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A Chelate Silylene-Silyl Ligand Can Boost Rhodium-Catalyzed C-H Bond Functionalizations

Zhenbo Mo,[+] Arseni Kostenko,[+] Yu-Peng Zhou, Shenglai Yao, and Matthias Driess*

Abstract: *The first N-heterocyclic silylene (NHSi)-silane scaffold LSi-R-Si(H)Mes$_2$* ***1*** *(L = PhC(NtBu)$_2$; -R- = 1,12-xanthendiyl spacer; Mes = 2,4,6-Me$_3$C$_6$H$_2$) was synthesized and used to form the unique rhodium(III) complex (LSi-R-SiMes$_2$)Rh(H)Cl* ***2*** *through its reaction with 0.5 molar equivalents of [Rh(coe)$_2$Cl]$_2$ (coe = cyclooctene). An X-ray diffraction analysis revealed that* ***2*** *has a (Si^{II}Si^{IV})Rh(H)Cl core with three short Rh···H-C contacts with Me groups of the ligand* ***1****, which cause a distorted pentagonal-bipyramidal coordination of the Rh center. Unexpectedly, the reaction of* ***2*** *with ^{t}BuONa yields the novel bis(silyl)hydridorhodium(III) complex* ***4****. Due to the strong donor ability of the chelate Si^{II}-Si^{IV} ligand,* ***2*** *and* ***4*** *can act as highly efficient pre-catalysts in the Rh-mediated selective C-H functionalization of 2-phenylpyridines with C-C-unsaturated organic substrates under mild reaction conditions. A DFT-derived mechanism for the model alkylation reaction of 2-phenylpyridine with ethylene using the pre-catalyst* ***2*** *is presented.*

Ligands can play a decisive role in determining the nature of the active site of catalysts through stabilizing specific oxidation states of metal centers, and defining the size and shape of the catalytic entity.[1] In the wide variety of ligands, strongly electron-donating ligands are among the favorites in the chemists' ligand arsenal. Such ligands can facilitate oxidative addition steps of substrates through enhanced nucleophilicity of the metal center in homogeneous catalysis.[1] In this context, silyl ligands are of particular interest due to their strong σ-donor ability, which generate electron-rich metal sites and concomitantly labilize trans substituents.[2] Thus far, monoanionic silyl ligands that feature pendant donor groups (Chart 1, left) such as phosphine,[3b] pyridine,[3c] quinoline,[3c] olefin,[3d] and *N*-heterocyclic carbenes (NHCs) moieties,[3e,f] have been developed and applied in transition-metal (TM) mediated activation of inert bonds (i.e., H-H, N-H, C-H, N≡N) in catalysis.[3] *N*-Heterocyclic silylenes (NHSis), the heavy analogues of NHCs, represent a new type of stronger σ-donors than NHCs and phosphines that have already been demonstrated to be effective in homogeneous catalysis.[4] Thus, the unique electronic properties of all silicon-based donors prompted us to investigate whether the presence of a silylene and silyl donor in a chelate ligand can boost metal-mediated catalytic transformations of organic substrates. To the best of our knowledge, an intramolecular silylene-silyl ligand remained elusive as yet. Inspired by the ability of the 9,9-dimethylxanthene backbone which enabled the synthesis of an intramolecular silylene borane[5] and a versatile coordination chemistry of the xanthsil ligands developed by Tobita et al.,[6] we attempted the realization of a silyl-functionalized silylene ligand scaffold featuring the 9,9-dimethylxanthene backbone (Chart 1, right).

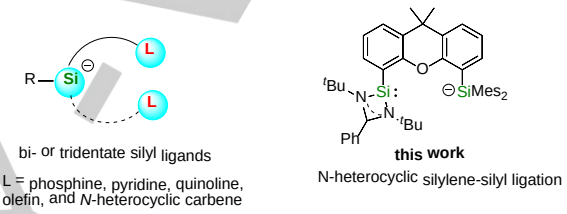

Chart 1. Examples of silyl-functionalized chelate ligands.

C-H bond coordination to a TM center is considered to be a central event in TM-mediated C-H bond activation and functionalization. [7, 8] Important recent advances include the studies of σ-alkane complexes in solutions by time-resolved infrared spectroscopy or in situ NMR spectroscopy, and characterization of σ-alkane, agostic, and anagostic complexes in the solid states by X-ray diffraction techniques.[7,9] TM agostic and anagostic complexes have been considered as possible candidates for catalytic C-H bond functionalization, olefin polymerization, hydrocyclization and more.[10] However, the application of such well-defined TM complexes as (pre)catalyst is scarce. [7]

Herein we report the synthesis and characterization of the first chelate silylene silane LSi-R-SiHMes$_2$ **1** bearing the 9,9-dimethylxanthene spacer and its unexpected ligation properties towards rhodium. Oxidative addition of Rh^I in [RhCl(coe)]$_2$ into the Si-H bond of **1** leads to a pentagonal-bipyramidal Rh^{III} site in (LSi-R-SiMes$_2$)Rh(H)Cl **2** featuring one agostic and two anagostic interactions. Remarkably, **2** exhibits a high catalytic efficiency and selectivity in alkylation of 2-phenylpyridine with norbornene via C-H bond activation under mild reaction conditions. In addition, the selective alkenylation of 2-phenylpyridine with diphenylacetylene could also be achieved. The high activity of **2** surpasses those of previously known rhodium analogues bearing phosphine, NHC, and bis(NHSi) ligands, respectively. DFT calculations revealed that the NHSi-silyl ligand might be the key for the unique performance of the Rh-mediated C-H bond functionalization.

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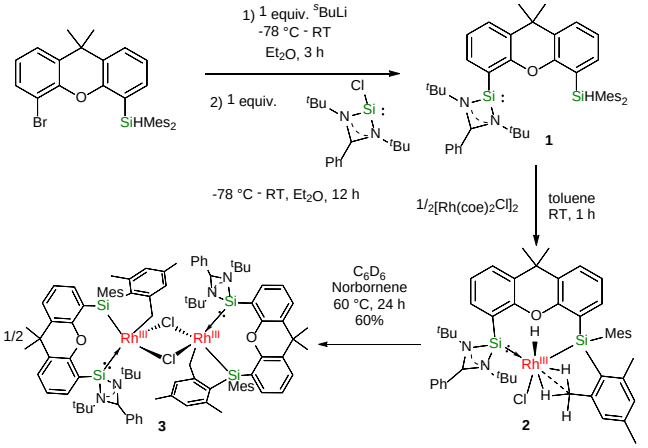

Scheme 1. Synthesis of the silylene-silane **1** and its reaction with $[Rh(coe)Cl]_2$ to give the Rh^{III} complex **2**. coe = cyclooctene.

The silylene-silane **1** is accessible from the corresponding bromosilane precursor via its lithiation and subsequent salt metathesis reaction with one molar equivalent of N,N′-di-tert-butyl(phenylamidinato)-chlorosilylene. It can be isolated as a pale yellow solid in 70% yields in hexane solutions at 0 °C. Its ^{29}Si NMR spectrum features a signal at δ = 13.9 ppm for the silylene group and at δ = -41.1 ppm assignable to the silyl group. The molecular structure of **1** was confirmed by a single-crystal X-ray diffraction analysis (see Fig. S14 in SI), revealing a Si-Si distance of 4.255(1) Å.

As mentioned above, treatment of **1** with 0.5 molar equivalent of $[Rh(coe)_2Cl]_2$ (coe = cyclooctene) in toluene at room temperature leads to (LSi-R-SiMes$_2$)Rh(H)Cl **2** as orange crystals in 64% yields. The diagnostic resonance in the ^1H NMR spectrum at δ = -16.6 ppm with the J_{Rh-H} coupling constant of 27.6 Hz indicates the formation of a RhH moiety. Variable temperature ^1H NMR measurements show that the *o*-CH_3 (mesityl group) proton resonance signal at δ = 2.84 ppm at 298 K splits into four peaks at 213 K, which might be due to the restricted rotation of the mesityl groups at low temperatures. Two ^{29}Si NMR resonances are observed at δ = 33.3 (Si^{II}) and 2.36 (Si^{IV}) ppm with J_{Rh-H} coupling constants of 110.1 and 35.8 Hz, respectively. The solid-state structure of **2** shows a ($Si^{II}Si^{IV}$)Rh(H)Cl core with Rh-Si^{II} and Rh-Si^{IV} distances of 2.2273(7) and 2.3289(6) Å, respectively. Complex **2** is formally a 14e complex without interaction between the Rh and O. Heating of a C_6D_6 solution of **2** at 60 °C in the presence of norbornene as a hydrogen acceptor leads to the formation of the chloride-bridged Rh^{III} dimer **3** via intramolecular C-H bond activation.

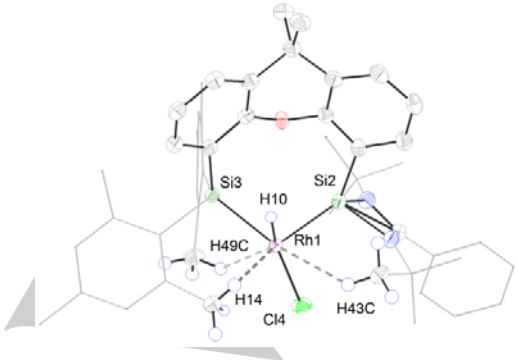

Figure 1. Molecular structure (left) and selected distances (Å) of **2**: Rh1-Si2 2.2273(7), Rh1-Si3 2.3289(6), Rh1-Cl4 2.4060(6), Rh1-H10 1.45(3).

In order to shed more light into the electronic structure and bonding pattern of **2**, quantum chemical calculations were performed. Based on the experimentally determined structure of **2**, a constrained optimization of only the hydrogen atoms was carried out at the RI-ZORA-B3LYP-D3/def2-TZVP level of theory. The constrainedly optimized geometry is only 0.9 kcal mol^{-1} higher in energy than the fully optimized one which is in excellent agreement with the experimentally obtained metric data (see *Supporting Information*). The constrainedly optimized geometry was used for further quantum chemical analyses.

Interestingly, the short distance of 2.634 Å between Rh1 and the mesityl carbon C28 atom implies the presence of an agostic interaction between Rh and the C28-H hydrogen atom. The agostic M-H-C interactions imply relatively short M-H distances of ~1.8–2.3 Å and small M-H-C bond angles of ~90–140°.[11] Thus, the Rh1-H14 distance of 2.018 Å and the Rh1-C28-H14 angle of 111.32° (Table 1) fall in the common geometric range of agostic M-H interactions. In fact, the 'Quantum Theory of Atoms in Molecules' (QTAIM) molecular graph (Figure 1a) displays a bond critical point (BCP) between the H14 and the Rh1 with electron density ρ = 0.046 e Bohr^{-3} and the Laplacian $\nabla^2\rho$ = 0.15 e Bohr^{-5} (Table 1) that are typical of those detected for agostic interactions.[12] The NBO second order perturbation analysis reveals a significant amount of donor-acceptor interactions that are responsible for the Rh1-H14 bonding with the major donations from σ(C-H) to σ*(Rh-Si2) ($E^{(2)}$ = 9.1 kcal mol^{-1}), from σ (Rh-H10) to σ*(C-H) to ($E^{(2)}$ = 4.7 kcal mol^{-1}) and from the σ(Rh-Si3) and σ(Rh-H10) to the extra-valence-shell orbitals of H14 ($E^{(2)}$ = 7.0, 6.4) kcal mol^{-1}.

Table 1. Calculated parameters of the Rh1 agostic and anagostic interactions.

H	r(Rh1-H) Å	α(Rh-H-C) (deg)	ρ (e Bohr^{-3})	$\nabla^2\rho$ (e Bohr^{-5})
H14	2.018	111.32	0.046	0.15
H43C	2.825	129.59	0.010	0.03
H49C	2.702	136.11	0.012	0.03

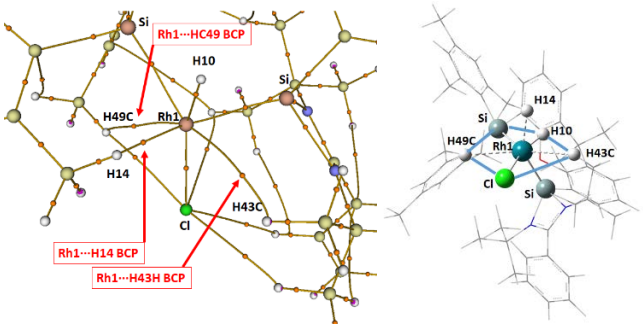

Figure 2. (a) QTAIM molecular graph of **2** focusing on the Rh-H interactions at B3LYP/def2-TZVP level of theory, based on constrained optimization of hydrogen atoms of the X-ray structure of **2** at RI-ZORA-B3LYP-D3/def2-TZVP level of theory. BCPs are shown in orange. (b) The pentagonal-bipyramidal geometry of **2**. The pentagonal plane is highlighted with blue lines.

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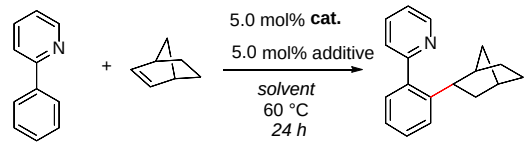
Furthermore, QTAIM calculations show two additional BCPs associated with the Rh1-H43C and Rh1-H49C contacts (Figure 1a) with ρ = 0.010 e Bohr^{-3}, $\nabla^2\rho$ = 0.03 e Bohr^{-5} and ρ = 0.012 e Bohr^{-3}, $\nabla^2\rho$ = 0.03 e Bohr^{-5}, respectively. With r(Rh1-H43C) = 2.825 Å, α(Rh1-H43C-C43) = 129.59° and r(Rh1-H49C) = 2.825 Å, α(Rh1-H49C-C49) = 136.11° (Table 1), these contacts fall in the range of anagostic interactions that are characterized by relatively long M-H distances of ~2.3–2.9 Å and large M–H–C bond angles of ~110–170°.[11] The NBO analysis shows only weak donor acceptor interactions that comprise the Rh1-H43C and Rh1-H49C contacts with total $E^{(2)}$ of 13.2 and 3.5 kcal mol^{-1}, respectively (see the full description in *Supporting Information*).

With its four substituents (Si3, Si4, Cl and H10), one agostic (H14) and two anagostic (H43C, H49C) interactions, the Rh center in **2** adopts a distorted pentagonal-bipyramidal geometry, with H10, Si3, H49C, Cl and H43C lying in the pentagonal plane and H13, Si2 in the axial positions (Figure 1b). The readiness of **2** to interact with C-H bonds in agostic and anagostic manners can promote reactions that involve C-H bond activation as discussed below.

Table 2. Catalytic performance of various Rh complexes in the alkylation of 2-phenylpyridine with norbornene.[a]



Entry	catalyst	solvent	additive	yield[b]
1	**2**	C_6D_6	^{t}BuONa	84
2	$Rh(PPh)_3Cl$	C_6D_6	-	<5
3[c]	$[Rh(coe)_2Cl]_2/PPh_3$	C_6D_6	-	nd
4	$[Rh(coe)_2Cl]_2$/IPr	C_6D_6	-	35
5	$[Rh(coe)_2Cl]_2$/IPr	C_6D_6	^{t}BuONa	15
6	$[Rh(coe)_2Cl]_2$/NHSi	C_6D_6	-	nd
7	**2**	C_6D_6	-	nd
8	**2**	d_8-THF	^{t}BuONa	25
9[d]	**2**	C_6D_6	^{t}BuONa/Hg	80
10	**4**	C_6D_6	-	85

[a] Reaction conditions: Rh complexes (5 mol%), 2-phenylpyridine (0.1 mmol), and norbornene (0.2 mmol) in 0.5 mL solvent. [b] Yield is based on 2-phenylpyridine determined by ^{1}H NMR using ferrocene as internal standard. [c] 0.05 mmol $[Rh(coe)_2Cl]_2$ and 0.03 mmol PPh_3 were used, nd (not detectable). [d] 40 mmol Hg was added. IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), NHSi = bis(NHSi)xanthene ligand, see ref.8b.

Since the pioneering work of Murai and coworkers,[13] TM-mediated C-H bond functionalization has become a useful method in natural product and drug synthesis driven by the ubiquity of C-H bonds.[14] However, most of the known systems generally need high temperature and strong oxidants as additives.[15] The strongly electron donating NHSi-silyl ligand scaffold present in **2** prompted us to study whether C-H bond activation steps and subsequent functionalization could be achieved under milder reaction conditions. Choosing 2-phenylpyridine and norbornene as standard substrates the catalytic alkylation competency of **2** with other related rhodium complexes bearing phosphine, NHC, and NHSi ligands (Table 2) was compared. In fact, **2** proved to be an efficient pre-catalyst for alkylation of 2-phenylpyridine with norbornene in the presence of ^{t}BuONa as an additive at 60 °C, affording the corresponding ortho-monoalkylated product in 84% yield after 24 hours (Table 1, entry 1). In sharp contrast, the analogous reactions applying $Rh(PPh_3)_3Cl$ or the combination of $[Rh(coe)_2Cl]_2$ with different ligands such as PPh_3, and IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) as pre-catalysts furnished the desired product in much lower yields at 60 °C (Table 1, entries 2-5).

Recently, our group reported the synthesis of the corresponding chelating bis(NHSi)xanthene ligand, which is a strikingly efficient ligand in nickel-catalyzed hydrogenation of olefins.[8b] However, under similar reaction conditions, the combination of $[Rh(coe)_2Cl]_2$ with bis(NHSi)xanthene ligand was ineffective in promoting C-H bond alkylation (Table 1, entry 6). We assume that the higher catalytic activity of **2** stems from the more effective donor ability of the NHSi-silyl ligand. This strong effect of the ligand scaffold **1** in alternation of the catalytic activity of the Rh catalyst points to the nature of the active catalytic species in the C-H bond alkylation. High-valent late transition metals, that are known to be highly active in catalytic functionalization by C-H bond activation such as Pd^{II}, Rh^{III}, Ir^{III} and Ru^{II} typically react via an electrophilic pathway that requires a catalyst to be rather electron-poor.[16] In contrast, similar metal sites in lower oxidation state such as Rh^I and Ir^I typically react via oxidative addition with C–H bonds, which is facilitated through the presence of strong donor ligands that increase the electron-density at the metal center (e.g., phosphines or NHCs).[16] Thus, the catalytic activity through the presence of the strong σ-donor NHSi-silyl ligand **1** is a key factor to achieve the good performance of the rhodium catalyst for the alkylation of 2-phenylpyridine and may indicates that the active catalyst contains low-valent Rh^I.

Furthermore, we probed the influence of the additive (base) and solvent on the reaction progress. Without addition of ^{t}BuONa, **2** is incapable of promoting C-H bond alkylation. As we discuss below, the addition of a base may facilitates the formation of the catalytically active Rh^I species. The different performance of **2** in C_6D_6 and THF suggests the importance of the nature of solvent in stabilizing the catalytic intermediates. In THF, the reaction proceeds with lower yields, i.e. 25% vs. 84% in toluene (Table 2, Entry 1 and 8). This observation is also concurrent with the conclusion that the active catalytic species is Rh^I that operates via oxidative addition into C-H bond, rather than Rh^{III} operating in a electrophilic pathway. Control experiments showed the addition of mercury does not affect the reaction yield in accordance with a homogenously catalyzed process.[17]

Encouraged by the high catalytic activity of **2** in alkylation of 2-phenylpyridine, we examined its ability with other substituted arylpyridines; it turned out that the corresponding monoalkylated products are produced in good yields of 80-86% (Scheme S1). In addition to the reactions with norbornene, selective alkenylation of 2-phenylpyridine with diphenylacetylene could also be achieved, affording an ortho-monoalkenylated product in 82% yields. To our delight, a pyrazole group can also serve as a directing group to produce monoalkenylated and monoalkylated products but in somewhat lower yields.

In order to shed light on the mechanism for the C-H bond functionalization with **2**, stoichiometric reactions of **2** with ^{t}BuONa were carried out. The reaction of **2** with ^{t}BuONa in THF occurred immediately at room temperature with the formation of the bis(silyl)HRh^{III} complex **4** in 65% isolated yields (Scheme 2).[19] The ^{1}H NMR spectrum of **4** in C_6D_6 displays six sets of singlets for the methyl of mesityl groups due to

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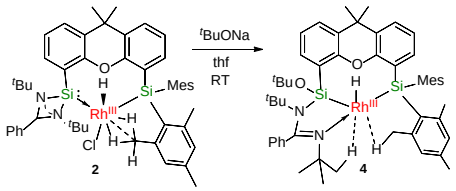
the restricted rotation of the mesityl groups. The ^{29}Si NMR spectrum of **4** reveals two resonance signals at δ = 9.1 and 2.9 ppm, one at lower-field (δ = 9.1 ppm) is downfield shifted compared with that of **2**. A single-crystal X-ray diffraction analysis reveals that the central structural motive of **4** features a distorted tetrahedral ($Si^{II}Si^{IV}$)Rh(H)N core with Rh-Si^{IV} distances of 2.3131(8) and 2.2273(8) Å, respectively, (see Figure S16).



Scheme 2. Synthesis of **4** from the reaction of 2 with tBuONa..

One possible rout to complex **4** is outlined in Scheme 2, migration of imine from silicon to rhodium could be followed by 1,2-shift of tert-butoxide group from rhodium to silicon. Testing the catalytic performance of the **4** revealed that it has very similar catalytic activity to that of **2** in the reaction of 2-phenylpyridine with norbornene. In situ ^{1}H-NMR studies on the catalytic reactions also proved the formation of **4** as an intermediate in the catalytic process. For oxidant free rhodium-catalyzed C-H bond functionalization, Rh^I species is always proposed to be the catalytic active species.[14] We supposed that **4** might undergo Si-O bond activation, via a ^{t}BuOH elimination, to form an olefin stabilized Rh^I intermediate **A** (Scheme S3). Such cleavage reactions of Si-O bonds of silyl ligands to form silylene complexes were proposed by Ogino, Tilley, and Braun et al.[19] The routes of formation of the proposed catalytically active Rh^I intermediate from **2** and **4** are presented in Scheme S3. A tentative calculated mechanism of model catalytic alkenylation reaction of phenylpyridine with ethylene using the Rh^I intermediate **A** is shown in Scheme S4. Attempts to detect these genuine catalytically active species were hitherto unsuccessful.

In summary, the reaction of the first chelate NHSi-silane **1** with $[Rh(coe)_2Cl]_2$ led to the unusual rhodium(III) complex (LSi-R-$SiMes_2$)RhHCl **2** featuring one agostic and two anagostic Rh-H-C interactions. Notably, **2** can boost the selective catalytic alkenylation and alkylation of a C-H bond in the 3-position of 2-phenylpyridine with high catalytic efficiency under relatively mild reaction conditions. Reactivity investigations on the pre-catalyst **2** towards ^{t}BuONa furnished the new agostic bis(silyl) hydridorhodium(III) complex **4**, which is likely to act as intermediate in the catalytic transformations. The high catalytic activity of **2** surpasses those of related rhodium complexes bearing phosphines, NHCs and bis(NHSis) as supporting ligands. The promising steering potential of this new type of strong σ-donor NHSi-silyl scaffold is expected to open new doorways in other catalytic transformations of organic substrates.

Keywords: *N*-Heterocyclic Silylene • DFT Calculations • Agostic Complex • Alkenylation • Atoms in Molecules

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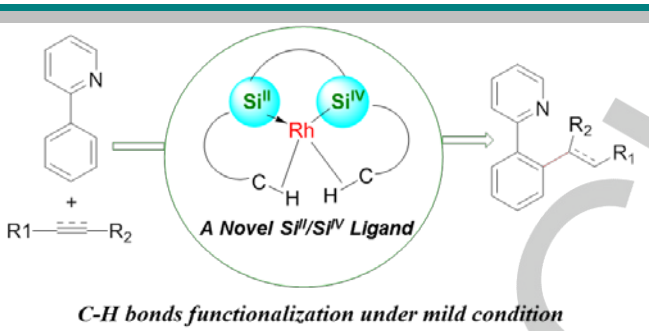
A pentagonal- bipyramidal rhodium(III) complex featuring one agostic and two anagostic interactions with a novel Si^{II}-Si^{IV} ligand has been synthesized, which can be used as pre-catalyst for alkenylation and alkylation of C-H bonds with high catalytic efficiency under mild reaction conditions.



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A Chelate Silylene-Silyl Ligand Can Boost the Rhodium-Catalyzed C-H Bond Functionalizations