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Cationic Dirhodium Complexes Bridged by 2-Phosphinopyridines Having an Exquisitely Positioned Axial Shielding Group: A Molecular Design for Enhancing the Catalytic Activity of the Dirhodium Core

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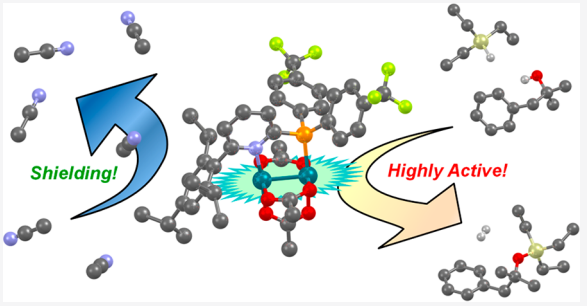
ABSTRACT: This report describes a strategy to create highly electrophilic dirhodium catalysts. The electrophilicity of lantern-type dirhodium complexes is generally decreased by the coordination of a ligand to the axial site, which often causes a reduction in the catalytic activity. We designed and synthesized a series of cationic dirhodium complexes bridged by 2-diarylphosphinopyridines having a bulky 2,4,6-triisopropylphenyl (Tip) group that can prevent the attack of external molecules to the closest axial site. Theoretical calculations indicated that the Tip group weakly interacts with the axial site but hardly reduces the electrophilicity of the dirhodium core. The complexes served as excellent catalyst precursors for the dehydrogenative silylation of alcohols using hydrosilanes under mild conditions and a low metal loading, producing the silyl ethers in higher yields in comparison to conventional dirhodium complexes.



INTRODUCTION

Lantern-type dirhodium complexes, shown in Figure 1A, are useful catalysts for various organic transformations: e.g., Lewis acid catalysis and rhodium carbenoid mediated reactions.[1−6] The electrophilic nature and the surrounding steric environments of the dirhodium core greatly influence the catalytic properties.[1,2a−d,3b,c,4d,e,6a,b] These factors can be adjusted by changing the bridging ligands, leading to an improvement in the catalytic activity, selectivity, and stability in various reactions. Therefore, dirhodium complexes with various bridging ligands such as carboxylates, carboxamidates, phosphonates, 1,8-naphthyridines, *ortho*-metalated phosphines, thienylphosphines, and oxothioethers have been synthesized and their catalytic properties investigated.[1b,5a,7,8] The axial ligand modification has also been studied as another strategy for improving the catalytic performance.[9] However, in most cases, the coordination of axial ligands, usually solvents containing N and O atoms, diminishes the catalytic activity for the following reasons (Figure 1B). (i) The ligands quickly occupy both axial sites and prevent the generation of a coordinatively unsaturated and catalytically active rhodium center.[5c,10,11] (ii) The active rhodium center is electronically influenced by the axial ligand on the opposite rhodium atom, resulting in a decrease in the electrophilicity in comparison with the corresponding dirhodium core without axial ligands.[10,12] These imply that a rational catalyst design for preventing the coordination of axial ligands to the dirhodium core may lead to the development of highly active dirhodium complex catalysts.[13]

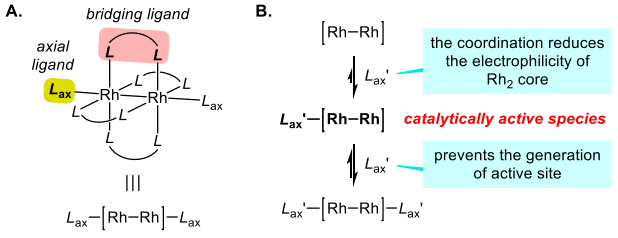


Figure 1. (A) Structural representation of lantern-type dirhodium complexes. (B) Coordination of axial ligands to the Rh_2 core and the influence on the catalytic activity. L_{ax}' is a molecule that is in a coordination equilibrium with Rh_2.

2-Phosphinopyridine derivatives constitute an important class of bridging ligands for the construction of various homo- and heteronuclear dimetal complexes.[14] A few reports for the preparation of lantern-type dirhodium complexes with diphenylphosphinopyridine (**1**) as a ligand are known (Figure 2A). Kühn et al. reported that the reaction of commercially available $Rh_2(OAc)_4$ with **1** gave the diaxial adduct **2**, whereas the preparation of the monoaxial adduct and **1**-bridged

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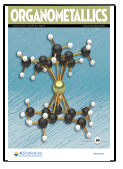

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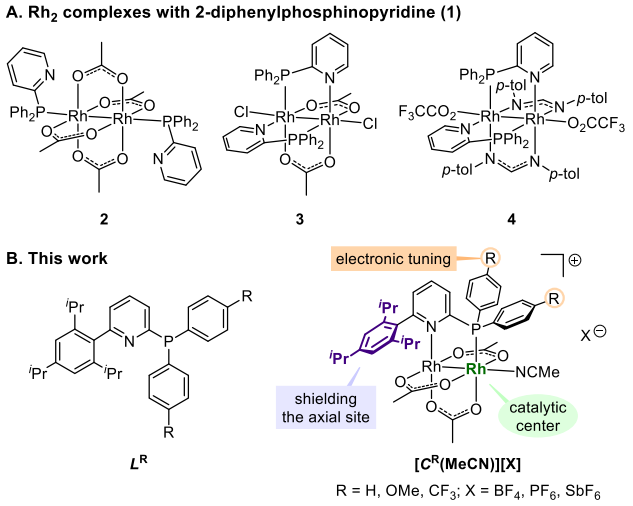


Figure 2. Lantern-type dirhodium complexes with 2-phosphinopyridines.

complexes was not successful.[15] Cotton et al. found that their complexation in the presence of lithium chloride afforded doubly **1**-bridged dirhodium complex **3**.[16] Piraino et al. also synthesized complex **4** from **1** and a specially prepared dirhodium precursor.[17] Further molecular conversions and the catalytic properties of this class of dirhodium complexes are of interest; however, they have not been explored.

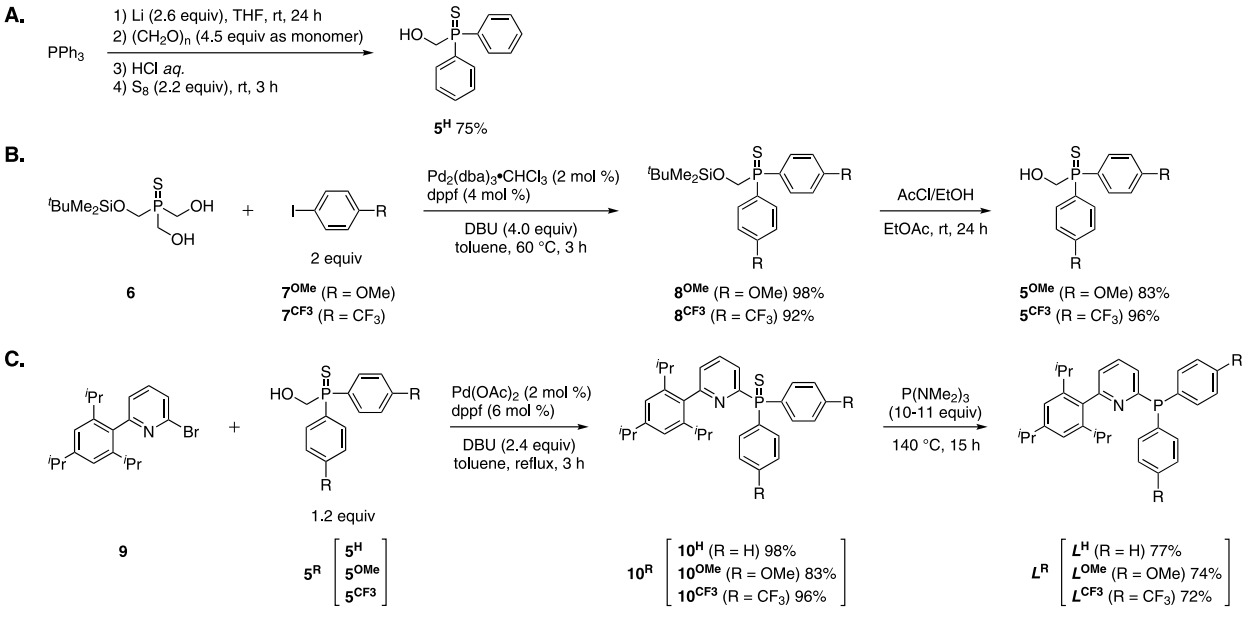
Herein, we wish to report the synthesis, characterization, and catalytic application of novel lantern-type dirhodium complexes $[\mathbf{C^R(MeCN)}][\mathbf{X}]$ bridged by 2-diarylphosphino-6-(2,4,6-triisopropylphenyl)pyridines[18] $\boldsymbol{L^R}$ (Figure 2B). The bridging ligands $\boldsymbol{L^R}$ are selected to enhance the electrophilicity of the dirhodium core. Thus, a bulky 2,4,6-triisopropylphenyl (Tip) group on the pyridine ring shields the closest rhodium atom from the axial coordination which reduces the electrophilicity of the dirhodium core. On the other hand, the axial site of the opposite rhodium atom can work as a catalytic center after the dissociation of the initially coordinated acetonitrile ligand. The complexes have electrophilic cationic character and weakly coordinating counteranions (X = BF_4, PF_6, SbF_6). In addition, the electronic tuning of the dirhodium core is possible by changing the substituents (R = H, OMe, CF_3) on the phosphorus atom in $\boldsymbol{L^R}$. Therefore, the designed complexes are expected to become highly electrophilic catalyst precursors. $[\mathbf{C^R(MeCN)}][\mathbf{X}]$ were successfully prepared from $Rh_2(OAc)_4$ and $\boldsymbol{L^R}$ as starting materials in a few steps. The experimental and quantum chemical studies revealed that the Tip group weakly interacts with the dirhodium core and protects the axial site from the coordination of external molecules but it hardly reduces the electrophilicity. The complexes were more effective catalyst precursors for the dehydrogenative silylation of alcohols using hydrosilanes in comparison to conventional dirhodium complexes.

RESULTS AND DISCUSSION

Synthesis of Ligands. In order to achieve the synthesis of the novel cationic dirhodium complexes $[\mathbf{C^R(MeCN)}][\mathbf{X}]$, we prepared 2-phosphinopyridine ligands $\boldsymbol{L^R}$ from 2-bromo-6-(2,4,6-triisopropylphenyl)pyridine (**9**) and diaryl(hydroxymethyl)phosphine sulfides $\mathbf{5^R}$ (R = H, OMe, CF_3) as shown in Scheme 1. First, $\mathbf{5^H}$ was obtained from triphenylphosphine through *in situ* generation and reaction of lithium diphenylphosphide (Scheme 1A). $\mathbf{5^{OMe}}$ and $\mathbf{5^{CF3}}$ were produced by the Pd-catalyzed P−C cross-coupling[19] of bis(hydroxymethyl)(*tert*-butyldimethylsilyl)phosphine sulfide (**6**) with aryl iodides $\mathbf{7^{OMe}}$ and $\mathbf{7^{CF3}}$ followed by the deprotection of the silyl groups (Scheme 1B). The P−C cross-coupling between **9** and $\mathbf{5^R}$ into thiophosphinopyridines $\mathbf{10^R}$ and the subsequent reduction by tris(dimethylamino)-phosphine proceeded to give $\boldsymbol{L^R}$ in good yields (Scheme 1C).

Synthesis of Dirhodium Complexes. $\boldsymbol{L^R}$-bridged dirhodium complexes $\mathbf{C^RCl}$ were prepared as precursors for $[\mathbf{C^R(MeCN)}][\mathbf{X}]$ through a one-pot reaction shown in Scheme 2. Thus, the treatment of $Rh_2(OAc)_4$ with an equimolar amount of $\boldsymbol{L^R}$ in acetic acid under reflux conditions yielded the $\boldsymbol{L^R}$-bridged complexes $\mathbf{C^ROAc}$.[20] After the solvent was removed under vacuum, the crude $\mathbf{C^ROAc}$ was dissolved

Scheme 1. Synthesis of 2-Phosphinopyridine Ligands $\boldsymbol{L^R}$



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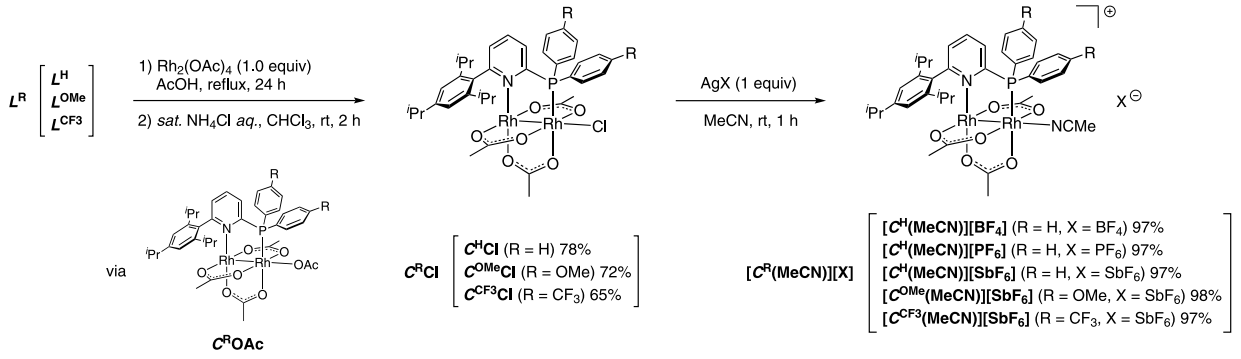
Scheme 2. Synthesis of Cationic Dirhodium Complexes $[C^R(MeCN)][X]$



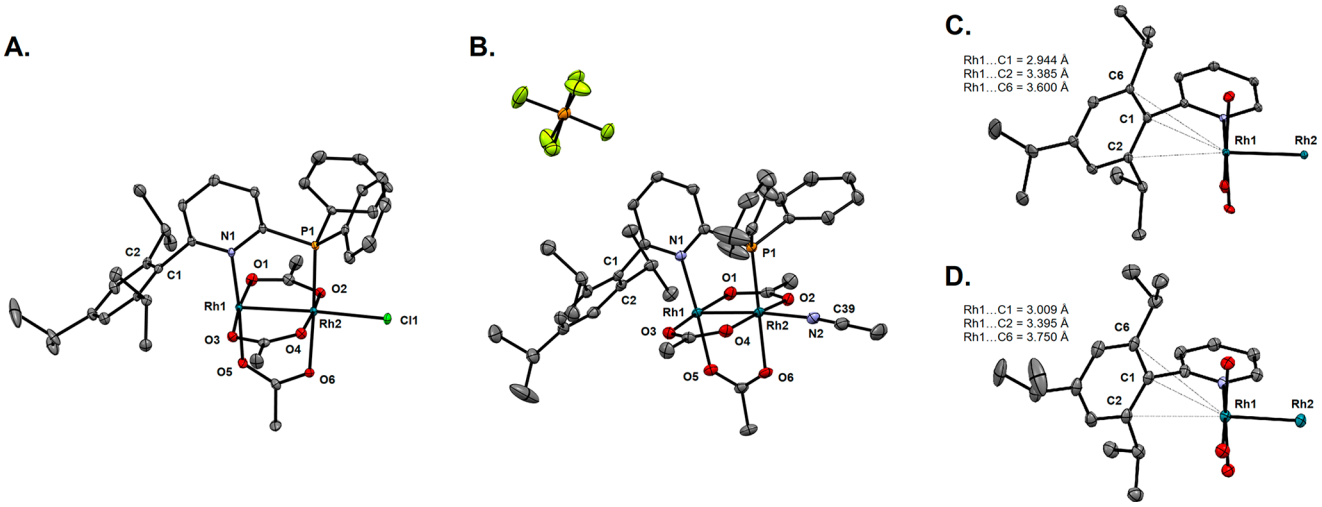


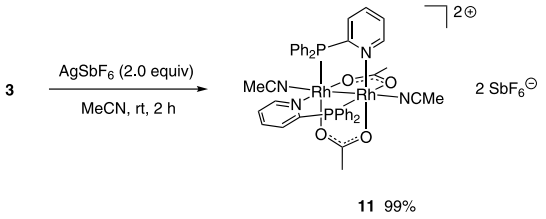
Figure 3. X-ray crystal structures of (A) C^H**Cl** and (B) $[C^H(MeCN)][PF_6]$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules (CH_2Cl_2) are omitted for clarity. Partial structures showing the coordination geometry around Rh1 center for (C) C^H**Cl** and (D) $[C^H(MeCN)][PF_6]$.

with chloroform and reacted with ammonium chloride to give C^R**Cl** in 65−78% isolated yields. The anion exchange of C^R**Cl** with AgX (X = BF_4, PF_6, SbF_6) proceeded efficiently in acetonitrile at room temperature, affording $[C^R(MeCN)][X]$ in 97−98% isolated yields. The isolated complexes were characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR, FAB-MS, and elemental analysis. Furthermore, the molecular structures of C^H**Cl** and $[C^H(MeCN)][PF_6]$ were successfully determined by X-ray crystallographic analyses, as shown in Figure 3 (the details are described in the next section).

To evaluate the influence of the axial shielding Tip group of $[C^R(MeCN)][X]$ on the catalytic activity, we attempted to synthesize singly **1**-bridged dirhodium complexes by the same synthetic procedure for $[C^R(MeCN)][X]$. However, the reactions using **1** and $Rh_2(OAc)_4$ (1−3 equiv) as the starting materials did not give singly **1**-bridged complexes, and mixtures containing doubly **1**-bridged complexes were obtained. The results suggest that the Tip group controls the coordination behavior of L^R toward the dirhodium core and is important to produce singly L^R-bridged complexes. Therefore, instead of singly **1**-bridged complexes, we prepared the doubly **1**-bridged dicationic complex **11** from **3** for comparison in catalytic activity testing (Scheme 3).

Structural Evaluation. The X-ray crystal structures of C^H**Cl** and $[C^H(MeCN)][PF_6]$ are shown in Figure 3. The crystallographic data and selected structural parameters are given in Tables S1 and S2 (Supporting Information). The

Scheme 3. Synthesis of Dicationic Dirhodium Complex 11



crystal structures showed that L^H bridges two rhodium centers via both nitrogen and phosphorus atoms by occupying the equatorial positions. The Rh1−Rh2 bond lengths of C^H**Cl** and $[C^H(MeCN)][PF_6]$ are 2.4401(5) and 2.4246(4) Å, respectively. These bond lengths are similar to those of reported dirhodium triacetate complexes (2.405−2.439 Å).[4d,5a,21] The Rh2−P1 bond length of C^H**Cl** (2.209(1) Å) is shorter than that of $[C^H(MeCN)][PF_6]$ (2.2270(10) Å), suggesting that the rhodium atom of $[C^H(MeCN)][PF_6]$ is more electron deficient than that of C^H**Cl** and has lower back-donating ability toward the phosphine moiety. The most noteworthy structural feature of these complexes is that the rhodium atom Rh2 has an axial acetonitrile ligand, whereas no ligand coordinates to the axial position of Rh1 near the Tip group.[22] The carbon atoms C1, C2, and C6 in the Tip group are close to Rh1, and the interatomic distances are shorter than the sum of the van

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der Waals radii of Rh and C atoms (4.21 Å),[23] suggesting the existence of interactions between Rh1 and the Tip group.

Density functional theory (DFT) calculations for the $[C^{H}(MeCN)]^{+}$ cation at the M06-L/Def2TZVP//ωB97XD/Def2SVP level of theory were performed to elucidate the interactions between the Rh1 and the Tip group (Figure 4 and

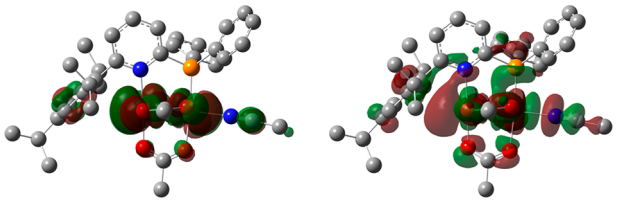

Figure 4. Frontier orbitals of the $[C^{H}(MeCN)]^{+}$ cation: HOMO (left) and LUMO (right) (isovalue 0.013). Hydrogen atoms are omitted for clarity.

Table 1. Stabilization Energies of Selected NBO Pairs as Given by Second-Order Perturbation Theory Analysis of the Fock Matrix in NBO Basis for $[C^{H}(MeCN)]^{+}$[a]

donor NBO	ED (e)	acceptor NBO	ED (e)	$E^{(2)}$ (kcal/mol)
π(C1−C2)	1.65807	σ*(Rh1−Rh2)	0.44164	1.01
LP(Rh1)	1.96967	π*(C1−C2)	0.40259	0.52
LP(N2)	1.79940	σ*(Rh1−Rh2)	0.44164	52.38
σ(N2−C39)	1.99633	σ*(Rh1−Rh2)	0.44164	2.13
LP(Rh2)	1.95502	π*(N2−C39)	0.07251	3.23
LP(Rh2)	1.95502	π*(N2−C39)	0.07257	0.99

[a]The atom numbering is shown in Figure 3. Abbreviations: LP, lone pair orbital; ED, electron density; $E^{(2)}$, stabilization energy (energy of delocalization).

Table 1). Figure 4 shows that the calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are delocalized over the dirhodium core and the Tip group. A natural bond orbital (NBO) analysis revealed the existence of weak donor−acceptor interactions between them: π(C1−C2) → σ*(Rh1−Rh2) and LP(Rh1) → π*(C1−C2).[24] The total stabilization energy is 1.53 kcal/mol, which is much lower than the energy between the dirhodium core and the axial acetonitrile ligand, 58.73 kcal/mol.

To confirm the axial shielding effect of the Tip group, we measured a series of ^{1}H NMR spectra of $[C^{H}(MeCN)][PF_6]$ in the absence and presence of excess acetonitrile. As shown in Figure 5, the addition of acetonitrile increased the signal intensity of free acetonitrile, and no new signals derived from the acetonitrile coordinated to Rh1 were observed.

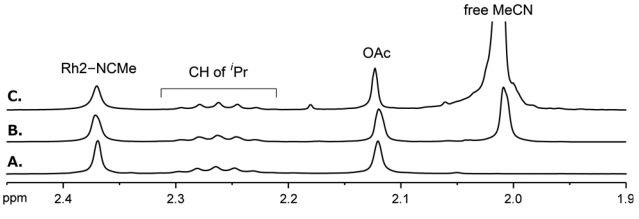

Figure 5. ^{1}H NMR spectra of $[C^{H}(MeCN)][PF_6]$ in the absence (A) and presence of 2 (B) and 18 (C) equiv of MeCN in $CDCl_3$ solution.

The above results indicate that the Tip group in $[C^{H}(MeCN)][PF_6]$ weakly interacts with the dirhodium core and can protect the axial site of Rh1 from the coordination of an external polar molecule such as acetonitrile.

Evaluation of Electrophilic Nature. Lewis acidity and electrophilicity are crucial factors for determining the catalytic performance of dirhodium complexes. We employed the Gutmann−Beckett method[25] for the evaluation of the Lewis acidity of $[C^{R}][X]$,in which the structure of the cation part $[C^{R}]^{+}$ is shown in Figure 6. For the tests, $[C^{R}(MeCN)][X]$

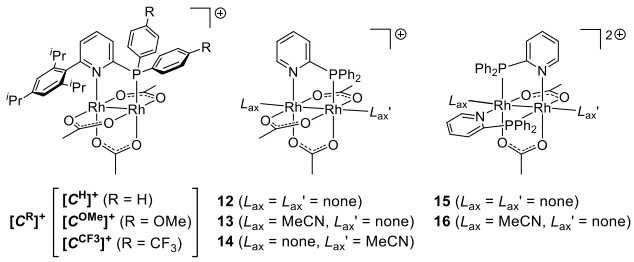

Figure 6. Structures of dirhodium cations bridged by L^{R} or **1**.

were reacted with an equimolar amount of triethylphosphine oxide (TEPO) in CD_2Cl_2 at room temperature to form the Lewis acid−base adducts $[C^{R}(TEPO)][X]$, and the $^{31}P\{^{1}H\}$ NMR chemical shifts for the phosphorus atom of the TEPO were measured (Figure 7 and Table 2). The stronger the Lewis

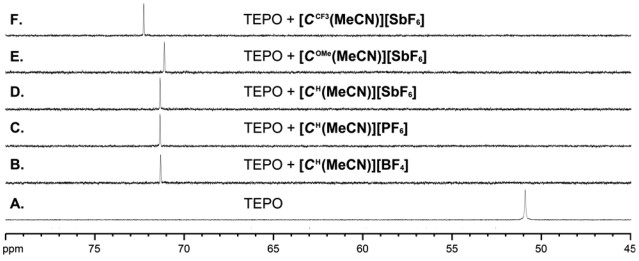

Figure 7. $^{31}P\{^{1}H\}$ NMR spectra of (A) TEPO and (B−F) 1:1 molar mixtures of TEPO and $[C^{R}(MeCN)][X]$ in CD_2Cl_2 at rt.

acid, the more downfield the signal for the corresponding adduct appears from that of free TEPO and the larger the Gutmann−Beckett acceptor number (AN). As a result, this method provided the order of the relative Lewis acidity as follows: $[C^{CF3}][SbF_6]$ > $[C^{H}][SbF_6]$ = $[C^{H}][PF_6]$ ≈ $[C^{H}][BF_4]$ > $[C^{OMe}][SbF_6]$. This result indicates that the electron-

Table 2. Experimental Evaluation of the Lewis Acidity of $[C^{R}][X]$ by the Gutmann−Beckett Method[a]

Lewis acid	$\delta_{Rh\text{-}TEPO}$ (ppm)[b]	Δδ (ppm)[c]	AN[d]
$[C^{H}][BF_4]$	71.3	20.4	67.2
$[C^{H}][PF_6]$	71.4	20.5	67.4
$[C^{H}][SbF_6]$	71.4	20.5	67.4
$[C^{OMe}][SbF_6]$	71.1	20.2	66.7
$[C^{CF3}][SbF_6]$	72.3	21.4	69.4

[a]$[C^{R}(TEPO)][X]$ were generated *in situ* by mixing a 1:1 molar ratio of $[C^{R}(MeCN)][X]$ and TEPO in CD_2Cl_2 at rt, then the $^{31}P\{^{1}H\}$ NMR spectra were recorded at rt. [b]$^{31}P\{^{1}H\}$ NMR chemical shift for the phosphorus atom of the coordinated TEPO. [c]The difference in chemical shifts between coordinated and free TEPO. [d]AN = $(\delta_{Rh\text{-}TEPO} - 41.0) \times \{100/(86.1-41.0)\}$.

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withdrawing *p*-trifluoromethylphenyl groups on the phosphorus atom in $[C^{CF3}]^+$ increase the Lewis acidity of the dirhodium core. For reference, the ANs of typical Lewis acids are shown: $SnCl_4$ (AN = 59), BPh_3 (AN = 66), $B(C_6F_5)_3$ (AN = 78).[25b]

To investigate the effect of the axial shielding Tip group in $[C^R]^+$ on the electrophilic nature of the dirhodium core, we compared $[C^R]^+$ and **1**-bridged dirhodium cations **12**−**14** (Figure 6) by the global electrophilicity index (GEI, ω)[26] calculated from the HOMO and LUMO energies obtained at the M06-L/Def2TZVP(SMD,CH_2Cl_2)//ωB97XD/Def2SVP level of theory (Table 3). GEI is used to estimate the electrophilicity of a molecule without considering the influence of a Lewis base, and a stronger electrophile has a larger ω value. In Table 3, we also give ω', which is a relative percentage of the ω value of an electrophile over that of $[C^H]^+$. First, the order of electrophilicity between $[C^R]^+$ cations was found to be $[C^{CF3}]^+ > [C^H]^+ > [C^{OMe}]^+$, which is consistent with the above results for Lewis acidity by the Gutmann−Beckett method.[26a,b] **12** is the derivative of $[C^H]^+$ without a Tip group, and the ω' value (103%) is slightly higher than that of $[C^H]^+$. However, the actual electrophilic species formed during catalytic reactions using **12** is considered to be complexes such as **13** and **14** having one axial ligand, and the ω' values are 64% and 59%, respectively. These results indicate that axial-ligand-free **12** is highly electrophilic but axial coordination to the dirhodium core significantly reduces the electrophilicity. On the other hand, $[C^H]^+$ retains an electrophilicity similar to that of **12**, although the Tip group is weakly interacting with the axial site as mentioned above. To further evaluate the electrophilicity of $[C^R]^+$, the GEI values of **15** and **16** (Figure 6), commonly used dirhodium catalysts ($Rh_2(OAc)_4$, $Rh_2(tfa)_4$, $Rh_2(pfb)_4$), and their monoadducts with typical solvents were calculated. **15**, the cation of **11** without the acetonitrile ligands, has a high ω' value (123%) that is probably due to the dicationic character; however, the ω' value (78%) of the monoacetonitrile adduct **16** is lower than that of $[C^R]^+$. Similarly, the ω' values of $Rh_2(OAc)_4$ (69%), $Rh_2(tfa)_4$ (109%), and $Rh_2(pfb)_4$ (109%) are greatly reduced by the axial coordination of polar molecules. These results suggest that $[C^R(MeCN)][SbF_6]$ would serve as a more effective catalyst precursor in comparison to **11** and the commonly used dirhodium complexes in a catalytic reaction.

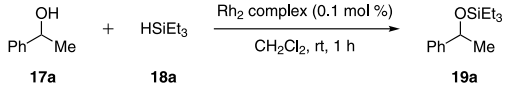
Table 3. GEI Value (ω) Calculated from the Energies of the HOMO and LUMO (E_{HOMO}, E_{LUMO}) for Electrophilic Dirhodium Complexes[a]

Rh_2 complex	E_{HOMO} (eV)	E_{LUMO} (eV)	ω (eV)[b]	ω' (%)[c]
$[C^{CF3}]^+$	−5.172	−3.875	7.884	105
$[C^H]^+$	−5.087	−3.776	7.494	100
$[C^{OMe}]^+$	−5.015	−3.706	7.265	97
12	−5.140	−3.838	7.741	103
13	−5.013	−3.238	4.793	64
14	−4.964	−3.113	4.405	59
15	−5.943	−4.473	9.224	123
16	−5.788	−3.821	5.866	78
$Rh_2(OAc)_4$	−4.438	−3.073	5.165	69
$Rh_2(OAc)_4(H_2O)$	−4.209	−2.489	3.261	44
$Rh_2(OAc)_4(MeOH)$	−4.161	−2.419	3.108	42
$Rh_2(OAc)_4(MeCN)$	−4.259	−2.382	2.936	39
$Rh_2(tfa)_4$	−5.530	−4.106	8.151	109
$Rh_2(tfa)_4(H_2O)$	−5.269	−3.484	5.363	72
$Rh_2(tfa)_4(MeOH)$	−5.213	−3.409	5.151	69
$Rh_2(tfa)_4(MeCN)$	−5.296	−3.364	4.851	65
$Rh_2(pfb)_4$	−5.566	−4.131	8.191	109
$Rh_2(pfb)_4(H_2O)$	−5.311	−3.520	5.444	73
$Rh_2(pfb)_4(MeOH)$	−5.259	−3.451	5.245	70
$Rh_2(pfb)_4(MeCN)$	−5.335	−3.398	4.922	66

[a]Abbreviations: tfa, trifluoroacetate; pfb, perfluorobutyrate. [b]$\omega = \chi^2/2\eta$, $\chi = -(E_{HOMO} + E_{LUMO})/2$, $\eta = E_{LUMO} - E_{HOMO}$. [c]$\omega'$ = 100(ω of the Rh_2 complex)/(ω of $[C^H]^+$).

Catalysis. Doyle et al. reported that electrophilic $Rh_2(pfb)_4$ was an effective catalyst precursor for the dehydrogenative silylation of alcohols with hydrosilanes to afford silyl ethers under mild conditions (room temperature, 1.0 mol % Rh_2 loading).[5f] Therefore, we evaluated $[C^R(MeCN)][X]$ as a catalyst precursor for the dehydrogenative silylation of 1-phenylethanol (**17a**) using triethylsilane (**18a**) in dichloromethane at room temperature for 1 h with a lower Rh_2 loading of 0.1 mol % (Table 4). As shown in entries 1−3, representative dirhodium complexes such as $Rh_2(OAc)_4$, $Rh_2(tfa)_4$, and $Rh_2(pfb)_4$ did not work as effective catalyst precursors under the conditions. C^HCl, having no available axial sites, gave no product (entry 4), and thus we performed the reaction with $[C^H(MeCN)][X]$ (entries 5−7). The complexes having BF_4^-, PF_6^-, and SbF_6^- anions gave the silyl ether **19a** in 2%, 87%, and 94% yields, respectively. The much lower yield by $[C^H(MeCN)][BF_4]$ is probably due to the stronger affinity of $[C^H]^+$ with BF_4^- than with PF_6^- and SbF_6^-.[27] Next, we compared the reactions of $[C^R(MeCN)][SbF_6]$ having different aryl groups on the phosphorus atom (entries 7−9). The complexes having $[C^H]^+$, $[C^{OMe}]^+$, and $[C^{CF3}]^+$ cations exhibited a difference in yield, and $[C^{CF3}(MeCN)][SbF_6]$ was found to be the best catalyst precursor. Doubly **1**-bridged complex **11** having SbF_6^- anions also provided **19a** in 82% yield (entry 10). Interestingly, the product yields obtained with the cationic dirhodium complexes are well explained by the order of electrophilicity of the species having one available axial site described above ($[C^{CF3}]^+ > [C^H]^+ > [C^{OMe}]^+ >$ **16**). Another noteworthy point is that $[C^{CF3}(MeCN)][SbF_6]$ worked well in the reaction using *N*,*N*-

Table 4. Dehydrogenative Silylation of 17a with 18a[a]



entry	Rh_2 complex	yield (%)[b]
1	$Rh_2(OAc)_4$	0
2	$Rh_2(tfa)_4$	1
3	$Rh_2(pfb)_4$	4
4	C^HCl	0
5	$[C^H(MeCN)][BF_4]$	2
6	$[C^H(MeCN)][PF_6]$	87
7	$[C^H(MeCN)][SbF_6]$	94
8	$[C^{OMe}(MeCN)][SbF_6]$	91
9	$[C^{CF3}(MeCN)][SbF_6]$	99
10	**11**	82
11[c]	$[C^{CF3}(MeCN)][SbF_6]$	94

[a]Reaction conditions unless specified otherwise: **17a** (1.0 mmol), **18a** (1.1 mmol, 1.1 equiv), Rh_2 complex (0.1 mol %), CH_2Cl_2 (1.0 mL), rt, 1 h. [b]GC yield. [c]The reaction was performed at 60 °C for 1 h using DMF (1.0 mL) as a solvent.

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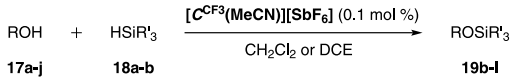
Table 5. Dehydrogenative Silylation of Various Alcohols[a]



entry	alcohol **17**	hydrosilane **18**	product **19**	solvent	temperature (°C)	time (h)	yield (%)[b]
1	benzyl alcohol (**17b**)	**18a**	**19b**	CH_2Cl_2	rt	1	99
2	2-phenylethanol (**17c**)	**18a**	**19c**	CH_2Cl_2	rt	1	99
3	3-phenyl-1-propanol (**17d**)	**18a**	**19d**	CH_2Cl_2	rt	1	(99)
4	1-phenyl-1-propanol (**17e**)	**18a**	**19e**	CH_2Cl_2	rt	1	(99)
5	3-phenyl-2-propanol (**17f**)	**18a**	**19f**	CH_2Cl_2	rt	1	(98)
6[c]	2-methyl-4-phenyl-2-butanol (**17g**)	**18a**	**19g**	DCE	60	9	97
7[c]	2-methyl-3-phenyl-2-propanol (**17h**)	**18a**	**19h**	DCE	60	9	(91)
8[c]	4-propylphenol (**17i**)	**18a**	**19i**	DCE	40	25	99
9[c]	4-phenylphenol (**17j**)	**18a**	**19j**	DCE	40	25	(96)
10[c]	**17b**	$HSiMe_2{}^tBu$ (**18b**)	**19k**	DCE	60	24	(99)
11[c]	**17a**	**18b**	**19l**	DCE	60	24	(24)

[a]Reaction conditions unless specified otherwise: **17** (1.0 mmol), **18** (1.1 mmol, 1.1 equiv), $[C^{CF3}(MeCN)][SbF_6]$ (0.1 mol %), CH_2Cl_2 (1.0 mL) or DCE (0.5 mL). [b]GC yield of **19**. Isolated yields are given in parentheses. [c]1.5 mmol (1.5 equiv) of **18** was used.

dimethylformamide (DMF) as a solvent at 60 °C, although the activity of conventional dirhodium catalysts is usually suppressed by coordinating solvents.[5c] It is known that Biffis's monocationic dirhodium complexes bridged by oxothioether ligands are one of the most effective dirhodium catalyst precursors for the dehydrogenative silylation of alcohols, which proceeds at 50 °C with a Rh_2 loading of 0.1 mol % or below.[5a] The catalyst generated from $[C^{CF3}(MeCN)][SbF_6]$ has quite high activity, comparable to that of the Biffis catalysts.

The efficacy of $[C^{CF3}(MeCN)][SbF_6]$ was further investigated by the reaction of various alcohols using dichloromethane or 1,2-dichloroethane (DCE) as a solvent (Table 5). Primary alcohols **17b−d** and secondary alcohols **17e,f** reacted with **18a** at room temperature for 1 h, giving the corresponding products **19b−f** in excellent yields (entries 1−5). Although the silylation of tertiary alcohols hardly proceeds by conventional dirhodium catalysts,[5a,f] the reaction of **17g,h** using $[C^{CF3}(MeCN)][SbF_6]$ afforded **19g,h** in high yields by optimizing the reaction conditions (entries 6 and 7). Phenol derivatives **17i,j** were converted to **19i,j** at 40 °C after 25 h (entries 8 and 9). *tert*-Butyldimethylsilane (**18b**) could be used for the silylation of **17b** and **17a** to form **19k** and **19l** in 99% and 24% isolated yields, respectively (entries 10 and 11).

CONCLUSION

In conclusion, novel cationic lantern-type dirhodium complexes $[C^{R}(MeCN)][X]$ bridged by 2-diarylphosphinopyridines having an axial shielding Tip group at the 6-position were designed, synthesized, and evaluated as catalyst precursors for the dehydrogenative silylation of alcohols using hydrosilanes. It was found that the Tip group weakly interacts with the dirhodium core and prevents the closest axial site from the coordination of external molecules. Experimental and quantum chemical studies suggested that the unique structural features and the electron-withdrawing *p*-trifluoromethylphenyl groups on the phosphorus atom make the complexes highly electrophilic. Actually, $[C^{CF3}(MeCN)][SbF_6]$ was a superior catalyst precursor for the dehydrogenative silylation of various alcohols in comparison with conventional dirhodium complexes. Currently, studies on further catalytic reactions using $[C^{R}(MeCN)][X]$ are ongoing in our laboratory.

EXPERIMENTAL SECTION

General Information. Reagents were obtained from commercial suppliers (Aldrich, Kanto, TCI, Wako) and used without further purification unless otherwise noted. Toluene, tetrahydrofuran (THF), DMF, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were refluxed over drying agents and purified by distillation under an inert gas (Na for toluene under Ar; Na/benzophenone for THF under N_2; BaO for DMF under Ar; CaH_2 for DBU under Ar). Superdehydrated dichloromethane (Wako) and DCE (Kanto) were used for catalytic reactions. Oily alcohols were dried over MS4A and purified by distillation. **6** (CAS registry number 1420040-42-1) was prepared according to our previous report.[19b] ^1H NMR (400 MHz), $^{31}P\{^1H\}$ NMR (162 MHz), and $^{13}C\{^1H\}$ NMR (101 or 126 MHz) spectra were measured with Bruker AVANCE 400 and Bruker AVANCE III HD 500 spectrometers. The ^1H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm) or residual protiated solvent (7.26 ppm for $CDCl_3$; 5.32 ppm for CD_2Cl_2; 1.94 ppm for CD_3CN).[28] The $^{13}C\{^1H\}$ NMR chemical shifts are reported relative to $CDCl_3$ (77.16 ppm), CD_2Cl_2 (53.84 ppm), and CD_3CN (1.32 ppm).[28] Fast atom bombardment (FAB) low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were measured on a JEOL JMS-700V instrument by using 3-nitrobenzyl alcohol as a matrix. X-ray diffraction data collections were performed with a Rigaku VariMax SaturnCCD724/α diffractometer using multilayer mirror monochromated Mo Kα radiation (λ = 0.71073 Å) at −173 °C. Elemental analyses were performed on a J-SCIENCE LAB MICRO CORDER JM10T instrument. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-2014 instrument with a flame ionization detector (FID) equipped with a capillary column (DB-FFAP, 0.25 mm i.d. × 30 m, df 0.25 μm). Analyses by GC coupled to electron impact mass spectrometry (EI-MS) were conducted on a Shimadzu GCMS-2020 NX instrument (capillary column: DB-FFAP, 0.25 mm i.d. × 30 m, df 0.50 μm). Column chromatography was performed on Kanto silica gel 60 (spherical, 40−50 μm).

Synthesis of 5^H. A mixture of triphenylphosphine (9.97 g, 38.0 mmol, 1.0 equiv), lithium (0.673 g, 97.0 mmol, 2.6 equiv), and THF (38 mL) was stirred at room temperature for 24 h under Ar. Then, the solution was placed in another reactor containing paraformaldehyde (5.14 g, 171 mmol as the monomer, 4.5 equiv) under Ar by cannula transfer. After completion of the addition, water (Ar bubbled, 10 mL), 1 N HCl(aq) (Ar bubbled, 90 mL), and S_8 (2.73 g, 85.1 mmol as S, 2.2 equiv) were successively added to the mixture, and the resulting mixture was stirred at room temperature for 3 h under Ar. The mixture was extracted with ethyl acetate, and the combined organic layers were washed successively with water, saturated $NaHCO_3$(aq), and brine. After the solution was dried over Na_2SO_4,

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the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (eluent: ethyl acetate/*n*-hexane 1/3). The obtained solid was recrystallized from ethyl acetate/*n*-hexane to give the product as a white solid (7.10 g, 28.6 mmol, 75%). CAS registry number: 96620-51-8. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95−3.00 (m, 1H, OH), 4.33−4.35 (m, 2H, CH_2), 7.46−7.57 (m, 6H, PhH), 7.79−7.85 (m, 4H, PhH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 63.1 (d, J = 60.7 Hz, CH_2), 128.9 (d, J = 12.2 Hz, *m*-C of Ph × 4), 130.4 (d, J = 79.1 Hz, *ipso*-C of Ph × 2), 131.6 (d, J = 9.9 Hz, *o*-C of Ph × 4), 132.2 (d, J = 2.9 Hz, *p*-C of Ph × 2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 42.9.

Synthesis of 8^{OMe}. A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (41.4 mg, 0.040 mmol, 2 mol %) and 1,1′-bis(diphenylphosphino)ferrocene (dppf; 44.4 mg, 0.080 mmol, 4 mol %) in toluene (8 mL) was stirred at room temperature for 15 min under Ar. To the solution were added successively **6** (0.542 g, 2.00 mmol, 1.0 equiv), 7^{OMe} (1.04 g, 4.42 mmol, 2.2 equiv), toluene (12 mL), and DBU (1.22 g, 8.00 mmol, 4.0 equiv). The mixture was stirred at 60 °C for 3 h under Ar. After it was cooled to room temperature, the resulting mixture was quenched with 1 N HCl(aq) and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (eluent: ethyl acetate/*n*-hexane 1/29) to give the product as a white solid (0.827 g, 1.96 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.09 (s, 6H, Si-CH_3), 0.81 (s, 9H, ^{t}Bu), 3.84 (s, 6H, OCH_3), 4.37 (d, J = 4.8 Hz, 2H, CH_2), 6.95 (dd, J = 8.8 and 2.2 Hz, 4H, *m*-H of *p*-An), 7.83 (dd, J = 12.0 and 8.6 Hz, 4H, *o*-H of *p*-An). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ − 5.8 (s, Si-CH_3 × 2), 18.3 (s, quat C of ^{t}Bu), 25.8 (s, CH_3 of ^{t}Bu × 3), 55.5 (s, OCH_3 × 2), 67.5 (d, J = 72.7 Hz, CH_2), 114.0 (d, J = 13.2 Hz, *m*-C of *p*-An × 4), 122.4 (d, J = 86.8 Hz, *ipso*-C of *p*-An × 2), 134.2 (d, J = 11.1 Hz, *o*-C of *p*-An × 4), 162.5 (d, J = 2.9 Hz, *p*-C of *p*-An × 2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 37.8. HRMS (FAB+): m/z calcd for $C_{21}H_{32}O_3PSSi$, 423.1579 $[M + H]^+$; found, 423.1574.

Synthesis of 8^{CF3}. The compound was prepared by following the synthetic procedure for 8^{OMe}, using $Pd_2(dba)_3{\cdot}CHCl_3$ (0.104 g, 0.10 mmol, 2 mol %), dppf (0.111 g, 0.20 mmol, 4 mol %), toluene (20 mL), **6** (1.35 g, 5.01 mmol, 1.0 equiv), 7^{CF3} (2.86 g, 10.5 mmol, 2.1 equiv), toluene (30 mL), and DBU (3.04 g, 20.0 mmol, 4.0 equiv). Isolation by column chromatography gave the product as a white solid (2.31 g, 4.63 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.06 (s, 6H, Si-CH_3), 0.82 (s, 9H, ^{t}Bu), 4.49 (d, J = 4.6 Hz, 2H, CH_2), 7.74 (dd, J = 8.3 and 2.2 Hz, 4H, *o*-H of *p*-$CF_3C_6H_4$), 8.06 (dd, J = 12.2 and 8.1 Hz, 4H, *m*-H of *p*-$CF_3C_6H_4$). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ −5.8 (s, Si-CH_3 × 2), 18.2 (s, quat C of ^{t}Bu), 25.7 (s, CH_3 of ^{t}Bu × 3), 67.0 (d, J = 72.0 Hz, CH_2), 123.6 (q, J = 273.2 Hz, CF_3 × 2), 125.4 (dq, J = 12.1 and 3.9 Hz, *m*-C of *p*-$CF_3C_6H_4$ × 4), 132.8 (d, J = 10.3 Hz, *o*-C of *p*-$CF_3C_6H_4$ × 4), 134.0 (qd, J = 32.9 and 3.0 Hz, *p*-C of *p*-$CF_3C_6H_4$ × 2), 135.1 (d, J = 78.6 Hz, *ipso*-C of *p*-$CF_3C_6H_4$ × 2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 38.7. HRMS (FAB+): m/z calcd for $C_{21}H_{26}F_6OPSSi$, 499.1115 $[M + H]^+$; found, 499.1133.

Synthesis of 5^{OMe}. 8^{OMe} (1.91 g, 4.52 mmol, 1.0 equiv) was dissolved in a small amount of ethyl acetate. To the solution was added a solution of acetyl chloride (5.3 mL) in ethanol (50 mL). The mixture was stirred at room temperature for 24 h in air, neutralized with KOH, and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (eluent: ethyl acetate/*n*-hexane 1/2) to give the product as a white solid (1.15 g, 3.73 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.09−3.11 (br, 1H, OH), 3.81 (s, 6H, OCH_3), 4.24 (br s, 2H, CH_2), 6.95−6.96 (m, 4H, *m*-H of *p*-An), 7.72 (dd, J = 12.0 and 8.7 Hz, 4H, *o*-H of *p*-An). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 55.4 (s, OCH_3 × 2), 63.5 (d, J = 62.2 Hz, CH_2), 114.4 (d, J = 13.2 Hz, *m*-C of *p*-An × 4), 121.4 (d, J = 85.6 Hz, *ipso*-C of *p*-An × 2), 133.4 (d, J = 11.3 Hz, *o*-C of *p*-An × 4), 162.5 (d, J = 2.9 Hz, *p*-C of *p*-An × 2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 41.0. HRMS (FAB+): m/z calcd for $C_{15}H_{17}O_3PS$: 308.0636 $[M]^+$; found: 308.0636.

Synthesis of 5^{CF3}. The compound was prepared by following the synthetic procedure for 5^{OMe}, using 8^{CF3} (1.50 g, 3.00 mmol, 1.0 equiv), acetyl chloride (4 mL), and ethanol (38 mL). Isolation by column chromatography (eluent: ethyl acetate/*n*-hexane 1/5) gave the product as a white solid (1.10 g, 2.87 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.90−2.92 (br, 1H, OH), 4.43 (br s, 2H, CH_2), 7.76 (dd, J = 8.3 and 2.0 Hz, 4H, *o*-H of *p*-$CF_3C_6H_4$), 7.97 (dd, J = 12.3 and 8.2 Hz, 4H, *m*-H of *p*-$CF_3C_6H_4$). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 63.5 (d, J = 62.1 Hz, CH_2), 123.5 (q, J = 273.0 Hz, CF_3 × 2), 125.9 (dq, J = 12.0 and 3.9 Hz, *m*-C of *p*-$CF_3C_6H_4$ × 4), 132.2 (d, J = 10.4 Hz, *o*-C of *p*-$CF_3C_6H_4$ × 4), 134.4 (qd, J = 32.9 and 3.0 Hz, *p*-C of *p*-$CF_3C_6H_4$ × 2), 134.4 (d, J = 76.6 Hz, *ipso*-C of *p*-$CF_3C_6H_4$ × 2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 41.0. HRMS (FAB+): m/z calcd for $C_{15}H_{12}F_6OPS$, 385.0251 $[M + H]^+$; found, 385.0267.

Synthesis of 9. **9** was prepared by a modified procedure described in the literature.[18b] A solution of 2-bromo-1,3,5-triisopropylbenzene (2.39 g, 8.43 mmol, 1.2 equiv) in THF (8 mL) was slowly added to a suspension of magnesium (0.223 g, 9.18 mmol, 1.3 equiv) in THF (3 mL) at room temperature under Ar. The resulting mixture was stirred at reflux for 3 h under Ar. The Grignard reagent prepared was cannulated into a solution of 2,6-dibromopyridine (1.66 g, 7.00 mmol, 1.0 equiv) and $NiCl_2(PCy_3)_2$ (14.5 mg, 0.021 mmol, 0.3 mol %) in toluene (14 mL). After the resulting mixture was stirred at room temperature for 43 h under Ar, the reaction was quenched successively by dilution with toluene, saturated NH_4Cl(aq), and dichloromethane. Then, the mixture was extracted with dichloromethane. The combined organic layers were washed successively with saturated NH_4Cl(aq), water, and brine. After the solution was dried over Na_2SO_4, the solvent was removed *in vacuo*. The resulting solid was recrystallized from toluene/diethyl ether. The precipitate that formed was filtered, washed with diethyl ether/ethanol, and dried under vacuum to give the product as a white solid (1.87 g, 5.19 mmol, 74%). CAS registry number: 833453-21-7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 1.14 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.26 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 2.47 (sep, J = 6.8 Hz, 2H, CH of ^{i}Pr), 2.91 (sep, J = 6.9 Hz, 1H, CH of ^{i}Pr), 7.05 (s, 2H, *m*-H of Tip), 7.24 (d, J = 7.4 Hz, 1H, PyH), 7.45 (d, J = 7.9 Hz, 1H, PyH), 7.56−7.60 (m, 1H, PyH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 24.0 (CH_3 of ^{i}Pr × 2), 24.2 (CH_3 of ^{i}Pr × 2), 24.3 (CH_3 of ^{i}Pr × 2), 30.6 (CH of ^{i}Pr × 2), 34.6 (CH of ^{i}Pr × 2), 120.9 (*m*-C of Tip × 2), 124.1 (5-C of Py), 126.1 (3-C of Py), 135.0 (*ipso*-C of Tip), 138.1 (4-C of Py), 141.6 (2-C of Py), 146.3 (*o*-C of Tip × 2), 149.4 (*p*-C of Tip), 161.5 (6-C of Py).

Synthesis of 10^H. A solution of $Pd(OAc)_2$ (18.9 mg, 0.084 mmol, 2 mol %) and dppf (140 mg, 0.25 mmol, 6 mol %) in toluene (20 mL) was stirred at room temperature for 0.5 h under Ar. To the solution were added successively 5^H (1.25 g, 5.05 mmol, 1.2 equiv), **9** (1.51 g, 4.20 mmol, 1.0 equiv), toluene (30 mL), and DBU (1.54 g, 10.1 mmol, 2.4 equiv). The mixture was stirred at reflux for 3 h under Ar. After it was cooled to room temperature, the resulting mixture was quenched with water and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (eluent: ethyl acetate/*n*-hexane 1/29) to give the product as a white solid (2.05 g, 4.13 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.01 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.29 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 2.29 (sep, J = 6.8 Hz, 2H, CH of ^{i}Pr), 2.93 (sep, J = 6.9 Hz, 1H, CH of ^{i}Pr), 7.03 (s, 2H, *m*-H of Tip), 7.27−7.30 (m, 1H, ArH), 7.36−7.31 (m, 4H, ArH), 7.39−7.43 (m, 2H, ArH), 7.86−7.89 (m, 1H, ArH), 7.91−7.96 (m, 4H, ArH), 8.70−8.74 (m, 1H, ArH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 24.0 (s, CH_3 of ^{i}Pr × 4), 24.2 (s, CH_3 of ^{i}Pr × 2), 30.5 (s, CH of ^{i}Pr × 2), 34.4 (s, CH of ^{i}Pr), 120.7 (s, *m*-C of Tip × 2), 126.6 (d, J = 3.1 Hz, 5-C of Py), 126.9 (d, J = 26.0 Hz, 4-C of Py), 128.2 (d, J = 12.7 Hz, *m*-C of Ph × 4), 131.4 (d, J = 3.0 Hz, *p*-C of Ph × 2), 132.5−133.4 (m, *ipso*-C × 4 and *o*-C of Ph × 2), 135.7 (s, *ipso*-C of Tip), 136.2 (d, J = 11.1 Hz, 3-C of Py), 146.3 (s, *o*-C of Tip × 2), 149.1 (s, *p*-C of Tip), 155.7 (d, J = 111.0 Hz, 2-C of Py), 160.5 (d, J = 17.9 Hz, 6-C of Py). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ

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36.0. HRMS (FAB+): m/z calcd for $C_{32}H_{37}NPS$, 498.2384 $[M + H]^+$; found, 498.2369.

Synthesis of 10^{OMe}. The compound was prepared by following the synthetic procedure for $\mathbf{10^H}$, using $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 2 mol %), dppf (33.3 mg, 0.060 mmol, 6 mol %), toluene (4 mL), $\mathbf{5^{OMe}}$ (0.370 g, 1.20 mmol, 1.2 equiv), **9** (0.360 g, 1.00 mmol, 1.0 equiv), toluene (6 mL), and DBU (0.366 g, 2.41 mmol, 2.4 equiv). Isolation by column chromatography (eluent: ethyl acetate/*n*-hexane 1/9) gave the product as a white solid (0.466 g, 0.835 mmol, 83%). ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.01 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.29 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 2.30 (sep, J = 6.8 Hz, 2H, CH of ^{i}Pr), 2.93 (sep, J = 6.9 Hz, 1H, CH of ^{i}Pr), 3.77 (s, 6H, OCH_3), 6.83−6.86 (m, 4H, *m*-H of *p*-An), 7.03 (s, 2H, *m*-H of Tip), 7.25−7.28 (m, 1H, PyH), 7.83−7.88 (m, 5H, ArH), 8.67−8.71 (m, 1H, PyH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 24.01 (s, CH_3 of ^{i}Pr × 2), 24.04 (s, CH_3 of ^{i}Pr × 2), 24.2 (s, CH_3 of ^{i}Pr × 2), 30.4 (s, CH of ^{i}Pr × 2), 34.4 (s, CH of ^{i}Pr), 55.4 (s, OCH_3 × 2), 113.8 (d, J = 13.8 Hz, *m*-C of *p*-An × 4), 120.7 (s, *m*-C of Tip × 2), 124.3 (d, J = 92.3 Hz, *ipso*-C of *p*-An × 2), 126.3 (d, J = 2.7 Hz, 5-C of Py), 126.5 (d, J = 26.0 Hz, 4-C of Py), 134.3 (d, J = 11.8 Hz, *o*-C of *p*-An × 4), 135.8 (s, *ipso*-C of Tip), 136.1 (d, J = 11.1 Hz, 3-C of Py), 146.3 (s, *o*-C of Tip × 2), 149.0 (s, *p*-C of Tip), 156.5 (d, J = 111.7 Hz, 2-C of Py), 160.3 (d, J = 18.2 Hz, 6-C of Py), 162.1 (d, J = 3.1 Hz, *p*-C of *p*-An × 2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 34.6. HRMS (FAB+): m/z calcd for $C_{34}H_{41}NO_2PS$, 558.2596 $[M + H]^+$; found, 558.2586.

Synthesis of 10^{CF3}. The compound was prepared by following the synthetic procedure for $\mathbf{10^H}$, using $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 2 mol %), dppf (33.3 mg, 0.060 mmol, 6 mol %), toluene (4 mL), $\mathbf{5^{CF3}}$ (0.461 g, 1.20 mmol, 1.2 equiv), **9** (0.360 g, 1.00 mmol, 1.0 equiv), toluene (6 mL), and DBU (0.366 g, 2.41 mmol, 2.4 equiv). Isolation by column chromatography gave the product as a white solid (0.606 g, 0.957 mmol, 96%). ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.02 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.30 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 2.22 (sep, J = 6.8 Hz, 2H, CH of ^{i}Pr), 2.94 (sep, J = 6.9 Hz, 1H, CH of ^{i}Pr), 7.04 (s, 2H, *m*-H of Tip), 7.34−7.36 (m, 1H, PyH), 7.61−7.62 (m, 4H, ArH), 7.93−7.98 (m, 1H, PyH), 8.06−8.11 (m, 4H, ArH), 8.68−8.72 (m, 1H, PyH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 23.9 (s, CH_3 of ^{i}Pr × 2), 24.0 (s, CH_3 of ^{i}Pr × 2), 24.1 (s, CH_3 of ^{i}Pr × 2), 30.6 (s, CH of ^{i}Pr × 2), 34.5 (s, CH of ^{i}Pr), 120.9 (s, *m*-C of Tip × 2), 123.7 (q, J = 273.4 Hz, CF_3 × 2), 125.2 (dq, J = 12.8 and 3.8 Hz, *m*-C of *p*-$CF_3C_6H_4$ × 4), 127.2 (d, J = 26.5 Hz, 4-C of Py), 127.3 (d, J = 3.3 Hz, 5-C of Py), 133.0 (d, J = 10.7 Hz, *o*-C of $CF_3C_6H_4$ × 4), 133.5 (qd, J = 32.9 and 3.0 Hz, *p*-C of $CF_3C_6H_4$ × 2), 135.2 (s, *ipso*-C of Tip), 136.6 (d, J = 11.5 Hz, 3-C of Py), 136.9 (d, J = 84.2, *ipso*-C of $CF_3C_6H_4$) 146.2 (s, *o*-C of Tip × 2), 149.5 (s, *p*-C of Tip), 154.3 (d, J = 113.0 Hz, 2-C of Py), 161.1 (d, J = 18.3 Hz, 6-C of Py). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 34.3. HRMS (FAB+): m/z calcd for $C_{34}H_{35}F_6NPS$, 634.2132 $[M + H]^+$; found, 634.2134.

Synthesis of L^H. A mixture of $\mathbf{10^H}$ (0.372 g, 0.747 mmol, 1.0 equiv) and tris(dimethylamino)phosphine (1.5 mL) was stirred at 140 °C for 15 h under Ar. After the volatiles were removed *in vacuo*, the reactor was cooled to room temperature. The residue was purified twice by reprecipitation using degassed chloroform and degassed methanol under Ar, giving the product as a white solid (0.268 g, 0.576 mmol, 77%). CAS registry number: 919091-19-3. ^1H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.09 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 1.27 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 2.51 (sep, J = 6.9 Hz, 2H, CH of ^{i}Pr), 2.91 (sep, J = 6.9 Hz, 1H, CH of ^{i}Pr), 7.00−7.03 (m, 1H, PyH), 7.03 (s, 2H, *m*-H of Tip), 7.15−7.17 (m, 1H, PyH), 7.32−7.35 (m, 6H, PhH), 7.38−7.45 (m, 4H, PhH), 7.57−7.61 (m, 1H, PyH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 24.1 (s, CH_3 of ^{i}Pr × 2), 24.2 (s, CH_3 of ^{i}Pr × 2), 24.3 (s, CH_3 of ^{i}Pr × 2), 30.5 (s, CH of ^{i}Pr × 2), 34.5 (s, CH of ^{i}Pr), 120.8 (s, *m*-C of Tip × 2), 123.9 (s, 5-C of Py), 125.7 (d, J = 15.6 Hz, 3-C of Py), 128.6 (d, J = 7.2 Hz, *m*-C of Ph × 4), 129.0 (s, *p*-C of Ph × 2), 134.4 (d, J = 19.7 Hz, *o*-C of Ph × 4), 135.4 (d, J = 2.5 Hz, 4-C of Py), 136.5 (s, *ipso*-C of Tip), 136.8 (d, J = 11.1 Hz, *ipso*-C of Ph × 2), 146.3 (s, *o*-C of Tip × 2), 148.8 (s, *p*-C of Tip), 160.9 (d, J = 12.6 Hz, 6-C of Py), 163.6 (d, J = 4.5 Hz, 2-C of Py). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ −4.91.

Synthesis of L^{OMe}. The compound was prepared by following the synthetic procedure for $\mathbf{L^H}$, using $\mathbf{10^{OMe}}$ (0.413 g, 0.740 mmol, 1.0 equiv) and tris(dimethylamino)phosphine (1.5 mL). Isolation by reprecipitation gave the product as a white solid (0.2897 g, 0.551 mmol, 74%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.01 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.07 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.25 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 2.48 (sep, J = 6.8 Hz, 2H, CH of ^{i}Pr), 2.89 (sep, J = 6.9 Hz, 1H, CH of ^{i}Pr), 3.80 (s, 6H, OCH_3), 6.87 (d, J = 8.5 Hz, 4H, *m*-H of *p*-An), 6.97 (d, J = 7.7 Hz, 1H, PyH), 7.01 (s, 2H, *m*-H of Tip), 7.11 (d, J = 7.7 Hz, 1H, PyH), 7.31−7.35 (m, 4H, *o*-H of *p*-An), 7.54−7.58 (m, 1H, PyH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 24.1 (s, CH_3 of ^{i}Pr × 2), 24.2 (s, CH_3 of ^{i}Pr × 2), 24.3 (s, CH_3 of ^{i}Pr × 2), 30.47 (s, CH of ^{i}Pr × 2), 34.53 (s, CH of ^{i}Pr), 55.3 (s, OCH_3 × 2), 114.3 (d, J = 8.0 Hz, *m*-C of *p*-An × 4), 120.8 (s, *m*-C of Tip ×2), 123.6 (s, 5-C of Py), 125.3 (d, J = 15.3 Hz, 3-C of Py), 128.0 (d, J = 8.0 Hz, *ipso*-C of *p*-An × 2), 135.3 (s, 4C of Py), 135.9 (d, J = 21.2 Hz, *o*-C of *p*-An × 4), 136.5 (d, J = 1.3 Hz, *ipso*-C of Tip), 146.3 (s, *o*-C of Tip × 2), 148.8 (s, *p*-C of Tip), 160.4 (s, *p*-C of *p*-An × 2), 160.7 (d, J = 12.6 Hz, 6-C of Py), 164.7 (d, J = 4.4 Hz, 2-C of Py). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ −8.1. HRMS (FAB+): m/z calcd for $C_{34}H_{41}NO_2P$, 526.2875 $[M + H]^+$; found, 526.2875.

Synthesis of L^{CF3}. The compound was prepared by following the synthetic procedure for $\mathbf{L^H}$, using $\mathbf{10^{CF3}}$ (0.507 g, 0.800 mmol, 1.0 equiv) and tris(dimethylamino)phosphine (1.5 mL). Isolation by reprecipitation gave the product as a white solid (0.349 g, 0.579 mmol, 72%). ^1H NMR (400 MHz, $CDCl_3$): δ 0.91 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 0.99 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.19 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 2.33 (sep, J = 6.7 Hz, 2H, CH of ^{i}Pr), 2.83 (sep, J = 6.8 Hz, 1H, CH of ^{i}Pr), 6.95 (s, 2H, *m*-H of Tip), 7.09−7.14 (m, 2H, PyH), 7.43−7.51 (m, 8H, ArH), 7.61−7.57 (m, 1H, PyH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 24.0 (s, CH_3 of ^{i}Pr × 2), 24.2 (s, CH_3 of ^{i}Pr × 2), 30.6 (s, CH of ^{i}Pr × 2), 34.5 (s, CH of ^{i}Pr), 120.9 (s, *m*-C of Tip × 2), 124.1 (q, J = 272.4 Hz, CF_3 × 2), 124.9 (s, 5-C of Py), 125.4 (dq, J = 7.2 and 3.6 Hz, *m*-C of *p*-$CF_3C_6H_4$ × 4), 126.9 (d, J = 24.5 Hz, 3-C of Py), 131.3 (br q, J = 32.4 Hz, *p*-C of *p*-$CF_3C_6H_4$ × 2), 134.5 (d, J = 19.9 Hz, *o*-C of *p*-$CF_3C_6H_4$ × 4), 135.8 (d, J = 5.4 Hz, 4-C of Py), 136.0 (s, *ipso*-C of Tip), 141.2 (d, J = 14.2 Hz, *ipso*-C of *p*-$CF_3C_6H_4$ × 2), 146.2 (s, *o*-C of Tip × 2), 149.1 (s, *p*-C of Tip), 161.0 (d, J = 3.2 Hz, 2-C of Py), 161.7 (d, J = 11.1 Hz, 6-C of Py). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ −5.7. HRMS (FAB+): m/z calcd for $C_{34}H_{35}F_6NP$, 602.2411 $[M + H]^+$; found, 602.2412.

Synthesis of C^HCl. A solution of $Rh_2(OAc)_4$ (0.442 g, 1.00 mmol, 1.0 equiv) and $\mathbf{L^H}$ (0.466 g, 1.00 mmol, 1.0 equiv) in acetic acid (40 mL) was stirred at reflux for 24 h under Ar. After the solvent was removed *in vacuo*, the residue was dissolved with chloroform (50 mL) at room temperature. Saturated NH_4Cl(aq) (100 mL) was added to the solution, and the mixture was stirred at room temperature for 2 h in air. Then, the resulting mixture was extracted with chloroform, and the combined organic layers were washed successively with saturated $NaHCO_3$(aq) and brine. After the solution was dried over Na_2SO_4, the solvent was removed *in vacuo*. The residue was purified successively by washing with diethyl ether/*n*-hexane (1/2) and recrystallizing from dichloromethane/diethyl ether, giving the product as a green solid (0.690 g, 0.780 mmol, 78%). Single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of diethyl ether into a dichloromethane solution of $\mathbf{C^HCl}$. ^1H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, J = 6.6 Hz, 6H, CH_3 of ^{i}Pr), 1.31−1.33 (m, 12H, CH_3 of ^{i}Pr and OAc), 1.40 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 2.09 (s, 3H, OAc), 2.31 (sep, J = 6.5 Hz, 2H, CH of ^{i}Pr), 3.09 (sep, J = 6.8 Hz, 1H, CH of ^{i}Pr), 7.29−7.32 (m, 1H, ArH), 7.32−7.41 (m, 6H, ArH), 7.47−7.51 (m, 3H, ArH), 7.58−7.63 (m, 4H, ArH), 7.84−7.88 (m, 1H, ArH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 22.1 (s, CH_3 of ^{i}Pr × 2), 23.1 (s, CH_3 of OAc × 2), 23.7 (d, J = 3.6 Hz, CH_3 of OAc), 24.0 (s, CH_3 of ^{i}Pr × 2), 26.5 (s, CH_3 of ^{i}Pr × 2), 31.3 (s, CH of ^{i}Pr × 2), 34.7 (s, CH of ^{i}Pr), 121.8 (s, *m*-C of Tip × 2), 127.6 (s, *ipso*-C of Tip), 128.1−128.7 (m, *m*-C of Ph × 4 and *ipso*-C of Ph × 2), 128.4 (br s, 5-C of Py), 130.06−130.14 (m, 3-C of Py), 131.5 (d, J = 2.6 Hz, *p*-C of Ph × 2), 134.4 (d, J = 10.3 Hz, *o*-C of Ph × 4), 135.6 (d, J =

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4.7 Hz, 4-C of Py), 148.6 (s, *o*-C of Tip × 2), 152.5 (s, *p*-C of Tip), 165.8−166.4 (m, 2-C and 6-C of Py), 187.0 (d, J = 4.2 Hz, CO_2 of OAc), 190.9 (s, CO_2 of OAc × 2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 34.1 (dd, J_{P-Rh} = 143.5 and 2.1 Hz). HRMS (FAB+): m/z calcd for $C_{38}H_{45}{}^{35}ClNO_6PRh_2$, 883.0783 $[M]^+$; found, 883.0797.

Synthesis of $C^{OMe}Cl$. The compound was prepared by following the synthetic procedure for $C^{H}Cl$, using $Rh_2(OAc)_4$ (0.177 g, 0.400 mmol, 1.0 equiv), L^{OMe} (0.219 g, 0.416 mmol, 1.0 equiv), acetic acid (16 mL), $CHCl_3$ (40 mL), and saturated NH_4Cl(aq) (50 mL). Isolation by recrystallization gave the product as a green solid (0.270 g, 0.286 mmol, 72%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, J = 6.7 Hz, 6H, CH_3 of ^{i}Pr), 1.32 (d, J = 6.4 Hz, 6H, CH_3 of ^{i}Pr), 1.37 (s, 6H, OAc), 1.40 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 2.09 (s, 3H, OAc), 2.30 (sep, J = 6.5 Hz, 2H, CH of ^{i}Pr), 3.09 (sep, J = 6.5 Hz, 1H, CH of ^{i}Pr), 3.82 (s, 6H, OCH_3), 6.92 (br d, J = 7.6 Hz, 4H, *m*-H of *p*-An), 7.32−7.36 (m, 3H, ArH), 7.46−7.48 (m, 1H, ArH), 7.50−7.55 (m, 4H, ArH), 7.78−7.82 (m, 1H, ArH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 22.2 (s, CH_3 of ^{i}Pr × 2), 23.1 (s, CH_3 of OAc × 2), 23.7 (d, J = 4.2 Hz, CH_3 of OAc), 24.1 (s, CH_3 of ^{i}Pr × 2), 26.5 (s, CH_3 of ^{i}Pr × 2), 31.3 (s, CH of ^{i}Pr × 2), 34.7 (s, CH of ^{i}Pr), 55.5 (s, OCH_3 × 2), 114.3 (d, J = 12.3 Hz, *o*-C of *p*-An × 4), 119.3 (d, J = 62.0 Hz, *ipso*-C of *p*-An × 2), 121.8 (s, *m*-C of Tip × 2), 127.8 (s, *ipso*-C of Tip), 128.1−128.2 (m, 5-C of Py), 129.8−129.9 (m, 3-C of Py), 135.3 (d, J = 5.9 Hz, 4-C of Py), 136.1 (d, J = 11.8 Hz, *o*-C of *p*-An × 4), 148.6 (s, *o*-C of Tip × 2), 152.5 (s, *p*-C of Tip), 162.2 (d, J = 2.8 Hz, *p*-C of *p*-An × 2), 166.2−167.3 (m, 6-C of Py), 167.1 (d, J = 65.3 Hz, 2-C of Py), 186.9 (d, J = 3.8 Hz, CO_2 of OAc), 190.8 (s, CO_2 of OAc × 2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 32.2 (dd, J_{P-Rh} = 142.5 and 2.7 Hz). HRMS (FAB+): m/z calcd for $C_{40}H_{49}{}^{35}ClNO_8PRh_2$, 943.0994 $[M]^+$; found, 943.1003.

Synthesis of $C^{CF3}Cl$. The compound was prepared by following the synthetic procedure for $C^{H}Cl$, using $Rh_2(OAc)_4$ (0.177 g, 0.400 mmol, 1.0 equiv), L^{CF3} (0.248 g, 0.412 mmol, 1.0 equiv), acetic acid (16 mL), $CHCl_3$ (40 mL), and saturated NH_4Cl(aq) (50 mL). Isolation by recrystallization gave the product as a green solid (0.267 g, 0.261 mmol, 65%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.34 (d, J = 6.6 Hz, 6H, CH_3 of ^{i}Pr), 1.36 (s, 6H, OAc), 1.41 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 2.11 (s, 3H, OAc), 2.26 (sep, J = 6.7 Hz, 2H, CH of ^{i}Pr), 3.11 (sep, J = 6.9 Hz, 1H, CH of ^{i}Pr), 7.32−7.35 (m, 1H, ArH), 7.38 (s, 2H, *m*-H of Tip), 7.57−7.59 (m, 1H, ArH), 7.68−7.70 (m, 4H, ArH), 7.78−7.83 (m, 4H, ArH), 7.85−7.90 (m, 1H, ArH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 22.1 (s, CH_3 of ^{i}Pr × 2), 23.3 (s, CH_3 of OAc × 2), 23.7 (d, J = 3.9 Hz, CH_3 of OAc), 24.1 (s, CH_3 of ^{i}Pr × 2), 26.6 (s, CH_3 of ^{i}Pr × 2), 31.5 (s, CH of ^{i}Pr × 2), 34.8 (s, CH of ^{i}Pr), 122.0 (s, *m*-C of Tip × 2), 123.6 (q, J = 272.7 Hz, CF_3 × 2), 125.6 (dq, J = 11.3 and 3.7 Hz, *m*-C of *p*-$CF_3C_6H_4$ × 4), 127.0 (s, *ipso*-C of Tip), 129.0 (br s, 5-C of Py), 130.1−130.2 (m, 3-C of Py), 132.6 (d, J = 54.1 Hz, *ipso*-C of *p*-$CF_3C_6H_4$ × 2), 133.8 (qd, J = 33.1 and 2.3 Hz, *p*-C of *p*-$CF_3C_6H_4$ × 2), 134.9 (d, J = 10.8 Hz, *o*-C of *p*-$CF_3C_6H_4$), 135.8 (d, J = 4.8 Hz, 4-C of Py), 148.6 (s, *o*-C of Tip × 2), 153.1 (s, *p*-C of Tip), 164.5 (d, J = 67.2 Hz, 2-C of Py), 167.3−167.4 (m, 6-C of Py), 187.7 (d, J = 3.9 Hz, CO_2 of OAc), 191.3 (s, CO_2 of OAc × 2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 35.1 (br d, J_{P-Rh} = 145.5 Hz). HRMS (FAB+): m/z calcd for $C_{40}H_{44}{}^{37}ClF_6NO_6PRh_2$, 1022.0580 $[M + H]^+$; found, 1022.0608.

Synthesis of $[C^{H}(MeCN)][BF_4]$. A solution of $C^{H}Cl$ (0.106 g, 0.120 mmol, 1.0 equiv) and $AgBF_4$ (25.3 mg, 0.130 mmol, 1.1 equiv) in acetonitrile (3 mL) was stirred at room temperature for 1 h under Ar. The resulting mixture was filtered through a pad of Celite. The filtrate was evaporated to dryness, and the residue was recrystallized from dichloromethane/diethyl ether to give the product as a blue solid (0.114 g, 0.117 mmol, 98%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, J = 6.7 Hz, 6H, CH_3 of ^{i}Pr), 1.30 (d, J = 6.4 Hz, 6H, CH_3 of ^{i}Pr), 1.38−1.40 (m, 12H, CH_3 of ^{i}Pr and OAc), 2.12 (s, 3H, OAc), 2.26 (sep, J = 6.5 Hz, 2H, CH of ^{i}Pr), 2.41 (s, 3H, CH_3CN), 3.09 (sep, J = 6.8 Hz, 1H, CH of ^{i}Pr), 7.36−7.42 (m, 6H, ArH), 7.51−7.57 (m, 5H, ArH), 7.62−7.66 (m, 2H, ArH), 7.72−7.74 (m, 1H, ArH), 8.22−8.26 (m, 1H, ArH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 3.1 (s, CH_3 of CH_3CN), 21.8 (s, CH_3 of ^{i}Pr × 2), 23.2 (s, CH_3 of OAc × 2), 23.4 (d, J = 3.4 Hz, CH_3 of OAc × 2), 24.0 (s, CH_3 of ^{i}Pr × 2), 26.7 (s, CH_3 of ^{i}Pr × 2), 31.4 (s, CH of ^{i}Pr × 2), 34.8 (s, CH of ^{i}Pr), 116.4 (s, CN of CH_3CN), 121.9 (s, *m*-C of Tip × 2), 125.6 (s, *ipso*-C of Tip), 126.1 (d, J = 55.9 Hz, *ipso*-C of Ph × 2), 129.6 (d, J = 11.3 Hz, *m*-C of Ph × 4), 130.1 (br s, 5-C of Py), 131.5−131.6 (m, 3-C of Py), 132.8 (d, J = 2.6 Hz, *p*-C of Ph × 2), 133.7 (d, J = 10.5 Hz, *o*-C of Ph × 4), 138.2 (d, J = 5.6 Hz, 4-C of Py), 149.0 (s, *o*-C of Tip × 2), 153.2 (s, *p*-C of Tip), 163.1 (d, J = 71.9 Hz, 2-C of Py), 165.6−165.7 (m, 6-C of Py), 187.8 (d, J = 3.8 Hz, CO_2 of OAc), 192.0 (s, CO_2 of OAc × 2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 30.1 (dd, J_{P-Rh} = 138.6 and 3.3 Hz). LRMS (FAB+) m/z calcd for $C_{38}H_{45}NO_6PRh_2$, 848 $[M - CH_3CN - BF_4]^+$); found, 848. Anal. Calcd for $C_{40}H_{48}BF_4N_2O_6PRh_2{\cdot}0.5CH_2Cl_2{\cdot}H_2O$: C, 46.91; H, 4.96; N, 2.70. Found: C, 46.98; H, 4.91; N, 2.53.

Synthesis of $[C^{H}(MeCN)][PF_6]$. The compound was prepared by following the synthetic procedure for $[C^{H}(MeCN)][BF_4]$ using $C^{H}Cl$ (0.106 g, 0.120 mmol, 1.0 equiv), $AgPF_6$ (33.3 mg, 0.132 mmol, 1.1 equiv), and acetonitrile (3 mL). Isolation by recrystallization gave the product as a blue solid (0.121 g, 0.117 mmol, 98%). Single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of diethyl ether into a dichloromethane solution of $[C^{H}(MeCN)][PF_6]$. ^1H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.31 (d, J = 6.5 Hz, 6H, CH_3 of ^{i}Pr), 1.38−1.40 (m, 12H, CH_3 of ^{i}Pr and OAc), 2.12 (s, 3H, OAc), 2.26 (sep, J = 6.5 Hz, 2H, CH of ^{i}Pr), 2.37 (s, 3H, CH_3CN), 3.09 (sep, J = 6.9 Hz, 1H, CH of ^{i}Pr), 7.36−7.42 (m, 6H, ArH), 7.48−7.51 (m, 1H, ArH), 7.53−7.57 (m, 4H, ArH), 7.62−7.65 (m, 2H, ArH), 7.70−7.72 (m, 1H, ArH), 8.14−8.18 (m, 1H, ArH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 3.1 (s, CH_3 of CH_3CN), 21.8 (s, CH_3 of ^{i}Pr × 2), 23.3 (s, CH_3 of OAc × 2), 23.5 (d, J = 2.8 Hz, CH_3 of OAc), 24.0 (s, CH_3 of ^{i}Pr × 2), 26.7 (s, CH_3 of ^{i}Pr × 2), 31.5 (s, CH of ^{i}Pr × 2), 34.8 (s, CH of ^{i}Pr), 116.3 (s, CN of CH_3CN), 121.9 (s, *m*-C of Tip × 2), 125.7 (s, *ipso*-C of Tip), 126.0 (d, J = 56.1 Hz, *ipso*-C of Ph × 2), 129.7 (d, J = 11.4 Hz, *m*-C of Ph × 4), 130.0 (br s, 5-C of Py), 131.5−131.6 (m, 3-C of Py), 132.9 (d, J = 2.6 Hz, *p*-C of Ph × 2), 133.7 (d, J = 10.7 Hz, *o*-C of Ph × 4), 138.1 (d, J = 5.9 Hz, 4-C of Py), 149.1 (s, *o*-C of Tip × 2), 153.3 (s, *p*-C of Tip), 163.2 (d, J = 72.1 Hz, 2-C of Py), 165.7−165.8 (m, 6-C of Py), 187.9 (d, J = 3.6 Hz, CO_2 of OAc), 192.1 (s, CO_2 of OAc × 2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ −144.4 (sep, J_{P-F} = 712.2 Hz, PF_6), 30.1 (dd, J_{P-Rh} = 138.6 and 3.5 Hz). HRMS (FAB+): m/z calcd for $C_{38}H_{45}NO_6PRh_2$, 848.1095 $[M - CH_3CN - PF_6]^+$; found, 848.1073. Anal. Calcd for $C_{40}H_{48}F_6N_2O_6P_2Rh_2{\cdot}H_2O$: C, 45.64; H, 4.79; N, 2.66. Found: C, 45.53; H, 4.73; N, 2.47.

Synthesis of $[C^{H}(MeCN)][SbF_6]$. The compound was prepared by following the synthetic procedure for $[C^{H}(MeCN)][BF_4]$ using $C^{H}Cl$ (0.354 g, 0.400 mmol, 1.0 equiv), $AgSbF_6$ (0.139 g, 0.404 mmol, 1.0 equiv), and acetonitrile (10 mL). Isolation by recrystallization gave the product as a blue solid (0.437 g, 0.388 mmol, 97%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.31 (d, J = 6.5 Hz, 6H, CH_3 of ^{i}Pr), 1.38−1.40 (m, 12H, CH_3 of ^{i}Pr and OAc), 2.12 (s, 3H, OAc), 2.27 (sep, J = 6.6 Hz, 2H, CH of ^{i}Pr), 2.35 (s, 3H, CH_3CN), 3.09 (sep, J = 6.9 Hz, 1H, CH of ^{i}Pr), 7.36−7.42 (m, 6H, ArH), 7.46−7.49 (m, 1H, ArH), 7.53−7.57 (m, 4H, ArH), 7.62−7.66 (m, 2H, ArH), 7.69−7.70 (m, 1H, ArH), 8.09−8.13 (m, 1H, ArH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 3.1 (s, CH_3 of CH_3CN), 21.8 (s, CH_3 of ^{i}Pr × 2), 23.3 (s, CH_3 of OAc × 2), 23.5 (d, J = 2.8 Hz, CH_3 of OAc), 24.1 (s, CH_3 of ^{i}Pr × 2), 26.7 (s, CH_3 of ^{i}Pr × 2), 31.5 (s, CH of ^{i}Pr × 2), 34.8 (s, CH of ^{i}Pr), 116.1 (s, CN of CH_3CN), 121.9 (s, *m*-C of Tip × 2), 125.7 (s, *ipso*-C of Tip), 126.0 (d, J = 55.9 Hz, *ipso*-C of Ph × 2), 129.7 (d, J = 11.4 Hz, *m*-C of Ph × 4), 129.9 (br s, 5-C of Py), 131.4−131.5 (m, 3-C of Py), 132.9 (d, J = 2.7 Hz, *p*-C of Ph × 2), 133.7 (d, J = 10.6 Hz, *o*-C of Ph × 4), 137.9 (d, J = 5.9 Hz, 4-C of Py), 149.1 (s, *o*-C of Tip × 2), 153.3 (s, *p*-C of Tip), 163.3 (d, J = 72.2 Hz, 2-C of Py), 165.8−165.9 (m, 6-C of Py), 187.9 (d, J = 3.5 Hz, CO_2 of OAc), 192.1 (s, CO_2 of OAc × 2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 30.1 (dd, J_{P-Rh} = 138.5 and 3.6 Hz). HRMS (FAB+): m/z calcd for $C_{38}H_{45}NO_6PRh_2$, 848.1095 $[M - CH_3CN - SbF_6]^+$; found, 848.1076. Anal. Calcd for $C_{40}H_{48}F_6N_2O_6PRh_2Sb{\cdot}$

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0.5CH_2Cl_2·H_2O: C, 41.02; H, 4.34; N, 2.36. Found: C, 41.21; H, 4.21; N, 2.28.

Synthesis of [C^{OMe}(MeCN)][SbF_6]. The compound was prepared by following the synthetic procedure for [C^{H}(MeCN)][BF_4] using C^{OMe}Cl (0.142 g, 0.150 mmol, 1.0 equiv), $AgSbF_6$ (53.5 mg, 0.156 mmol, 1.0 equiv), and acetonitrile (4 mL). Isolation by recrystallization gave the product as a blue solid (0.175 g, 0.147 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.31 (d, J = 6.5 Hz, 6H, CH_3 of ^{i}Pr), 1.39 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 1.43 (s, 6H, OAc), 2.10 (s, 3H, OAc), 2.26 (sep, J = 6.5 Hz, 2H, CH of ^{i}Pr), 2.37 (s, 3H, CH_3CN), 3.09 (sep, J = 6.9 Hz, 1H, CH of ^{i}Pr), 3.87 (s, 6H, OCH_3), 7.04−7.06 (m, 4H, m-H of p-An), 7.28−7.34 (m, 4H, o-H of p-An), 7.36 (s, 2H, m-H of Tip), 7.45−7.48 (m, 1H, PyH), 7.64−7.65 (m, 1H, PyH), 8.04−8.09 (m, 1H, PyH). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 3.1 (s, CH_3 of CH_3CN), 21.8 (s, CH_3 of ^{i}Pr × 2), 23.3 (s, CH_3 of OAc × 2), 23.5 (d, J = 2.0 Hz, CH_3 of OAc), 24.1 (s, CH_3 of ^{i}Pr × 2), 26.7 (s, CH_3 of ^{i}Pr × 2), 31.5 (s, CH of ^{i}Pr × 2), 34.8 (s, CH of ^{i}Pr), 55.8 (s, OCH_3 × 2), 115.4 (d, J = 12.5 Hz, m-C of p-An × 4), 116.1−116.7 (m, $ipso$-C of p-An × 2 and CN of CH_3CN), 121.9 (s, m-C of Tip × 2), 125.9 (s, $ipso$-C of Tip), 129.6 (br s, 5-C of Py), 131.0−131.1 (m, 3-C of Py), 135.5 (d, J = 12.1 Hz, o-C of p-An × 4), 137.6 (d, J = 5.7 Hz, 4-C of Py), 149.1 (s, o-C of Tip × 2), 153.2 (s, p-C of Tip), 163.1 (d, J = 2.7 Hz, p-C of p-An × 2), 164.4 (d, J = 71.4 Hz, 2-C of Py), 165.5−165.6 (m, 6-C of Py), 187.7 (d, J = 2.7 Hz, CO_2 of OAc), 191.9 (s, CO_2 of OAc × 2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 28.1 (dd, J_{P-Rh} = 136.6 and 1.8 Hz). HRMS (FAB+): m/z calcd for $C_{40}H_{49}NO_8PRh_2$, 908.1300 [M − CH_3CN − SbF_6]$^+$; found, 908.1345. Anal. Calcd for $C_{42}H_{52}F_6N_2O_8PRh_2Sb$·$CH_2Cl_2$: C, 40.66; H, 4.28; N, 2.21. Found: C, 40.61; H, 4.33; N, 2.19.

Synthesis of [C^{CF3}(MeCN)][SbF_6]. The compound was prepared by following the synthetic procedure for [C^{H}(MeCN)][BF_4] using C^{CF3}Cl (0.204 g, 0.200 mmol, 1.0 equiv), $AgSbF_6$ (68.8 mg, 0.200 mmol, 1.0 equiv), and acetonitrile (5 mL). Isolation by recrystallization gave the product as a blue solid (0.246 g, 0.195 mmol, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (d, J = 6.8 Hz, 6H, CH_3 of ^{i}Pr), 1.32 (d, J = 6.5 Hz, 6H, CH_3 of ^{i}Pr), 1.39 (d, J = 6.9 Hz, 6H, CH_3 of ^{i}Pr), 1.42 (s, 6H, OAc), 2.12 (s, 3H, OAc), 2.24 (sep, J = 6.4 Hz, 2H, CH of ^{i}Pr), 2.41 (s, 3H, CH_3CN), 3.09 (sep, J = 6.9 Hz, 1H, CH of ^{i}Pr), 7.37 (s, 2H, m-H of Tip), 7.55−7.64 (m, 5H, PyH and o-H of p-$CF_3C_6H_4$), 7.73−7.75 (m, 1H, PyH), 7.81−7.83 (m, 4H, m-H of p-$CF_3C_6H_4$), 8.14−8.18 (m, 1H, PyH). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 3.1 (s, CH_3 of CH_3CN), 21.7 (s, CH_3 of ^{i}Pr × 2), 23.3 (s, CH_3 of OAc × 2), 23.5 (d, J = 2.3 Hz, CH_3 of OAc), 24.1 (s, CH_3 of ^{i}Pr × 2), 26.8 (s, CH_3 of ^{i}Pr × 2), 31.6 (s, CH of ^{i}Pr × 2), 34.9 (s, CH of ^{i}Pr), 116.4 (s, CN of CH_3CN), 122.0 (s, m-C of Tip × 2), 123.3 (q, J = 274.1 Hz, CF_3 × 2), 125.1 (s, $ipso$-C of Tip), 126.5 (dq, J = 11.5 and 3.7 Hz, m-C of p-$CF_3C_6H_4$ × 4), 130.0−130.5 (m, $ipso$-C of p-$CF_3C_6H_4$ × 2 and 5-C of Py), 132.1−132.2 (m, 3-C of Py), 134.0−135.1 (m, p-C of p-$CF_3C_6H_4$ × 2 and o-C of p-$CF_3C_6H_4$ × 4), 138.5 (d, J = 5.7 Hz, 4-C of Py), 149.3 (s, o-C of Tip × 2), 153.5 (s, p-C of Tip), 161.7 (d, J = 74.1 Hz, 2-C of Py), 166.1−166.2 (m, 6-C of Py), 188.2 (d, J = 4.1 Hz, CO_2 of OAc), 192.3 (s, CO_2 of OAc × 2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 30.6 (br d, J_{P-Rh} = 141.0 Hz). HRMS (FAB+): m/z calcd for $C_{40}H_{43}F_6NO_6PRh_2$, 984.0837 [M − CH_3CN − SbF_6]$^+$; found, 984.0885. Anal. Calcd for $C_{42}H_{46}F_{12}N_2O_6PRh_2Sb$: C, 39.99; H, 3.68; N, 2.22. Found: C, 39.68; H, 3.73; N, 2.07.

Synthesis of 3. **3** was prepared by a modified procedure described in the literature.[16] A solution of $Rh_2(OAc)_4$ (0.177 g, 0.400 mmol, 1.0 equiv), **1** (0.316 g, 1.20 mmol, 3.0 equiv), and lithium chloride (0.170 g, 4.01 mmol, 10 equiv) in toluene (8 mL) was stirred at reflux for 24 h under Ar. After the mixture was cooled to room temperature, the resulting precipitate was collected by filtration. Then, the product in the obtained solid was extracted with dichloromethane until the washings became colorless. The organic liquid was washed with brine and dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue was washed with diethyl ether to give the product as a pink solid (0.253 g, 0.275 mmol, 69%). CAS registry number: 114411-83-5. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.14 (s, 6H, OAc), 6.91−6.96 (m, 4H, ArH), 7.02−7.06 (m, 2H, ArH), 7.20−7.26 (m, 6H, ArH), 7.43−7.47 (m, 2H, ArH), 7.47−7.57 (m, 6H, ArH), 7.63−7.67 (m, 2H, ArH), 8.14−8.19 (m, 4H, ArH), 9.51−9.53 (m, 2H, ArH). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 22.9 (d, J = 2.6 Hz, CH_3 of OAc × 2), 126.0 (d, J = 54.4 Hz, $ipso$-C of Ph × 2), 127.6 (br s, 5-C of Py × 2), 128.7 (d, J = 10.9 Hz, m-C of Ph × 4), 129.0 (d, J = 10.3 Hz, m-C of Ph × 4), 129.4 (d, J = 50.7 Hz, $ipso$-C of Ph × 2), 131.1 (d, J = 2.6 Hz, p-C of Ph × 2), 131.7 (d, J = 2.7 Hz, p-C of Ph × 2), 132.7 (d, J = 9.1 Hz, o-C of Ph × 4), 134.1−134.2 (m, 3-C of Py × 2), 135.3 (d, J = 9.9 Hz, o-C of Ph × 4), 135.7 (d, J = 5.0 Hz, 4-C of Py × 2), 160.7 (d, J = 10.4 Hz, 6-C of Py × 2), 166.4 (d, J = 71.7 Hz, 2-C of Py × 2), 189.6 (d, J = 3.0 Hz, CO_2 of OAc × 2). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 30.6-31.6 (m). HRMS (FAB+): m/z calcd for $C_{38}H_{34}{}^{35}ClN_2O_4P_2Rh_2$, 884.9792 [M − Cl]$^+$; found, 884.9821. LRMS (FAB+): m/z 885 [M − Cl]$^+$, 850 [M − 2Cl]$^+$. Anal. Calcd for $C_{38}H_{34}ClN_2O_4P_2Rh_2$·$H_2O$: C, 48.59; H, 3.86; N, 2.98. Found: C, 48.87; H, 3.74; N, 2.99.

Synthesis of 11. A solution of **3** (93.9 mg, 0.102 mmol, 1.0 equiv) and $AgSbF_6$ (70.0 mg, 0.204 mmol, 2.0 equiv) in acetonitrile (30 mL) was stirred at room temperature for 2 h under Ar. The resulting mixture was filtered through a pad of Celite. Then, the filtrate was evaporated to dryness *in vacuo* to give the product as an orange solid (0.142 g, 0.101 mmol, 99%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.43 (s, 6H, OAc), 2.37 (s, 6H, CH_3CN), 6.81−6.86 (m, 4H, ArH), 7.32−7.39 (m, 6H, ArH), 7.44−7.52 (m, 6H, ArH), 7.54−7.59 (m, 6H, ArH), 7.62−7.66 (m, 2H, ArH), 7.92−7.97 (m, 2H, ArH), 8.53−8.54 (m, 2H, ArH). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 3.3 (d, J = 1.8 Hz, CH_3 of CH_3CN × 2), 23.2 (d, J = 1.7 Hz, CH_3 of OAc × 2), 119.6 (d, J = 2.3 Hz, CN of CH_3CN × 2), 125.3 (d, J = 53.4 Hz, $ipso$-C of Ph × 4), 129.7 (d, J = 11.4 Hz, m-C of Ph × 4), 130.1 (br s, 5-C of Py × 2), 130.7 (d, J = 10.9 Hz, m-C of Ph × 4), 132.0 (d, J = 9.8 Hz, o-C of Ph × 4), 132.8 (d, J = 2.8 Hz, p-C of Ph × 2), 132.9 (d, J = 2.9 Hz, p-C of Ph × 2), 133.8 (d, J = 10.1 Hz, o-C of Ph × 4), 135.7 (d, J = 7.9 Hz, 3-C of Py × 2), 138.6 (d, J = 5.4 Hz, 4-C of Py × 2), 158.5 (d, J = 9.7 Hz, 6-C of Py × 2), 163.3 (d, J = 75.0 Hz, 2-C of Py × 2), 190.6 (d, J = 3.1 Hz, CO_2 of OAc × 2). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 25.7−26.7 (m). HRMS (FAB+): m/z calcd for $C_{38}H_{34}N_2O_4P_2Rh_2$, 850.0104 [M − 2$CH_3CN$ − 2SbF_6]$^+$; found, 850.0130. Anal. Calcd for $C_{42}H_{40}F_{12}N_4O_4P_2Rh_2Sb_2$: C, 35.93; H, 2.87; N, 3.99. Found: C, 35.65; H, 3.11; N, 3.83.

General Procedure for the Dehydrogenative Silylation of Alcohols with Hydrosilanes. The dehydrogenative silylation of alcohols with hydrosilanes was performed under Ar in a 10 mL Schlenk flask for the reaction at room temperature or a closed system using a 10 mL borosilicate glass screw-top vial sealed by a melamine plastic screw cap with Teflon liner (screw-top test tube, NR-10: Maruemu Corporation) for the reaction with heating. A Rh_2 complex (1.0 μmol, 0.1 mol %) was placed in the reaction vessel and dissolved with a solvent (0.50 or 0.25 mL) under Ar. Then, the vessel was charged successively with an alcohol (1.0 mmol, 1.0 equiv), the solvent (0.50 or 0.25 mL), and a trialkylsilane (1.1 or 1.5 mmol, 1.1 or 1.5 equiv) via syringe. After the resulting mixture was stirred under the reaction conditions indicated in each case (Tables 4 and 5), n-tridecane (0.10 mmol, as an internal standard for GC analysis) and the solvent (4.0−4.5 mL, for dilution) were added to the mixture in atmospheric air. Then, the liquid part was analyzed by GC/FID to determine the GC yield of the product. The isolation of the product was performed by column chromatography on silica gel (eluent: ethyl acetate/n-hexane 1/9) without adding the internal standard. All of the reaction products are known compounds, and the CAS registry numbers and analytical data are given in the Supporting Information.

Computational Details. DFT calculations were performed with the Gaussian 16 (Revision C. 01) program package.[29] All structures were optimized as a singlet state in the gas phase with the ωB97XD functional[30] using the Def2SVP basis set[31] for all atoms. All obtained stationary points were confirmed by frequency calculations at the same level of theory as geometry optimization. Single-point energy calculations of the optimized structures were conducted with the M06-L functional[32] using the Def2TZVP basis set[31] for all atoms. All

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of the calculations shown in Figure 4 and Table 1 were performed in the gas phase, while the results shown in Table 3 were obtained by single-point energy calculations with the SMD solvation model,[33] where dichloromethane was selected as the solvent to consider the results of the Gutmann–Beckett tests and catalytic reactions described above. On the basis of the optimized structure, NBO calculations were performed at the M06-L/Def2TZVP level of theory using the NBO 7.0[34] program in Gaussian 16.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00314.

Crystallographic and additional computational data, characterization data of silyl ethers, and NMR spectra (PDF)

Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 2084570–2084571 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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