# **ORGANOMETALLICS**

# Multiple Si–H Bond Activations by <sup>t</sup>Bu<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub> and <sup>t</sup>Bu<sub>2</sub>PCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub> Di(phosphine) Complexes of Rhodium and Iridium

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**Supporting Information** 

**ABSTRACT:** Reactions of the di(*tert*-butylphosphino)ethane complex (dtbpe)Rh(CH<sub>2</sub>Ph) with Ph<sub>2</sub>SiH<sub>2</sub> and Et<sub>2</sub>SiH<sub>2</sub> resulted in isolation of (dtbpe)Rh(H)<sub>2</sub>(SiBnPh<sub>2</sub>) (**1**; Bn = CH<sub>2</sub>Ph) and (dtbpe)Rh(H)<sub>2</sub>(SiBnEt<sub>2</sub>) (**2**), respectively. Both **1** and **2** feature strong interactions between the rhodium hydride and silyl ligands, as indicated by large <sup>2</sup>J<sub>SiH</sub> values (44.4 and 52.1 Hz). The reaction of (dtbpm)Rh(CH<sub>2</sub>Ph) (dtbpm = di(*tert*-butylphosphino)methane) with Mes<sub>2</sub>SiH<sub>2</sub> gave the pseudo-three-coordinate Rh complex (dtbpm)Rh(SiHMes<sub>2</sub>) (**3**), which is stabilized in the solid state by agostic interactions



between the rhodium center and two C–H bonds of a methyl substituent on the mesityl group. The analogous germanium compound (dtbpm)Rh(GeHMes<sub>2</sub>) (4) is also accessible. Complex 3 readily undergoes reactions with diphenylacetylene, phenylacetylene, and 2-butyne to give the silaallyl complexes (dtbpm)Rh[Si(CPh=CHPh)Mes<sub>2</sub>] (5), (dtbpm)Rh[Si(CH=CHPh)Mes<sub>2</sub>] (7), and (dtbpm)Rh(Si(CMe=CHMe)Mes<sub>2</sub>) (8) via net insertions into the Si–H bond. The germaallyl complexes (dtbpm)Rh[Ge(CPh=CHPh)Mes<sub>2</sub>] (6) and (dtbpm)Rh[Ge(CMe=CHMe)Mes<sub>2</sub>] (9) were synthesized under identical conditions starting from 4. The reaction of (dtbpm)Rh(CH<sub>2</sub>Ph) with 1 equiv of TripPhSiH<sub>2</sub> yielded (dtbpm)Rh(H)<sub>2</sub>[5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1H-silaindenyl- $\kappa$ Si] (11), and catalytic investigations indicate that both (dtbpm)Rh(CH<sub>2</sub>Ph) and 11 are competent catalysts for the conversion of TripPhSiH<sub>2</sub> to 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1H-silaindenyl- $\kappa$ Si] (12), was used to access the dinuclear bridging silylene complexes [(dtbpm)IrH]( $\mu$ -SiPh<sub>2</sub>)( $\mu$ -Cl)<sub>2</sub>[(dtbpm)IrH] (12) and [(dtbpm)IrH]( $\mu$ -SiMesCl)( $\mu$ -Cl)( $\mu$ -H)[(dtbpm)-IrH] (13). The reaction of [(dtbpm)IrCl]<sub>2</sub> with a sterically bulky primary silane, (dmp)SiH<sub>3</sub> (dmp = 2,6-dimesitylphenyl), allowed isolation of the mononuclear complex (dtbpm)Ir(H)<sub>4</sub>(10-chloro-1-mesityl-5,7-dimethyl-9,10-dihydrosilaphenanthrene- $\kappa$ Si), in which the dmp substituent has undergone C–H activation.

# INTRODUCTION

Catalytic transformations involving organosilanes, such as hydrosilation, are commercially significant,<sup>1</sup> and much of this catalysis involves the activation of a silane at a transition-metal center.<sup>2</sup> Within this context, a thorough understanding of the fundamental steps in such reactions, such as Si–H bond activation and Si–C bond formation,<sup>3</sup> can be highly valuable in the design of new catalysts.<sup>4</sup>

Complexes of rhodium and iridium supported by pincer ligands display rich chemistry with regard to silane activation and catalysis.<sup>5</sup> However, while related di(phosphine) rhodium complexes have been implicated as catalysts for a number of reactions, such as the dehydrocoupling of phosphines,<sup>6</sup> CO<sub>2</sub> hydrogenation,<sup>7</sup> and the hydroboration of alkenes,<sup>8</sup> their silicon chemistry has not been as extensively explored. Promisingly, complexes supported by the di(isopropylphosphino)ethane ligand (dippe) have demonstrated both stoichiometric and catalytic reactivity toward silanes.<sup>9</sup> The dinuclear complex [(dippe)Rh( $\mu$ -H)]<sub>2</sub> undergoes reactions with primary and secondary silanes to give complexes such as [(dippe)Rh]<sub>2</sub>( $\mu$ -SiPh<sub>2</sub>)<sub>2</sub> and [(dippe)Rh]<sub>2</sub>( $\mu$ - $\eta$ <sup>2</sup>-SiHMe<sub>2</sub>)<sub>2</sub>.<sup>9</sup> A number of these dinuclear complexes also display various Si-H bond

activations, resulting in terminal hydrides, hydrides that bridge two rhodium atoms, and hydrides that bridge between rhodium and silicon. Additionally, transformations catalyzed by this family of complexes include olefin hydrosilation, redistribution of substituents at silicon, dehydrocoupling of silanes, and H/D exchange.<sup>9</sup>

Although (dippe)Rh complexes display interesting reactivity toward primary and secondary silanes, the resulting metal– silicon products are consistently dinuclear and feature bridging silyl or silylene ligands.<sup>9</sup> Given the interesting possibility of observing and/or isolating related, mononuclear silylene species, it is reasonable to explore silane activations by more sterically hindered diphosphine complexes. Rhodium complexes supported by the di(*tert*-butylphosphino)methane (dtbpm) ligand, such as [(dtbpm)RhCl]<sub>2</sub> and (dtbpm)RhCl-(PPh<sub>3</sub>), have previously been reported to be active catalysts for the hydrosilation of alkynes, and synthesis of the silyl complex (dtbpm)Rh[Si(OEt)<sub>3</sub>](PMe<sub>3</sub>) has been described.<sup>10</sup> Despite these interesting results, the silicon chemistry of such

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Scheme 1



complexes remains relatively unexplored. Herein we report investigations that target (dtbpe)Rh and (dtbpm)Rh complexes and associated activations of silanes and germanes.

# RESULTS AND DISCUSSION

**Reaction of (dtbpe)Rh(CH<sub>2</sub>Ph) with Secondary Silanes.** The mononuclear complex (dtbpe)Rh(CH<sub>2</sub>Ph)<sup>11</sup> was envisioned as a potentially useful starting material and precursor to hydrido(silylene) complexes, as outlined in Scheme 1. Oxidative addition of an Si–H bond to this complex would give a (dtbpe)Rh<sup>III</sup> benzyl silyl hydride, which could then undergo reductive elimination of toluene. This would result in a reactive three-coordinate (dtbpe)Rh<sup>I</sup> silyl species, and  $\alpha$ hydrogen migration from the silicon to the rhodium center could provide a pathway to a (dtbpe)Rh silylene complex.<sup>12</sup>

Reactions of (dtbpe)Rh(CH<sub>2</sub>Ph) with secondary silanes were found to result in conversion to new, isolable products. For example, a pentane solution of 1 equiv of Ph<sub>2</sub>SiH<sub>2</sub> was added to a pentane solution of (dtbpe)Rh(CH<sub>2</sub>Ph) at room temperature, and after 24 h the resulting orange-red solution was cooled to -35 °C to give (dtbpe)Rh(H)<sub>2</sub>(SiBnPh<sub>2</sub>) (1; Bn = CH<sub>2</sub>Ph) as orange crystals in 69% yield (eq 1). The <sup>1</sup>H NMR spectrum of



1 displays peaks in the aromatic region corresponding to two phenyl groups and one benzyl group, and the methylene group of the benzyl substituent appears as a singlet at 3.28 ppm. Two equivalent hydrides appear as a multiplet at -5.35 ppm ( $J_{PH} =$ 19.6 Hz,  $J_{RhH} =$  33.8 Hz) and exhibit a large  $J_{SiH}$  value of 44.4 Hz, indicating a strong interaction with Si (cf.  $J_{SiH}$  values of ca. 200 Hz for free silanes<sup>13</sup>). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum exhibits a single resonance as a doublet at 111.3 ppm ( $J_{RhP} =$ 114 Hz), and the single <sup>29</sup>Si NMR peak at -5.6 ppm is consistent with a silyl group.<sup>13</sup> Complex 1 can be stored at room temperature for 4 weeks before significant decomposition is observed.

The identity of **1** was confirmed by X-ray crystallography (Figure 1). The Rh(1), P(1), P(2), H(1), and H(2) atoms are coplanar ( $\pm 0.04$  Å), and the Rh–Si bond forms an angle of 22.1° with this plane. The Rh–Si bond length of 2.3536(19) Å is typical for Rh–Si single bonds,<sup>13</sup> and the Rh–P bond lengths are nearly identical (2.327(2) and 2.323(2) Å). The rhodium hydride ligands, H(1) and H(2), were located in the Fourier map, but the difference in the observed Rh(1)–H(1) (1.67(4) Å) and Rh(1)–H(2) bond distances (1.49(4) Å) may not be



**Figure 1.** Two views of the molecular structure of **1** displaying thermal ellipsoids at the 50% probability level. Selected H atoms have been omitted for clarity. Selected bond lengths (Å): Rh(1)-Si(1) = 2.3536(19), Rh(1)-P(1) = 2.327(2), Rh(1)-P(2) = 2.323(2), Rh(1)-H(1) = 1.67(4), Rh(1)-H(2) = 1.49(4), Si(1)-H(1) = 1.84(4), Si(1)-H(2) = 1.88(4).

statistically meaningful. The Si–H bonds (1.84(4) and 1.88(4) Å) are elongated with respect to a typical Si–H bond distance of ~1.5 Å.<sup>13</sup> The geometry about Si(1) is approximately square pyramidal (ignoring the Rh atom), with a phenyl group in the apical position. This type of structure therefore resembles those of related  $\sigma$  complexes such as [RuH<sub>2</sub>{( $\eta^2$ -HSiMe<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}-(PCy<sub>3</sub>)<sub>2</sub>].<sup>14a</sup> Like Cp(PiPr<sub>2</sub>Me)Fe(H<sub>2</sub>SiR<sub>3</sub>),<sup>14b</sup> 1 may be regarded as a [ $\eta^3$ -H<sub>2</sub>SiR<sub>3</sub><sup>-</sup>] hydrosilicate complex. Alternatively,

given the short Rh–H and long Si–H bond distances, 1 may be described as a silvl dihydride complex, with strong intramolecular interactions between the hydride ligands and the silicon atom.<sup>13</sup> Thus, Rh(I) and Rh(III) resonance forms may be considered (eq 1).

The analogous complex  $(dtbpe)Rh(H)_2(SiBnEt_2)$  (2) was obtained similarly, by reaction of 1 equiv of Et<sub>2</sub>SiH<sub>2</sub> with  $(dtbpe)Rh(CH_2Ph)$  in pentane, followed by cooling to -35 °C to give yellow crystals in 70% yield. The <sup>1</sup>H NMR spectrum of 2 is similar to that of 1, and most notably the hydride ligands appear as one multiplet (-5.63 ppm,  $J_{PH} = 19.1$  Hz,  $J_{RhH} = 27.3$ Hz) and retain a large coupling to Si with a  $J_{SiH}$  value of 52.1 Hz. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum displays a doublet at 114.7 ppm ( $J_{RhP} = 136$  Hz), and the silicon resonance appears at 0.8 ppm in the <sup>29</sup>Si NMR spectrum. Complex 2 is much more thermally sensitive than 1 and decomposes in solution over 2 h.

Complexes 1 and 2 may form via a series of oxidative addition and reductive elimination steps. Initial oxidative addition of an Si-H bond to (dtbpe)Rh(CH<sub>2</sub>Ph) may give (dtbpe)RhH(CH<sub>2</sub>Ph)(SiHPh<sub>2</sub>), which would rapidly undergo Si-C bond reductive elimination to produce Ph<sub>2</sub>(CH<sub>2</sub>Ph)SiH and a rhodium hydride species. Finally, Ph<sub>2</sub>(CH<sub>2</sub>Ph)SiH would add to [(dtbpe)RhH] to give the product. This mechanism is supported by several observations. A solution of (dtbpe)Rh- $(CH_2Ph)$  with 1 equiv of  $Ph_2SiH_2$  in  $C_6D_6$  was monitored by multinuclear NMR spectroscopy over the course of the reaction and was found to contain Ph<sub>2</sub>(PhCH<sub>2</sub>)SiH, as compared to an independently synthesized sample. After 15 min, ca. 0.25 equiv of Ph<sub>2</sub>(PhCH<sub>2</sub>)SiH was present, and this amount remained constant throughout most of the course of the reaction, until it was finally consumed in formation of the final product. However, no organometallic species corresponding to an intermediate was definitively identified. Additionally, the reaction of (dtbpe)Rh(CH<sub>2</sub>Ph) with 0.5 equiv of Ph<sub>2</sub>SiH<sub>2</sub> and 0.5 equiv of  $Ph_2SiD_2$  in  $C_6D_6$  resulted in 3 isotopomers— $(dtbpe)Rh(H)_2(SiBnPh_2)$ , (dtbpe)Rh- $(D)_2(SiBnPh_2)$ , and  $(dtbpe)Rh(H)(D)[SiBnPh_2)]$ , as determined by <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy. This H/D scrambling suggests a mechanism in which Ph<sub>2</sub>(CH<sub>2</sub>Ph)Si(H/D) leaves the coordination sphere of a [(dtbpe)Rh(H/D)] species.

**Reactions of (dtbpm)Rh(CH<sub>2</sub>Ph) with Mes<sub>2</sub>EH<sub>2</sub> (E = Si, Ge).** In light of the limited number of clean reactions observed for hydrosilanes with (dtbpe)Rh(CH<sub>2</sub>Ph), and on the basis of the previous successful synthesis of (dtbpm)Rh[Si(OEt)<sub>3</sub>]-(PMe<sub>3</sub>),<sup>10</sup> silane and germane activations by the related benzyl derivative (dtbpm)Rh(CH<sub>2</sub>Ph)<sup>10</sup> were examined. In screening the reactivity of (dtbpm)Rh(CH<sub>2</sub>Ph) with a number of primary and secondary silanes, it was found that certain sterically hindered secondary silanes provided isolable reaction products, while primary silanes and other secondary silanes resulted in complex reaction mixtures. Thus, reaction of 1 equiv of Mes<sub>2</sub>SiH<sub>2</sub> with (dtbpm)Rh(CH<sub>2</sub>Ph) gave orange crystals of **3** from pentane, isolated in 81% yield (eq 2). The <sup>31</sup>P{<sup>1</sup>H} NMR



spectrum of 3 reveals two resonances, a doublet of doublets at 45.9 ppm ( ${}^{2}J_{PP}$  = 17.9 Hz,  ${}^{1}J_{RhP}$  = 226.6 Hz) and a doublet of doublets at 10.6 ppm ( ${}^{2}J_{PP} = 17.9$  Hz,  ${}^{1}J_{RhP} = 89.7$  Hz), indicating that each P atom of the dtbpm ligand is in a unique environment. A large difference in Rh-P couplings has previously been observed for (dtbpm)Rh complexes, <sup>5</sup> and lower coupling is attributed to the presence of a ligand that displays a strong trans influence.<sup>16</sup> The <sup>29</sup>Si NMR spectrum displays a single peak at -12.4 ppm, in the region expected for silvl ligands.<sup>13</sup> However, the <sup>1</sup>H NMR spectrum of 3 at room temperature is difficult to interpret, since it contains no observable Si-H resonance but two broad peaks at 2.56 and 2.24 ppm for the methyl groups of the mesityl substituents, which together integrate to only 15 H. In addition, a singlet at 6.81 ppm integrates for 4 H and arises from the aromatic protons of the mesityl substituents on Si.

The <sup>1</sup>H NMR spectrum of **3** in toluene- $d_8$  solution at -80 °C is more informative, as it contains four aromatic resonances (7.06–6.74 ppm) and a broad singlet at 6.21 ppm attributed to the Si–H group. Additionally, there are five singlets in the methyl region: four that integrate for 3 H each and one that integrates for 6 H (*p*-Me groups). No Rh–H coupling is observed for these methyl resonances. The *tert*-butyl groups of the dtbpm ligand are split into four sets of doublets, each integrating to 9 H. These NMR data indicate that complex **3** may be formulated as (dtbpm)Rh(SiHMes<sub>2</sub>), possessing a geometry that renders the P atoms and the mesityl groups inequivalent.

Single crystals of 3 suitable for X-ray crystallography were grown by slow evaporation from a pentane solution at -35 °C (Figure 2). Surprisingly, the structure of 3 was found to involve agostic interactions, such that two C–H bonds of one mesityl methyl group interact with the Rh center. The coordination geometry about Rh is square planar, with C(18) constituting one corner of the square. The Rh–Si bond length of 2.3777(7) Å is typical for a Rh–Si single bond.<sup>13</sup> The Rh–P(1) bond



**Figure 2.** Molecular structure of 3 displaying thermal ellipsoids at the 50% probability level. Selected H atoms have been omitted for clarity. Selected bond lengths (Å): Rh(1)-Si(1) = 2.3777(7), Rh(1)-P(1) = 2.2181(7), Rh(1)-P(2) = 2.3462(7), Rh(1)-H(100) = 2.01(3), Rh(1)-H(101) = 2.01(3), Si(1)-H(1) = 1.38(3).

length (2.2181(7) Å) is shorter than that of Rh-P(2) (2.3462(7) Å), due to the trans influence of Si. The hydrogen atoms H(1), H(100), H(101), and H(102) were located in the Fourier map, and the Rh-H(100) and Rh-H(101) distances are both 2.01(3) Å. The third C-H bond does not interact with Rh, nor does the Si-H bond, as it is not in an appropriate position. For comparison, the alkyl complexes (dtbpm)- $RhCH_2CMe_3^{17}$  and  $[(dtbpe)NiCH_2CMe_3][PF_6]^{18}$  display very similar geometries but feature a single  $\gamma$ -CH agostic interaction. The Rh-C(18) distance of 2.377(3) Å is significantly shorter than the corresponding distance observed for (dtbpm)RhNp (2.491(4) Å), which is likely due to the presence of an additional agostic interaction for 3. A weak absorption at 2728 cm<sup>-1</sup> in the infrared spectrum of a crystalline sample indicates that the agostic interactions remain present at room temperature.<sup>19a</sup>

The analogous germyl complex 4 was prepared by reaction of (dtbpm)Rh(CH<sub>2</sub>Ph) with Mes<sub>2</sub>GeH<sub>2</sub>, and dark red crystals were isolated in 71% yield from pentane (eq 2). Unlike 3, the <sup>1</sup>H NMR spectrum of 4 displays all expected resonances at room temperature. A singlet at 6.89 ppm is assigned to the aromatic protons of the mesityl substituents, the resonance for the Ge-H group appears at 5.98 ppm, and three singlets at 2.71, 2.32, and 2.25 ppm each integrate for 6 H, accounting for all methyl groups of the mesityl substituents. The peaks associated with the dtbpm ligand appear as a triplet at 2.97 ( $J_{\rm PH}$ = 7.5 Hz) for the methylene protons and as two doublets at 1.21 ( $J_{\rm PH}$  = 13.4 Hz) and 1.17 ppm ( $J_{\rm PH}$  = 12.3 Hz). The methyl(mesityl) resonances for this complex are quite broad at room temperature, but at -80 °C in toluene- $d_8$  they are resolved into five sharp singlets, four that integrate as 3 H and one that integrates as 6 H (p-Me groups). In addition, two singlets at 7.01 and 6.69 ppm for the aromatic mesityl protons are observed. The Ge-H resonance changes very little, remaining as a doublet at 5.94 ppm (J = 14.2 Hz). At room temperature, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum reveals two doublets at 42.6 ( ${}^{2}J_{PP}$  = 20.9 Hz,  ${}^{1}J_{RhP}$  = 218.6 Hz) and 9.6 ppm ( ${}^{2}J_{PP}$  = 20.9 Hz,  ${}^{1}J_{\text{RhP}}$  = 109.1 Hz). The structure of 4 obtained by Xray crystallography differs very little from that of 3 (Figure 3). The infrared spectrum of a crystalline solid sample contains a weak absorption at 2720 cm<sup>-1</sup>, consistent with the agostic interactions.

**Reactions of (dtbpm)Rh(EHMes<sub>2</sub>) with Alkynes.** Reactions of 3 and 4 with alkynes were examined, given the literature precedent for alkyne hydrosilation by (dtbpm)Rh complexes.<sup>10</sup> A solution of 1 equiv of diphenylacetylene in  $C_6H_6$  was added to 3 in  $C_6H_6$  at room temperature to afford (dtbpm)Rh[Si(CPh=CHPh)Mes<sub>2</sub>] (5) in high yield (eq 3).



The identity of **5** was determined by multinuclear NMR spectroscopy. At room temperature, four peaks in the aromatic region are associated with two phenyl groups and two mesityl groups (one peak is comprised of overlapping resonances correlating to both a phenyl group and mesityl group). Five resonances attributed to methyl protons reflect the presence of



**Figure 3.** Molecular structure of 4 displaying thermal ellipsoids at the 50% probability level. Selected H atoms have been omitted for clarity. Selected bond lengths (Å): Rh(1)-Ge(1) = 2.4433(6), Rh(1)-P(1) = 2.2098(7), Rh(1)-P(2) = 2.3079(8), Rh(1)-H(100) = 1.99(2), Rh(1)-H(101) = 2.05(2), Ge(1)-H(1) = 1.41(2).

inequivalent mesityl groups, and the *tert*-butyl resonances for the dtbpm ligand are present as three broad singlets (18 H:9 H:9 H). A new singlet at 5.36 ppm is attributed to a vinylic CHPh proton, determined by a 2D <sup>1</sup>H,<sup>1</sup>H NOESY experiment to be in the cis position relative to the Si atom. No Si–H resonance appears in this spectrum or in a spectrum of the sample cooled to -60 °C in toluene- $d_8$ . However, at -60 °C the vinylic resonance at 5.36 ppm appears as a multiplet, likely due to coupling to Rh and P, indicating coordination of the vinyl group. Thus, complex 5 may be viewed as the product of net insertion of the alkyne into the Si–H bond. An infrared absorption at 1550 cm<sup>-1</sup> (Nujol) may reflect weak coordination of the vinyl group (cf.  $\nu_{C=C}$  for free *cis*-stilbene at 1628 cm<sup>-1</sup>).<sup>19b</sup>

In an analogous manner, the reaction of diphenylacetylene with 4 gave (dtbpm)Rh[Ge(CPh=CHPh)Mes<sub>2</sub>] (6) as a dark orange solid. The <sup>1</sup>H NMR spectrum at room temperature contains a new resonance at 5.62 ppm, corresponding to the CHPh proton. A resonance associated with a Ge–H bond is not observed at room temperature or at -60 °C. The resonance at 5.62 ppm broadens significantly (fwhh = 34 Hz) upon cooling but does not display a clear splitting from coupling to Rh or P. The <sup>31</sup>P NMR spectrum displays two doublets of doublets at 31.4 (<sup>2</sup>J<sub>PP</sub> = 8.2 Hz, <sup>1</sup>J<sub>RhP</sub> = 136.7 Hz) and 7.8 ppm (<sup>2</sup>J<sub>PP</sub> = 8.2 Hz, <sup>1</sup>J<sub>RhP</sub> = 88.0 Hz). In general, the spectroscopic properties for complexes 5 and 6 are very similar.

Complex 3 reacted with phenylacetylene under analogous conditions to yield (dtbpm)Rh[Si(CH=CHPh)Mes<sub>2</sub>] (7) as a bright orange solid. The arrangement of substituents on the allyl group was determined by  $J_{\rm HH}$  coupling constants. In the <sup>1</sup>H NMR spectrum, a doublet at 5.23 ppm and a doublet of doublets at 4.16 ppm for the vinylic protons are associated with a relatively large  $J_{\rm HH}$  coupling constant (J = 16.2 Hz) consistent with a trans arrangement.<sup>20</sup> The additional splitting of the resonance at 4.16 ppm ( $J_{\rm RhH} = 6.7$  Hz) arises from an interaction with Rh. This trans arrangement of vinylic protons indicates that Si–H addition to the alkyne has occurred in an anti-Markovnikov manner. Like 5 and 6, the phosphine ligand of 7 appears as two doublets of doublets at 37.4 ( $^{2}J_{\rm PP} = 15.9$  Hz,

Scheme 2



 ${}^{1}J_{\rm RhP} = 187.5 \text{ Hz}$ ) and 6.8 ppm ( ${}^{2}J_{\rm PP} = 15.9 \text{ Hz}$ ,  ${}^{1}J_{\rm RhP} = 127.4 \text{ Hz}$ ) in the  ${}^{31}{\rm P}{}^{1}{\rm H}$  NMR spectrum, and the silvl group is observed at 0.6 ppm by  ${}^{29}{\rm Si}$  NMR spectroscopy. The reaction of complex 4 with phenylacetylene resulted in an intractable mixture of products.

Reactions of complexes 3 and 4 with 2-butyne in benzene resulted in color changes from orange to dark red. However, attempts to isolate products from the reaction solutions resulted only in quantitative recovery of the starting materials, 3 and 4. The products of these reactions were therefore characterized in situ by NMR spectroscopy as the E-H insertion products (dtbpm)Rh[Si(CMe=CHMe)Mes<sub>2</sub>] (8) and  $(dtbpm)Rh[Ge(CMe=CHMe)Mes_2]$  (9). Complex 8 displays new <sup>1</sup>H NMR resonances at 3.91 (CHMe), 2.14, and 2.12 ppm (inequivalent methyl groups on the silaallyl moiety), and all appear as broad singlets at room temperature. At -60°C, the CHMe proton shifts to 3.47 ppm and appears as a multiplet due to H-H and Rh-H coupling. The dtbpm ligand appears as two doublets of doublets in the  $^{31}\mathrm{P}\{^1\mathrm{H}\}$  NMR spectrum (30.2 ppm,  ${}^{2}J_{PP} = 7.5$  Hz,  ${}^{1}J_{RhP} = 154.9$  Hz; 13.95 ppm,  ${}^{2}J_{PP} = 7.5$  Hz,  ${}^{1}J_{RhP} = 99.4$  Hz), and the  ${}^{29}$ Si NMR spectrum contains a single peak at 5.2 ppm. The <sup>1</sup>H NMR spectrum for complex 9 exhibits a broad multiplet at 4.39 ppm for the CHMe proton, a multiplet at 2.15 ppm for one  $CH_3$ group due to couplings to the terminal CH proton, P and Rh, and a singlet at 2.13 ppm for the other  $CH_3$  group. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum contains two doublets of doublets at 32.6 ( ${}^{2}J_{PP}$  = 9.8 Hz,  ${}^{1}J_{RhP}$  = 117.4 Hz) and 13.7 ppm ( ${}^{2}J_{PP}$  = 9.8 Hz,  ${}^{1}J_{RhP}$  = 92.9 Hz). When complexes 8 and 9 were exposed to vacuum in the solid state, 3 and 4 were regenerated and 2butyne was removed (by <sup>1</sup>H NMR spectroscopy).

Silaallyl complexes are quite rare,<sup>21<sup>1</sup></sup> and **5**, **7**, and **8** appear to represent the first family of such complexes with rhodium. The

terminal vinyl protons of these complexes display coupling to Rh, which provides evidence for coordination of the vinyl group. This type of complex has been targeted for a number of years due to the similarity to the well-known  $\eta^3$ -allyl complexes.<sup>22</sup> The synthesis of silaallyl species has typically relied on the reaction of a suitable metal precursor with a vinyl silane, such as (dimethylvinyl)dimethylsilane. Thus, the formation of silaallyl complexes from the addition of alkynes to a metal silyl species is unprecedented. Additionally, complexes **6** and **9** represent the first reported germaallyl complexes. Unfortunately, further structural data could not be obtained because all efforts to grow X-ray-quality crystals of **5**–**9** were unsuccessful.

Two possible routes to complexes 5-9 are outlined in Scheme 2. In route A, complex 3 first binds the alkyne, and then the coordinated alkyne inserts into the Rh–Si bond. The Si–H bond could then add to the rhodium center to produce a metallacycle, and reductive elimination of the C–H bond would generate the observed product. Alternatively, as indicated by route B,  $\alpha$ -hydrogen migration to a Rh silylene complex could be followed by a [2 + 2] cycloaddition with the alkyne to form the same metallacycle proposed in route A. Again, reductive elimination would give the silaallyl complex. Interestingly, the process by which these reactions occur must be reversible (at least in the case of 2-butyne).

To probe which of these possible reaction pathways might be operative, the reaction between complex **3** and the Lewis base DMAP (*p*-dimethylaminopyridine) was examined. This Lewis base has been observed to interact with a number of silylene complexes via coordination to silicon,<sup>23</sup> and it was hypothesized that DMAP may act as a trap for a transient silylene complex. A solution of DMAP in pentane was added to a solution of **3** in  $C_6H_{6}$ , and the reaction mixture was cooled to -35 °C to afford

 $(dtbpm)Rh(SiHMes_2)(DMAP)$  (10) as yellow crystals (eq 4). The <sup>1</sup>H NMR spectrum at room temperature contains



resonances for DMAP and the dtbpm ligand but none for the silyl group. However, upon cooling to -60 °C, peaks corresponding to two mesityl groups and an Si–H group (6.06 ppm) appear. No hydride ligands are observed. The dtbpm ligand displays two doublets of doublets in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at 39.14 (<sup>2</sup>*J*<sub>PP</sub> = 9.0, *J*<sub>RhP</sub> = 169.5 Hz) and 3.63 ppm (<sup>2</sup>*J*<sub>PP</sub> = 8.9, *J*<sub>RhP</sub> = 97.8 Hz). The <sup>29</sup>Si NMR resonance at -33.8ppm confirms the presence of a silyl group.<sup>13</sup> Given this result, the precedents for alkyne insertions into metal–silicon bonds,<sup>24</sup> and the limited precedent for 2 + 2 cycloadditions involving alkynes and silylene complexes,<sup>12a,25</sup> we currently favor the mechanism of route A.

**Reaction of (dtbpm)Rh(CH<sub>2</sub>Ph) with TripPhSiH<sub>2</sub>.** The benzyl complex (dtbpm)Rh(CH<sub>2</sub>Ph) was also found to undergo a clean reaction with TripPhSiH<sub>2</sub> (Trip = 2,4,6-triisopropylphenyl). A pentane solution of 1 equiv of TripPhSiH<sub>2</sub> was added to a pentane solution of (dtbpm)Rh-(CH<sub>2</sub>Ph), and cooling the reaction solution to -35 °C afforded (dtbpm)Rh(H)<sub>2</sub>[5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindenyl- $\kappa$ Si] (11) as orange crystals in 65% isolated yield (eq 5). Because complex 11 is not stable at room



temperature in solution, multinuclear NMR experiments were performed on solutions of 11 cooled to 0 °C in toluene- $d_8$ . The <sup>1</sup>H NMR spectrum displays typical resonances for the dtbpm ligand: a triplet at 3.14 ppm ( $J_{PH} = 6.9 \text{ Hz}$ ) for the methylene protons and two doublets at 1.23 ( $J_{PH}$  = 12.6 Hz) and 1.10 ppm  $(J_{\rm PH} = 12.8 \text{ Hz})$  for inequivalent *tert*-butyl groups. Three peaks in the aromatic region correspond to the phenyl substituent on Si, and one peak corresponds to the aryl protons of the Trip group. Only five CH<sub>3</sub> groups from the Trip substituent are apparent, indicating C-H activation at one of the methyl groups, and two resonances at 1.99 and 1.61 ppm correspond to diastereotopic protons for the new methylene group. No Si-H group is observed, and two hydrides are present at -7.04ppm as a complex multiplet, that displays strong coupling to Si  $(J_{SiH} = 51.8 \text{ Hz})$ . The multiplet arises from the presence of inequivalent hydrides (due to the chiral silicon center) and coupling to the Rh and inequivalent P atoms. Unlike complexes 3-10, the  ${}^{31}P{}^{1}H$  NMR spectrum displays only one doublet at 19.8 ( $J_{RhP}$  = 113.9 Hz), presumably due to a rapid dynamic process. Additionally, the <sup>29</sup>Si NMR resonance of 0.89 is typical for a silyl ligand. Taken together, the NMR data indicate that activation of one Trip methyl group has occurred to create a new Si-C bond. The two new rhodium hydride ligands originate from the activation of Si-H and C-H bonds. Like complexes 1 and 2, 11 appears to best be represented as a

(dtbpm)Rh<sup>1</sup> complex with an  $[\eta^3$ -H<sub>2</sub>SiR<sub>3</sub>]<sup>-</sup> ligand (eq 5; one bonding representation shown). Interestingly, the decomposition of **11** in C<sub>6</sub>D<sub>6</sub> over 24 h at room temperature gives an unidentified Rh complex and 5,7-diisopropyl-3-methyl-1phenyl-2,3-dihydro-1*H*-silaindole (vide infra).

Single-crystal X-ray diffraction confirms the identity of 11 (Figure 4). The Rh–Si distance of 2.3163(15) Å is quite a bit



**Figure 4.** Molecular structure of **11** displaying thermal ellipsoids at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å): Rh(1)-Si(1) = 2.3163(15), Rh(1)-P(1) = 2.3249(13), Rh(1)-P(2) = 2.3381(16), Si(1)-C(24) = 1.901(5), Si(1)-C(38) = 1.906(5).

shorter than that observed for 3, and the Rh–P bond lengths are very similar (2.3249(13) and 2.3381(16) Å). Like complexes 1 and 2, the Si atom is not coplanar with the dtbpm phosphorus atoms and Rh. The Si–C bonds of the fivemembered ring are nearly identical, with Si(1)–C(24) at 1.901(5) Å and Si(1)–C(38) at 1.906(5) Å. Although the rhodium hydride ligands were not located, the strong coupling to Si observed by NMR spectroscopy indicates that the hydrides likely occupy positions similar to those located for complex 1.

The proposed formation of 11 is outlined in Scheme 3. Oxidative addition of TripPhSiH<sub>2</sub> followed by reductive elimination of toluene can result in a (dtbpm)Rh(SiHTripPh) complex, which can then undergo C–H activation of a methyl group to give a cyclometalated species. Reductive elimination from this species would result in a (dtbpm)RhH species and 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole. Finally, the latter compound would add via Si–H oxidative

Scheme 3



addition to give **11**. Note that the related complex (dippe)Rh-(CH<sub>2</sub>Ph) (dippe = bis(diisopropylphosphino)ethane) undergoes a similar reaction with [2,4,6-tri(*tert*-butyl)phenyl]phosphine to afford (dippe)Rh(H)[5,7-di(*tert*-butyl)-2,3-dihydro-3,3-dimethyl-1*H*-phosphindole- $\kappa P$ ].<sup>6b</sup>

The observation of 5,7-diisopropyl-3-methyl-1-phenyl-2,3dihydro-1*H*-silaindole in 15% yield from the decomposition of **11** led to investigations on the catalytic production of this species. A solution of TripPhSiH<sub>2</sub> in benzene- $d_6$  with a 10% loading of (dtbpm)Rh(CH<sub>2</sub>Ph) was monitored at room temperature (eq 6). Over 48 h, a yield of 90% of 5,7-



diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole was observed, along with the concurrent release of hydrogen (by <sup>1</sup>H NMR spectroscopy). Longer reaction times did not increase the product yield. Complex **11** also acts as a competent catalyst for this transformation. After 20 h at room temperature with 10% of **11**, 49% conversion was observed. For comparison, after 20 h with (dtbpm)Rh(CH<sub>2</sub>Ph), 55% conversion was observed. This result suggests that (dtbpm)Rh(CH<sub>2</sub>Ph) and **11** function as precatalysts to the same active species. However, further catalytic studies were hindered by decomposition of the rhodium complexes in this system.

A proposed mechanism is outlined in Scheme 4. When  $(dtbpm)Rh(CH_2Ph)$  is used as the precatalyst, the reaction of (dtbpm)Rh(CH<sub>2</sub>Ph) and TripPhSiH<sub>2</sub> can give 11 and enter into the catalytic cycle by reductive elimination to form [(dtbpm)RhH] and 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1H-silaindole. Similarly, 11 would function as a precatalyst by reductive elimination to form [(dtbpm)RhH] and 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1H-silaindole. The [(dtbpm)RhH] species could then oxidatively add TripPhSiH<sub>2</sub> to give a (dtbpm)Rh(H)<sub>2</sub>(SiHTripPh) complex, which could then lose 1 equiv of H<sub>2</sub> via reductive elimination. The resulting (dtbpm)Rh(SiHTripPh) could then activate a methyl C-H bond to form a cyclometalated species. Reductive elimination of the Si and C groups would release 5,7diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1H-silaindole and re-form [(dtbpm)RhH].

**Reactions of [(dtbpm)IrCl]\_2 with Silanes.** Silane activations related to those above were investigated for the (dtbpm)Ir fragment, using  $[(dtbpm)IrCl]_2^{26}$  as a starting





material. The complex  $[(dtbpm)IrCl]_2$  reacted with 2 equiv of  $H_2SiPh_2$  in benzene at room temperature over 40 min to give the bridging silylene complex  $[(dtbpm)IrH](\mu$ -SiPh<sub>2</sub>)( $\mu$ -Cl)<sub>2</sub>[(dtbpm)IrH] (12) as a yellow-orange solid in 89% yield (eq 7). The identity of 12 was determined by X-ray



crystallography (Figure 5), with single crystals grown from a toluene solution at -35 °C. The Ir–Si bond distances of 2.425(2) and 2.427(2) Å are quite long compared to most Ir–Si single bonds.<sup>13</sup> The hydride ligands were not located in the Fourier map. Neglecting the hydride ligands, the coordination environment for Ir(1) can be described as an approximate square pyramid, with P(3), P(4), Si(1), and Cl(1) forming the square plane. The empty coordination site trans to Cl(2) is presumed to contain a hydride ligand (see below). In a similar manner, Ir(2) adopts an octahedral geometry with P(1), P(2), Si(1), and Cl(2) defining a coordination plane and the coordination site trans to Cl(1) being occupied by a hydride



**Figure 5.** Molecular structure of **12** displaying thermal ellipsoids at the 50% probability level. H atoms and *tert*-butyl groups have been omitted for clarity. Selected bond lengths (Å): Ir(1)-Si(1) = 2.427(2), Ir(1)-P(3) = 2.406(2), Ir(1)-P(4) = 2.233(2), Ir(1)-Cl(1) = 2.503(2), Ir(1)-Cl(2) = 2.551(2), Ir(2)-Si(1) = 2.425(2), Ir(2)-P(1) = 2.237(2), Ir(2)-P(2) = 2.412(2), Ir(2)-Cl(1) = 2.555(2), Ir(2)-Cl(2) = 2.502(2).

ligand. The strong trans influence of Si is manifested in different Ir–P bond lengths; the Ir(1)-P(4) bond length is 2.233(2) Å, while the Ir(1)-P(3) bond length is significantly longer at 2.406(2) Å. The same trend is observed for the Ir(2)-P(1) (2.237(2) Å) and Ir(2)-P(2) (2.412(2) Å) bonds.

The NMR spectroscopic data for 12 are consistent with the observed X-ray structure. By <sup>1</sup>H NMR spectroscopy, two sets of tBu resonances are observed, as well as resonances associated with equivalent phenyl groups. Two equivalent hydride ligands give rise to a doublet at -23.3 ppm, due to splitting by <sup>31</sup>P ( $J_{PH}$ = 24.8 Hz). Coupling to the second  $^{31}$ P nucleus is likely too small to be observed, which is supported by an analogously small coupling in 14 (vide infra). As discussed above, the terminal Ir-H ligands are in coordination sites trans to a Cl atom, and the small coupling to <sup>31</sup>P supports a cis arrangement of the phosphine and hydride ligands. The  $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$  spectrum displays two doublets at 8.9 and -3.7 ppm ( $J_{PP} = 6.1$  Hz), and a single resonance at -34.4 ppm in the <sup>29</sup>Si NMR spectrum is in a region consistent with a bridging silvlene complex of iridium.<sup>13,27</sup> Additionally, two terminal hydride stretches are observed by infrared spectroscopy (2328, 2288 cm<sup>-1</sup>, Nujol mull). Overall, complex 12 can be considered to be the product of two Si-H oxidative additions across the two Ir centers of [(dtbpm)IrCl]<sub>2</sub>, and such complexes are typical products of the reactivity of binuclear complexes of Rh and Ir with silanes.<sup>28</sup>

Under analogous conditions,  $[(dtbpm)IrCl]_2$  undergoes clean conversion to a new product with 2 equiv of MesSiH<sub>3</sub> (eq 8). The yellow-orange solid, isolated in 90% yield, was characterized as  $[(dtbpm)IrH](\mu$ -SiMesCl) $(\mu$ -Cl) $(\mu$ -H)-[(dtbpm)IrH] (13) via multinuclear NMR experiments. The <sup>1</sup>H NMR spectrum of complex 13 contains resonances corresponding to one mesityl group and two dtbpm ligands. There is no resonance at ca. 5 ppm, indicating that an Si–H



bond is not present in the molecule. A triplet of triplets at -12.59 ppm ( $J_{PH} = 5.3, 63.3$  Hz) arises from a bridging hydride ligand due to coupling to each dtbpm ligand, and a doublet of doublets integrating to 2H at -24.66 ppm ( $J_{PH} = 2.4$ , 18.0 Hz) results from the two terminal Ir-H ligands. No J<sub>SiH</sub> coupling constant was observed for these hydride ligands. The presence of terminal hydrides is further supported by infrared spectroscopy (2391, 2327 cm<sup>-1</sup>, Nujol mull). In contrast to the common trend, by <sup>1</sup>H NMR spectroscopy the terminal hydride ligands appear far upfield from the bridging hydride ligand,<sup>2</sup> but this is consistent with the hydride ligands observed for 12. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum contains doublets at 18.50 and 3.28 ppm ( $J_{PP} = 14.5$  Hz). By <sup>29</sup>Si NMR spectroscopy, a pseudotriplet at 75.0 ppm ( $J_{SiP} \sim 150$  Hz) is observed for the bridging silvlene ligand. On the basis of previous reports, this resonance is much further downfield than one would expect for a bridging SiMesCl moiety.<sup>13,27</sup> However, the connectivity of 13 was confirmed by a low-quality X-ray structure. Additionally, low-valent Ir-Cl and Rh-Cl have been shown to undergo facile oxidative addition of an Si-H bond, followed by reductive elimination of an Si-Cl bond in the context of catalytic hydrosilation of various substrates.<sup>30</sup>

In an effort to synthesize a mononuclear (dtbpm)Ir silyl complex, an extremely bulky primary silane was utilized. The reaction of  $[(dtbpm)IrCl]_2$  with 2 equiv of H<sub>3</sub>Si(dmp) (dmp = 2,6-dimesitylphenyl) in benzene at 55 °C for 18 h afforded (dtbpm)Ir(H)<sub>4</sub>(10-chloro-1-mesityl-5,7-dimethyl-9,10-dihydro-silaphenanthrene- $\kappa$ Si) (14) as a yellow solid in moderate (72%) isolated yield (eq 9). The identity of 14 was determined by a



combination of X-ray crystallography (Figure 6) and multinuclear NMR spectroscopy. Single crystals of 14 were grown from a concentrated toluene solution at -35 °C. The Ir-Si bond length of 2.323(4) Å is in the region expected for Ir silyl species, and unlike 12, the Ir-P bond lengths are very similar (2.378(4) and 2.365(4) Å). The Si-Cl bond length (2.142(6) Å) is normal, and the Si-C bond lengths are very similar (1.890(15) and 1.868(14) Å). The hydride ligands were not located. The <sup>1</sup>H NMR spectrum at room temperature displays five distinct methyl groups, correlating to the CH<sub>3</sub> groups of the dmp ligand. Additionally, two new  $\mathrm{CH}_2$  resonances are present at 3.64 and 2.64 ppm, each integrating to 1 H. Four equivalent hydride ligands appear as a triplet at -11.58 ppm  $(J_{\rm PH} = 18.0 \text{ Hz})$ , and the integration of the hydrides was confirmed under varying relaxation times. The 29Si NMR spectrum displays a resonance at -1.96 ppm that is typical for metal silvl complexes.

The mechanism for the formation of 14 likely involves a series of oxidative additions and reductive eliminations,



**Figure 6.** Molecular structure of **14** displaying thermal ellipsoids at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å): Ir(1)-Si(1) = 2.323(4), Ir(1)-P(1) = 2.378(4), Ir(1)-P(2) = 2.365(4), Si(1)-Cl(1) = 2.142(6), Si(1)-C(1) = 1.890(15), Si(1)-C(15) = 1.868(14).

including an intramolecular C-H activation related to that of Scheme 4. For example, initial addition of the silane followed by Si-Cl reductive elimination could produce (dtbpm)IrH and the chlorosilane. These species could then recombine to form (dtbpm)IrH<sub>2</sub>(SiHCldmp), which could undergo hydrogen loss and then intramolecular C-H activation at Ir. Finally, Si-C reductive elimination of the cyclic silane, followed by Si-H and H-H oxidative additions, would produce the product. Unlike 11, complex 14 is stable at elevated temperatures and does not release a silane product upon heating to 80 °C for 18 h. A similar complex was reported from the reaction of (Et<sub>2</sub>PhP)<sub>3</sub>IrCl with (dmp)SiH<sub>3</sub> and was suggested to form via an Ir silvlene complex.<sup>31</sup> While both of these postulated mechanisms are reasonable, the reaction mixture must be heated to achieve the synthesis of 14, which is not consistent with conditions typically observed for reactive silvlene intermediates.

### CONCLUSION

The complexes (dtbpe)Rh(CH<sub>2</sub>Ph), (dtbpm)Rh(CH<sub>2</sub>Ph), and [(dtbpm)IrCl]<sub>2</sub> have been shown to undergo reactions with various organosilanes, and several themes emerge from the reactivity patterns for these hindered, bis(phosphine)-supported group 9 metal complexes. Most notable is the prevalence of Si-C bond formation in these systems. The complex (dtbpe)Rh(CH<sub>2</sub>Ph) undergoes reactions with secondary silanes in which the benzyl group is transferred to the silicon atom to give the tertiary silyl complexes 1 and 2. Benzyl reagents often lose the benzyl group as toluene (e.g., in the reaction of (dtbpm)Rh(CH<sub>2</sub>Ph) with Mes<sub>2</sub>SiH<sub>2</sub>). The sila- and germaallyl complexes 5-9 result from the net insertion of an alkyne into an E-H bond. Interestingly, this Si-C bond formation appears to be reversible on the basis of the conversion of 8 and 9 back to 3 and 4, respectively, under an applied vacuum. Complex 11 is produced from a C-H bond activation and subsequent Si-C bond formation to give a silacycle, and both (dtbpm)Rh(CH<sub>2</sub>Ph) and 11 have been demonstrated to catalyze Si-C bond formation in the transformation of TripPhSiH<sub>2</sub> to 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole. Like **11**, the iridium complex **14** also contains a silacycle produced by an intramolecular Si–C bond formation.

Another common theme encountered in this study is the apparent participation of reactive [(diphosphine)MH] species as key intermediates in many of the observed transformations. In the proposed mechanisms for the formations of 1, 2, and 11, the Si-C bond-forming step appears to produce a [(diphosphine)RhH] species, which can then undergo further reaction with the released silane. Similarly, the Si-C bond-forming step in the synthesis of 14 appears to generate a [(dtbpm)IrH<sub>3</sub>] species. Several [(diphosphine)MH] complexes with group 9 metals have been isolated as dinuclear complexes, such as [(dippe)RhH]<sub>2</sub><sup>9</sup> and [(dippe)NiH]<sub>2</sub>,<sup>32</sup> and these are active catalysts for H/D exchange or the dehydrocoupling of silanes. Current efforts to synthesize [(dtbpm)RhH]<sub>2</sub> and [(dtbpm)IrH]<sub>2</sub> and explore their catalytic reactivity are underway.

#### EXPERIMENTAL SECTION

**General Considerations.** All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N<sub>2</sub>) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H<sub>2</sub>SO<sub>4</sub>, 0.5 N KMnO<sub>4</sub> in 3 M H<sub>2</sub>SO<sub>4</sub>, and then NaHCO<sub>3</sub>. Pentane was then dried over MgSO<sub>4</sub> and stored over activated 4 Å molecular sieves and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H<sub>2</sub>SO<sub>4</sub> and saturated NaHCO<sub>3</sub>. Benzene and toluene by treatment with H<sub>2</sub>SO<sub>4</sub> and saturated NaHCO<sub>3</sub>. Benzene and toluene were then dried over CaCl<sub>2</sub> and further dried over alumina. Tetrahydrofuran, diethyl ether, dichloromethane, and hexanes were dried over alumina. Benzene-*d*<sub>6</sub> was dried by vacuum distillation from Na/K alloy. The complexes (dtbpe)Rh(CH<sub>2</sub>Ph),<sup>10</sup> (dtbpm)Rh-(CH<sub>2</sub>Ph),<sup>11</sup> and [(dtbpm)IrCl]<sub>2</sub><sup>26</sup> were prepared according to literature methods. All other chemicals were purchased from commercial sources and used without further purification.

NMR spectra were recorded using Bruker AV-500 and AV-600 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room temperature and referenced to the residual protonated solvent for <sup>1</sup>H unless otherwise noted. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced relative to 85% H<sub>3</sub>PO<sub>4</sub> external standard ( $\delta = 0$ ). <sup>19</sup>F{<sup>1</sup>H} spectra were referenced relative to a  $C_6F_6$  external standard. <sup>13</sup>C{<sup>1</sup>H} NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For  ${}^{13}C{}^{1}H$  NMR spectra, resonances obscured by the solvent signal are omitted. <sup>29</sup>Si NMR spectra were referenced relative to a tetramethylsilane standard and obtained via 2D <sup>1</sup>H,<sup>29</sup>Si HMBC unless specified otherwise. The following abbreviations have been used to describe peak multiplicities in the reported NMR spectroscopic data: "m" for complex multiplet, and "br" for broadened resonances. Infrared spectra for 3 and 4 were collected on a Perkin-Elmer Spectrum 400 FTIR spectrometer with an attenuated total reflectance accessory. Infrared spectra for all other complexes were recorded on a Nicolet Nexus 6700 FTIR spectrometer with a liquidnitrogen-cooled MCT-B detector. Measurements were made at a resolution of 4.0 cm<sup>-1</sup>. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

(dtbpe)Rh(H)<sub>2</sub>(SiBnPh<sub>2</sub>) (1). To a 2 mL pentane solution of (dtbpe)Rh(CH<sub>2</sub>Ph) (0.030 g, 0.058 mmol) was added a 1 mL pentane solution of Ph<sub>2</sub>SiH<sub>2</sub> (0.011 g, 0.060 mmol). The reaction mixture was allowed to stand for 24 h at room temperature, after which the resulting orange-red solution was cooled to -35 °C. After 3 days, orange crystals were collected by filtration in 69% yield (0.028 g). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  7.93 (4H, d, *J* = 7.0 Hz, ArH), 7.29 (4H, t, *J* = 7.5 Hz, ArH), 7.20 (4H, t, *J* = 7.5 Hz, ArH), 7.08 (2H, t, *J* = 7.5 Hz, ArH), 6.98 (1H, t, *J* = 7.0 Hz, ArH), 3.28 (2H, s, CH<sub>2</sub>Ar), 1.37 (4H, d, *J* = 12.0 Hz, PCH<sub>2</sub>CH<sub>2</sub>P), 1.00 (36H, m, PC(CH<sub>3</sub>)<sub>3</sub>), -5.35 (2H, m,

 $\begin{array}{l} J_{\rm PH} = 19.6 \ {\rm Hz}, \ J_{\rm RhH} = 33.8 \ {\rm Hz}, \ J_{\rm SiH} = 44.4 \ {\rm Hz}, \ {\rm Rh}H). \ ^{13}{\rm C}\{^{1}{\rm H}\} \ {\rm NMR} \\ ({\rm C}_6{\rm D}_6, \ 150.9 \ {\rm MHz}): \ \delta \ 147.9 \ ({\rm ArC}), \ 143.4 \ ({\rm ArC}), \ 136.1 \ ({\rm ArC}), \ 130.4 \\ ({\rm ArC}), \ 127.3 \ ({\rm ArC}), \ 123.8 \ ({\rm ArC}), \ 37.4 \ ({\rm CH}_2), \ 35.2 \ ({\rm PC}({\rm CH}_3)_3), \ 35.0 \\ ({\rm P}({\rm CH}_2)_2{\rm P}), \ 30.5 \ ({\rm PC}({\rm CH}_3)_3). \ ^{31}{\rm P}\{^{1}{\rm H}\} \ {\rm NMR} \ ({\rm C}_6{\rm D}_{6\prime}, \ 163.0 \ {\rm MHz}): \ \delta \\ 111.3 \ ({\rm d}, \ ^{1}J_{\rm RhP} = 114 \ {\rm Hz}). \ ^{29}{\rm Si} \ {\rm NMR} \ ({\rm C}_6{\rm D}_{6\prime}, \ 99.4 \ {\rm MHz}): \ \delta \ -5.6 \ {\rm Anal}. \\ {\rm Calcd \ for} \ {\rm C}_{37}{\rm H}_{59}{\rm P}_2{\rm RhSi}: \ {\rm C}, \ 63.78; \ {\rm H}, \ 8.53. \ {\rm Found}: \ {\rm C}, \ 63.39; \ {\rm H}, \ 8.70. \end{array}$ 

(dtbpe)Rh(H)<sub>2</sub>(SiBnEt<sub>2</sub>) (2). To a 2 mL pentane solution of (dtbpe)Rh(H)<sub>2</sub>(SiBnEt<sub>2</sub>) (2). To a 2 mL pentane solution of Et<sub>2</sub>SiH<sub>2</sub> (0.009 g, 0.098 mmol) was added a 1 mL pentane solution of Et<sub>2</sub>SiH<sub>2</sub> (0.009 g, 0.10 mmol). The reaction mixture was cooled to -35 °C. After 3 days, yellow crystals were collected in 70% yield (0.041 g). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  7.36 (2H, d, J = 7.6 Hz, ArH), 7.22 (2H, t, J = 7.6 Hz, ArH), 7.04 (1H, t, J = 7.6 Hz, ArH), 2.81 (2H, s, CH<sub>2</sub>), 1.40 (10H, m, CH<sub>2</sub>CH<sub>3</sub>), 1.11 (36H, d, J = 12.2 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 0.88 (4H, t, J = 7.0 Hz, PCH<sub>2</sub>CH<sub>2</sub>P), -5.63 (2H, m,  $J_{PH}$  = 19.1 Hz,  $J_{RhH}$  = 27.3 Hz,  $J_{SiH}$  = 52.1 Hz, RhH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.9 MHz):  $\delta$  144.3 (ArC), 141.6 (ArC), 139.9 (ArC), 132.5 (ArC), 125.8 (ArC), 123.1 (ArC), 37.8 (CH<sub>2</sub>), 34.6 (P(CH<sub>2</sub>)<sub>2</sub>P), 31.5 (PC(CH<sub>3</sub>)<sub>3</sub>), 30.3 (PC(CH<sub>3</sub>)<sub>3</sub>), 7.8 (CH<sub>2</sub>CH<sub>3</sub>), 2.4 (CH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 163.0 MHz):  $\delta$  114.7 (d, <sup>1</sup> $J_{RhP}$  = 136 Hz). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 99.4 MHz):  $\delta$  0.8 ppm. Anal. Calcd for C<sub>29</sub>H<sub>59</sub>P<sub>2</sub>RhSi: C, 57.98; H, 9.90. Found: C, 57.70; H, 10.36.

(dtbpm)Rh(SiHMes<sub>2</sub>) (3). A solution of Mes<sub>2</sub>SiH<sub>2</sub> (0.040 g, 0.15 mmol) in 2 mL of pentane was added to a solution of (dtbpm)Rh-(CH<sub>2</sub>Ph) (0.075 g, 0.15 mmol) in 2 mL of pentane. After 1 h, the solution was concentrated (to ca. 2 mL) and cooled to -35 °C to afford orange crystals in 81% yield (0.081 g). <sup>1</sup>H NMR (20 °C, toluene- $d_{8}$ , 500 MHz):  $\delta$  6.81 (4H, s, ArH), 3.01 (2H, t, J = 7.5 Hz, PCH<sub>2</sub>P), 2.56 (9H, br s, ArCH<sub>3</sub>), 2.24 (6H, s, ArCH<sub>3</sub>), 1.21 (36H, d, J = 15.0 Hz, PC(CH<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H NMR (-80 °C, toluene- $d_8$ , 500 MHz):  $\delta$ 7.06 (1H, s, ArH), 6.96 (1H, s, ArH), 6.76 (1H, s, ArH), 6.74 (1H, s, ArH), 6.81 (1H, br s, SiH), 3.15 (3H, s, ArCH<sub>3</sub>), 2.77 (5H, s, ArCH<sub>3</sub> + PCH<sub>2</sub>P), 2.60 (3H, s, ArCH<sub>3</sub>), 2.34 (3H, s, ArCH<sub>3</sub>), 2.30 (3H, s, ArCH<sub>3</sub>), 1.44 (9H, d, J = 12.5 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.18 (9H, d, J = 11.5Hz,  $PC(CH_3)_3$ , 1.05 (9H, d, J = 11.5 Hz,  $PC(CH_3)_3$ ), 0.95 (9H, d,  $PC(CH_3)_3$ ), 0.95 (9H, d, PC(CH\_3)\_3), 0.95 (9H, d, PC(CH\_3)\_3), 0.95 (9H, d, PC(CH\_3 12.5 Hz, PC(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (-80 °C, toluene-d<sub>8</sub>, 150.9 MHz): δ 144.8 (ArC), 144.2 (ArC), 144.1 (ArC), 143.4 (ArC), 142.8 (ArC), 142.2 (ArC), 136.3 (ArC), 134.9 (ArC), 126.1 (ArC), 36.3 (PC(CH<sub>3</sub>)<sub>3</sub>), 36.0 (PC(CH<sub>3</sub>)<sub>3</sub>), 34.0 (PC(CH<sub>3</sub>)<sub>3</sub>), 33.8 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.9 (PCH<sub>2</sub>P), 31.0 (PC(CH<sub>3</sub>)<sub>3</sub>), 30.7 (PC(CH<sub>3</sub>)<sub>3</sub>), 30.3 (PC-(CH<sub>3</sub>)<sub>3</sub>), 25.8 (ArCH<sub>3</sub>), 25.0 (ArCH<sub>3</sub>), 23.5 (ArCH<sub>3</sub>), 21.4  $(ArCH_3)$ , 21.2  $(ArCH_3)$ . <sup>31</sup>P{<sup>1</sup>H} NMR  $(C_6D_6$ , 163.0 MHz):  $\delta$  45.9  $(dd, {}^{2}J_{PP} = 17.9 \text{ Hz}, {}^{1}J_{RhP} = 226.6 \text{ Hz}), 10.6 (dd, {}^{2}J_{PP} = 17.9 \text{ Hz}, {}^{1}J_{RhP} =$ 89.7 Hz). <sup>29</sup>Si NMR ( $C_6D_6$ , 99.4 MHz):  $\delta$  –12.4. Anal. Calcd for C35H61P2RhSi: C, 62.30; H, 9.11. Found: C, 61.94; H, 9.30.

(dtbpm)Rh(GeHMes<sub>2</sub>) (4). A solution of Mes<sub>2</sub>GeH<sub>2</sub> (0.047 g, 0.15 mmol) in 2 mL of pentane was added to a solution of (dtbpm)Rh-(CH<sub>2</sub>Ph) (0.075 g, 0.15 mmol) in 2 mL of pentane. After 1 h, the solution was concentrated (ca. 2 mL) and cooled to -35 °C to afford dark red crystals in 71% yield (0.077 g). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600 MHz):  $\delta$  6.89 (4H, s, ArH), 5.98 (1H, d, J = 14.0 Hz, GeH), 2.97 (2H, t, J = 7.5 Hz, PCH<sub>2</sub>P), 2.71 (6H, br s, ArCH<sub>3</sub>), 2.32 (6H, br s, ArCH<sub>3</sub>), 2.25  $(6H, s, ArCH_3)$ , 1.21 (18H, d, J = 13.4 Hz,  $PC(CH_3)_3$ ), 1.17 (18H, d, J= 12.3 Hz,  $PC(CH_3)_3$ ). <sup>1</sup>H NMR (-80 °C, toluene- $d_{80}$ , 500 MHz):  $\delta$  7 0.01 (2H, s, ArH), 6.69 (2H, s, ArH), 5.94 (1H, d, J = 14.2 Hz, GeH), 3.05 (3H, s, ArCH<sub>3</sub>), 2.71 (2H, m, PCH<sub>2</sub>P), 2.56 (6H, s, ArCH<sub>3</sub>), 2.28 (3H, s, ArCH<sub>3</sub>), 2.23 (3H, s, ArCH<sub>3</sub>), 1.99 (3H, s, ArCH<sub>3</sub>), 1.33 (9H, d, J = 12.8 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.11 (9H, d, J = 12.2 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 0.99  $(9H, d, J = 11.8 \text{ Hz}, \text{PC}(CH_3)_3), 0.88 (9H, d, J = 13.0 \text{ Hz}, \text{PC}(CH_3)_3).$  $^{13}C{^{1}H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 150.9 MHz):  $\delta$  146.5 (ArC), 142.5 (ArC), 135.4 (ArC), 37.6 (PCH<sub>2</sub>P), 36.5 (PC(CH<sub>3</sub>)<sub>3</sub>), 34.6 (PC(CH<sub>3</sub>)<sub>3</sub>), 34.0 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.7 (PC(CH<sub>3</sub>)<sub>3</sub>), 30.9 (PC(CH<sub>3</sub>)<sub>3</sub>), 22.3 (ArCH<sub>3</sub>), 20.8 (ArCH<sub>3</sub>), 13.8 (ArCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 163.0 MHz):  $\delta$  42.6  $(dd, {}^{2}J_{PP} = 20.9 \text{ Hz}, {}^{1}J_{RhP} = 218.6 \text{ Hz}), 9.6 (dd, {}^{2}J_{PP} = 20.9 \text{ Hz}, {}^{1}J_{RhP} =$ 109.1 Hz). Anal. Calcd for C<sub>35</sub>H<sub>61</sub>GeP<sub>2</sub>Rh: C, 58.44; H, 8.55. Found: C, 58.26; H, 8.78.

(dtbpm)Rh(Si(CPh=CHPh)Mes<sub>2</sub>) (5). A solution of diphenylacetylene (0.008 g, 0.04 mmol) in 1 mL of  $C_6H_6$  was added to a solution of 3 (0.030 g, 0.04 mmol) in 2 mL of  $C_6H_6$ . The red reaction solution was stirred for 30 min before being filtered through a Celite plug. The resulting solution was stripped to dryness to give a bright

orange solid in 85% yield (0.032 g). <sup>1</sup>H NMR ( $C_6D_{67}$  500 MHz):  $\delta$ 7.52 (4H, d, J = 7.4 Hz, ArH), 6.98 (4H, t, J = 7.4 Hz, ArH), 6.86 (4H, ov m, ArH), 6.66 (2H, s, ArH), 5.36 (1H, s, CHPh), 3.18 (5H, br s, ArCH<sub>3</sub> + PCH<sub>2</sub>P), 2.79 (3H, br s, ArCH<sub>3</sub>), 2.67 (6H, s, ArCH<sub>3</sub>), 2.20 (3H, s, ArCH<sub>3</sub>), 2.04 (3H, s, ArCH<sub>3</sub>), 1.27 (18H, br s, PC(CH<sub>3</sub>)<sub>3</sub>), 1.10 (9H, br s, PC(CH<sub>3</sub>)<sub>3</sub>), 0.92 (9H, br s, PC(CH<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H NMR (-60 °C, toluene-d<sub>8</sub>, 500 MHz): δ 7.46 (4H, s, ArH), 6.95 (4H, s, ArH), 6.80 (4H, s, ArH), 6.59 (2H, s, ArH), 5.24 (1H, t, J<sub>RhH</sub> = 6.3 Hz, CHPh), 3.11 (5H, br s, ArCH<sub>3</sub> + PCH<sub>2</sub>P), 2.72 (3H, s, ArCH<sub>3</sub>), 2.59 (6H, s, ArCH<sub>3</sub>), 2.19 (3H, s, ArCH<sub>3</sub>), 2.01 (3H, s, ArCH<sub>3</sub>), 1.21 (18H, d, J = 11.5 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.05 (9H, d, J = 11.3 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 0.95 (9H, d, J = 11.0 Hz, PC(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.9 MHz): δ 145.7 (ArC), 143.8 (ArC), 143.0 (ArC), 136.9 (ArC), 132.0 (ArC), 130.8 (ArC), 125.0 (ArC), 124.3 (ArC), 124.0 (ArC), 90.3 (CPhSi), 83.6 (CHPh), 37.4 (PCH<sub>2</sub>P), 36.5 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.4 (PC(CH<sub>3</sub>)<sub>3</sub>), 27.1 (ArCH<sub>3</sub>), 21.3 (ArCH<sub>3</sub>), 21.1 (ArCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 163.0 MHz): δ 27.8 (dd,  ${}^{2}J_{PP} = 9.1$  Hz,  ${}^{1}J_{RhP} = 145.1$  Hz), 7.9 (dd,  ${}^{2}J_{PP} = 9.1$  Hz,  ${}^{1}J_{RhP} = 89.7$  Hz).  ${}^{29}$ Si NMR (C<sub>6</sub>D<sub>6</sub>, 99.4 MHz): δ 3.8. IR: 1550 cm<sup>-1</sup> ( $\nu$ (C=C)). Anal. Calcd for C<sub>49</sub>H<sub>71</sub>P<sub>2</sub>RhSi: C, 68.99; H, 8.39. Found: C, 68.38; H, 8.72.

(dtbpm)Rh(Ge(CPh=CHPh)Mes<sub>2</sub>) (6). A solution of diphenylacetylene (0.008 g, 0.04 mmol) in 1 mL of C<sub>6</sub>H<sub>6</sub> was added to a solution of 4 (0.030 g, 0.04 mmol) in 2 mL of  $C_6H_6$ . The reaction solution was stirred for 30 min before being filtered through a Celite plug. The resulting solution was stripped to dryness to give a dark orange solid in 83% yield (0.029 g). <sup>1</sup>H NMR ( $C_6D_{61}$  600 MHz):  $\delta$ 7.52 (4H, d, J = 6.9 Hz, ArH), 6.99 (4H, m, ArH), 6.88 (2H, br s, ArH), 6.83 (2H, t, J = 7.5 Hz, ArH), 6.70 (2H, br s, ArH), 5.62 (1H, s, CHPh), 3.19 (2H, br s, PCH<sub>2</sub>P), 2.94 (6H, br s, ArCH<sub>3</sub>), 2.47 (6H, br s, ArCH<sub>3</sub>), 2.19 (3H, br s, ArCH<sub>3</sub>), 2.10 (3H, br s, ArCH<sub>3</sub>), 1.26 (18H, br s, PC(CH\_3)\_3), 1.11 (18H, br s, PC(CH\_3)\_3). <sup>1</sup>H NMR (-60  $^\circ\text{C},$ toluene- $d_{81}$  500 MHz):  $\delta$  7.31 (2H, t, J = 7.0 Hz, ArH), 7.04 (2H, d, J= 7.0 Hz, ArH), 6.83 (2H, m, ArH), 6.77 (4H, t, J = 7.0 Hz, ArH), 6.63 (4H, s, ArH), 5.46 (1H, s, CHPh), 3.12 (2H, dd, J = 16.0, 8.1 Hz, PCH<sub>2</sub>P), 2.38 (6H, s, ArCH<sub>3</sub>), 2.04 (12H, s, ArCH<sub>3</sub>), 1.24 (9H, d, J = 10.0 Hz,  $PC(CH_3)_3$ , 1.13 (9H, d, J = 13.0 Hz,  $PC(CH_3)_3$ ), 1.06 (9H, d, J = 11.7 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 0.93 (9H, d, J = 12.0 Hz, PC(CH<sub>3</sub>)<sub>3</sub>).  $^{13}C{^{1}H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 150.9 MHz):  $\delta$  147.7 (ArC), 143.6 (ArC), 142.3 (ArC), 135.8 (ArC), 130.2 (ArC), 124.9 (ArC), 123.9 (ArC), 91.1 (CHPh), 92.6 (CHPh), 35.9 (PCH<sub>2</sub>P), 34.6 (PC(CH<sub>3</sub>)<sub>3</sub>), 34.0  $(PC(CH_3)_3)$ , 31.5  $(PC(CH_3)_3)$ , 31.3  $(PC(CH_3)_3)$ , 30.9  $(PC(CH_3)_3)$ , 22.6  $(ArCH_3)$ , 22.3  $(ArCH_3)$ , 20.7  $(ArCH_3)$ . <sup>31</sup>P{<sup>1</sup>H} NMR  $(C_6D_6)$ 163.0 MHz):  $\delta$  31.4 (dd,  ${}^{2}J_{PP}$  = 8.2 Hz,  ${}^{1}J_{RhP}$  = 136.7 Hz), 7.8 (dd,  ${}^{2}J_{PP}$ = 8.2 Hz,  ${}^{1}J_{RhP}$  = 88.0 Hz). Anal. Calcd for C<sub>49</sub>H<sub>71</sub>GeP<sub>2</sub>Rh: C, 65.57; H, 7.97. Found: C, 65.78; H, 8.04.

(dtbpm)Rh(Si(CH=CHPh)Mes<sub>2</sub>) (7). An excess of phenylacetylene (ca. 0.1 mL) was added to a solution of 3 (0.030 g, 0.04 mmol) in 1 mL of  $C_6H_6$ . The reaction solution was stirred for 30 min before being filtered through a Celite plug. The resulting solution was stripped to dryness to give a bright orange solid in 88% yield (0.030 g). <sup>1</sup>H NMR ( $C_6D_6$ , 500 MHz)  $\delta$  7.45 (2H, d, J = 7.4 Hz, PhH), 7.06 (2H, t, J = 7.4 Hz, PhH), 6.89 (1H, d, J = 7.4 Hz, PhH), 6.81 (4H, s, ArH), 5.23 (1H, d, J = 16.2 Hz, =CH), 4.16 (1H, dd, J = 16.2, J<sub>RhH</sub> = 6.7 Hz, =CH), 3.12 (2H, t, J = 6.8 Hz, PCH<sub>2</sub>P), 3.01 (6H, br s, ArCH<sub>3</sub>), 2.69 (6H, s, ArCH<sub>3</sub>), 2.18 (3H, s, ArCH<sub>3</sub>), 2.16 (3H, s, ArCH<sub>3</sub>), 1.34 (9H, d, J = 12.2 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.26 (9H, d, J = 12.0 Hz,  $C(CH_3)_3)$ , 1.04 (9H, d, J = 12.7 Hz,  $C(CH_3)_3)$ , 0.76 (9H, d, J = 11.8Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.9 MHz):  $\delta$  145.3 (ArC), 144.4 (ArC), 144.0 (ArC), 139.1 (ArC), 131.5 (ArC), 130.6 (ArC), 128.6 (ArC), 127.2 (ArC), 100.7 (CSi), 76.9 (CHPh), 36.1 (PCH<sub>2</sub>P), 35.4 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.6 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.0 (PC(CH<sub>3</sub>)<sub>3</sub>), 30.8 (PC- $(CH_3)_3)$ , 30.3  $(PC(CH_3)_3)$ , 26.9  $(ArCH_3)$ , 23.1  $(ArCH_3)$ , 20.8 (ArCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 163.0 MHz):  $\delta$  37.4 (dd, <sup>2</sup>J<sub>PP</sub> = 15.9 Hz,  ${}^{1}J_{RhP} = 187.5$  Hz), 6.8 (dd,  ${}^{2}J_{PP} = 15.9$  Hz,  ${}^{1}J_{RhP} = 127.4$  Hz).  $^{29}\text{Si}$  NMR (C<sub>6</sub>D<sub>6</sub>, 99.4 MHz):  $\delta$  0.6. Anal. Calcd for C\_{37}H\_{59}P\_2RhSi: C, 63.78; H, 8.53. Found: C, 63.39; H, 8.70.

In Situ Formation of (dtbpm)Rh(Si(CMe=CHMe)Mes<sub>2</sub>) (8). With a 10  $\mu$ L syringe, 2-butyne (3.1  $\mu$ L, 0.04 mmol) was added to a solution of 3 (0.030 g, 0.04 mmol) in 1 mL of C<sub>6</sub>D<sub>6</sub>. The reaction solution was stirred for 30 min before being filtered through a Celite

plug. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 6.81 (4H, s, ArH), 3.91 (1H, s, CHMe), 3.10 (2H, s, PCH<sub>2</sub>P), 2.88 (12H, s, ArCH<sub>3</sub>), 2.17 (6H, s, ArCH<sub>3</sub>), 2.14 (3H, s, CH<sub>3</sub>), 2.12 (3H, s, CH<sub>3</sub>), 1.28 (12H, br s, PC(CH<sub>3</sub>)<sub>3</sub>), 1.18 (12H, br s, PC(CH<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H NMR (-60 °C, toluened<sub>8</sub>, 500 MHz): δ 6.83 (1H, s, ArH), 6.74 (2H, s, ArH), 6.58 (1H, s, ArH), 3.47 (1H, m, CHMe), 3.33 (3H, s, ArCH<sub>3</sub>), 2.99 (2H, m, PCH<sub>2</sub>P), 2.81 (6H, s, ArCH<sub>3</sub>), 2.10 (3H, s, ArCH<sub>3</sub>), 1.32 (9H, d, *J* = 11.5 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.17 (9H, d, *J* = 11.4 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.07 (9H, d, *J* = 10.8 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 0.94 (9H, d, *J* = 12.1 Hz, PC(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.9 MHz): δ 143.5 (ArC), 136.5 (ArC), 89.8 (CMeSi), 79.9 (CHMe), 37.2 (PCH<sub>2</sub>P), 36.0 (PC(CH<sub>3</sub>)<sub>3</sub>), 34.9 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.5 (PC(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 163.0 MHz): δ 30.2 (dd, <sup>2</sup>J<sub>PP</sub> = 7.5 Hz, <sup>1</sup>J<sub>RhP</sub> = 154.9 Hz), 13.95 (dd, <sup>2</sup>J<sub>PP</sub> = 7.5 Hz, <sup>1</sup>J<sub>RhP</sub> = 99.4 Hz). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 99.4 MHz): δ 5.2.

In Situ Formation of (dtbpm)Rh(Ge(CMe=CHMe)Mes<sub>2</sub>) (9). With a 10 μL syringe, 2-butyne (3.3 μL, 0.04 mmol) was added to a solution of 4 (0.030 g, 0.04 mmol) in 1 mL of  $C_6D_6$ . The dark red reaction solution was stirred for 30 min before being filtered through a Celite plug. <sup>1</sup>H NMR ( $C_6D_6$ , 600 MHz):  $\delta$  6.83 (4H, s, ArH), 4.39 (1H, br m, CHMe), 3.14 (2H, t, J = 6.6 Hz, PCH<sub>2</sub>P), 2.80 (12H, s, ArCH<sub>3</sub>), 2.18 (6H, s, ArCH<sub>3</sub>), 2.15 (3H, m, CH<sub>3</sub>), 2.13 (3H, s, CH<sub>3</sub>), 1.27 (18H, d, J = 11.4 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.19 (18H, d, J = 12.4 Hz, PC(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , 150.9 MHz):  $\delta$  142.4 (ArC), 135.5 (ArC), 87.7 (CMeSi), 79.5 (CHMe), 38.2 (PCH<sub>2</sub>P), 35.4 (PC(CH<sub>3</sub>)<sub>3</sub>), 34.8 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.5 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.1 (PC(CH<sub>3</sub>)<sub>3</sub>), 30.8 (PC(CH<sub>3</sub>)<sub>3</sub>), 26.4 (ArCH<sub>3</sub>), 23.6 (CHMe=CMeGe), 22.6 (CHMe=CMeGe), 20.7 (ArCH<sub>3</sub>), 18.4 (ArCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR ( $C_6D_6$ , 163.0 MHz):  $\delta$  32.6 (dd, <sup>2</sup>J<sub>PP</sub> = 9.8 Hz, <sup>1</sup>J<sub>RhP</sub> = 117.4 Hz), 13.7 (dd, <sup>2</sup>J<sub>PP</sub> = 9.8 Hz, <sup>1</sup>J<sub>RhP</sub> = 92.9 Hz).

(dtbpm)Rh(SiHMes<sub>2</sub>)(DMAP) (10). A solution of DMAP (0.009 g, 0.07 mmol) in 1 mL of pentane was added to a solution of 3 (0.050 g, 0.07 mmol) in 2 mL of C<sub>6</sub>H<sub>6</sub>. After 30 min, the solution was concentrated (ca. 2 mL) and cooled to -35 °C to afford yellow crystals in 95% yield (0.053 g). <sup>1</sup>H NMR ( $C_6D_6$ , 500 MHz):  $\delta$  8.48 (1H, d, J = 5.6 Hz, ArH), 8.10 (1H, d, J = 6.0 Hz, ArH), 6.10 (1H, d, J = 5.6 Hz, ArH), 5.53 (1H, d, J = 6.0 Hz, ArH), 2.87 (2H, t, J = 6.9 Hz, PCH<sub>2</sub>P), 2.23 (3H, s, NCH<sub>3</sub>), 2.04 (3H, s, NCH<sub>3</sub>), 1.48 (18H, br s,  $PC(CH_3)_3$ , 1.25 (18H, d, J = 10.0 Hz,  $PC(CH_3)_3$ ). <sup>1</sup>H NMR (-60 °C, toluene-d<sub>8</sub>, 500 MHz):  $\delta$  8.38 (1H, br s, ArH), 7.59 (1H, br s, ArH), 7.21 (1H, s, MesH), 6.95 (1H, s, MesH), 6.78 (1H, s, MesH), 6.14 (1H, s, MesH), 6.06 (1H, m, SiH), 5.40 (1H, br s, ArH), 5.15 (1H, br s, ArH), 4.48 (3H, s, MesCH<sub>3</sub>), 3.20 (3H, s, MesCH<sub>3</sub>), 2.70 (5H, s, ArCH<sub>3</sub> + PCH<sub>2</sub>P), 2.26 (3H, s, MesCH<sub>3</sub>), 2.19 (3H, s, ArCH<sub>3</sub>), 2.03 (3H, s, ArCH<sub>3</sub>), 1.76 (9H, d, J = 10.8 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.44 (3H, s, MesCH<sub>3</sub>), 1.38 (9H, d, J = 10.6 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.18  $(9H, d, J = 11.0 \text{ Hz}, \text{PC}(CH_3)_3), 0.95 (9H, d, J = 10.6 \text{ Hz}, \text{PC}(CH_3)_3).$ <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.9 MHz):  $\delta$  152.3 (ArC), 151.9 (ArC), 105.4 (ArC), 37.8 (PCH<sub>2</sub>P), 34.0 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.1 (PC(CH<sub>3</sub>)<sub>3</sub>), 22.3  $(PC(CH_3)_3)$ , 20.9  $(ArCH_3)$ , 13.9  $(ArCH_3)$ , 8.6  $(ArCH_3)$ . <sup>13</sup>C{<sup>1</sup>H} NMR (-60 °C, toluene-d<sub>8</sub>, 150.9 MHz): δ 151.9 (ArC), 145.5 (ArC), 145.3 (ArC), 143.5 (ArC), 105.8 (ArC), 105.4 (ArC), 38.5 (ArCH<sub>3</sub>), 37.6 (PCH<sub>2</sub>P), 36.1 (PC(CH<sub>3</sub>)<sub>3</sub>), 35.6 (PC(CH<sub>3</sub>)<sub>3</sub>), 35.1 (PC(CH<sub>3</sub>)<sub>3</sub>), 33.9 (PC(CH<sub>3</sub>)<sub>3</sub>), 33.3 (PC(CH<sub>3</sub>)<sub>3</sub>), 32.3 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.3 (PC(CH<sub>3</sub>)<sub>3</sub>), 30.8 (PC(CH<sub>3</sub>)<sub>3</sub>), 26.5 (ArCH<sub>3</sub>), 25.8 (ArCH<sub>3</sub>), 24.8 (ArCH<sub>3</sub>), 23.7 (ArCH<sub>3</sub>), 21.9 (ArCH<sub>3</sub>), 15.2 (ArCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR ( $C_6D_6$ , 163.0 MHz):  $\delta$  39.1 (dd,  ${}^2J_{PP} = 9.0$ ,  ${}^1J_{RhP} = 169.5$  Hz), 3.63 (dd,  ${}^{2}J_{PP} = 9.0$ ,  ${}^{1}J_{RhP} = 97.8$  Hz).  ${}^{29}Si$  NMR (C<sub>6</sub>D<sub>6</sub>, 99.4 MHz):  $\delta$ -33.8. Anal. Calcd for C<sub>42</sub>H<sub>71</sub>N<sub>2</sub>P<sub>2</sub>RhSi: C, 63.30; H, 8.98; N, 3.52. Found: C, 62.96; H, 9.23; N, 3.24.

(dtbpm)Rh(H)<sub>2</sub>[5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindenyl- $\kappa$ Si] (11). A solution of TripPhSiH<sub>2</sub> (0.032 g, 0.10 mmol) in 2 mL of pentane was added to a solution of (dtbpm)Rh(CH<sub>2</sub>Ph) (0.050 g, 0.10 mmol) in 2 mL of pentane. The solution was immediately cooled to -35 °C to afford orange crystals in 65% yield (0.047 g). <sup>1</sup>H NMR (0 °C, toluene- $d_8$ , 500 MHz):  $\delta$  8.14 (2H, d, J = 6.7 Hz, PhH), 7.26 (2H, m, PhH), 7.08 (1H, s, PhH), 7.03 (2H, s, ArH), 3.76 (1H, sept, J = 6.7 Hz, CH), 3.58 (1H, sextet, J = 6.9 Hz, CH), 3.14 (2H, t, J = 6.9 Hz, PCH<sub>2</sub>P), 2.96 (1H, sept, J = 6.8 Hz, CH), 1.99 (1H, dd, J = 13.5, 6.9 Hz, SiCH<sub>2</sub>), 1.76 (3H, d, J = 6.7 Hz, CH<sub>3</sub>), 1.61 (1H, m, SiCH<sub>2</sub>), 1.50 (3H, d, J = 6.9 Hz, CH<sub>3</sub>), 1.39 (6H, d, J = 6.8, CH<sub>3</sub>), 1.23 (18H, d, J = 12.6 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.10 (18H, d, J = 12.8 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.05 (3H, d, J = 6.9 Hz, CH<sub>3</sub>), -7.04 (2H, m,  $J_{SiH} = 51.8$  Hz, RhH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (0 °C, toluene- $d_8$ , 150.9 MHz):  $\delta$  155.5 (ArC), 152.9 (ArC), 148.8 (ArC), 144.5 (ArC), 126.63 (ArC), 120.4 (ArC), 118.9 (ArC), 37.8 (CH<sub>2</sub>), 35.1 (PCH<sub>2</sub>P), 34.9 (PC(CH<sub>3</sub>)<sub>3</sub>), 34.6 (PC(CH<sub>3</sub>)<sub>3</sub>), 33.8 (PC(CH<sub>3</sub>)<sub>3</sub>), 32.9 (PC(CH<sub>3</sub>)<sub>3</sub>), 30.5 (PC(CH<sub>3</sub>)<sub>3</sub>), 30.3 (PC(CH<sub>3</sub>)<sub>3</sub>), 25.2 (ArCH<sub>3</sub>), 24.5 (ArCH<sub>3</sub>), 24.3 (ArCH<sub>3</sub>), 23.8 (ArCH<sub>3</sub>), 22.8 (ArCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (0 °C, toluene- $d_8$ , 163.0 MHz):  $\delta$  19.8 (d, <sup>1</sup> $J_{RhP} = 113.9$  Hz). <sup>29</sup>Si NMR (0 °C, toluene- $d_8$ , 99.4 MHz):  $\delta$  0.89. Anal. Calcd for C<sub>38</sub>H<sub>67</sub>P<sub>2</sub>RhSi: C, 63.67; H, 9.42. Found: C, 63.73; H, 9.54.

[(dtbpm)lrH](µ-SiPh<sub>2</sub>)(µ-Cl)<sub>2</sub>[(dtbpm)lrH] (12). A solution of  $H_2SiPh_2$  (0.023 g, 0.12 mmol) in  $C_6H_6$  was added to a stirred solution of  $[(dtbpm)IrCl]_2$  (0.10 g, 0.09 mmol) in C<sub>6</sub>H<sub>6</sub>. The solution was stirred at room temperature for 40 min. The solvent was removed under reduced pressure. The resulting yellow-orange solid was washed twice with 1 mL of cold pentane to remove remaining H<sub>2</sub>SiPh<sub>2</sub>. Further drying gave 12 as a yellow-orange powder in 89% yield (0.102 g). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 8.89 (4H, br s, ArH), 7.44 (4H, t, J = 7.4 Hz, ArH), 7.26 (2H, t, J = 7.4 Hz, ArH), 3.15 (2H, m, PCH<sub>2</sub>P), 2.85 (2H, m, PCH<sub>2</sub>P), 1.55 (18H, d,  $J_{PH}$  = 11.5 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.43 (18, d,  $J_{PH} = 11.5$  Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.03 (18H, d,  $J_{PH} = 13.5$  Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 0.85 (18H, d,  $J_{PH}$  = 13.5 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), -23.3 (2H, d,  $J_{PH}$  = 24.8 Hz, IrH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.9 MHz):  $\delta$  136.5 (ArC), 135.6 (ArC), 134.5 (ArC), 129.7 (ArC), 128.1 (ArC), 36.0 (PCH<sub>2</sub>P), 35.3 (PCH<sub>2</sub>P), 33.3 (PC(CH<sub>3</sub>)<sub>3</sub>), 32.3 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.1  $(PC(CH_3)_3)$ , 30.9  $(PC(CH_3)_3)$ , 30.3  $(PC(CH_3)_3)$ , 29.1  $(PC(CH_3)_3)$ .  $^{31}P{^{1}H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 202 MHz):  $\delta$  8.9 (d,  $^{2}J_{PP}$  = 6.1 Hz), -3.7 (d,  ${}^{2}J_{\rm PP} = 6.1$  Hz).  ${}^{29}$ Si NMR (C<sub>6</sub>D<sub>6</sub>, 99.4 MHz):  $\delta$  –34.4. IR: 2328, 2288 (*v*(Ir-H)). Anal. Calcd for C<sub>46</sub>Cl<sub>2</sub>H<sub>88</sub>Ir<sub>2</sub>P<sub>4</sub>Si: C, 44.25; H, 7.10. Found: C, 44.42; H, 7.08.

[(dtbpm)IrH](µ-SiMesCI)(µ-CI)(µ-H)[(dtbpm)IrH] (13). A solution of H<sub>3</sub>SiMes (0.018 g, 0.12 mmol) in C<sub>6</sub>H<sub>6</sub> was added to a stirred solution of [(dtbpm)IrCl]<sub>2</sub> (0.102 g, 0.096 mmol) in C<sub>6</sub>H<sub>6</sub>. The solution was stirred at room temperature for 40 min. The solvent was removed under reduced pressure. The resulting yellow-orange solid was washed twice with 1 mL of cold pentane to remove the remaining H<sub>3</sub>SiMes. Further drying under reduced pressure gave 13 as a yellow powder in 90% yield (0.104 g). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  6.92 (1H, s, ArH), 6.83 (1H, s, ArH), 3.72 (2H, m, PCH<sub>2</sub>P), 3.51 (2H, m, PCH<sub>2</sub>P), 3.36 (3H, s, ArCH<sub>3</sub>), 3.16 (3H, s, ArCH<sub>3</sub>), 2.17 (3H, s, ArCH<sub>3</sub>), 1.51 (18H, d, J<sub>PH</sub> = 11.9 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.41 (18H, d, J<sub>PH</sub> = 9.9 Hz,  $PC(CH_3)_3$ ), 1.35 (18H, d,  $J_{PH} = 9.9$  Hz,  $PC(CH_3)_3$ ), 1.08 (18H, d,  $J_{PH} = 11.6$  Hz, PC(CH<sub>3</sub>)<sub>3</sub>), -12.59 (1H, tt,  $J_{PH} = 5.3$ , 63.3 Hz,  $\mu$ -IrH), -24.66 (2H, dd,  $J_{PH}$  = 2.4, 18.0 Hz, IrH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.9 MHz): δ 144.5 (ArC), 139.1 (ArC), 135.6 (ArC), 130.5 (ArC), 37.3 (PCH<sub>2</sub>P), 35.2 (PCH<sub>2</sub>P), 32.3 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.6 (PC(CH<sub>3</sub>)<sub>3</sub>), 30.8 (PC(CH<sub>3</sub>)<sub>3</sub>), 30.2 (PC(CH<sub>3</sub>)<sub>3</sub>), 29.9 (PC(CH<sub>3</sub>)<sub>3</sub>), 29.3 (PC(CH<sub>3</sub>)<sub>3</sub>), 26.5 (ArCH<sub>3</sub>), 24.0 (ArCH<sub>3</sub>), 22.3 (ArCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 162 MHz):  $\delta$  18.5 (d, <sup>2</sup>J<sub>PP</sub> = 14.5), 3.28 (d, <sup>2</sup>J<sub>PP</sub> = 14.5). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 99.4 MHz):  $\delta$  75.0 (t,  $J_{SiP} \approx$  150 Hz). IR: 2391, 2327 (*v*(Ir–H)). Anal. Calcd for C<sub>43</sub>Cl<sub>2</sub>H<sub>92</sub>Ir<sub>2</sub>P<sub>4</sub>Si: C, 42.45; H, 7.62. Found: C, 42.69; H, 7.24.

(dtbpm)Ir(H)<sub>4</sub>(10-chloro-1-mesityl-5,7-dimethyl-9,10-dihydrosilaphenanthrene- $\kappa Si$ ) (14). A solution of H<sub>3</sub>Si(dmp) (0.032 g, 0.094 mmol) in C<sub>6</sub>H<sub>6</sub> was added to a stirred solution of [(dtbpm)IrCl]<sub>2</sub> (0.050 g, 0.046 mmol) in C<sub>6</sub>H<sub>6</sub>. The solution was stirred at 55 °C for 18 h. The solvent was removed under reduced pressure. The resulting yellow-orange solid was washed twice with 1 mL of cold pentane to remove remaining H<sub>3</sub>Si(dmp). Further drying under reduced pressure gave 14 as a yellow powder in 72% yield (0.058 g). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  7.34 (1H, s, ArH), 7.25 (1H, t, *J* = 7.5 Hz, ArH), 7.06 (1H, s, ArH), 7.01 (1H, d, *J* = 7.5, ArH), 6.92 (2H, d, *J* = 7.5 Hz, ArH), 6.79 (1H, s, ArH), 3.64 (1H, d, *J* = 13.4 Hz, CH<sub>2</sub>), 3.13 (2H, t, *J* = 7.7 Hz, PCH<sub>2</sub>P), 2.64 (1H, d, *J* = 13.4 Hz, CH<sub>2</sub>), 2.56 (3H, s, ArCH<sub>3</sub>), 2.20 (3H, s, ArCH<sub>3</sub>), 1.10 (18H, d, *J*<sub>PH</sub> = 13.5 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), 1.00 (18H, d, *J*<sub>PH</sub> = 13.6 Hz, PC(CH<sub>3</sub>)<sub>3</sub>), -11.58 (4H, t,  $J_{PH}$  = 15.1 Hz, IrH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.9 MHz):  $\delta$ 145.6 (ArC), 145.1 (ArC), 142.9 (ArC), 140.6 (ArC), 139.8 (ArC), 138.2 (ArC), 136.4 (ArC), 135.4 (ArC), 135.1 (ArC), 134.9 (ArC), 129.8 (ArC), 129.7 (ArC), 125.6 (ArC), 41.6 (CH<sub>2</sub>), 37.6 (PCH<sub>2</sub>P), 33.5 (PC(CH<sub>3</sub>)<sub>3</sub>), 32.8 (PC(CH<sub>3</sub>)<sub>3</sub>), 31.9 (PC(CH<sub>3</sub>)<sub>3</sub>), 30.5 (PC(CH<sub>3</sub>)<sub>3</sub>), 29.7 (PC(CH<sub>3</sub>)<sub>3</sub>), 24.0 (ArCH<sub>3</sub>), 23.0 (ArCH<sub>3</sub>), 22.7 (ArCH<sub>3</sub>), 21.4 (ArCH<sub>3</sub>), 21.1 (ArCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 163.0 MHz):  $\delta$  –2.1. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 99.4 MHz):  $\delta$  –1.96. Anal. Calcd for C<sub>41</sub>H<sub>66</sub>ClIrP<sub>2</sub>Si: C, 56.17; H, 7.59. Found: C, 55.86; H, 7.86.

# ASSOCIATED CONTENT

#### **S** Supporting Information

CIF files giving crystallographic data for the crystal structure studies in the paper. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

#### Notes

The authors declare no competing financial interest.

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