the interaction between the iridium metal center and the *N*-xylyl moiety. The overall molecular structure was determined by X-ray analysis.

Figure 3 shows the molecular structure of the iridium complex **8d-Cl**. The iridium atom possessed a square pyramidal

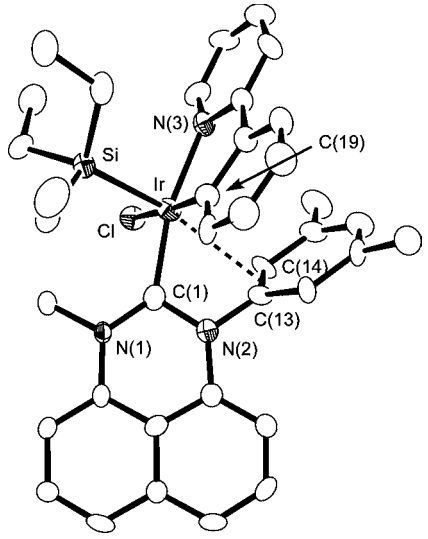


Figure 3. ORTEP drawing of the molecular structure of **8d-Cl**. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir−Cl, 2.461(3); Ir−C(1), 1.988(12); Ir−Si, 2.356(4); Ir−C(19), 2.014(11); Ir−N(3), 2.100(10); Ir−C_{cent}, 2.664 (C_{cent} = midpoint of C(13)−C(14)); Cl−Ir−C(1), 89.9(3); Si−Ir−N(3), 89.9(3); C(1)−Ir−C(19), 94.8(5); C(19)−Ir−N(3), 82.1(4).

penta-coordinated structure supported by C and N atoms of cyclometalated 2-phenylpyridine, a carbene carbon of the neutral perimidine-based carbene ligand, a Si atom of the triethylsilyl group, and a chloride atom. A phenyl ring on a nitrogen atom of the perimidine-based carbene ligand interacts with an iridium atom *trans* to the Ir−$SiEt_3$ moiety to form an octahedral structure, and the distance of Ir−C_{cent} (C_{cent} = midpoint of C(13)−C(14)) is 2.664 Å, which is consistent with the lower-field shift of one of two ortho-C−H singlet signals in the ^1H NMR spectrum. A silyl group coordinates to the metal center at the *cis*-position to 2-phenylpyridine and a perimidine-based carbene ligand. The Ir−Si distance is 2.356(4) Å, consistent with typical M−Si (M = Ir and Rh) bonds.[29,30] The distance of Ir−C(1) in **8d-Cl** is 1.989(12) Å, indicating a typical M−$C_{carbene}$ bond but it is noticeably shorter than the Ir−$C_{carbene}$ distance in $[(^{Ph}C\hat{}C:)_2Ir(\mu\text{-}Cl)]_2$ ($^{Ph}C\hat{}C$: = cyclometalated *N*-methyl-*N*-phenylperimidine carbene) (2.042(3) Å).[10]

Figure 2c clearly shows that the addition of norbornene induced a decrease in the hydride signal due to **8d** at room temperature. Upon prolonged standing of the reaction mixture for 4 days at room temperature, we obtained a new complex, bis(cyclometalated)Ir($SiEt_3$) complex (**10d**), as sparingly soluble dark red crystals in 54% yield (eq 6). Complex **10d** was fully characterized by spectroscopic measurements along with X-ray diffraction studies, which revealed that complex **10d** has a cyclometalated *N*-methyl group of the perimidine-carbene

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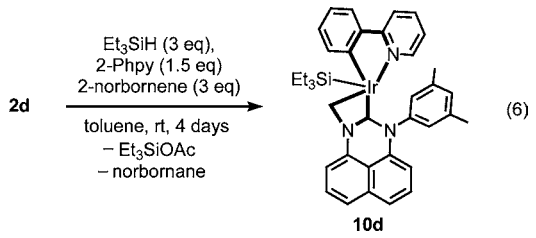


ligand, to form a four-membered ring as a consequence of unique C(sp^3)−H bond activation.[31] Notable spectral data were that two hydrogen atoms on a cyclometalated methylene group of the carbene ligand, forming a four-membered metallacycle, separately appeared at δ_H 3.45 and 3.39 as doublet signals, and the resonance for $C_{carbene}$ was observed at δ_C 169.9, which was shifted to lower field than that in **2d**.

Figure 4 clearly shows that the coordination environment around the iridium center of **10d** adopts a unique square

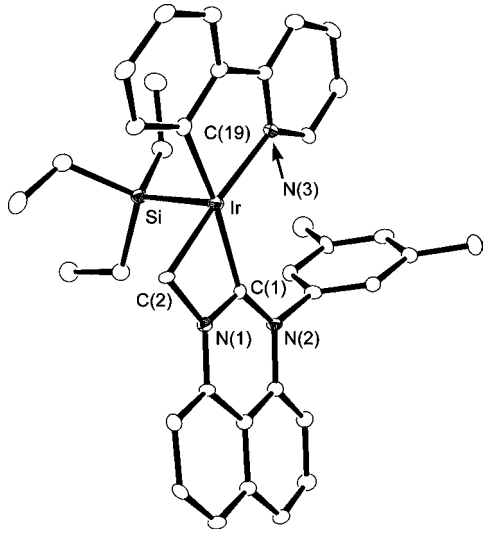
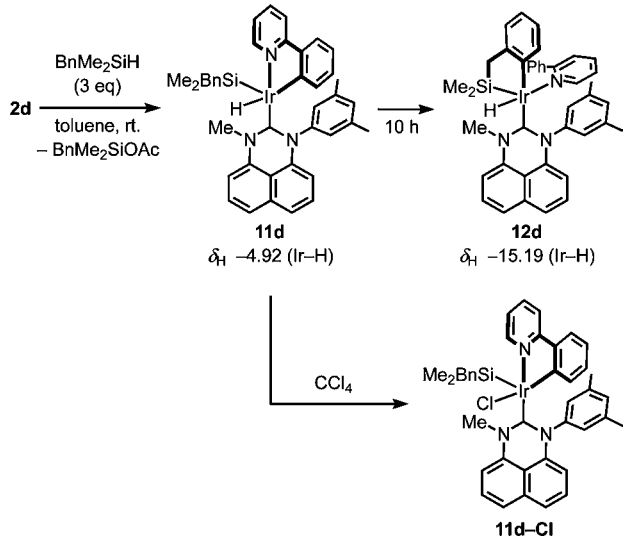


Figure 4. ORTEP drawing of the molecular structure of **10d**. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir−C(1), 2.086(5); Ir−C(2), 2.083(5); Ir−C(19), 2.042(5); Ir−Si, 2.3106(15); Ir−N(3), 2.141(5); C(1)−Ir−C(2), 65.35(19); C(1)−Ir−C(19), 164.3(2); C(1)−Ir−N(3), 114.93(18); C(1)−Ir−Si, 92.00(15); C(19)−Ir−N(3), 78.57(19).

pyramidal geometry where an iridium atom is surrounded by two cyclometalated fragments of 2-phenylpyridine and the perimidine-based carbene ligand at the basal position in addition to a triethylsilyl group occupying an apex position.[30] The distances of Ir−C(1) and Ir−C(2) for **10d** are 2.086(5) and 2.082(5) Å, respectively, indicating elongation of an Ir−C(1) bond compared with an Ir−$C_{carbene}$ bond of **2d** (1.987(7) Å) and a shorter Ir−C(2) bond distance compared with a normal Ir−C_{methyl} bond distance due to formation of the four-membered metallacycle via C(sp^3)−H bond activation of a *N*-methyl group of the perimidine-based carbene ligand. The Ir−Si distance of 2.3108(16) Å is normal and comparable to that found in the pentacoordinated complexes Ir(acac)H($SiPh_3$)(PCy_3) (2.307(1) Å)[30] and IrHCl(Si^iPr_2OH)(PEt_3)$_2$ (2.313.(6) Å).[32] The angles of C(1)−Ir−C(2) and N(3)−Ir−C(27) are 65.29(19)° and 78.56(19)°, respectively, and such environments thus enforce the complex to adopt an unusual, distorted square pyramidal geometry.

*Minor Product **9d** and Its Related Complexes.* For minor product **9d**, we could not isolate **9d** even by treatment with CCl_4 followed by a separation trial. Thus, we conducted the reaction of **2d** with the other silane, $BnMe_2SiH$.[33] The ^{1}H NMR spectrum of the reaction mixture of **2d** with $BnMe_2SiH$ (3 equiv) at room temperature displayed two signals at δ_H −4.92 (**11d**) and −15.28 (**12d**), corresponding to the previous observation of the reaction of **2d** with Et_3SiH (3 equiv). At room temperature, the hydride signal due to **11d** gradually disappeared and only the hydride signal assignable to **12d** was observed (Scheme 2, Figure 5).[25c,26,34]

Scheme 2. Reaction of 2d with Me_2BnSiH



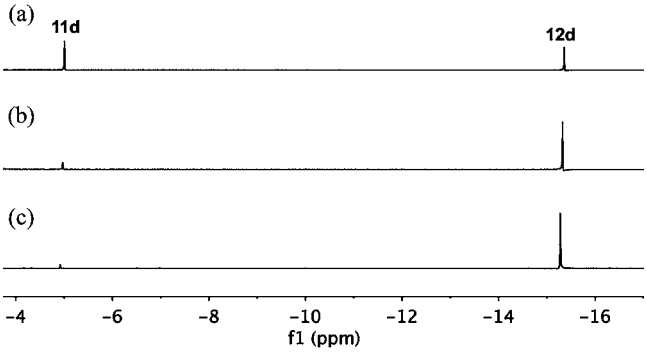


Figure 5. The ^{1}H NMR hydride resonances for **11d** and **12d**: (a) **2d** with Me_2BnSiH (3 equiv) at room temperature, (b) 6 h, and (c) 10 h.

Although complex **11d** and its chlorination product **11d-Cl** were characterized in the similar manner as **8d** and **8d-Cl**, complex **12d** was characterized spectroscopically to be a five-membered iridasilacycle, in which C(sp^2)−H activation was rather favored over C(sp^3)−H activation of the four-membered iridasilacycle of the Ir−$SiEt_3$ moiety.[35] The resonances of **12d** for two methyl groups bound to the silicon atom were separately observed at δ_H 0.00 and 0.22 in the ^{1}H NMR spectrum and at δ_C 4.9 and 5.5 in the ^{13}C NMR spectrum. The six signals for aromatic carbons of the benzyl group were inequivalently observed as well due to the rigid iridasilacycle structure. The signal for the metalated carbon appeared at δ_C 144.5 with correlations to resonances of methylene bound to the silicon atom in 2D ^{1}H−^{13}C HMQC and 2D ^{1}H−^{13}C HMBC measurement, clearly supporting the formation of iridasilacycle (see Supporting Information). Milstein et al. reported

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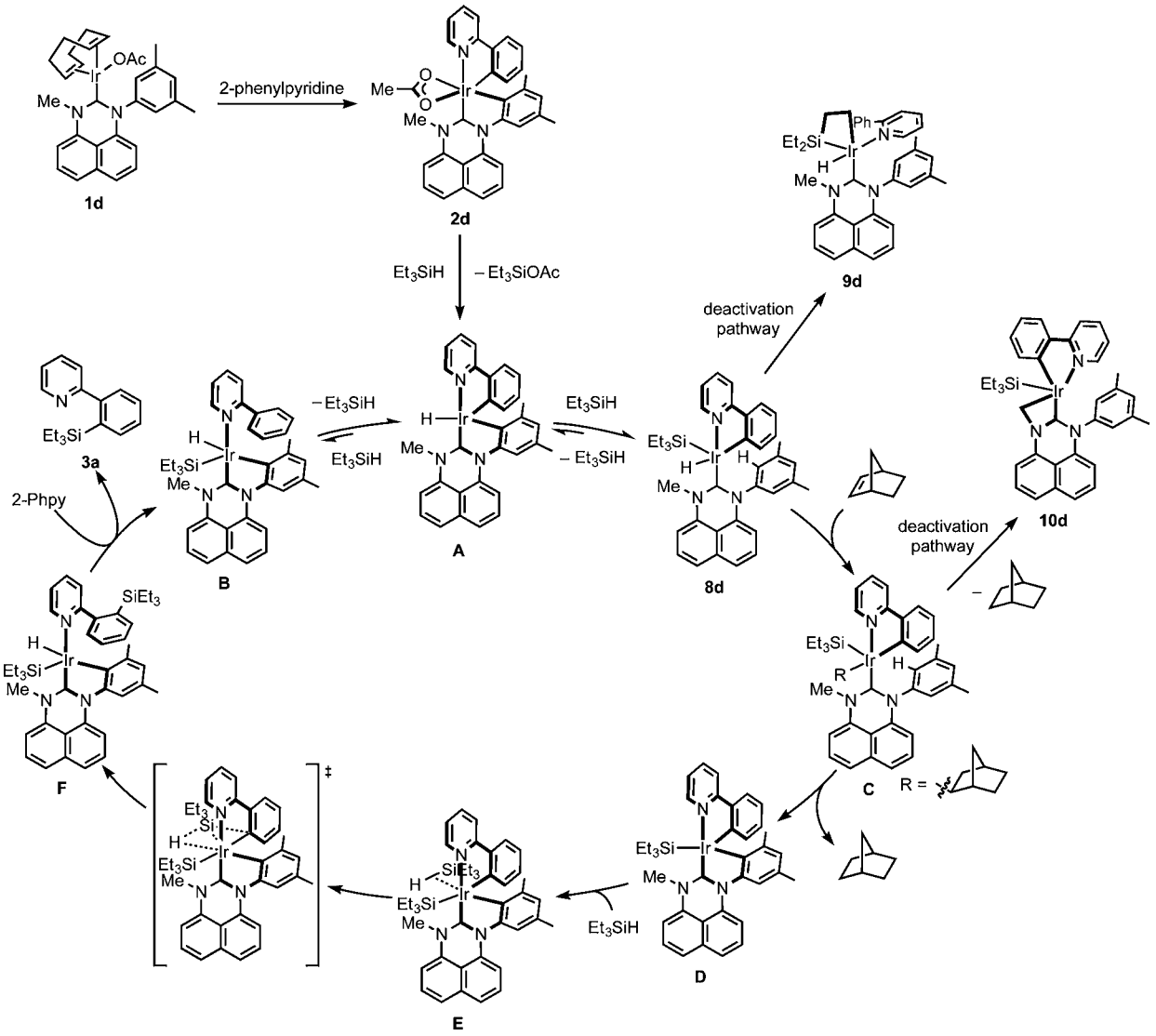
Scheme 3. Proposed Mechanism for Iridium-Catalyzed Dehydrogenative Silylation



that an iridasilacycle, $(PMe_3)_3(H)\overline{Ir(o\text{-}C_6H_4SiPh_2)}$, proceeded via ortho-metalation of the silyl ligand attached to the transient Ir(I) species in situ generated by the elimination of CH_4 from $(PMe_3)_3Ir(SiPh_3)(Me)(H)$.[36] Similarly, it was likely assumed that complex **12d** was formed via an intramolecular C(sp^2)–H activation of $SiBnMe_2$ by Ir(I) species generated by reductive elimination of 2-phenylpyridine from **11d**. Thus, though this was not direct evidence, we assumed that **9d** was a four-membered iridasilacycle, as depicted in eq 4, via an intramolecular C(sp^3)–H activation. Similar C(sp^3)–H activation of alkyl groups on the silicon atom was observed for $(Me_3P)_3(H)\overline{IrSiMe_2SiMe(SiMe_3)SiMe_2CH_2}$ from $(PMe_3)_3IrSi(SiMe_3)_3$.[27]

Proposed Mechanism. Scheme 3 shows a plausible catalytic cycle for the dehydrogenative silylation of 2-phenylpyridine. At the beginning, the catalyst precursor **2d** reacted with 1 equiv of Et_3SiH to give a five-coordinated Ir–H species **A** along with the formation of Et_3SiOAc. The addition of 1 equiv of Et_3SiH to **A** induced the demetalation of the *N*-3,5-xylyl ring of the carbene ligand or the phenyl ring of the substrate via concerted Ir–Si and C–H bond formations after coordination of the Si–H σ-bond to the iridium atom to give **B** and complex **8d**, respectively, the latter of which was thermally unstable to afford **9d**. The iridium species **A**, **B**, and **8d** were in equilibrium, and such reversible cyclometalation and decyclometalation reactions for the iridium species were confirmed by a deuterium labeling experiment using Et_3SiD (vide infra). The second step was the insertion of 2-norbornene into the Ir–H bond of **8d**, forming norbornyliridium species **C**, which was thermally unstable even at room temperature and C(sp^3)–H activation of the *N*-methyl group of the carbene ligand slowly proceeded to give **10d**, presumably due to the difficulty for the free rotation of the *N*-aryl ring to approach the ortho-C(sp^2)–H bond at the iridium metal center. Heating the reaction mixture induced rotation of the *N*-3,5-xylyl ring of the carbene ligand, and subsequent ortho-C(sp^2)–H bond activation of the *N*-aryl ring of the carbene ligand afforded the five-coordinated Ir–$SiEt_3$ intermediates **D** along with a release of norbornane. In this step, C–H bond activation of the carbene ligand was expected to proceed through either an oxidative addition of the C–H bond to form an Ir(V) intermediate[37,38] or a σ-bond metathesis pathway between Ir-norbornyl and the ortho-C–H bond, suggested by Bergman[39] and Periana,[40] respectively. In the next step, from **D** to **F** via **E**, the σ-bond of Et_3Si–H coordinated to the five-coordinated iridium metal center of **D** to form the σ-bond coordinated species **E**. The silicon atom of the

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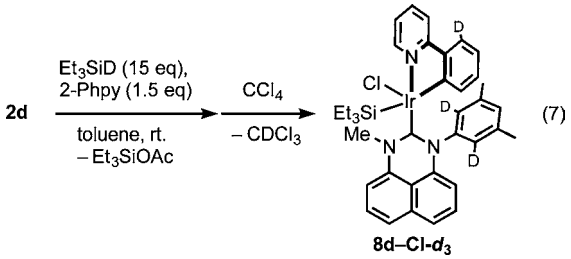
coordinating Et_3Si-H began to interact with the carbanion of the 2-pyridylphenyl moiety to form a σ-complex-assisted metathesis (σ-CAM) intermediate, and both Ir−H and C−Si bond formations proceeded together with cleavage of the Si−H bond to give an ortho-silylated 2-phenylpyridine-coordinated iridium species **F**. The σ-CAM pathway is often proposed for late transition metal catalyzed reactions involving H−E bond cleavage (E = H, B, Si, C) proposed by Sabo-Etienne and co-workers, and bond formation and cleavage reactions proceed without changing the oxidation state of the metal center.[41] Due to the presence of the bulky $SiEt_3$ group attached to the iridium center and the *N*-3,5-xylyl group of the carbene ligand, C−Si bond formation of the substrate proceeded selectively. At the final stage, exchange of the ortho-silylated 2-phenylpyridine to 2-phenylpyridine regenerated the catalytically active species **B**.

Deuterium labeling of **2d** with excess Et_3SiD (15 equiv) in the presence of 2-phenylpyridine (1.5 equiv) at room temperature demonstrated the reversibility of cyclometalation/decyclometalation steps for iridium species **A**, **B**, and **8d** in Scheme 3. Three deuterium atoms were incorporated at the two ortho-positions of the *N*-3,5-xylyl ring of the carbene ligand and one ortho-position of the phenyl ring of 2-phenylpyridine, and after 3 h, we added CCl_4 to give **8d-Cl-d_3** in 69% yield (eq 7). The D-content of the



8d–Cl-d_3 (7)

3,5-xylyl ring and phenyl ring of the substrate was estimated to be 90% and 40%, respectively.[42] The high deuterium content suggests the rapid equilibrium among **8d**, **A**, and **B** in the proposed cycle, and each step in the equilibrium involves reversible Ir−Si/C−H bond formation and cleavage through the σ-CAM pathway without a change in the oxidation state of the metal center.[25a−c]

CONCLUSIONS

We developed an Ir(carbene)-catalyzed direct dehydrogenative silylation of pyridyl- and iminyl-ligated arenes with triethylsilane via C−H bond functionalization, which selectively afforded a mono-ortho-silylation product in good to excellent yield. A variety of aromatic compounds containing a nitrogen atom as a directing group can be used for the dehydrogenative silylation. Noteworthy was that the intramolecular C−H bond activation of an *N*-xylyl ring of the perimidine-based carbene ligand, leading to cyclometalated iridium species, efficiently enhanced the dehydrogenative silylation reaction. During the catalytic cycle, the perimidine-based carbene ligand changed its electronic and structural properties via a cyclometalation/decyclometalation reaction. In this context, cyclometalated monoanionic carbene increased the steric crowding around the iridium metal center and acted as a hydride acceptor returning back to neutral carbene, demonstrating the utility of the carbanion as a labile coordination site of hemilabile ligation, which is, to the best of our knowledge, the first example of the hemilabile nature of carbene ligands bearing a labile carbanion site.

EXPERIMENTAL SECTION

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using the standard Schlenk technique or an argon-filled glovebox. All iridium complexes and perimidine-based carbene ligands were prepared according to the literature, including (L)Ir(cod)(X) (L = perimidine-based carbene, X = OAc, OCOPh, and Cl) complexes.[10] 2-Phenylpyridine, 1-phenylpyrazol, *N*-benzylidenemethylamine, *N*-benzylidene-*tert*-butylamine, dimethylphenylsilane, and benzyldimethylsilane were purchased from Sigma-Aldrich and purified by distillation over CaH_2. 2-Methyl-6-phenylpyridine and triethylsilane were purchased from TCI and dried over CaH_2, degassed by a freeze−pump−thaw cycle (3 times), and vacuum-transferred from CaH_2. *N*-Benzylideneaniline was purchased from Sigma-Aldrich and used as received. Benzo[*h*]quinoline was purchased from TCI and used as received. 2-(4-Methoxyphenyl)pyridine, 2-(4-trifluoromethylphenyl)pyridine, 4-methyl-2-phenylpyridine, (3-(pyridin-2-yl)phenyl)methylium, (3-methyl-5-(pyridin-2-yl)phenyl)methylium, and *N*-benzylidenecyclohexanamine were prepared according to previously published procedures.[43,44] 2-Phenylpyridine-d_9 was prepared according to a previously reported procedures.[45] Toluene, THF, CH_2Cl_2, and hexane were dried and deoxygenated by passing through a Grubbs column (Glass Counter Solvent Dispending System, Nikko Hansen & Co, Ltd.). Benzene-d_6 was dried over CaH_2 and degassed by a freeze−pump−thaw cycle (3 times) and vacuum-transferred from CaH_2. CD_2Cl_2 and DMSO-d_6 were degassed and stored under Ar. ^1H NMR (400 MHz), ^2H NMR (61 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were measured on BRUKER AVANCEIII−400 spectrometer. ^{29}Si NMR (85 MHz) spectra were referenced relative to a tetramethylsilane standard. Assignments for ^1H and ^{13}C NMR peaks for some of the complexes were aided by 2D $^1H-^1H$ COSY, 2D $^1H-^{13}C$ HMQC, and 2D $^1H-^{13}C$ HMBC spectra. GC−MS measurement performed out using a DB-1 capillary column (0.25 mm × 30 m) on a Shimadzu GCMS−QP2010Plus. Mass spectra were recorded on Bruker Daltonics MicroTOF II-HB and JEOL JMS−700. IR spectra were recorded on a JASCO FT/IR−230 spectrometer. The elemental analyses were recorded by a Perkin-Elmer 2400 at the Faculty of Engineering Science, Osaka University. All melting points were recorded on Yanaco micro melting point apparatus. Flash column chromatography was performed using silica gel 60 (0.040−0.0663 nm, 230−400 mesh ASTM).

Preparation of (L^4)Ir(cod)(OAc) (1d) (L^4 = *N*-CH_3, *N*-3,5-$(CH_3)_2C_6H_3$ Perimidine Carbene). THF (30 mL) was added to a Schlenk containing $LiN(SiMe_3)_2$ (167 mg, 9.98×10^{-1} mmol), $[IrCl(cod)]_2$ (336 mg, 4.99×10^{-1} mmol), *N*-methyl-*N*-3,5-dimethylphenylperimidium iodide (L^4)[I] (414 mg, 1.00 mmol), and AgOAc (1.67 g, 10 mmol) at room temperature, and then the resulting reaction mixture was stirred for 6 h at room temperature. After all volatiles were removed under reduced pressure, the resulting solids were extracted with CH_2Cl_2, which was concentrated to give the title product **1d** (551 mg, 8.52×10^{-1} mmol) as yellow powder. Yield: 85%. Mp 224 °C (dec). ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 7.59 (s, 1H, CH of NAr), 7.09 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, perimidine ring), 7.00−7.05 (m, 2H, perimidine ring), 6.91 (s, 1H, CH of NAr), 6.83 (dd, $^3J_{H-H}$ = 8.0 Hz, $^3J_{H-H}$ = 7.9 Hz, 1H, perimidine ring), 6.73 (s, 1H, CH of NAr), 6.26 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, perimidine ring), 6.14 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, perimidine ring), 4.45−4.51 (m, 2H, =CH of cod), 4.12 (s, 3H, NCH_3), 2.91 (t, $^3J_{H-H}$ = 6.6 Hz, 1H, =CH of cod), 2.31−2.40 (m, 2H, CH_2 of cod and =CH of cod), 2.25 (s, 3H, CH_3 of NAr), 2.23 (s, 3H, CH_3COO), 2.15 (s, 3H, CH_3 of NAr), 1.92−1.97 (m, 2H, CH_2 of cod), 1.54−1.63 (m, 3H, CH_2 of cod), 1.21−1.25 (m, 2H, CH_2 of cod). ^{13}C NMR (100 MHz, C_6D_6, 30 °C) δ 207.2 (Ir=C), 176.1 (C=O), 142.2, 140.8, 140.5, 138.5, 138.4, 137.1, 135.3, 130.2 (CH), 130.0 (CH), 127.9 (CH, perimidine ring), 125.8 (CH), 125.6 (CH), 121.1 (CH), 120.7 (CH), 120.3 (CH), 107.0 (CH, perimidine ring), 105.2 (CH of NAr), 86.1 (=CH of cod), 81.2 (=CH of cod), 53.9 (=CH of cod), 49.0 (=CH of cod), 43.8 (NCH_3), 36.7 (CH_2 of cod), 30.9 (CH_2 of cod), 30.4 (CH_2 of cod), 27.3 (CH_2 of cod), 24.1 (two CH_3 of NAr), 21.6 ($OCCH_3$). IR (KBr tablet, cm^{-1}): 3448, 2916, 1635, 1583, 1420, 1380, 1341, 1307, 813, 760. Anal. Calcd for $C_{30}H_{33}IrN_2O_2$: C, 55.79; H, 5.15; N, 4.34. Found: C, 55.48; H, 5.18; N, 4.52.

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Preparation of (L^5)Ir(cod)(OAc) (1e) (L^5 = *N*-CH_3, *N*-3,5-$(OCH_3)_2C_6H_3$ Perimidine Carbene). The synthesis of **1e** was identical to that of **1d** except that *N*-methyl-*N*-3,5,-dimethoxylphenylperimidium iodide, (L^5)[I], was used as a carbene precursor. Yield: 83%. Yellow powder, mp 198 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 7.45 (dd, $^4J_{H-H}$ = 2.3 Hz, $^4J_{H-H}$ = 1.7 Hz, 1H, CH of NAr), 7.09−6.99 (m, 3H, perimidine ring), 6.86−6.81 (m, 1H, perimidine ring (1H) and CH of NAr (1H)), 6.48 (dd, $^4J_{H-H}$ = 2.3 Hz, $^4J_{H-H}$ = 1.7 Hz, 1H, CH of NAr), 6.30 (dd, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 0.9 Hz, 1H, perimidine ring), 6.24 (dd, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.0 Hz, 1H, perimidine ring), 4.60−4.50 (m, 2H, =CH of cod), 4.10 (s, 3H, NCH_3), 3.62 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 2.97 (t, $^3J_{H-H}$ = 6.4 Hz, 1H, =CH of cod), 2.50 (td, ^3J = 7.9 Hz, $^3J_{H-H}$ = 4.1 Hz, 1H, =CH of cod), 2.41−2.31 (m, 1H, CH_2 of cod), 2.15 (s, 3H, CH_3COO), 1.98−1.90 (m, 2H, CH_2 of cod), 1.87−1.77 (m, 1H, CH_2 of cod), 1.74−1.61 (m, 2H, CH_2 of cod), 1.21−1.11 (m, 2H, CH_2 of cod). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 206.3 (Ir=C), 175.7 (C=O), 162.7, 161.5, 142.2, 137.7, 136.6, 134.9, 128.0 (CH), 127.7 (CH), 120.9 (CH), 120.5 (CH), 120.0, 108.3 (CH of NAr), 106.9 (CH of NAr), 106.7 (CH of perimidine ring), 104.9 (CH of perimidine ring), 102.3 (CH of perimidine ring), 85.4 (=CH of cod), 81.3 (=CH of cod), 55.5 (OCH_3), 55.3 (OCH_3), 54.0 (=CH of cod), 49.1 (=CH of cod), 43.3 (NCH_3), 36.5 (CH_2 of cod), 30.6 (CH_2 of cod), 30.4 (CH_2 of cod), 26.9 (CH_2 of cod), 23.8 ($OCCH_3$). IR (KBr tablet, cm^{-1}) ν = 3438, 3002, 2957, 2877, 2834, 1631, 1609, 1582, 1469, 1425, 1379, 1348, 1330, 1307, 1234, 1205, 1193, 1154, 1081, 1056, 816, 764, 670. Anal. Calcd for $C_{30}H_{33}IrN_2O_4$: C, 53.16; H, 4.91; N, 4.13. Found: C, 53.12; H, 5.06; N, 4.31.

Preparation of (L^6)Ir(cod)(OAc) (1f) (L^6 = *N*-CH_3, *N*-3,5-(^{t}Bu)$_2C_6H_3$ Perimidine Carbene). The synthesis of **1f** was identical to that of **1d** except that *N*-methyl-*N*-3,5-di-*tert*-butylphenylperimidium iodide (L^6)[I] was used as a carbene precursor. Yield: 87%. Yellow powder, mp 252 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 8.05 (t, $^4J_{H-H}$ = 1.9 Hz, 1H, CH of NAr), 7.66 (t, $^4J_{H-H}$ = 1.9 Hz, 1H, CH of NAr), 7.09−6.99 (m, 4H, perimidine ring and CH of NAr), 6.77 (t, $^3J_{H-H}$ = 8.1 Hz, 1H, perimidine ring), 6.27 (d, $^3J_{H-H}$ = 7.3 Hz, 1H, perimidine ring), 6.12 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, perimidine ring), 4.57 (q, $^3J_{H-H}$ = 7.7 Hz, 1H, =CH of cod), 4.46 (t, $^3J_{H-H}$ = 6.5 Hz, 1H, =CH of cod), 4.17 (s, 3H, NCH_3), 2.96 (t, ^3J = 6.6 Hz, 1H, =CH of cod), 2.50−2.46 (m, 1H, =CH of cod), 2.40−2.32 (m, 1H, CH_2 of cod), 2.28 (s, 3H, CH_3COO), 2.04−1.87 (m, 2H, CH_2 of cod), 1.69−1.58 (m, 1H, CH_2 of cod), 1.57−1.44 (m, 2H, CH_2 of cod), 1.43 (s, 9H, *t*Bu), 1.30 (s, 9H, ^{t}Bu), 1.16−1.05 (m, 2H, CH_2 of cod). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 206.3 (Ir=C), 175.6 (C=O), 153.5, 151.5, 140.5, 138.4, 136.8, 134.9, 127.6 (CH of NAr), 126.7 (CH of NAr), 122.5 (CH of NAr), 122.1 (CH of a perimidine ring), 120.7 (CH of perimidine ring), 120.4 (CH of perimidine ring), 120.2, 106.6 (CH of perimidine ring), 104.8 (CH of perimidine ring), 84.7 (=CH of cod), 81.5 (=CH of cod), 53.6 (=CH of cod), 48.8 (=CH of cod), 43.2 (NCH_3), 36.1 (CH_2 of cod), 35.5 (N-3,5-{$C(CH_3)_3$}$_2C_6H_3$), 35.1 (N-3,5-{$C(CH_3)_3$}$_2C_6H_3$), 31.6 (CH_3 of N-3,5-{$C(CH_3)_3$}$_2C_6H_3$), 31.5 (CH_3 of N-3,5-{$C(CH_3)_3$}$_2C_6H_3$), 30.7 (CH_2 of cod), 30.0 (CH_2 of cod), 27.3 (CH_2 of cod), 23.9 ($OCCH_3$). One carbon resonance is overlapped with C_6D_6 signals. IR (KBr tablet, cm^{-1}) ν = 3421, 2961, 2877, 2831, 1634, 1583, 1527, 1475, 1428, 1381, 1361, 1340, 1297, 1136, 1079, 816, 765, 713, 670. Anal. Calcd for $C_{36}H_{45}IrN_2O_2$: C, 59.23; H, 6.21; N, 3.84. Found: C, 59.66; H, 5.93; N, 4.29.

Preparation of (^{Xy}C^C:)(C^N) Ir(OAc) (^{Xy}C^C: = Cyclometalated Perimidine-Based Carbene, C^N = Cyclometalated 2-Phenylpyridine) (2d). Toluene was added to a Schlenk containing a corresponding (L^4)Ir(cod)OAc (L^4 = perimidine-based carbene) **1d** (170 mg, 2.63 × 10^{-1} mmol) and 2-phenylpyridine (50.0 mg, 3.22 × 10^{-1} mmol) at room temperature. The reaction mixture was stirred under toluene refluxing conditions for 48 h under an argon atmosphere. The mixture was cooled to ambient temperature, and the solvent was evaporated under vacuum. The resulting solid was washed by hexane (3 times) to give a corresponding bis(cyclometalated)iridium complex **2d** in 93% yield (169 mg, 2.45 × 10^{-1} mmol). Yellow powder, mp > 270 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 8.75 (dd, $^3J_{H-H}$ = 5.4 Hz, $^4J_{H-H}$ = 1.7 Hz, 1H, py), 7.54$_2$ (d, $^3J_{H-H}$ = 7.6 Hz, 1H, Ar), 7.54$_1$ (s, 1H, CH of NAr), 7.49 (dd, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 1.4 Hz, 1H, Ar), 7.34 (d, $^3J_{H-H}$ = 8.3 Hz, 1H, perimidine ring), 7.10 (t, $^3J_{H-H}$ = 8.0 Hz, 2H, Ar), 7.02−6.91 (m, 5H, Ar), 6.77 (td, $^3J_{H-H}$ = 7.4, $^4J_{H-H}$ = 1.4 Hz, 1H, perimidine ring), 6.56 (ddd, $^3J_{H-H}$ = 7.1, 5.6 Hz, $^4J_{H-H}$ = 1.3 Hz, 1H, py), 6.39 (s, 1H, CH of NAr), 6.18 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, perimidine ring), 3.70 (s, 3H, NCH_3), 2.22 (s, 3H, CH_3 of NAr), 1.76 (s, 3H, CH_3COO), 1.67 (s, 3H, CH_3 of NAr). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 193.7 (Ir=C), 186.6 (C=O), 166.0, 153.4, 147.5 (HC=N of 2-Ph*py*), 145.4, 144.6, 139.5 (CH), 137.6, 135.4, 134.9, 130.5, 130.0 (CH of perimidine ring), 128.9, 128.6, 127.4 (CH), 127.3 (CH of NAr), 127.1 (CH), 124.2 (CH), 122.0, 121.7, 121.6, 121.4 (CH of perimidine ring), 120.7 (CH of perimidine ring), 120.0, 118.6 (CH of perimidine ring), 110.9 (CH), 110.8 (CH), 106.0 (CH of perimidine), 42.4 (NCH_3), 25.8 ($OCCH_3$), 23.4 (CH_3 of NAr), 21.2 (CH_3 of NAr). IR (KBr tablet, cm^{-1}) ν = 3446, 2923, 1610, 1584, 1542, 1457, 1423, 1384, 1345, 1325, 1091, 1049, 1019, 817, 749, 736, 677. Anal. Calcd for $C_{33}H_{29}IrN_3O_2$: C, 57.29; H, 4.23; N, 6.07. Found: C, 56.81; H, 4.38; N, 6.15.

Synthesis of (^{Xy}C^C:)(C^N)Ir(OAc) (^{Xy}C^C: = Cyclometalated Perimidine-Based Carbene, C^N = Cyclometalated Benzo[*h*]-quinoline) (4d). The synthesis of **4d** was identical to that of **2d** except that benzo[*h*]quinoline was used as a substrate (83% yield). Yellow powder, mp > 270 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 8.98 (d, $^3J_{H-H}$ = 4.8 Hz, 1H, HC=N of benzo[*h*]quinoline), 7.57 (d, $^3J_{H-H}$ = 4.4 Hz, 1H, Ar), 7.55 (d, $^3J_{H-H}$ = 6.0 Hz, 1H, Ar), 7.51 (dd, $^3J_{H-H}$ = 7.9, $^4J_{H-H}$ = 1.0 Hz, 1H, CH of benzo[*h*]quinoline), 7.36 (d, J = 7.7 Hz, 1H, Ar), 7.21 (d, $^3J_{H-H}$ = 7.2 Hz, 1H, Ar), 7.18 (s, 1H, CH of NAr), 7.14−7.12 (m, 2H, Ar), 7.11 (d, $^3J_{H-H}$ = 4.0 Hz, 1H, Ar), 6.96−7.04 (m, 3H, Ar), 6.91 (dd, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 5.2 Hz, 1H, CH of benzo[*h*]quinoline), 6.27 (s, 1H, CH of NAr), 6.21 (d, J = 7.7 Hz, 1H, perimidine ring), 3.72 (s, 3H, NCH_3), 2.19 (s, 3H, CH_3 of NAr), 1.82 (s, 3H, CH_3COO), 1.31 (s, 3H, CH_3 of NAr). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 192.4 (Ir=C), 186.7 (C=O), 153.3, 146.5 (HC=N of benzo[*h*]quinoline), 145.2, 141.7, 140.5, 136.5 (CH), 136.3 (CH), 135.6, 134.9, 134.2, 133.1, 130.5, 129.8, 129.7, 129.3, 128.7, 128.6, 127.4, 127.3, 127.1 (CH of NAr), 126.8, 123.4, 121.8 (CH), 121.0 (CH), 120.8 (CH), 119.8, 111.0 (CH), 110.8 (CH), 106.1 (CH of perimidine ring), 42.7 (NCH_3), 25.9 ($OCCH_3$), 22.7 (CH_3 of NAr), 21.1 (CH_3 of NAr). IR (KBr tablet, cm^{-1}) ν = 3431, 2918, 1631, 1583, 1525, 1479, 1453, 1427, 1383, 1346, 1327, 1230, 1190, 1139, 1085, 1037, 929, 834, 816, 764, 719, 677. Anal. Calcd for $C_{35}H_{29}IrN_3O_2$: C, 58.72; H, 4.08; N, 5.87. Found: C, 59.21; H, 3.89; N, 5.48.

Preparation of (^{Xy}C^C:)(C^N) Ir(OAc) (^{Xy}C^C: = Cyclometalated Perimidine-Based Carbene, C^N = Cyclometalated *N*-Benzylidenemethylamine) (5d). The synthesis of **5d** was identical to that of **5a** except that **1d** was used as a precursor (93% yield). Orange powder, mp > 270 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 7.77 (s, 1H, MeN=C*H*Ph), 7.49 (s, 1H, CH of NAr), 7.48 (d, $^3J_{H-H}$ = 6.9 Hz, 1H, Ar), 7.20 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, perimidine ring), 7.09 (t, $^3J_{H-H}$ = 8.5 Hz, 2H, Ar), 6.99 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, perimidine ring), 6.95 (d, ^3J = 7.9 Hz, 1H, perimidine ring), 6.87−6.81 (m, 2H, Ar), 6.67 (td, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.6 Hz, 1H, perimidine ring), 6.46 (s, 1H, CH of NAr), 6.15 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, perimidine ring), 3.64 (s, 3H, NCH_3 of perimidine ring), 3.35 (s, 3H, NCH_3 of *N*-benzylidenemethylamine), 2.24 (s, 3H, CH_3 of NAr), 2.07 (s, 3H, CH_3 of NAr), 1.78 (s, 3H, CH_3COO). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 193.0 (Ir=C), 186.2 (C=O), 175.4 (MeN=CHPh), 153.1, 148.4, 146.3, 145.7, 138.5 (CH), 135.4, 134.9, 132.9, 130.9 (CH), 130.6, 129.3, 128.7, 128.6, 128.6, 127.4, 127.2 (CH), 126.9 (CH of NAr), 121.7, 121.4, 121.0 (CH), 120.8 (CH), 110.9 (CH of perimidine ring), 110.7 (CH of NAr), 106.0 (CH of perimidine ring), 44.5 (NCH_3 of *N*-benzylidenemethylamine), 42.3 (NCH_3 of perimidine ring), 25.2 ($OCCH_3$), 23.5 (CH_3 of NAr), 21.2 (CH_3 of NAr). IR (KBr tablet, cm^{-1}) ν = 3446, 3056, 2919, 1631, 1607, 1583, 1526, 1457, 1428, 1382, 1345, 1325, 1228, 1141, 1089, 1049, 1034, 1019, 815, 760, 749, 736, 679. Anal. Calcd for $C_{30}H_{29}IrN_3O_2$: C, 54.94; H, 4.46; N, 6.41. Found: C, 55.25; H, 4.32; N, 6.17.

Preparation of (^{Xy}C^C:)(C^N) Ir(OAc) (^{Xy}C^C: = Cyclometalated Perimidine-Based Carbene, C^N = Cyclometalated 2-Vinylpyridine) (6d). The synthesis of **6d** was identical to that of **6a** except that **1d** was used as a precursor (92% yield). Yellow powder, mp > 270 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 9.05 (d, $^3J_{H-H}$ = 7.5 Hz,

1H, py), 8.58 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, py), 7.50 (s, 1H, CH of NAr), 7.48 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, perimidine ring), 7.11−7.05 (m, 3H, Ar), 7.01−6.93 (m, 3H, Ar), 6.87 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, perimidine ring), 6.56 (dd, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.4 Hz, 1H, py), 6.51 (s, 1H, CH of NAr), 6.15 (d, *J* = 7.6 Hz, 1H, perimidine ring), 3.62 (s, 3H, NCH_3), 2.23 (s, 3H, CH_3 of NAr), 1.93 (s, 3H, CH_3 of NAr), 1.75 (s, 3H, CH_3COO). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 192.0 (Ir═C), 186.4 (C═O), 167.3, 157.2, 153.4, 147.5, 145.8, 137.7 (CH), 135.4, 134.8, 132.9, 132.4 (CH), 130.8, 127.3 (CH), 127.2 (CH), 127.0 (CH of NAr), 121.6, 121.4, 120.8 (CH), 119.7 (CH), 118.6 (CH of perimidine ring), 113.5, 110.8 (CH of perimidine ring), 110.7, 105.9 (CH of perimidine ring), 41.7 (NCH_3), 25.7 ($OCCH_3$), 23.1 (CH_3 of NAr), 21.2 (CH_3 of NAr). IR (KBr tablet, cm^{-1}) ν = 3448, 3058, 2959, 1632, 1604, 1595, 1584, 1526, 1469, 1441, 1426, 1383, 1325, 1222, 1139, 1087, 1037, 816, 798, 763, 677. Anal. Calcd for $C_{29}H_{27}IrN_3O_2$: C, 54.27; H, 4.24; N, 6.55. Found: C, 54.53; H, 4.12; N, 6.80.

Preparation of (^{xy}C^C:)(C^N) Ir(OAc) (^{xy}C^C: = Cyclometalated Perimidine-Based Carbene, C^N = Cyclometalated *N*-(3-Phenylallylidene)aniline) (7d). The synthesis of **7d** was identical to that of **7a** except **1d** was used as a precursor (94% yield). Bright pink powder, mp > 270 °C (dec). ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 8.27 (d, $^3J_{H-H}$ = 2.4 Hz, 1H, N═CH), 7.71 (s, 1H, CH of NAr), 7.60−7.55 (m, 3H, Ar), 7.14−7.10 (m, 4H, Ar), 7.05−6.93 (m, 5H, Ar), 6.84−6.75 (m, 4H, Ar), 6.68 (s, 1H, CH of NAr), 5.86 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, perimidine ring), 3.18 (s, 3H, NCH_3), 2.61 (s, 3H, CH_3 of NAr), 2.31 (s, 3H, CH_3 of NAr), 1.22 (s, 3H, CH_3COO). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 195.3 (Ir═C), 193.0, 186.8, 169.6 (N═CH), 153.4, 152.2, 148.8, 148.4, 134.7, 134.6, 132.7, 132.1, 130.1, 129.0 (CH), 127.4, 127.3 (CH), 127.2, 126.6, 125.9 (CH), 124.0 (CH), 121.7 (CH), 121.6, 121.1 (CH), 116.2, 111.2 (CH), 110.9 (CH), 105.8 (CH of perimidine), 41.5 (NCH_3), 24.5 ($OCCH_3$), 23.1 (CH_3 of NAr), 21.4 (CH_3 of NAr). IR (KBr tablet, cm^{-1}) ν = 3445, 2916, 1633, 1583, 1526, 1483, 1474, 1459, 1441, 1381, 1365, 1361, 1355, 1342, 1334, 1327, 1316, 1306, 1201, 1086, 816, 760, 697, 687, 682. Anal. Calcd for $C_{37}H_{33}IrN_3O_2$: C, 59.74; H, 4.47; N, 5.65. Found: C, 59.60; H, 4.21; N, 5.49. Some carbon resonances are overlapped with C_6D_6 signals.

Characterization of [(C^N)Ir(L)($SiEt_3$)H] (C^N = Cyclometalated 2-Phenylpyridine, L = *N*-CH_3, *N*-3,5-$(CH_3)_2C_6H_3$ Perimidine-Based Carbene) (8d). Triethylsilane (5.05 mg, 4.35×10^{-2} mmol) was added to benzene solution of **2d** (10.0 mg, 1.45×10^{-2} mmol) in the presence of 2-phenylpyridine-d_9 (2.38 mg, 1.45×10^{-2} mmol) in a J-Young tube. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 8.29 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, py), 8.03 (d, $^3J_{H-H}$ = 7.3 Hz, 1H, Ar), 7.66 (d, $^3J_{H-H}$ = 7.7 Hz, 1H, perimidine ring), 7.33 (td, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.3 Hz, 1H, perimidine ring), 7.28 (s, 1H, ortho CH of NAr), 7.25 (d, *J* = 8.9 Hz, 1H, Ar), 7.20−7.15 (m, 2H, Ar), 7.15−7.09 (m, 2H, Ar), 7.01−6.96 (m, 1H, Ar), 6.90 (m, 1H, Ar, overlapped with CH of NAr), 6.88 (s, 1H, ortho CH of NAr), 6.51 (s, 1H, para CH of NAr), 6.42 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, perimidine ring), 6.26 (dd, $^3J_{H-H}$ = 7.3 Hz, $^4J_{H-H}$ = 1.3 Hz, 1H, py), 6.18 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, perimidine ring), 3.99 (s, 3H, NCH_3), 2.16 (s, 3H, CH_3 of NAr), 1.22 (s, 3H, CH_3 of NAr), 0.99−0.95 (m, 9H, $Si(CH_2CH_3)_3$, overlapped with free $HSiEt_3$) 0.79−0.73 (m, 6H, $Si(CH_2CH_3)_3$, overlapped with free Et_3SiOAc), −5.55 (s, 1H, Ir−H). ^{29}Si NMR (85 MHz, C_6D_6, 30 °C): δ 5.35.

Preparation of [(C^N)Ir(L)($SiEt_3$)Cl] (C^N = Cyclometalated 2-Phenylpyridine, L = *N*-CH_3, *N*-3,5-$(CH_3)_2C_6H_3$ Perimidine-Based Carbene) (8d-Cl). Triethylsilane (50.3 mg, 4.33×10^{-1} mmol) was added to **2d** (100 mg, 1.45×10^{-1} mmol) in the presence of 2-phenylpyridine (33.6 mg, 2.17×10^{-1} mmol) in 8 mL of toluene. The reaction mixture was stirred at room temperature for 30 min, and then, CCl_4 (111 mg, 7.22×10^{-1} mmol) was added to the reaction mixture. The reaction mixture was stirred for 20 h at ambient temperature, and all volatiles were removed under vacuum. The orange powder was washed by hexane (5 mL × 3 times) and was dried under vacuum. Bright orange powder was obtained in 69% yield (78.3 mg, 1.00×10^{-1} mmol). mp > 270 °C (dec). ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 10.08 (d, $^3J_{H-H}$ = 5.7 Hz, 1H, HC═N of 2-Ph*py*), 8.13 (s, 1H, ortho CH of NAr), 7.22 (d, $^3J_{H-H}$ = 7.7 Hz, 1H, perimidine ring), 7.17−7.13 (m, 1H, Ar, overlapped with C_6D_6), 7.08 (d, $^3J_{H-H}$ = 8.3 Hz, 1H, Ar), 7.04 (m, 2H, Ar), 6.94 (d, $^3J_{H-H}$ = 8.3 Hz, 1H, CH of 2-Ph*py*), 6.88 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, Ar), 6.83 (t, $^3J_{H-H}$ = 8.2 Hz, 1H, Ar), 6.78 (d, $^3J_{H-H}$ = 7.0 Hz, 1H, Ar), 6.66 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, Ar), 6.43 (t, $^3J_{H-H}$ = 6.5 Hz, 1H, CH of 2-Ph*py*), 6.33 (t, $^3J_{H-H}$ = 7.7 Hz, 2H, Ar), 6.23 (s, 1H, ortho CH of NAr), 6.15 (s, 1H, para CH of NAr), 4.15 (s, 3H, NCH_3), 1.76 (s, 3H, CH_3 of NAr), 1.62 (s, 3H, CH_3 of NAr), 1.07 (t, $^3J_{H-H}$ = 7.8 Hz, 9H, $Si(CH_2CH_3)_3$), 0.88 (q, $^3J_{H-H}$ = 6.5 Hz, 6H, $Si(CH_2CH_3)_3$). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 183.8 (Ir═C), 167.0, 153.7, 150.9, 145.1, 145.0 (HC═N of 2-Ph*py*), 142.6, 142.5, 140.3, 140.2, 140.0, 137.5, 136.8 (CH), 136.6 (CH), 136.2, 135.0, 129.9 (CH), 129.7 (CH), 128.5, 127.5, 121.1 (CH), 120.9, 120.6, 120.5, 119.6, 117.5 (CH), 106.2, 105.0 (CH), 44.3 (NCH_3), 21.2 (CH_3 of NAr), 20.3 (CH_3 of NAr), 9.7 ($Si(CH_2CH_3)_3$), 8.4 ($Si(CH_2CH_3)_3$). Some carbon resonances are overlapped with C_6D_6 signals. ^{29}Si NMR (85 MHz, C_6D_6, 35 °C): δ 6.33. IR (KBr tablet, cm^{-1}) ν = 3447, 2944, 2869, 1634, 1603, 1585, 1477, 1422, 1380, 1345, 1316, 1089, 1004, 815, 762, 729, 661. Anal. Calcd for $C_{37}H_{41}ClIrN_3Si$: C, 56.72; H, 5.27; N, 5.36. Found: C, 56.41; H, 4.90; N, 5.33.

Reaction of 2d with Et_3SiD. Triethylsilane-d_1 (170 mg, 1.45 mmol) was added to benzene solution of **2d** (100 mg, 1.45×10^{-1} mmol) in the presence of 2-phenylpyridine (33.8 mg, 2.18×10^{-1} mmol) in a J-Young tube. ^2H NMR (61 MHz, C_6D_6, 30 °C): δ 8.06 (s, D of **8d**), 7.31 (br s), 7.15 (br s), 7.08(s, D of **8d**), 6.09 (br s, D of **9d**), −5.68 (s, Ir−D of **8d**), −15.35 (s, Ir−D of **9d**). The reaction mixture was stirred at room temperature for 30 min, and then, CCl_4 (112 mg, 7.25×10^{-1} mmol) was added to the reaction mixture. The reaction mixture was stirred for 20 h at ambient temperature, and all volatiles were removed under vacuum. The bright orange powder was obtained by washing with hexane (5 mL × 3 times) (see Figure S4, ^1H NMR spectra of **8d-Cl** and **8d-Cl-d_3** in Supporting Information).

Preparation of [(^{Me}C^C:)(C^N)Ir($SiEt_3$)] (^{Me}C^C: = Cyclometalated Perimidine-Based Carbene, C^N = Cyclometalated 2-Phenylpyridine) (10d). Triethylsilane (50.3 mg, 4.33×10^{-1} mmol) was added to **2d** (100 mg, 1.45×10^{-1} mmol) in the presence of 2-phenylpyridine (33.6 mg, 2.17×10^{-1} mmol) in 5 mL of toluene. 2-Norbornene (40.7 mg, 4.32×10^{-1} mmol) was added to the reaction mixture sequentially. The reaction mixture was kept at room temperature for 4 days, and all volatiles were removed under reduced pressure. Dark red crystals were obtained in 38% yield (41 mg, 5.49×10^{-2} mmol) by recrystallization with toluene/hexane. mp > 270 °C (dec). ^1H NMR (400 MHz, CD_2Cl_2, 30 °C): δ 7.66 (d, $^3J_{H-H}$ = 7.4 Hz, 1H, py), 7.59−7.53 (m, 3H, Ar), 7.39 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, Ar), 7.33 (d, *J* = 6.8 Hz, 2H, Ar), 7.26−7.20 (m, 3H, Ar), 7.11 (t, $^3J_{H-H}$ = 7.9 Hz, 1H, perimidine ring), 7.07−7.02 (m, 2H, Ar), 6.95 (d, $^3J_{H-H}$ = 7.0 Hz, 1H, Ar), 6.67 (d, $^3J_{H-H}$ = 7.4 Hz, 1H, perimidine ring), 6.37 (s, 1H, CH of NAr), 6.00 (d, $^3J_{H-H}$ = 7.7 Hz, 1H, perimidine ring), 3.45 (d, $^2J_{H-H}$ = 8.5 Hz, 1H, NCH_2Ir), 3.39 (d, $^2J_{H-H}$ = 8.5 Hz, 1H, NCH_2Ir), 2.50 (s, 3H, CH_3 of NAr), 2.32 (s, 3H, CH_3 of NAr), 0.57 (t, $^3J_{H-H}$ = 7.7 Hz, 9H, $Si(CH_2CH_3)_3$), 0.40 (q, $^3J_{H-H}$ = 7.8 Hz, 6H, $Si(CH_2CH_3)_3$). ^{13}C NMR (100 MHz, CD_2Cl_2, 30 °C): δ 189.0, 172.4, 169.3, 155.8, 151.1, 143.3, 142.5, 141.9, 141.2, 138.9, 138.9, 136.8, 135.5, 131.1, 128.9, 128.8, 128.0, 127.6, 127.5, 123.0, 122.9, 121.7, 120.9, 120.5, 119.7, 119.2, 118.0, 106.5, 101.4, 21.6, 21.5, 8.9, 7.9, 7.3. ^{29}Si NMR (85 MHz, C_6D_6, 30 °C): δ 7.02. IR (KBr tablet, cm^{-1}) ν = 3451, 3047, 2925, 2868, 1630, 1583, 1526, 1471, 1421, 1380, 1340, 1313, 1216, 1162, 1000, 815, 765, 750, 732. Anal. Calcd for $C_{37}H_{40}IrN_3Si$: C, 59.49; H, 5.40; N, 5.62. Found: C, 59.53; H, 5.41; N, 5.79.

Preparation of [(C^N)Ir(L)($SiMe_2$ Bn)Cl] (C^N = Cyclometalated 2-Phenylpyridine, L = *N*-CH_3, *N*-3,5-3,5-$(CH_3)_2C_6H_3$ Perimidine-Based Carbene) (11d-Cl). A similar procedure to that for **8d-Cl** was employed without excess of 2-phenylpyridine. The mixture was purified by silica-column chromatography (46% yield). Red powder, mp > 270 °C (dec). ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 9.11 (d, $^3J_{H-H}$ = 7.4 Hz, 1H, py), 7.98 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, Bn), 7.91 (s, 1H, CH of NAr), 7.35 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, Ar), 7.14−1.11 (m, 3H, Ar), 7.09−7.07 (m, 3H, Ar), 7.05−7.03 (m, 3H, Ar), 6.97 (t, $^3J_{H-H}$ = 7.1 Hz, 1H, Ar), 6.85 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, Ar), 6.78 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, Ar), 6.67 (t, $^3J_{H-H}$ = 7.7 Hz, 1H, Bn), 6.34 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, Ar), 6.24 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, perimidine ring), 6.16 (s, 1H, CH of NAr), 6.11 (s, 1H, CH of NAr), 5.89 (t, $^3J_{H-H}$ = 6.2 Hz, 1H, Bn), 4.09 (s, 3H, NCH_3), 2.74 (d, $^2J_{H-H}$ = 13.7 Hz, 1H, $Si(CH_2Ph)Me_2$), 2.57 (d, $^2J_{H-H}$ = 13.7 Hz, 1H, $Si(CH_2Ph)Me_2$), 1.68 (s, 3H, CH_3 of NAr),

1.43 (s, 3H, CH_3 of NAr), 0.18 (s, 3H, IrSi(CH_3)$_2$Bn), −0.26 (s, 3H, IrSi(CH_3)$_2$Bn). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 205.5 (Ir═C), 170.9, 166.8, 154.7 (C═N of 2-Ph*py*), 146.3, 145.5, 142.9, 139.6, 137.4, 137.0, 136.6 (CH), 136.1, 135.0 (CH), 130.5 (CH of NAr), 129.9, 129.1 (CH), 128.5, 127.6, 123.8 (CH), 123.6, 122.2 (CH of NAr), 122.0$_3$ (CH of NAr), 122.0 (CH of perimidine ring), 121.4$_3$ (CH), 121.4$_1$ (CH), 121.0, 120.4, 117.5 (CH of perimidine ring), 106.5 (CH of perimidine ring), 105.7 (CH of perimidine ring), 44.2 (NCH_3), 29.3 (Si(*C*HPh)-Me_2), 21.0 (CH_3 of NAr), 20.5 (CH_3 of NAr), 1.5 (SiBn(CH_3)$_2$), 1.0 (SiBn(CH_3)$_2$). Some carbon resonances are overlapped with C_6D_6 signals. ^{29}Si NMR (85 MHz, C_6D_6, 35 °C): δ −4.01. IR (KBr tablet, cm^{-1}) ν = 3450, 3056, 2949, 1634, 1603, 1491, 1474, 1424, 1380, 1347, 1317, 1231, 1147, 1080, 855, 815, 759, 734, 701. Anal. Calcd for $C_{40}H_{39}ClIrN_3Si$: C, 58.77; H, 4.81; N, 5.14. Found: C, 58.89; H, 4.39; N, 5.54.

Preparation of [(2-Phpy)Ir(L)(SiMe$_2$Bn)H] (2-Phpy = Coordinated 2-Phenylpyridine, L = *N*-CH_3, *N*-3,5-$(CH_3)_2C_6H_3$ Perimidine-Based Carbene) (12d). Benzyldimethylsilane (217 mg, 1.44 mmol) was added to **2d** (200 mg, 2.89×10^{-1} mmol) in 8 mL of toluene. The reaction mixture was stirred at room temperature for 10 h. All volatiles were removed under reduced pressure. The residue that formed was washed with cold pentane (8 mL × 2 times) and dried under vacuum. The orange powder was obtained in 61% yield (145 mg, 1.77×10^{-1} mmol). mp 194 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 8.35 (d, $^3J_{H-H}$ = 5.5 Hz, 1H, CH of 2-Ph*py*), 7.97 (d, $^3J_{H-H}$ = 7.3 Hz, 1H, CH of 2-*Ph*py), 7.41 (d, $^3J_{H-H}$ = 7.7 Hz, 1H, perimidine ring), 7.18−7.13 (m, 3H, Ar), 7.08−7.10 (m, 3H, Ar), 7.04−7.06 (m, 3H, Ar), 7.00−6.97 (m, 3H, ortho C*H* of SiCH$_2$*Ph* (1H) and Ar (3H)), 6.88 (t, $^3J_{H-H}$ = 8.0 Hz, 2H, Ar), 6.39 (s, 1H, CH of NAr), 6.32 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, Ar), 6.17 (s, 1H, CH of NAr), 6.16 (d, $^3J_{H-H}$ = 7.8 Hz, 1H, perimidine ring), 3.67 (s, 3H, NCH_3), 2.45 (d, $^2J_{H-H}$ = 12.9 Hz, 1H, Si(*C*H$_2$Ph)Me$_2$), 2.35 (d, $^2J_{H-H}$ = 12.9 Hz, 1H, Si(*C*H$_2$Ph)Me$_2$), 1.85 (s, 3H, CH_3 of NAr), 1.31 (s, 3H, CH_3 of NAr), 0.22 (s, 3H, SiBn(CH_3)$_2$), 0.00 (s, 3H, SiBn(CH_3)$_2$), −15.28 (s, 1H, Ir−H). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 203.5 (Ir═C), 172.9, 169.3, 152.4 (CH of 2-Ph*py*), 146.3, 145.0 (CH of 2-*Ph*py), 144.5 (Ir−*C* of SiCH$_2$*Ph*), 142.7, 141.1, 137.9, 136.3, 136.3, 135.6, 135.1, 131.1, 130.8 (CH of NAr), 130.0, 129.2, 129.0, 128.9 (ortho CH of SiCH$_2$*Ph*), 128.5, 124.0, 123.1, 122.0, 121.3 (CH of perimidine ring), 120.7, 120.0, 119.9, 119.3, 118.5 (CH of NAr), 118.2, 116.4, 105.7 (CH of perimidine ring), 103.7 (CH of perimidine ring), 43.9 (NCH_3), 33.6 (Si(*C*H$_2$Ph)Me$_2$), 21.3 (CH_3 of NAr), 20.7 (CH_3 of NAr), 5.5 (SiBn(CH_3)$_2$), 4.9 (SiBz(CH_3)$_2$). ^{29}Si NMR (85 MHz, C_6D_6, 30 °C): δ −9.98. Anal. Calcd for $C_{40}H_{40}IrN_3Si$: C, 61.35; H, 5.15; N, 5.37. Found: C, 61.30; H, 5.25; N, 5.15.

X-ray Crystallographic Analysis. All crystals were handled similarly. The crystals were mounted on the CryoLoop (Hampton ReseArCh Corp.) with a layer of mineral oil and placed in a nitrogen stream. Measurements were made on Rigaku R-AXIS RAPID imaging plate area detector or Rigaku AFC7R/Mercury CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71075). Crystal data and structure refinement parameters were listed in Supporting Information (Table S7). The structure was solved by direct methods on SIR97 or SHELXS97,[46] after being refined on F^2 by full-matrix least-squares methods using SHELXL-97.[47] Measured nonequivalent reflections with $I > 2.0\sigma(I)$ were used for the structure determination. The hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\max(F_o^2,0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions R_1 and wR_2 were $(\sum||F_o| - |F_c||)/\sum|F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw molecules.[48]

■ ASSOCIATED CONTENT

Supporting Information

Experimental and characterization details, tables for optimizing the catalytic conditions, and molecular structures of metal complexes **1d**−**1i**, **4d**, **5d**, **6d**, **7d**, and **11d-Cl** (PDF) and a CIF file for complexes **1d**−**1i**, **2d**, **4d**, **5d**, **6d**, **7d**, **8d-Cl**, **10d**, and **11d-Cl**. These materials are 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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