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Silacyclopropylideneplatinum(0) Complex as a Robust and Efficient Hydrosilylation Catalyst

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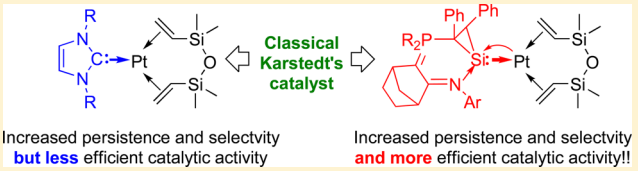
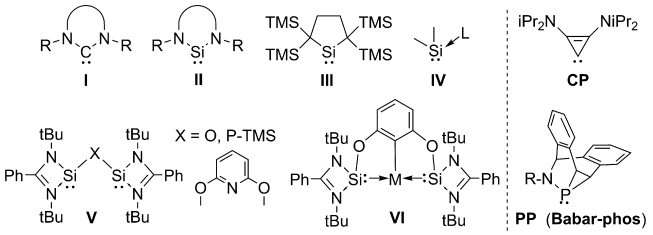
Supporting Information

ABSTRACT: The base-stabilized silacyclopropylidene **1** behaves as a versatile strongly nucleophilic ligand toward transition metals. The strong silylene−metal binding related to both increased σ-donating and π-accepting character of silylene **1** compared to N-heterocyclic carbenes (NHCs) allowed the synthesis of robust and air-stable silylene complexes. Of particular interest, the corresponding platinum(0) complex **6** exhibits high stability and a high level of selectivity and catalytic activity in hydrosilylation reactions that is superior to that of the related NHC-Pt^0 complexes.



INTRODUCTION

The development of new ligands for transition metals is obviously the key to improving further catalysis. Stable carbenes, especially N-heterocyclic carbenes (NHCs, **I**), have become a prominent class of ligands for transition-metal-based catalysts.[1] In marked contrast, their heavier analogues, stable silylenes (**II** and **III**),[2] present much higher reactivity and less coordinating ability.[3] Therefore, they often react with common metal precursors through M−X insertion reactions or MX_2 reduction, hampering their use as ligands.[4] The stability and nucleophilic character of silylenes can be improved by forming donor adducts (**IV**), which make it realistic to use silylenes as ligands[5] and actually allows the number of available stable silylene complexes to increase.[6,7] Furthermore, Driess et al. focused on bidentate and pincer architectures (**V** and **VI**) to overstep these limitations and trigger new catalytic reactions.[8] Nevertheless, stable monodentate silylene ligands, useful for the synthesis of robust transition-metal complexes, with potential applications in catalysis, are still very scarce.[9]



Ligands featuring a three-membered cyclic structure such as cyclopropylidene carbenes (CP)[10,11] and phosphiranes (Babar-phos PP)[12] present a unique combination of steric and electronic properties. The CP ligand shows high coordination abilities because of its acute carbene angle, which helps it to easily approach the metal. Moreover, it is much more nucleophilic than NHCs **I**.[13] In contrast, phosphirane ligands present weak σ-donating and enhanced π-accepting character.[12] The great s character of the phosphorus lone pair, owing to small bond angles (Σ_P° = 247°), increases the resistance to oxidation.[11,14] The small cyclic structure also leads to an enhanced π-accepting character, which makes them interesting ligands for hydrosilylation and hydroboration catalysts.[14] We have recently reported the synthesis of a donor-stabilized silacyclopropylidene **1** featuring a small polycyclic structure similar to that of PP developed by Grützmacher et al.[15] However, silylene **1** shows greater reactivity toward electrophiles compared to phosphiranes PP,[16,17] in agreement with a stronger electron-donating character. Here we report for the first time the use of silacyclopropylidene **1** as a robust and versatile ligand for transition metals. Of particular interest, the peculiar electronic properties of **1** allow the preparation of highly robust and efficient new hydrosilylation catalysts, highlighted by the superior catalytic activity of silacyclopropylideneplatinum(0) complex **6** compared to the classical Karstedt catalyst.

RESULTS AND DISCUSSION

One established method for measuring the electron-donor ability of ligands L is based on the carbonyl stretching frequencies of easy-to-handle *cis*-[RhCl(CO)$_2$L] complexes.[11b] Therefore, silacyclopropylidene **1** was reacted with 0.5 equiv of [RhCl(COD)]$_2$, leading to the corresponding rhodium(I) complex **2**, which was isolated as air-stable and thermally

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robust yellow crystals.[18] The ^{29}Si NMR spectrum displays a doublet signal with a typical large Rh−Si coupling constant [−50.8 ppm ($^{1}J_{SiRh}$ = 104.5 Hz)], indicating a direct Si−Rh interaction. The molecular structure of **2** was unambiguously confirmed by X-ray diffraction analysis (Figure 1). The related rhodium(I) dicarbonyl complex **3** was obtained quantitatively by bubbling carbon monoxide (CO) gas through a tetrahydrofuran (THF) solution of **2** (Scheme 1).

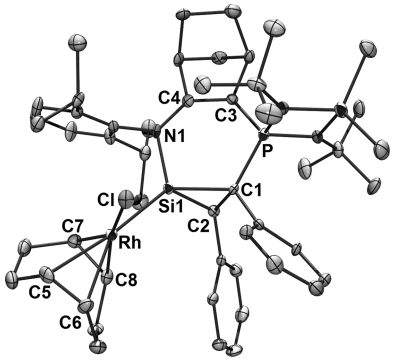
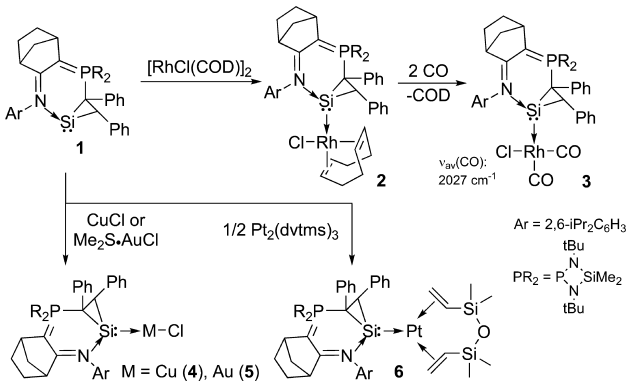


Figure 1. Molecular structure of complex **2**. Thermal ellipsoids represent 30% probability. Solvent molecules and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−Si1 2.334(2), Rh−C5 2.106(5), Rh−C6 2.127(6), Rh−C7 2.251(6), Rh−C8 2.217(5), Rh−Cl 2.390(2), P−C3 1.728(5), C1−P 1.777(5), Si1−C1 1.954(5), Si1−C2 1.884(5), C1−C2 1.599(6), Si1−N1 1.828(4), C3−C4 1.372(7), C4−N1 1.368(6); C1−Si1−C2 49.2(2), Si1−C2−C1 67.7(2), Si1−C1−C2 63.1(2), Si1−C1−P 118.7(2), N1−Si1−C2 102.8(2), N1−Si1−C1 105.2(2).

Scheme 1. Synthesis of Rhodium(I), Copper(I), Gold(I), and Platinum(0) Complexes 2−6 Featuring a Silacyclopropylidene Ligand (dvtms = Divinyltetramethyldisiloxane)



The IR spectrum of **3** shows the characteristic CO stretching frequencies with an average value of 2027 cm^{-1}, which suggests that silacyclipropylidene **1** has a donor capability superior not only to classical NHCs (2036−2060 cm^{-1}) but also to cyclic alkylaminocarbenes (CAAC; 2036 cm^{-1}) and cyclopropylidene (CP; 2031 cm^{-1}).[11b,20,21] The donor strength of **1** corresponds to those of abnormal NHCs (2025−2032 cm^{-1}).[22] This experimental observation is consistent with density functional theory (DFT) calculations, which demonstrate that the highest occupied molecular orbital (HOMO) energy level of **1** (−4.00 eV) is higher than those of NHC, CAAC, and CP (−4.44, −4.28, and −4.10 eV, respectively, in Figure 2). As expected, **1** is much more strongly nucleophilic than other silylenes substituted by electronegative π donors (N and O) such as NHSi (HOMO, −4.56 eV). In addition, its π-accepting character (lowest unoccupied molecular orbital LUMO+7, 0.50 eV) is superior to those of NHSi (LUMO+2, 0.67 eV) and NHC (LUMO+1, 1.00 eV). The remarkably enhanced electrophilic character of **1** can be attributed to the ring strain of the three-membered ring, similar to the case of phosphiranes PP. Indeed, both nonbonding (HOMO) and vacant (LUMO +7) orbitals of **1** are significantly lowered relative to those of the related acyclic analogue **1′** (HOMO, −3.36 eV; LUMO+9, 1.15 eV; Figure 2).

The potential usefulness of silacyclopropylidene **1** as an ancillary ligand was demonstrated by the selective formation of **1** → M−Cl complexes [M = Cu (**4**), Au (**5**)], which are particularly difficult to synthesize because of the easy silylene insertion into the M−Cl bond.[23,24] Complexes **4** and **5** were obtained in nearly quantitative yields (98 and 92%, respectively) by the reaction of **1** with CuCl and Me_2S·AuCl, respectively (Scheme 1). The ^{29}Si NMR spectrum of gold(I) complex **5** shows a resonance at lower field (−28.8 ppm) than that of copper(I) complex **4** (−51.1 ppm). X-ray diffraction analysis of both complexes reveals monomeric structures with essentially linear geometries (Si−M−Cl angle = 179° for **4** and 178° for **5**; Figure 3a,b).[25] The Si−Cu bond length [2.191(2) Å] is similar to those observed for previously reported cationic base-stabilized silylene-Cu^{I} complexes (2.17−2.20 Å).[26] The Si−Au bond length [2.246(1) Å] is similar to those observed for other donor-stabilized silylene-AuCl complexes (2.246−2.265 Å).[27] The extreme steric bulk of ligand **1** is clearly indicated by the space-filling representation of complex **4** (Figure 3c). Of particular interest, copper(I) complex **4** is robust enough to be used as a catalyst for the hydrosilylation of bulky ketones such as 1-adamantyl methyl ketone, in which the catalyst activity is directly related to the steric bulk provided by the ligand (Figure 3).[28] Copper(I) complex **4** is considerably more active than the corresponding Ph_3P-Cu^{I} complex and is as efficient as those with an extremely bulky bowl-shaped phosphine ligand (BSP-2), developed by Tsuji et al. (Figure 4).[29]

Silacyclopropylidene **1** also readily reacts at room temperature (RT) with 0.5 equiv of Karstedt complex [Pt_2(dvtms)$_3$] to afford the corresponding air-stable platinum(0) complex **6** (Scheme 1). The ^{29}Si resonance of **6** appears at lower field (δ = −24.4 ppm) compared to the free silylene **1** (δ = −87.4 ppm), similar to the case of gold(I) complex **5**. The ^{13}C NMR spectrum of **6** reveals signals for the vinyl groups at significantly high field [δ = 36.0 ppm, J_{C-Pt} = 51.0 Hz (CH), and 41.4 ppm (CH_2)] compared to those of the Karstedt complex (56.4−58.4 ppm),[29] which is in good agreement with the strong electron-donating character of the silacyclopropylidene ligand **1**. Indeed, these values are similar to those observed for NHC−Karstedt complex **7** (34.5−41.2 ppm)[30] rather than those of platinum(0) complexes with phosphine ligands (46.6−52.5 ppm).[31] The molecular structure of **6** shows a classical trigonal-planar arrangement around the Pt atom (Figure 5). The Si^{II}−Pt^{0} bond length [2.302(1) Å] is significantly longer than those observed for previously reported platinum(0) complexes with a base-free silylene ligand (2.207−2.212 Å),[32,33] suggesting a weak Pt═Si character. In agreement with the NMR data, the high electron density on the metal center, resulting from the strong Si → Pt donation is also indicated by the slightly short Pt−olefin distances [2.122(5)−2.150(5) Å] compared to the Karstedt complex (2.160−2.207 Å)[29] and to related R_3P−Pt(dvms)

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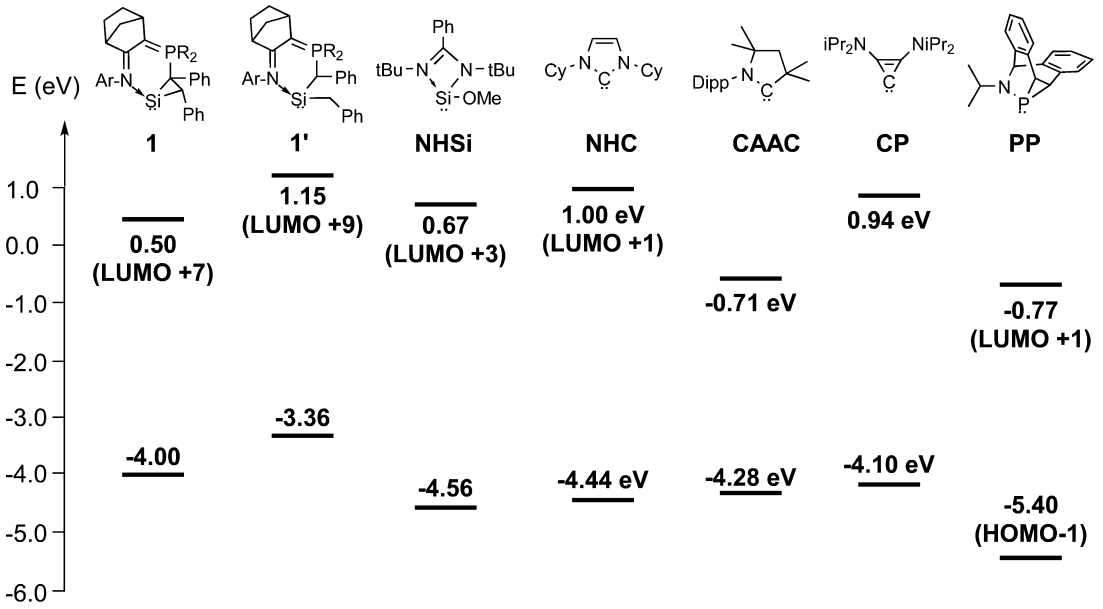


Figure 2. Calculated HOMO and LUMO energy levels of some donor-stabilized silylenes (**1**, **1′**, and NHSi), of carbenes (NHC, CAAC, and CP), and of a phosphirane (PP).

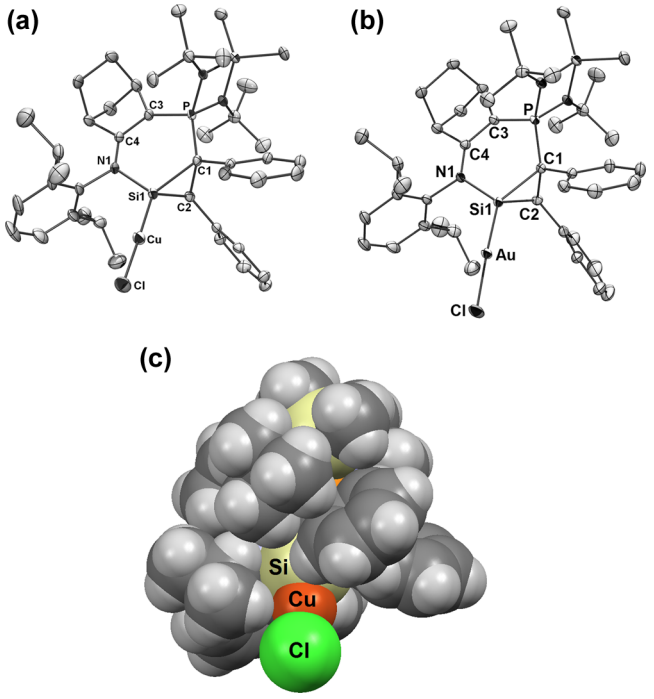
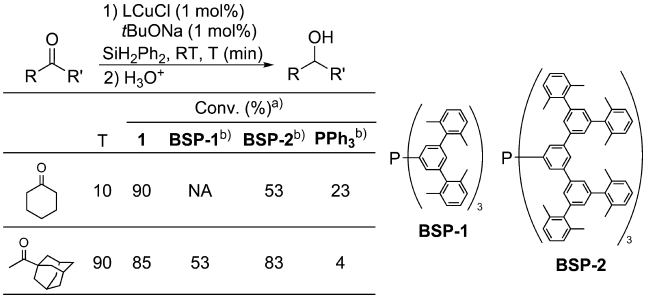


Figure 3. Molecular structure of complexes **4** (a) and **5** (b) and a space-filling representation of complex **4** (c). Selected bond lengths (Å) and angles (deg) for **4**: Si1−Cu 2,191(2), Cu−Cl 2,123(2), Si1−C1 1,941(4), Si1−C2 1,870(4), C1−C2 1.602(6), Si1−N1 1.783(4), C3−P 1,734(4); C1−Si1−C2 49.68(17), N1−Si1−C1 106.89(17), N1−Si1−C2 106.84(18), Si1−Cu−Cl 178.79(6). Selected bond lengths (Å) and angles (deg) for **5**: Si1−Au 2.246(1), Au−Cl 2.333(1), Si1−C1 1.918(2), Si1−C2 1.861(3), C1−C2 1.608(3), Si1−N1 1.766(2), C1−P 1.788(2); C1−Si1−C2 50.33(2), N1−Si1−C1 110.02(10), N1−Si1−C2 109.43(11), Si1−Au−Cl 177.61(3).

complexes [R = ArO, 2.155−2.187 Å;[34] R = tol, 2.124−2.160 Å).[31] Nevertheless, they are longer than those observed for NHC-Pt(dvms) **7** (2.114−2.132 Å)[30] probably because of the greater π-back-donation in **6** (Pt → Si) than in **7** (Pt → C_{NHC})



	T	Conv. (%)[a] 1	BSP-1[b]	BSP-2[b]	PPh_3[b]
	10	90	NA	53	23
	90	85	53	83	4

Figure 4. Hydrosilylation of ketones catalyzed by copper(I) complexes with different ligands (L = **1**, BSP-1,2, and PPh_3): (a) conversions determined by GC; (b) ref 28.

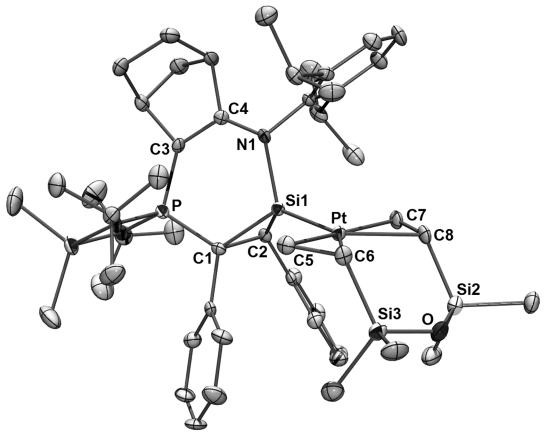


Figure 5. Molecular structure of complex **6**. Selected bond lengths (Å) and angles (deg) Thermal ellipsoids represent 30% probability. Solvent molecule and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt−Si1 2.3015(15), Pt−C5 2.120(5), Pt−C6 2.150(5), Pt−C7 2.136(5), Pt−C8 2.150(5), C5−C6 1.426(7),C7−C8 1.434(7), Si1−C2 1.887(5), Si1−C1 1.982(5) Si1−N1 1.823(4), N1−C4 1.358(6), C3−C4 1.381(6), P−C3 1.716(5), P−C1 1.763(5), N1−Si1−C2 101.0(2), N1−Si1−C1 106.1(2), C2−Si1−C1 48.89(19).

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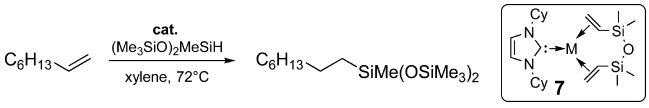
with a poorly electron-accepting NHC ligand. Indeed, DFT calculations indicate the thermally more favored formation of complex **6** than **7** (ΔE = −56.4 and −54.2 kcal/mol, respectively) and a greater stabilization energy gained by the M → L π-back-donation energy for **6** ($E_{M\rightarrow L}$ = −4.6 kcal/mol) than for **7** ($E_{M\rightarrow L}$ = −2.4 kcal/mol).[19]

Hydrosilylation of alkenes using platinum-based catalysts is one of the most important industrial applications of homogeneous catalysis.[34] Karstedt's complex is the most active catalyst currently used in the silicon industry, although it suffers from a few drawbacks, such as a number of side reactions and the formation of colloidal platinum species, causing undesired coloration and decreasing catalytic activity.[35] Markó et al. demonstrated that the use of Karstedt derivatives with a NHC ligand led to a dramatic improvement of the catalyst's stability and the selectivity of the reaction.[36] Nevertheless, these NHC-Pt^0 complexes are less active than the original Karstedt catalyst (Karstedt vs complex **7**; Table 1). Although the increasing bulkiness and π-accepting character of NHC ligands improve their performance, the catalytic activity of the NHC-Pt^0 complexes has never surpassed that of the original one.[30] In contrast, hydrosilylation of 1-octene catalyzed by the silacyclopropylidene complex **6** (30 ppm) is as fast as that with the Karstedt catalyst (>95% conversion = 20 vs 15 min) and proceeds in a more selective manner (isolated yield = 91% vs 78%; Table 1). With a catalyst loading of 3 ppm, the performances of the two complexes remain very similar. However, the most striking feature appears with the very low catalyst loading of 0.3 ppm, for which complex **6** is much more active than the Karstedt catalyst. Under these conditions, which require extended reaction time, a considerable decrease of the Karstedt catalyst efficiency has been observed, probably because of its degradation. Furthermore, in all cases, no colloidal platinum species have been visually observed during the reaction. These results clearly demonstrate the durability and high catalytic performance of the silacyclopropylidene complex **6**.

Table 1. Hydrosilylation Reactions of 1-Octene in the Presence of Karstedt's Catalyst and Complexes 6 and 7[a]



catalyst	catalyst (mol %)	T	conv (%)[b]	TOF (10^4 h^{-1})[c]	yield (%)[d]
Karstedt[d]	3×10^{-3}	15 min	>95	14.0	78
7[d]	3×10^{-3}	3 h			96
6	3×10^{-3}	20 min	>95	9.5	91
Karstedt	3×10^{-4}	4 h	>95	7.9	91
6	3×10^{-4}	4 h	>95	7.9	90
Karstedt	3×10^{-5}	24 h	50	6.9	48
6	3×10^{-5}	24 h	86	11.9	81

[a]Reaction conditions: 1-octene, 1.85 mmol; silane, 1.85 mmol; xylene, 1 mL. [b]Conversions were determined by ^{1}H NMR and GC. [c]With respect to the total reaction time. [d]Isolated yields. [e]Ref 36a.

These high catalytic performances can be related to the strong ligand−metal binding in **6**, which provides better protection to the highly reactive metallic species. Moreover, the higher steric congestion around the metal center provided by ligand **1** compared to NHCs (tricoordinate Si^{II} sp^3 center vs dicoordinate carbene sp^2) should promote the dissociation of other ligands to generate the active vacant sites. This effect, probably in addition to the enhanced π-accepting character of **1**, should also accelerate the olefin dissociation, providing a coordination site, as well as the reductive elimination, which is the rate-determining step in the Chalk−Harrod mechanism.[37]

CONCLUSION

In conclusion, we have successfully demonstrated that the stable silacyclopropylidene **1** is a versatile ligand with enhanced σ-donating and π-accepting properties, compared to those of NHCs, and, in addition, is able to bring an important bulk around the metal center. These features allow the synthesis of robust transition-metal complexes displaying, in some cases, high catalytic activity. Of particular interest, the corresponding platinum(0) complex **6** exhibits a high level of performance (durability, selectivity, and catalytic activity) in hydrosilylation reactions, superior to those of the classical Karstedt catalysts. Detailed mechanistic studies and other applications of the silacyclopropylidene ligand **1** in catalysis are under active investigation.

EXPERIMENTAL SECTION

General Consideration. All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were recorded on Avance 300 spectrometers, and the ^{195}Pt spectrum was recorded on an Avance 500 spectrometer. ^{1}H, ^{29}Si, and ^{13}C NMR chemical shifts are reported in ppm relative to CH_4Si as the internal standard. ^{31}P NMR downfield chemical shifts are expressed in ppm relative to 85% H_3PO_4. IR spectra were obtained as KBr pellets with a Varian 640-IR Fourier transform infrared spectrophotometer. The product **1** was synthesized as previously reported.[15]

*Silacyclopropylidene-Rh^{I}ClCOD Complex (**2**).* To a flask containing **1** (60.0 mg, 0.085 mmol) and the dimeric $[RhClCOD]_2$ (20.7 mg, 0.048 mmol) was added THF (1 mL) at RT. After stirring for 5 min at RT, all of the volatiles were removed under vacuum to give the analytically pure **2** as a yellow powder. Crystals of compound **2** suitable for X-ray diffraction analysis were obtained by slow crystallization in toluene at −30 °C (71.0 mg, 88%). Mp: 197−198 °C. Major isomer (92%). ^{1}H NMR (300.18 MHz, THF-d_8, 25 °C): δ −0.15 (s, 3H, CH_3Si), 0.51 (s, 3H, CH_3Si), 0.91 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.09 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.12 (m, 1H, $^1/_2CH_{2COD}$), 1.19 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.23 (br d, 1H, $^1/_2CH_{2Norb}$), 1.32 (overlapped with Me, 1H, $^1/_2CH_{2COD}$), 1.33 (1H, $^1/_2CH_2C_{bridgeheadCP}$), 1.35 (m, 1H, $^1/_2CH_{2COD}$), 1.36 (s, 9H, 3 × CH_{3tBu}), 1.41 (m, 1H, $^1/_2CH_{2COD}$), 1.41 (m, 1H, $^1/_2CH_{2COD}$), 1.49 (s, 9H, 3 × CH_{3tBu}), 1.57 (m, 1H, $^1/_2CH_2C_{bridgeheadCP}$), 1.58 (m, 1H, $^1/_2CH_{2Norb}$), 1.69 (m, 3H, 3 × $^1/_2CH_{2COD}$), 1.76 (m, 2H, $CH_2C_{bridgeheadCN}$), 1.81 (d, J_{HH} = 6.5 Hz, 3H, CH_{3iPr}), 1.97 (m, 1H, $^1/_2CH_{2COD}$), 2.36 (m, 1H, CH_{COD}), 2.52 (s, 1H, $PCCH_{bridgehead}$), 2.65 (m, 1H, CH_{COD}), 3.14 (sep, J_{HH} = 6.8 Hz, 1H, CH_{iPr}), 3.15 (d, J_{PH} = 31.4 Hz, 1H, SiCH), 3.36 (s, 1H, $NCCH_{bridgehead}$), 3.71 (sep, J_{HH} = 6.5 Hz, 1H, CH_{iPr}), 4.83 (m, 1H, CH_{COD}), 5.50 (m, 1H, CH_{COD}), 6.58 (2H, H_{Ar}), 6.70−6.83 (5H, H_{Ar}), 7.02−7.30 (5H, H_{Ar}), 9.82 (br, 1H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, THF-d_8, 25 °C): δ 2.5 (d, J_{PC} = 2.1 Hz, CH_3Si), 5.3 (br s, CH_3Si), 23.3 (s, CH_{3iPr}), 24.9 (s, CH_{2COD}), 25.2 (br, $CH_2C_{bridgeheadCP}$), 26.0 (s, CH_{3iPr}), 26.1 (s, CH_{3iPr}), 27.7 (s, CH_{3iPr}), 27.8 (s, $CH_2C_{bridgeheadCN}$), 28.0 (s, CH_{iPr}), 28.4 (s, CH_{iPr}), 29.9 (s, CH_{2COD}), 30.7 (m, SiCH), 31.1 (s, CH_{2COD}), 32.4 (d, J_{PC} = 5.0 Hz, 3C, 3 × CH_{3tBu}), 32.7 (d, J_{PC} = 4.5 Hz, 3C, 3 × CH_{3tBu}), 37.0 (s, CH_{2COD}), 42.8 (d, J_{PC} = 57.0 Hz, PCSi), 44.0 (d, J_{PC} = 8.7 Hz, $NCCH_{bridgehead}$), 46.6 (d, J_{PC} = 8.5 Hz, CH_{2Norb}), 47.1 (d, J_{PC} = 10.1 Hz, $PCCH_{bridgehead}$), 52.2 (d, J_{PC} = 0.7 Hz, C_{tBu}), 52.9 (d, J_{PC} = 1.2 Hz, C_{tBu}), 60.4 (d, J_{RhC} = 13.1 Hz, CH_{COD}), 65.9 (d, J_{RhC} = 13.7 Hz, CH_{COD}), 88.6 (d, J_{PC} = 120.9 Hz, PC═CN), 104.9 (d, J_{RhC} = 5.1 Hz, CH_{COD}), 106.9 (d, J_{RhC} = 5.8 Hz, CH_{COD}), 122.4 (s, CH_{Ar}), 124.0 (s, CH_{Ar}), 125.2 (s, CH_{Ar}), 125.5 (s, 2

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× CH_{Ar}), 126.2 (d, J_{PC} = 3.0 Hz, CH_{Ar}), 127.3 (s, CH_{Ar}), 130.0 (s, 2 × CH_{Ar}), 133.6 (d, J_{PC} = 4.9 Hz, C_{Ar}), 136.4 (br d, J_{PC} = 6.9 Hz, 2 × CH_{Ar}), 140.5 (d, J_{PC} = 0.9 Hz, C_{Ar}), 140.6 (br d, J_{PC} = 8.5 Hz, 2 × CH_{Ar}), 141.7 (d, J_{PC} = 0.6 Hz, C_{Ar}), 147.7 (s, C_{Ar}), 147.80 (s, C_{Ar}), 174.8 (dd, J_{PC} = 10.1 Hz, J_{RhC} = 0.8 Hz, PC═CN). $^{29}Si\{^1H\}$ NMR (59.63 MHz, THF-d_8, 25 °C): δ −50.8 (d, J_{SiRh} = 104.5 Hz, SiRh), 11.7 (d, J_{SiP} = 1.9 Hz, SiMe). $^{31}P\{^1H\}$ NMR (121.49 MHz, THF-d_8, 25 °C): δ 48.6 (s). Minor isomer (8%). $^{31}P\{^1H\}$ NMR (121.49 MHz, THF-d_8, 25 °C): δ 43.8 (s).

*Silacyclopropylidene-Rh^{I}Cl(CO$_2$)$_2$ Complex (**3**).* In a pressurized NMR tube, a solution of **2** (40.0 mg, 0.042 mmol) in $CDCl_3$ was exposed to a CO atmosphere (5 bar). After 5 min of stirring, the bright-yellow solution of **3** was analyzed by NMR. A solution of **2** (120.0 mg, 0.126 mmol) in CH_2Cl_2 (2 mL) was put under stirring at RT. After 10 min of CO bubbling in the solution, the resulting yellow solid of **3** was used to prepare KBr pellets suitable for IR analysis. Major isomer (92%) . ^1H NMR (300.18 MHz, THF-d_8, 25 °C): δ 0.01 (s, 3H, CH_3Si), 0.65 (s, 3H, CH_3Si), 1.16 (m, 6H, 2 × CH_{3iPr}), 1.29 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.43 (s, 9H, 3 × CH_{3tBu}), 1.46 (m, 1H, $^1/_2CH_{2Norb}$), 1.62 (overlapped with methyl, 3H, CH_{3iPr}), 1.63 (overlapped with tBu, 1H, $^1/_2CH_2C_{bridgeheadCP}$), 1.64 (s, 9H, 3 × CH_{3tBu}), 1.78 (m, 2H, $^1/_2CH_2C_{bridgeheadCP}$, $^1/_2CH_{2Norb}$), 1.91 (m, 2H, $CH_2C_{bridgeheadCN}$), 2.68 (s, 1H, $PCCH_{bridgehead}$), 3.28 (sep, J_{HH} = 6.7 Hz, 1H, CH_{iPr}), 3.41 (d, J_{PH} = 30.8 Hz, 1H, SiCH), 3.54 (s, 1H, $NCCH_{bridgehead}$), 3.64 (overlapped with THF, 1H, CH_{iPr}), 6.63 (m, 2H, H_{Ar}), 6.78 (m, 3H, H_{Ar}), 6.97−7.43 (m, 10H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, THF-d_8, 25 °C): δ 2.5 (d, J_{PC} = 2.1 Hz, CH_3Si), 5.3 (d, J_{PC} = 1.1 Hz, CH_3Si), 24.0 (s, CH_{3iPr}), 24.1 (s, CH_{3iPr}), 25.5 (br, $CH_2C_{bridgeheadCP}$), 25.6 (s, CH_{3iPr}), 26.1 (s, CH_{3iPr}), 27.8 (s, $CH_2C_{bridgeheadCN}$), 28.0 (s, CH_{iPr}), 28.6 (m, SiCH), 28.7 (s, CH_{iPr}), 32.2 (d, J_{PC} = 5.1 Hz, 3C, 3 × CH_{3tBu}), 32.8 (d, J_{PC} = 4.6 Hz, 3C, 3 × CH_{3tBu}), 44.1 (d, J_{PC} = 8.7 Hz, $NCCH_{bridgehead}$), 46.8 (d, J_{PC} = 8.2 Hz, CH_{2Norb}), 47.3 (d, J_{PC} = 10.0 Hz, $PCCH_{bridgehead}$), 47.9 (d, J_{PC} = 58.0 Hz, PCSi), 52.6 (br s, C_{tBu}), 52.9 (d, J_{PC} = 1.1 Hz, C_{tBu}), 90.1 (d, J_{PC} = 120.3 Hz, PC═CN), 123.3 (s, CH_{Ar}), 124.3 (s, CH_{Ar}), 124.8 (s, CH_{Ar}), 126.1 (s, 2 × CH_{Ar}), 126.6 (d, J_{PC} = 3.0 Hz, CH_{Ar}), 127.8 (s, CH_{Ar}), 128.3 (s, 2 × CH_{Ar}), 129.9 (s, 2 × CH_{Ar}), 132.5 (d, J_{PC} = 5.0 Hz, C_{Ar}), 137.0 (d, J_{PC} = 6.5 Hz, 2 × CH_{Ar}), 138.6 (s, C_{Ar}), 139.9 6(d, J_{PC} = 4.1 Hz, C_{Ar}), 148.2 (br s, 2 × C_{Ar}), 175.5 (d, J_{PC} = 10.0 Hz, PC═CN), 184.5 (br, CO). $^{29}Si\{^1H\}$ NMR (59.63 MHz, THF-d_8, 25 °C): δ −38.8 (d, J_{SiRh} = 74.1 Hz, SiRh), 13.6 (s, SiMe). $^{31}P\{^1H\}$ NMR (121.49 MHz, THF-d_8, 25 °C): δ 46.6 (s). IR (KBr pellets): ν_{CO} 1984.4 (CO_{trans}), 2070.2 (CO_{cis}) cm^{-1}. Minor isomer (8%). $^{31}P\{^1H\}$ NMR (121.49 MHz, THF-d_8, 25 °C): δ 42.7 (s).

*Silacyclopropylidene-Cu^{I}Cl Complex (**4**).* To a flask containing **1** (40.0 mg, 0.057 mmol) and CuCl (5.6 mg, 0.057 mmol) was added THF (1 mL) at RT. After stirring overnight at RT, all volatiles were removed under vacuum, and the solid was washed with pentane, to give the analytically pure **4** as a light-gray powder (45.0 mg, 98%). Crystals of compound **4** suitable for X-ray diffraction analysis were obtained by slow crystallization in a dichloromethane/diethyl ether mixture at −30 °C. Mp: 158−159 °C. Major isomer (92%). ^1H NMR (300.18 MHz, $CDCl_3$, 25 °C): δ 0.04 (s, 3H, CH_3Si), 0.49 (s, 3H, CH_3Si), 0.95 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.15 (overlapped with CH_{3tBu}, 6H, 2 × CH_{3iPr}), 1.16 (s, 9H, 3 × CH_{3tBu}), 1.25 (br d, J_{HH} = 7.7 Hz, 1H, $^1/_2CH_{2Norb}$), 1.34 (m, 1H, $^1/_2CH_2C_{bridgeheadCP}$), 1.49 (s, 9H, 3 × CH_{3tBu}), 1.60 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.61 (overlapped with CH_{3iPr}, 2H, $^1/_2CH_2C_{bridgeheadCP}$, $^1/_2CH_{2Norb}$), 1.74 (m, 2H, $CH_2C_{bridgeheadCN}$), 2.47 (s, 1H, $PCCH_{bridgehead}$), 2.97 (sep, J_{HH} = 7.0 Hz, 1H, CH_{iPr}), 3.20 (sep, J_{HH} = 7.2 Hz, 1H, CH_{iPr}), 3.24 (d, J_{PH} = 30.1 Hz, 1H, SiCH), 3.27 (s, 1H, $NCCH_{bridgehead}$), 6.38 (m, 2H, H_{Ar}), 6.77 (m, 3H, H_{Ar}), 7.04−7.24 (6H, H_{Ar}), 7.55 (br, 2H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ 3.5 (d, J_{PC} = 2.2 Hz, CH_3Si), 6.2 (br s, CH_3Si), 23.4 (s, CH_{3iPr}), 24.6 (s, CH_{3iPr}), 24.6 (s, $CH_2C_{bridgeheadCP}$), 26.2 (s, CH_{3iPr}), 26.7 (s, CH_{3iPr}), 27.9 (s, $CH_2C_{bridgeheadCN}$), 27.9 (s, CH_{iPr}), 28.5 (d, J_{PC} = 1.9 Hz, SiCH), 28.7 (s, CH_{iPr}), 32.4 (d, J_{PC} = 4.8 Hz, 3C, 3 × CH_{3tBu}), 33.4 (d, J_{PC} = 4.5 Hz, 3C, 3 × CH_{3tBu}), 44.0 (d, J_{PC} = 8.7 Hz, $NCCH_{bridgehead}$), 44.7 (d, J_{PC} = 63.8 Hz, PCSi), 46.9 (d, J_{PC} = 10.0 Hz, $PCCH_{bridgehead}$), 47.2 (d, J_{PC} = 8.2 Hz, CH_{2Norb}), 52.4 (d, J_{PC} = 1.5 Hz, C_{tBu}), 52.8 (br s, C_{tBu}), 89.6 (d, J_{PC} = 122.4 Hz, PC═CN), 123.5 (s, CH_{Ar}), 124.3 (s, CH_{Ar}), 124.9 (s, CH_{Ar}), 126.9 (s, 2 × CH_{Ar}), 127.4 (d, J_{PC} = 2.8 Hz, CH_{Ar}), 128.2 (s, 2 × CH_{Ar}), 128.3 (br, 3 × CHAr), 133.1 (d, J_{PC} = 4.3 Hz, C_{Ar}), 135.7 (br, 2 × CH_{Ar}), 138.3 (s, C_{Ar}), 140.7 (d, J_{PC} = 1.3 Hz, C_{Ar}), 145.0 (s, C_{Ar}), 148.1 (s, C_{Ar}), 174.9 (d, J_{PC} = 10.2 Hz, PC═CN). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$, 25 °C): δ −51.5 (s, SiCu), 11.7 (s, J = 12.18 Hz, SiMe). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C): δ 45.7 (s). Minor isomer (8%). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C): δ 41.1 (s).

*Silacyclopropylidene-Au^{I}Cl Complex (**5**).* To a flask containing **1** (24.3 mg, 0.034 mmol) and $AuCl(SMe_2)$ (10.1 mg, 0.034 mmol) was added THF (0.5 mL) at RT. After 15 min of stirring at RT, THF was removed, and the solid was washed with pentane, to give the analytically pure **5** as a light-violet powder (29.7 mg, 92%). Crystals of compound **5** suitable for X-ray diffraction analysis were obtained by slow crystallization in chloroform at RT. Mp: 240−241 °C. Major isomer (92%). ^1H NMR (300.18 MHz, $CDCl_3$, 25 °C): δ 0.08 (s, 3H, CH_3Si), 0.59 (s, 3H, CH_3Si), 1.04 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.22 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.26 (overlapped with CH_{3tBu}, 3H, CH_{3iPr}), 1.27 (s, 9H, 3 × CH_{3tBu}), 1.37 (br d, J_{HH} = 8.5 Hz, 1H, $^1/_2CH_{2Norb}$), 1.49 (m, 1H, $^1/_2CH_2C_{bridgeheadCP}$), 1.58 (s, 9H, 3 × CH_{3tBu}), 1.68 (br d, J_{HH} = 8.50 Hz, 1H, $^1/_2CH_{2Norb}$), 1.70 (overlapped with CH_{3iPr}, 1H, $^1/_2CH_2C_{bridgeheadCP}$), 1.73 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.74 (overlapped with CH_{3iPr}, 1H, $^1/_2CH_2C_{bridgeheadCN}$), 1.88 (m, 1H, $^1/_2CH_2C_{bridgeheadCN}$), 2.63 (s, 1H, $PCCH_{bridgehead}$), 3.09 (sep, J_{HH} = 6.8 Hz, 1H, CH_{iPr}), 3.28 (sep, J_{HH} = 6.8 Hz, 1H, CH_{iPr}), 3.36 (d, J_{PH} = 30.4 Hz, 1H, SiCH), 3.39 (s, 1H, $NCCH_{bridgehead}$), 6.61 (m, 2H, H_{Ar}), 6.90 (m, 3H, H_{Ar}), 7.13−7.33 (6H, H_{Ar}), 7.72 (br, 2H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ 3.5 (d, J_{PC} = 2.1 Hz, CH_3Si), 6.2 (d, J_{PC} = 0.9 Hz, CH_3Si), 23.5 (s, CH_{3iPr}), 24.7 (s, $CH_2C_{bridgeheadCP}$), 25.0 (s, CH_{3iPr}), 26.0 (s, CH_{3iPr}), 26.3 (s, CH_{3iPr}), 27.7 (s, $CH_2C_{bridgeheadCN}$), 28.0 (s, CH_{iPr}), 28.3 (d, J_{PC} = 3.0 Hz, SiCH), 28.9 (s, CH_{iPr}), 32.4 (d, J_{PC} = 5.0 Hz, 3C, 3 × CH_{3tBu}), 33.5 (d, J_{PC} = 4.5 Hz, 3C, 3 × CH_{3tBu}), 44.2 (d, J_{PC} = 8.7 Hz, $NCCH_{bridgehead}$), 44.5 (d, J_{PC} = 61.4 Hz, PCSi), 47.1 (d, J_{PC} = 9.9 Hz, $PCCH_{bridgehead}$), 47.4 (d, J_{PC} = 8.1 Hz, CH_{2Norb}), 52.6 (d, J_{PC} = 1.5 Hz, C_{tBu}), 52.9 (s, C_{tBu}), 90.8 (d, J_{PC} = 120.4 Hz, PC═CN), 124.0 (s, CH_{Ar}), 124.2 (s, CH_{Ar}), 125.1 (s, CH_{Ar}), 127.0 (s, 2 × CH_{Ar}), 127.5 (d, J_{PC} = 2.8 Hz, CH_{Ar}), 128.0 (br s, 2 × CH_{Ar}), 128.5 (s, CH_{Ar}), 128.8 (s, 2 × CH_{Ar}), 132.1 (d, J_{PC} = 4.6 Hz, C_{Ar}), 135.4 (br, 2 × CH_{Ar}), 138.0 (s, C_{Ar}), 139.2 (d, J_{PC} = 0.9 Hz, C_{Ar}), 145.6 (s, C_{Ar}), 147.9 (s, C_{Ar}), 175.1 (d, J_{PC} = 10.3 Hz, PC═CN). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$, 25 °C): δ −28.8 (d, J_{PSi} = 1.4 Hz, SiAu), 13.1 (d, J_{PSi} = 1.8 Hz, SiMe). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C): δ 45.5 (s). Minor isomer (8%). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C): δ 40.8 (s).

*Silacyclopropylidene-Pt^0(dvtms) Complex (**6**).* To a flask containing 1 (150 mg, 0.21 mmol) was added a platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylene (1.2 mL, 0.11 mmol) at room temperature. After stirring for 2 h, all volatiles were removed under vacuum, and the solid was washed with pentane to give the analytically pure **6** as a white powder (152 mg, 70%). Crystals of compound **6** suitable for X-ray diffraction analysis were obtained in a dichloromethane/pentane solution at room temperature. Mp: 244−245 °C (dec). Major isomer (94%). ^1H NMR (300.18 MHz, $CDCl_3$, 25 °C): δ −0.65 (s, 3H, CH_3Si), −0.43 (s, 3H, CH_3Si), −0.23 (s, 3H, CH_3Si), 0.16 (s, 3H, CH_3Si), 0.36 (s, 3H, CH_3Si), 0.55 (s, 3H, CH_3Si), 0.86 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr}), 0.97 (br s, overlapped with CH_{3iPr}, 1H, H_2CCH) 0.99 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr}), 1.10 (br s, 1H, $^1/_2H_2CCH$), 1.28 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr}), 1.29 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr}), 1.36 (br d, 1H, $^1/_2CH_{2Norb}$), 1.50 (overlapped with CH_{3tBu}, 1H, $CH_2C_{bridgeheadCP}$), 1.51 (s, 9H, 3 × CH_{3tBu}), 1.53 (overlapped with CH_{3tBu}, 1H, $^1/_2H_2CCH$), 1.56 (s, 9H, 3 × CH_{3tBu}), 1.66 (br s, 1H, $CH_2C_{bridgeheadCP}$), 1.67 (br s, 1H, H_2CCH), 1.74 (br d, 1H, $^1/_2CH_{2Norb}$), 1.84 (br d, 2H, $CH_2C_{bridgeheadCN}$), 2.59 (d, J_{HH} = 13.5 Hz, 1H, $^1/_2H_2CCH$), 2.63 (s, 1H, $PCCH_{bridgehead}$), 2.99 (d, J_{HH} = 11.4 Hz, 1H, $^1/_2H_2CCH$), 3.06 (m, 1H, CH_{iPr}), 3.34 (m, 1H, CH_{iPr}), 3.38 (d, J_{PH} = 31.8 Hz, 1H, SiCH), 3.48 (s, 1H, $NCCH_{bridgehead}$), 6.33 (m, 2H, HAr), 6.73 (m, 3H, H_{Ar}), 6.80−7.12 (6H, HAr), 7.51 (br, 2H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ −1.8 (s, CH_3Si),

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−1.5 (s, CH_3Si), 1.6 (s, CH_3Si), 1.7 (s, CH_3Si), 3.1 (d, J_{PC} = 1.5 Hz, CH_3Si), 6.0 (br s, CH_3Si), 23.5 (s, CH_{3iPr}), 24.3 (s, CH_{3iPr}), 25.5 (s, $CH_2C_{bridgeheadCP}$), 26.2 (s, CH_{3iPr}), 26.6 (s, CH_{3iPr}), 27.7 (s, CH_{iPr}), 28.2 (s, $CH_2C_{bridgeheadCN}$), 28.9 (s, CH_{iPr}), 32.4 (d, J_{PC} = 4.5 Hz, SiCH), 32.7 (d, J_{PC} = 5.2 Hz, 3C, 3 × CH_{3tBu}), 33.2 (d, J_{PC} = 4.5 Hz, 3C, 3 × CH_{3tBu}), 36.0 (t, J_{PtC} = 51.0 Hz, 2C, 2 × H_2CCH), 41.0 (s, H_2CCH), 41.4 (s, H_2CCH), 43.9 (d, J_{PC} = 8.7 Hz, $NCCH_{bridgehead}$), 47.0 (d, J_{PC} = 9.7 Hz, $PCCH_{bridgehead}$), 42.5 (d, J_{PC} = 125.2 Hz, PCSi), 47.1 (d, J_{PC} = 9.0 Hz, CH_{2Norb}), 52.1 (s, C_{tBu}), 52.5 (d, J_{PC} = 1.5 Hz, C_{tBu}), 87.8 (d, J_{PC} = 121.5 Hz, PCCN), 122.4 (s, CH_{Ar}), 123.8 (s, CH_{Ar}), 123.9 (s, CH_{Ar}), 126.0 (d, J_{PC} = 3 Hz, CH_{Ar}), 126.2 (s, 2 × CH_{Ar}), 126.2 (s, CH_{Ar}), 126.3 (s, CH_{Ar}), 127.0 (s, CH_{Ar}), 129.8 (s, 2 × CH_{Ar}), 134.0 (d, J_{PC} = 4.5 Hz, C_{Ar}), 136.7 (d, J_{PC} = 7.5 Hz, 2 × CH_{Ar}), 140.3 (s, C_{Ar}), 142.2 (s, C_{Ar}), 146.6 (s, C_{Ar}), 148.0 (s, C_{Ar}), 175.8 (d, J_{PC} = 9.4 Hz, PCCN). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$, 25 °C): δ −24.4 (s, SiPt), 2.4 (s, SiMe), 3.4 (s, SiMe), 10.4 (d, J_{PSi} = 1.8 Hz, SiMe). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C): δ 48.5 (d, J_{PPt} = 14.6 Hz). $^{195}Pt\{^1H\}$ NMR (107.55 MHz, $CDCl_3$, 25 °C): δ 5969 (s). Minor isomer (6%). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C): δ 43.1 (s). $^{195}Pt\{^1H\}$ NMR (107.55 MHz, $CDCl_3$, 25 °C): δ 5967 (s).

General Procedure for Hydrosilylation of Ketones with Diphenylsilane Using Copper Complex 4. To a solution of the complex **4** (17 mg, 0.02 mmol) in toluene (2.0 mL) was added tBuONa (1.9 mg, 0.02 mmol) at room temperature. After 0.5 h, diphenylsilane (0.45 mL, 2.4 mmol) was then added. After stirring at RT for an additional 0.5 h, the ketone (2.00 mmol) was added. After the reaction, hydrolysis was performed by adding HCl/MeOH (1 N, 1.0 mL), and the yield of the product was determined by gas chromatography (GC) analysis relative to an internal standard.

General Procedure for Hydrosilylation of 1-Octene with Bis(trimethylsiloxy)methylsilane Using Platinum Complex 6. A mixture of 1-octene (1.85 mmol), bis(trimethylsiloxy)methylsilane (1.85 mmol), and the corresponding xylene solution of the platinum complex was stirred in xylene (1 mL) at 72 °C. The reaction evolution was monitored by ^1H NMR spectroscopy and GC. When the reaction was over, pentane was added, the mixture was filtered through Celite, and the solvent was removed to give the crude product. 1,1,1,3,5,5,5-Heptamethyl-3-octyltrisiloxane was isolated by flash silica column chromatography, eluting with petrol ether to afford the product as a colorless oil. The product was identified according to previously reported spectroscopic data.[38]

Preparation of Platinum Complex Solutions. A 0.005 M solution of complex **6** was prepared by dissolving 26 mg (0.025 mmol) of **6** in 5 mL of xylene (solution A). Solutions of 0.0005 and 0.00005 M were prepared by diluting solution A with **1** and 10 mL of xylene, respectively. A 0.0005 M solution of the platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt) was prepared by dissolving 0.055 mL of a Karstedt solution (0.01 M) in 10 mL of xylene (solution B). A 0.00005 M solution was prepared by diluting this solution B (0.1 mL) with xylene (1 mL).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b01505.

X-ray crystallographic data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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