Reactions of the Square-Planar Compounds $Ir(C_2Ph)L_2(PCy_3)$ (L_2 = 2 CO, TFB) with $HSiR_3$ (R = Et, Ph) and $H_{x+1}SiPh_{3-x}$ (x = 1, 2): Stoichiometric and Catalytic Formation of Si−C Bonds

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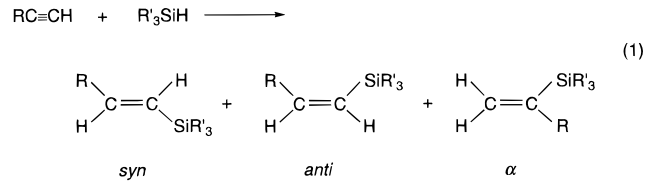
The square-planar *cis*-dicarbonyl complex $Ir(C_2Ph)(CO)_2(PCy_3)$ (**1**) reacts with ca. 1 equiv of $HSiR_3$ to give, in quantitative yield, the corresponding alkynyl−hydrido−silyl derivatives $Ir(C_2Ph)(H)(SiR_3)(CO)_2(PCy_3)$ (SiR_3 = $SiEt_3$ (**2**), $SiPh_3$ (**3**), $SiHPh_2$ (**4**), and SiH_2Ph (**5**)). The reactivity of the related tetrafluorobenzobarrelene compound $Ir(C_2Ph)(TFB)(PCy_3)$ (**6**) toward $HSiR_3$ has been also studied by NMR spectroscopy. The addition of ca. 2 equiv of $HSiEt_3$ to a benzene-d_6 solution of **6** affords $IrH_2(SiEt_3)(TFB)(PCy_3)$ (**7**) and PhC≡$CSiEt_3$ in a 1:1 molar ratio, while the reaction of **6** with ca. 1 equiv of $HSiPh_3$ yields, after 1 h and 30 min, $IrH_2(SiPh_3)(TFB)(PCy_3)$ (**10**, 8%), $Ir\{C(SiPh_3)=CHPh\}(TFB)(PCy_3)$ (**11**, 52%), and PhC≡$CSiPh_3$ (8%). The addition of ca. 1 equiv of H_2SiPh_2 to a benzene-d_6 solution of **6** leads, after 1 h, to $IrH_2\{Si(C_2Ph)Ph_2\}(TFB)(PCy_3)$ (**12**) in 90% yield. The alkynyl compounds **1** and **6** have been found to be active catalysts for the addition of triethylsilane to phenylacetylene. In all experiments, PhCH=CH_2, PhC≡$CSiEt_3$, *cis*-PhCH=CH($SiEt_3$), *trans*-PhCH=CH($SiEt_3$), and Ph($SiEt_3$)C=CH_2 were obtained. On the basis of the results from the stoichiometric reactions together those from the catalytic experiments, reaction pathways for the formation of these silylate products are discussed.

Introduction

The addition of silanes to alkynes catalyzed by transition metal complexes is one of the most important laboratory and industrial methods of forming vinylsilanes,[1] which have shown to be versatile intermediates in organic synthesis.[2] In the hydrosilylation of terminal alkynes, both the normal *syn*- and the unusual *anti*-addition products are formed, as well as the α isomer (eq 1), and much attention has received in an attempt to develop highly selective catalysts.[3]



The formation of the *anti*-addition product is interesting because the *cis* isomer is a result of the *trans*-addition of the silane to the alkyne. Ojima,[3n] Crabtree,[4] and we[3p,w] have proposed that the *anti*-addition product is formed by initial insertion of the unsaturated substrate into a M−Si bond, followed by isomerization of the (*Z*)-vinylsilyl intermediate to the less sterically congested (*E*)-vinylsilyl isomer (Scheme 1).

Recently, it has been also observed that in the presence of certain iridium catalysts the hydrosilylation reaction furthermore produces RC≡$CSiR'_3$, according to eq 2.[4,5]

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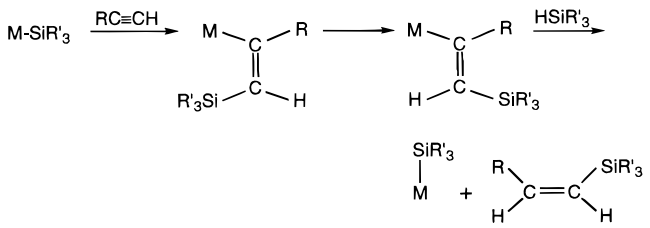
Scheme 1



Crabtree *et al.* have suggested that once the (*E*)-vinylsilyl intermediate has been formed, β-elimination of the *endo*-hydrogen atom of the vinylsilyl group could afford the silylation product.[4] Recently, we have examined the addition of triethylsilane to phenylacetylene catalyzed by $[Ir(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)]BF_4$.[6] This study has revealed that under the catalytic conditions both hydrido−alkynyl and hydrido−silyl species are formed. Hydrido−alkynyl species are the key intermediates for the formation of $PhC{\equiv}CSiEt_3$, while hydrido−silyl species are the key intermediates for the formation of *cis*-$PhCH{=}CH(SiEt_3)$.[6b] In addition, we note from some of our previous reports that the formation of the dehydrogenative silylation product takes place when the *cis*-vinylsilane is the major product of the catalytic reactions.[7] Interestingly, in these cases, the catalysts are alkynyl derivatives or complexes which react with terminal alkynes to give alkynyl compounds.[8] Thus, at the first glance, one could think that, in some cases, the formation of transition metal alkynyl compounds, during the catalytic hydrosilylation, plays a main role in the formation of the *anti*-addition product. In this respect, the investigation of the reactivity of alkynyl complexes with silanes is of great interest.

For several years, we have been exploring the reactivity of square-planar iridium(I) complexes toward silanes. Eight years ago, we reported that the alkoxy compounds $Ir(OR)(COD)(PR'_3)$ (COD = 1,5-cyclooctadiene; R = Me, $PR'_3 = PPh_3$; R = Et, $PR'_3 = PCy_3$) react with $HSiEt_3$ and $HSiMe_2Ph$ to give $ROSiR''_3$ ($SiR''_3 = SiEt_3$, $SiMe_2Ph$) and the dihydrido−silyl complexes $IrH_2(SiR''_3)(COD)(PR'_3)$.[9] Subsequently, we observed that the reactions of the acetato complex $Ir\{\eta^1\text{-}OC(O)CH_3\}(TFB)(PR_3)$ (TFB = tetrafluorobenzobarrelene; $PR_3 = PPh_3$, PCy_3, P^iPr_3) with $HSiR'_3$ also led to dihydrido−silyl derivatives of the formula $IrH_2(SiR'_3)(TFB)(PR_3)$ (R′ = Et, Ph). The same reactions with H_2SiPh_2 afford $IrH_2\{Si[OC(O)CH_3]Ph_2\}(TFB)(PR_3)$, which are the first iridium compounds containing an acetoxysilyl ligand.[7a] As a continuation of this work, the reactivity of the *cis*-dicarbonyl compound $Ir\{\eta^1\text{-}OC(O)CH_3\}(CO)_2(PCy_3)$ toward $HSiEt_3$, $HSiPh_3$, H_2SiPh_2, and H_3SiPh was examined. The study revealed that the *cis*-dicarbonyl complex undergoes reactions to give dihydrido−silyl and bis(silyl) derivatives depending upon the nature of the silane used. The complexes $IrH(SiHPh_2)_2(CO)_2(PCy_3)$ and $IrH(SiH_2Ph)_2(CO)_2(PCy_3)$, which were obtained by reaction of $Ir\{\eta^1\text{-}OC(O)CH_3\}(CO)_2(PCy_3)$ with H_2SiPh_2 and H_3SiPh, react with alcohols to afford $IrH_2\{Si(OR)Ph_2\}(CO)_2(PCy_3)$ and $IrH_2\{Si(OR)_2Ph\}(CO)_2(PCy_3)$, respectively.[10] Recently, it has been observed that the oxidative addition of H_2SiPh_2 to the complexes $Ir(acac)(\eta^2\text{-}CH_3O_2C\text{-}C{\equiv}CCO_2CH_3)(PR_3)$ ($PR_3 = P^iPr_3$, PCy_3) produces $Ir(acac)\{C[CH(OCH_3)OSiPh_2]{=}CHCO_2CH_3\}(PR_3)$, where the bonding situation in the Ir−Si−O sequence could be described as an intermediate state between metal-silylene stabilized by an oxygen base and a tetrahedral silicon.[11]

As a continuation of our work in this field, and with the idea of casting some light on the role of the transition metal alkynyl compounds in the formation of *cis*-$RCH{=}CH(SiR'_3)$ during the catalytic hydrosilylation of terminal alkynes, we have now studied the reactivity of the square-planar alkynyliridium(I) compounds $Ir(C_2Ph)(CO)_2(PCy_3)$ and $Ir(C_2Ph)(TFB)(PCy_3)$ toward $HSiEt_3$, $HSiPh_3$, H_2SiPh_2, and H_3SiPh. Although most of the hydridosilyliridium(III) complexes previously reported have been obtained by oxidative addition of silanes to square-planar iridium(I) compounds,[12] as far as we know, the oxidative addition of silanes to alkynyl derivatives of this type has not been previously studied.

In this paper, we report the characterization of the first alkynyl−hydrido−silyl and dihydrido−alkynylsilyl derivatives of iridium(III). The catalytic activity of $Ir(C_2Ph)(CO)_2(PCy_3)$ and $Ir(C_2Ph)(TFB)(PCy_3)$ in the addition of triethylsilane to phenylacetylene is also reported.

Results and Discussion

Reactions of $Ir(C_2Ph)(CO)_2(PCy_3)$ with $HSiR_3$. After 1 h, the addition of ca. 1 equiv of $HSiEt_3$, $HSiPh_3$,

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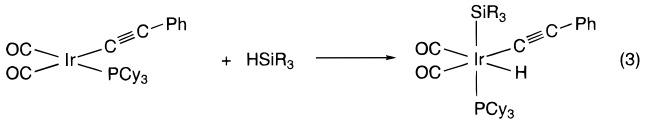
H_2SiPh_2, or H_3SiPh to yellow benzene-d_6 solutions of $Ir(C_2Ph)(CO)_2(PCy_3)$ (**1**) does not produce any change in the solution color. However, the IR spectra, as well as the ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra clearly indicate that the alkynyl−hydrido−silyl derivatives $Ir(C_2Ph)(H)(SiR_3)(CO)_2(PCy_3)$ have been formed in quantitative yield, according to eq 3. In solution, these compounds are stable up to 24 h if kept under an argon atmosphere at room temperature.

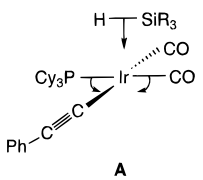


1

SiR_3 = $SiEt_3$ (**2**), $SiPh_3$ (**3**), $SiHPh_2$ (**4**), SiH_2Ph (**5**)

The presence of two carbonyl ligands mutually cis disposed and an alkynyl ligand is strongly supported by the IR and $^{13}C\{^1H\}$ NMR spectra. The IR spectra show two ν(CO) absorptions in the terminal carbonyl region (between 2060 and 1998 cm^{-1}), along with the ν(C≡C) and ν(Ir−H) vibrations between 2120 and 2140 cm^{-1}. Because the carbonyl ligands are chemically inequivalent, the $^{13}C\{^1H\}$ NMR spectra show two doublets at about 172 ppm. With regard to the values of the P−C coupling constants (about 5 Hz) there is no doubt about the mutually cis disposition of both carbonyl groups and the phosphine ligand. The $^{13}C\{^1H\}$ NMR spectra also contain the resonances due to the alkynyl ligand. The C_α carbon atoms appear as doublets at about 73 ppm with coupling constants of about 15 Hz, while the C_β carbon atoms also appear as doublets at about 107 ppm, but with P−C coupling constants of approximately 4 Hz. In the ^1H NMR spectra the most noticeable resonances are those corresponding to the hydrido ligands at about −9 ppm, which appear as doublets with P−H coupling constants between 14.7 and 15.6 Hz. The presence of only one hydrido ligand in these compounds was inferred from the $^{31}P\{^1H\}$ NMR spectra, which contain a singlet between 8.2 and 12.2 ppm which under off-resonance conditions due to P−H coupling is split into a doublet. The $^{31}P\{^1H\}$ NMR spectra also show the satellites due to the ^{29}Si isotope. The values of the P−Si coupling constants, between 73 and 91 Hz, strongly support the mutually trans disposition of the silyl and phosphine ligands.

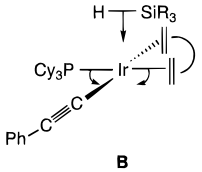
The oxidative addition of silanes to iridium(I) complexes is generally viewed as a diastereoselective concerted cis addition process with specific substrate orientation.[12k] The exclusive formation of **2**−**5** is in agreement with this. Thus, the addition of silanes to **1** seems to occur along the OC−Ir−P axis with the silicon atom above the carbonyl group (**A**). The basis of this



A

preference is probably steric and involves minimizing nonbonded interactions between the silyl ligands and the cyclohexyl groups of the phosphine. The same trend has been recently observed for the oxidative addition of $HSnPh_3$ and HSn^nBu_3 to **1**.[13]

Reactions of $Ir(C_2Ph)(TFB)(PCy_3)$ with $HSiR_3$. After 1 h the ^1H and $^{31}P\{^1H\}$ NMR spectra of the solution formed by addition of ca. 1 equiv of $HSiEt_3$ to $Ir(C_2Ph)(TFB)(PCy_3)$ (**6**) in benzene-d_6 show the resonances of **6** and the previously described dihydrido−silyl derivative $IrH_2(SiEt_3)(TFB)(PCy_3)$ (**7**)[7a] in a 1:1 intensity ratio. Analysis by gas chromatography of the solution also reveals the additional formation of PhC≡$CSiEt_3$, which was characterized by mass spectroscopy. The amount of PhC≡$CSiEt_3$ formed was similar to that of **7**. The addition of $HSiEt_3$ to the solution of **6** in a 2:1 molar ratio leads, in quantitative yield, to a mixture of **7** and PhC≡$CSiEt_3$ in a 1:1 molar ratio. During the reaction, the formation of phenylacetylene was not observed. The above mentioned data can be rationalized according to Scheme 2. In agreement with eq 3, the reaction could initially involve the oxidative addition of $HSiEt_3$ to **6**, along the olefin−Ir−P axis (**B**), to give **8** (SiR_3 = $SiEt_3$), followed by reductive elimination of PhC≡$CSiEt_3$ to give **9**. The subsequent oxidative addition of a second molecule of $HSiEt_3$ to **9** should lead to **7**.



B

The elimination of PhC≡$CSiEt_3$ from **8** merits further considerations. Due to the facial disposition of the silyl, hydrido, and alkynyl ligands, three unimolecular reductive eliminations are possible, leading to $HSiEt_3$, PhC≡CH, or PhC≡$CSiEt_3$. The first one again leads to **6**, and it is not our interest. However, of particular interest is the question of competitive PhC≡CH vs PhC≡$CSiEt_3$ reductive elimination. Whereas the reductive elimination of C−H bonds is a well-documented process,[12v,14] there are very few examples for the reductive elimination of Si−C bonds.[12o,15] Milstein *et al.*[12t] have recently studied the possible reductive elimination from complexes of type *fac*-$IrH(CH_3)(SiR_3)(PMe_3)_3$. While both the $Si(OEt)_3$ and $SiPh_3$ derivatives exclusively liberate CH_4 on heating, the $SiEt_3$ derivative gives CH_4 + $MeSiEt_3$ in a 4:1 molar ratio. The different behaviors of the SiR_3 complexes have been attributed to the different M−Si bond strengths. Electron-donating groups at the silicon atom weaken the M−Si bond and make the Si−C elimination competitive with the C−H one.

The intermediate **8** exclusively eliminates PhC≡$CSiR_3$, and the reductive elimination of phenylacetylene does not occur because of the cis constraint imposed by the chelating tetrafluorobenzobarrelene ligand and the fact

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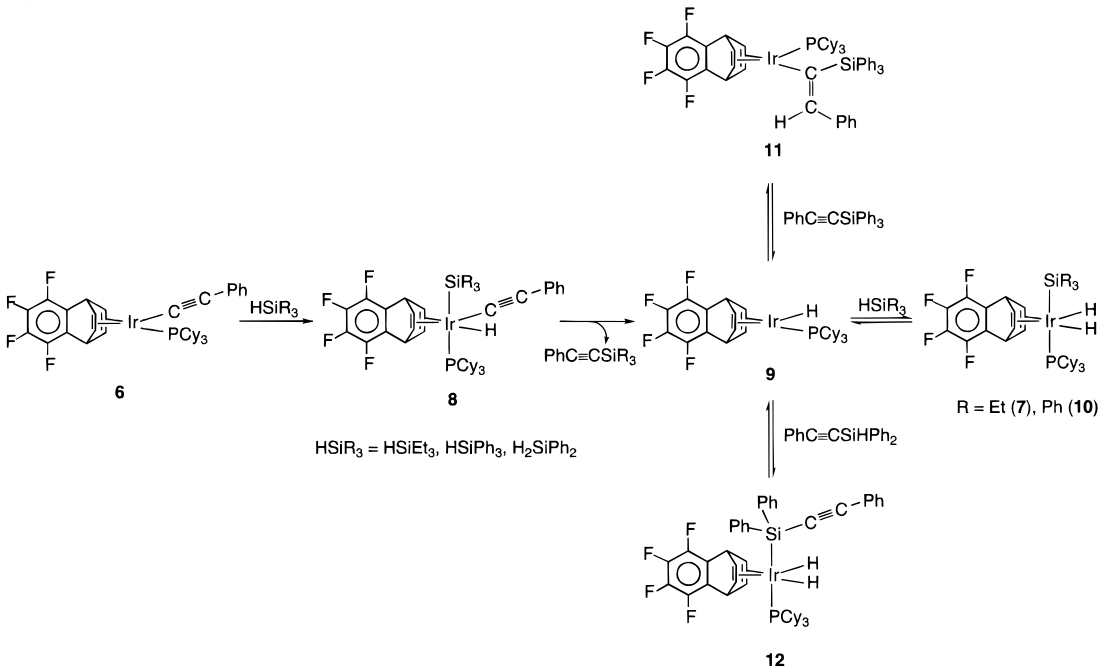
Scheme 2



that in a concerted reductive elimination the ligands trans to the leaving ligands move into mutually trans positions in the resulting four-coordinate complex.[12v,16] Thus the unfavorable elimination becomes the only possible alternative.

New Si−C bonds are also formed from the reactions of **6** with $HSiPh_3$ and H_2SiPh_2. After 30 min, the $^{31}P\{^1H\}$ NMR spectrum of the solution formed by addition of ca. 1 equiv of $HSiPh_3$ to **6** in benzene-d_6 shows the singlet of **6** at 23.2 ppm and a new singlet at 17.7 ppm. Satellites due to the ^{29}Si isotope are not observed, and the intensity ratio between the two resonances is 6:4. After 1 h and 30 min, a new singlet at 8.4 appear. This resonance was assigned to the previously reported dihydrido−silyl derivative $IrH_2(SiPh_3)(TFB)(PCy_3)$ (**10**) by comparison of this spectrum with a pure sample. The composition of the mixture was ca. 40% of **6**, 52% of the singlet at 17.7 ppm, and 8% of **10**. After 2 h and 30 min the new composition of the mixture was ca. 31%, 50%, and 19%. The ^1H NMR spectra and the analysis by gas chromatography of the three solutions show the presence of ca. 60% (30 min), 30% (1 h and 30 min), and 10% (2 h and 30 min) of unreacted $HSiPh_3$. In addition the formation of $PhC{\equiv}CSiPh_3$ in similar amounts to that of **10** was also observed.

Figure 1 shows the ^1H NMR spectrum of the solution obtained after 1 h and 30 min in the 2.5−6.5 ppm region. This spectrum contains the olefinic resonances of **6** and **10** along with a singlet at 6.50 (1 H) ppm, and three broad resonances at 5.31 (2 H), 3.45 (2 H), and 2.74 (2 H). The singlet at 6.50 is characteristic for a β-proton of an alkenyl group,[17] while the broad resonances are characteristic for a tetrafluorobenzobarrelene ligand, with chemically inequivalent olefinic bonds which are

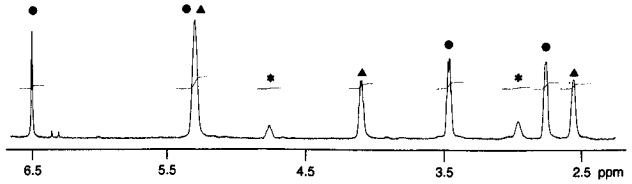


Figure 1. ^1H NMR spectrum in the 6.5−2.5 ppm region of the reaction of $Ir(C_2Ph)(TFB)(PCy_3)$ (**6**) with $HSiPh_3$ after 1 h and 30 min of reaction: $Ir(C_2Ph)(TFB)(PCy_3)$ (▲); $Ir\{C(SiPh_3){=}CHPh\}(TFB)(PCy_3)$ (●); $IrH_2(SiPh_3)(TFB)(PCy_3)$ (*).

coordinated to an iridium atom in a square-planar arrangement.[13] In the APT $^{13}C\{^1H\}$ NMR spectrum the resonances of the alkenyl group of this compound appear as a doublet with negative intensity at 146.16 ppm (J_{P-C} = 2.7 Hz), assigned to the α-carbon atom, and a singlet with positive intensity at 124.47 ppm, assigned to the β-carbon atom. Near the negative doublet the satellites due to the ^{29}Si isotope appear (J_{C-Si} = 35 Hz), suggesting that the α-carbon atom of the alkenyl group is also linked to a triphenylsilyl group. Therefore, the above spectroscopic data strongly support that the singlet at 17.7 ppm in the $^{31}P\{^1H\}$ NMR spectra corresponds to the square-planar alkenylsilyl derivative $Ir\{C(SiPh_3){=}CHPh\}(TFB)(PCy_3)$ (**11**).

Alkenylsilyl derivatives are rare. Eish, Lee, *et al.*[18] have reported that at −20 °C the chloroform solutions of the titanocene dichloride compound Cp_2TiCl_2 yield $[Cp_2Ti\{C(SiMe_3){=}CHPh\}]AlCl_4$, by treatment with $PhC{\equiv}CSiMe_3$ in the presence of CH_3AlCl_2. Tanaka *et al.*[19] have observed that alkynes undergo insertion reactions into the Me_3Si-Pt bond of $PtBr(SiMe_3)(PEt_3)_2$, to afford the β-alkenylsilyl derivatives $PtBr\{CR{=}CR(SiMe_3)\}(PEt_3)_2$. Suzuki *et al.*[20] have found that the

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treatment of the bis(μ-silylene) complex [Cp*Ru(μ-$SiPh_2$)(μ-H)]$_2$ with acetylene leads to the μ-2,5-1-disilaruthenacyclopentene complex Cp*Ru(μ-$SiPh_2$-$CH{=}CHSiPh_2$)(μ-H)$_2$RuCp* as a result of the insertion of C_2H_2 into a Ru−Si bond of [Cp*Ru(μ-$SiPh_2$)(μ-H)]$_2$, and very recently Jones *et al.*[21] described the synthesis of Cp*Ru{$C(SiHMe_2){=}CPh_2$}PR_3, which can be viewed as a 1-silaallene stabilized by both metal ligation and interaction with a metal−hydrogen bond.

The formation of **11** involves the insertion of $PhC{\equiv}CSiPh_3$, formed by reductive elimination from **8** ($SiR_3 = SiPh_3$), into the Ir−H bond of the intermediate **9** (Scheme 2). This reaction could proceed by a concerted mechanism involving a four-center intermediate, or, alternatively, via a vinylidene intermediate. In this context, it should be noted that Werner *et al.*[22] have recently observed that not only 1-alkynes $HC{\equiv}CR$ but also the trialkylsilyl derivatives $RC{\equiv}CSiR'_3$ can be transformed in the coordination sphere of rhodium into the isomeric disubstituted vinylidenes, $:C{=}C(SiR'_3)R$. The position of the triphenylsilyl group at the α-carbon atom of the alkenyl ligand of **11** rules out the possible participation of a vinylidene intermediate. In addition, it should be mentioned that **11** is the kinetically favored compound from the reaction of **6** with $HSiPh_3$. Furthermore, the dihydrido−silyl complex **11** is formed in a significant quantity (about 20%) after 2 h and 30 min. This suggests that in the presence of silane **11** is in equilibrium with **9** and **10**. The deinsertion of the alkyne from **11** most probably involves the β-elimination of the *endo*-hydrogen atom of the alkenylsilyl ligand, which is in agreement with the previously mentioned Crabtree proposal.

The addition of ca. 1 equiv of H_2SiPh_2 to a benzene-d_6 solution of **6** in an NMR tube leads to the dihydrido−silyl complex $IrH_2\{Si(C_2Ph)Ph_2\}(TFB)(PCy_3)$ (**12**) (Scheme 2) in 90% yield, after 1 h. The presence of two hydride ligands in **12** is strongly supported by the $^{31}P\{^1H\}$ NMR spectrum, which shows a singlet at 10.7 ppm, which at −60 °C, under off-resonance conditions due to the P−H coupling, is split into a triplet. Near this singlet, the satellites due to the ^{29}Si isotope appear. The value of the Si−P coupling constant (60 Hz) is in agreement with a mutually trans disposition for the tricyclohexylphosphine ligand and the silyl group. Similarly to the ^1H NMR spectra of **7** and **10**, the ^1H NMR spectrum of **12** is temperature-dependent (Figure 2). At room temperature the hydrido ligands appear as a broad resonance at −14.70 ppm, while the tetrafluorobenzobarrelene diolefin gives rise to two CH resonances, one aliphatic at 5.30 ppm and the other olefinic at 3.40 ppm. At −60 °C in toluene-d_8, the hydrido ligands appear at −14.80 ppm as a doublet with a P−H coupling constant of 19.9 Hz, suggesting that both hydrido ligands are chemically equivalent and are disposed cis to the phosphine ligand. This disposition leads to a situation where the aliphatic CH protons of the tetrafluorobenzobarrelene diolefin are chemically inequivalent; furthermore, the protons of each double carbon−carbon bond are also mutually

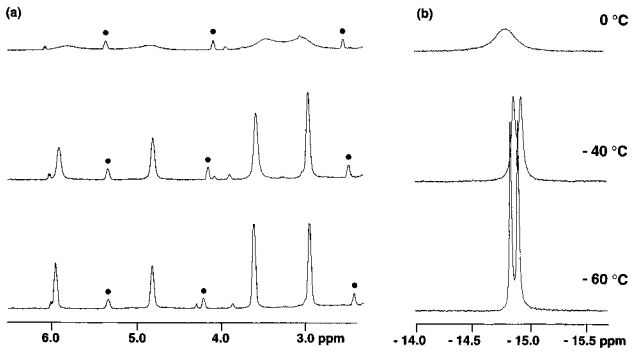

Figure 2. Variable-temperature ^1H NMR spectra (toluene-d_8) of $IrH_2\{Si(C_2Ph)Ph_2\}(TFB)(PCy_3)$ (**12**): (a) 6.5−2.5 ppm region (signals marked with ● correspond to $Ir(C_2Ph)$-$(TFB)(PCy_3)$ (**6**)) (b) hydride region.

inequivalent, although both olefinic bonds are chemically equivalent. As would be expected for this arrangement, the spectrum at −60 °C contains four resonances due to the diolefin, two aliphatic at 5.90 and 4.78 ppm and two olefinic at 3.95 and 2.92 ppm. This behavior suggests that **12** has a rigid structure (Scheme 2) only at low temperature. At room temperature an intramolecular exchange process takes place, which involves the relative positions of the atoms of the diolefin. This phenomenon is general for this type of compounds and is a consequence of the trend that they have to release the tricyclohexylphophine ligand.[7a,10,13]

In the $^{13}C\{^1H\}$ NMR spectrum the most noticeable resonances are those correspondig to the C_α and C_β carbon atoms of the $SiC{\equiv}CPh$ group, which appear as a doublet with a P−C coupling constant of 4.6 Hz at 99.53 and as a singlet at 109.00 ppm, respectively.

Previously, we have reported that the square-planar compound $Ir\{\eta^1\text{-}OC(O)CH_3\}(TFB)(PCy_3)$ reacts with H_2-$SiPh_2$ to give the acetoxysilyl derivative $IrH_2[Si\{OC(O)$-$CH_3\}Ph_2](TFB)(PCy_3)$. This reaction probably occurs via the silylene intermediate $IrH_2\{\eta^1\text{-}OC(O)CH_3\}$-$({=}SiPh_2)(TFB)$, which evolves by nucleophilic attack of the acetato group at the silicon atom.[7a,10] A similar reaction pathway for the formation of **12** from **6** and H_2SiPh_2 is not probable. It is well-known that electronic structures and reactivities of organic fragments change when they coordinate to transition metals to form organometallic complexes. For example, the coordination of $[RC{\equiv}C]^-$ to a metal center transfers the nucleophilicity from the α-carbon atom to the β-carbon atom.[23] Therefore, the attack of the C_α carbon atom of the alkynyl group at the silicon atom of a silylene derivative does not seem likely, given the electrophilicity of both centers. Hence, it can be proposed that the formation of **12** from **6** and H_2SiPh_2 occurs by initial oxidative addition of H_2SiPh_2 to **6** to give **8** ($SiR_3 = SiHPh_2$). The reductive elimination of $PhC{\equiv}CSiHPh_2$ and subsequent oxidative addition of the Si−H of $PhC{\equiv}CSiHPh_2$ to **9** should afford **12** (Scheme 2). A similar mechanism has been proposed for silane exchange reactions.[9b,12d,24]

Addition of $HSiEt_3$ to $PhC{\equiv}CH$ Catalyzed by 1 and 6. As expected from eq 3 and Scheme 2, the square planar alkynyl complexes **1** and **6** catalyze the hydrosilylation of phenylacetylene with triethylsilane. The

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Table 1. Hydrosilylation of Phenylacetylene Catalyzed by Ir(C₂Ph)(CO)₂(PCy₃) (1)[a]

[PhC≡CH] (M)	[HSiEt₃] (M)	[silylated products] (M)	[PhC≡CSiEt₃] (M)	[Ph(SiEt₃)C=CH₂] (M)	[*cis*-PhCH=CH(SiEt₃)] (M)	[*trans*-PhCH=CH(SiEt₃)] (M)
0.24	0.18	0.16	0.022	0.014	0.077	0.047
0.24	0.24	0.18	0.023	0.027	0.075	0.055
0.24	0.36	0.23	0.021	0.049	0.084	0.076
0.24	0.48	0.22	0.018	0.053	0.084	0.065
0.18	0.24	0.16	0.014	0.025	0.076	0.045
0.36	0.24	0.19	0.028	0.016	0.103	0.043
0.48	0.24	0.18	0.029	0.010	0.099	0.042

[a] [Catalyst] = 2.4×10^{-3} M; cyclohexane (0.125 M) was used as an internal standard; solvent 1,2-dichloroethane; argon atmosphere. The formed amount of PhCH=CH₂ is very similar to that of PhC≡CSiEt₃.

Table 2. Hydrosilylation of Phenylacetylene Catalyzed by Ir(C₂Ph)(TFB)(PCy₃) (6)[a]

[PhC≡CH] (M)	[HSiEt₃] (M)	[silylated products] (M)	[PhC≡CSiEt₃] (M)	[Ph(SiEt₃)C=CH₂] (M)	[*cis*-PhC H=CH(SiEt₃)] (M)	[*trans*-PhCH=CH(SiEt₃)] (M)
0.24	0.24	0.216	0.014	0.002	0.166	0.034
0.24	0.36	0.23	0.008	0.002	0.151	0.069
0.24	0.48	0.22	0.003		0.104	0.107
0.36	0.24	0.22	0.023	0.006	0.156	0.035
0.48	0.24	0.22	0.03	0.003	0.145	0.042
0.72	0.24	0.22	0.040	0.005	0.136	0.039

[a] [Catalyst] = 2.4×10^{-3} M; cyclohexane (0.125 M) was used as internal standard; solvent 1,2-dichloroethane; argon atmosphere. The formed amount of PhCH=CH₂ is very similar to that of PhC≡CSiEt₃.

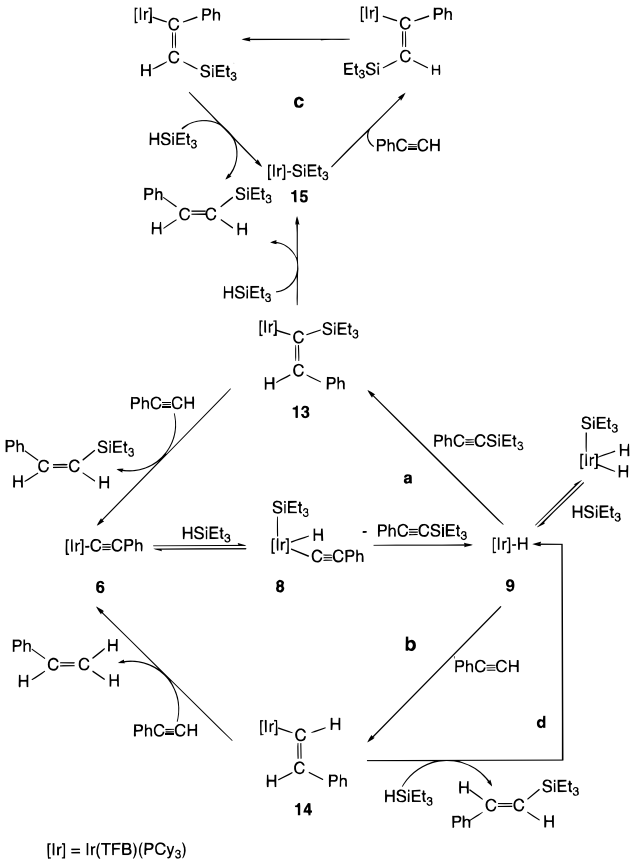
reactions were performed in 1,2-dichloroethane at 60 °C. In all experiments carried out PhCH=CH₂, PhC≡CSiEt₃, *cis*-PhCH=CH(SiEt₃), *trans*-PhCH=CH-(SiEt₃), and Ph(SiEt₃)C=CH₂ were obtained. The quantity of PhCH=CH₂ formed is very similar to that of PhC≡CSiEt₃. This can be rationalized in terms of a dehydrogenative silylation (eq 2), along with a normal hydrosilylation (eq 1). The rate and extent of the reactions are unaffected by the presence of hydroquinone, suggesting that the participation of radical-like species as catalytic intermediates is not significant.

Hydrosilylation experiments were performed at different concentrations of phenylacetylene and triethylsilane, and the results are collected in Tables 1 and 2. The dicarbonyl complex **1** is a less selective catalyst than **6**. In the presence of this complex, the relative amounts of each reaction product are not very dependent on phenylacetylene and triethylsilane concentrations and, in general, they do not show a clear trend. However, in the presence of the related tetrafluorobenzobarrelene derivative **6**, the relative amount of each reaction product clearly changes with the initial concentrations of the phenylacetylene and triethylsilane.

As seen from Table 2, in the initial presence of 0.24 M of triethylsilane, the concentration of *trans*-PhCH=CH(SiEt₃) is between 0.03 and 0.04 M and only traces of Ph(SiEt₃)C=CH₂ are formed. Under these conditions, the major product in all cases is *cis*-PhCH=CH(SiEt₃), resulting from the *anti*-addition of the silane to the alkyne. The amount of this product decreases as the phenylacetylene concentration increases. Contrary to this behavior, the amount of PhC≡CSiEt₃ rises. Scheme 3 illustrates different reaction sequences that allow us to rationalize the results recorded in Table 2.

The fact that the quantity of *trans*-PhCH=CH(SiEt₃) formed is independent of the phenylacetylene concentration and that the decrease of the amount of *cis*-PhCH=CH(SiEt₃) is similar to the increase of the amount of PhC≡CSiEt₃ suggests that the formation of the *syn*-addition product is independent of the formation of *cis*-PhCH=CH(SiEt₃) and PhC≡CSiEt₃ and, furthermore, suggests that the reaction pathways to afford the

Scheme 3



anti-addition product and PhC≡CSiEt₃ have some common point, which is sensitive to changes in the phenylacetylene concentration. According to Scheme 2, the dehydrogenative silylation product can be formed by reductive elimination from the alkynyl−hydrido−silyl intermediate **8**. The reductive elimination should afford **9**, which could inserts PhC≡CSiEt₃ (path **a**) to give an alkenyl intermediate **13**, similar to **11**, or alternatively could react with phenylacetylene to give the styryl derivative **14** (path **b**). At high phenylacetylene concentrations, both **13** and **14** could afford the corresponding olefins and **6**. The formation of olefins and alkynyl

compounds by reaction of alkenyl complexes and terminal alkynes is a well-known process.[25] Because the paths **a** and **b** are competitive and the path **b** would be favored with the increase of the phenylacetylene concentrations, the increase of this produces an increase in the amount of PhC≡CSiEt$_3$ and a decrease of the amount of *cis*-PhCH=CH(SiEt$_3$).

Alternatively to the reaction of **13** with phenylacetylene to give **6**, the intermediate **13** could also react with triethylsilane to give the silyl intermediate **15**, which could yield the *anti*-addition product by the Ojima's mechanism (path **c**). This reaction pathway should be favored at high triethylsilane concentrations and would produce a decrease in the amount of PhC≡CSiEt$_3$. Data collected in Table 2 show that the amount of dehydrogenative silylation product decreases as the triethylsilane concentration rises. However, the amount of *anti*-addition product also decreases. This decrease of the amount of *cis*-PhCH=CH(SiEt$_3$) on increasing the triethylsilane concentration is accompanied by an increase in the amount of *trans*-PhCH=CH(SiEt$_3$) formed. According to the Chalk−Harrod mechanism,[26] the *syn*-addition product could be formed by reaction of the styryl intermediate **14** with triethylsilane (path **d**), and its increase should involve a combined decrease of the amounts of PhC≡CSiEt$_3$ and *cis*-PhCH=CH(SiEt$_3$). Although this is observed, a decrease in the amount of *trans*-PhCH=CH(SiEt$_3$) on increasing the phenylacetylene concentration should be also expected, and as it has been previously mentioned, this does not occur. Hence, although it can not be rejected that some amount of *trans*-PhCH=CH(SiEt$_3$) is formed by path **d** of Scheme 3, the contribution of this reaction pathway to the overall *trans*-PhCH=CH(SiEt$_3$) is not significant. Thus, the *syn*-addition product should be formed by isomerization of *cis*-PhCH=CH(SiEt$_3$). In fact, we have also observed that, at 60 °C in the presence of **6** and triethylsilane, a mixture of 47% *cis*-PhCH=CH(SiEt$_3$) and 53% *trans*-PhCH=CH(SiEt$_3$) is converted into 4% *cis*-PhCH=CH(SiEt$_3$) and 96% *trans*-PhCH=CH(SiEt$_3$) after 30 min.

In summary, on the basis of eq 3 and Scheme 2, the results collected in Table 2 can be rationalized by Scheme 3, where the reaction pathways **a** and **c** explain the formation of *cis*-PhCH=CH(SiEt$_3$) and the reaction pathway **b** rationalizes the formation of PhC≡CSiEt$_3$. The *syn*-addition product, *trans*-PhCH=CH(SiEt$_3$), is mainly formed by isomerization of its *cis*-isomer.

Concluding Remarks

This study has revealed that the *cis*-dicarbonyl complex Ir(C$_2$Ph)(CO)$_2$(PCy$_3$) reacts with HSiR$_3$ to give Ir(C$_2$Ph)(H)(SiR$_3$)(CO)$_2$(PCy$_3$), which are the first examples of compounds of this type in iridium chemistry.

The reactions of the related tetrafluorobenzobarrelene derivative, Ir(C$_2$Ph)(TFB)(PCy$_3$), with HSiR$_3$ produce the selective formation of new Si−C bonds. The reaction with HSiEt$_3$ affords PhC≡CSiEt$_3$ and the dihydrido−silyl complex IrH$_2$(SiEt$_3$)(TFB)(PCy$_3$), while the reaction with HSiPh$_3$ and H$_2$SiPh$_2$ leads to Ir{C(SiPh$_3$)=CHPh}(TFB)(PCy$_3$) and IrH$_2${Si(C$_2$Ph)Ph$_2$}(TFB)(PCy$_3$), respectively, which are also the first examples of compounds of these types in iridium chemistry.

The complexes Ir(C$_2$Ph)(CO)$_2$(PCy$_3$) and Ir(C$_2$Ph)(TFB)(PCy$_3$) catalyze the addition of HSiEt$_3$ to phenylacetylene to give PhCH=CH$_2$, PhC≡CSiEt$_3$, *cis*-PhCH=CH(SiEt$_3$), *trans*-PhCH=CH(SiEt$_3$), and Ph(SiEt$_3$)C=CH$_2$. On the basis of the results obtained from the study of the reactivity of the catalysts toward HSiR$_3$ and from the catalytic experiments, we conclude that intermediates of the types M(H)(C$_2$R)(SiR$_3$) and M{C(SiR$_3$)=CHR} can play a main role in the formation of the dehydrogenative silylation (RC≡CSiR$_3$) and *anti*-addition (*cis*-RCH=CH(SiR$_3$)) products.

Experimental Section

General Data. All reactions were carried out with the use of standard Schlenk procedures. Solvents were dried and purified by known procedures and distilled under argon prior to use. Elemental analyses were performed with a Perkin-Elmer 2400 CHNS/O analyzer. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Varian UNITY 300 spectrometer. Chemical shifts are expressed in parts per million upfield from Si(CH$_3$)$_4$ (^{1}H and ^{13}C{^{1}H} NMR spectra) or 85% H$_3$PO$_4$ (^{31}P{^{1}H} NMR spectra). Infrared spectra were run on a Perkin-Elmer 783 spectrophotometer as either solids (Nujol mulls on polyethylene sheets) or solutions (NaCl cell windows). Mass spectra analyses were performed with a VG Autospec instrument. In FAB$^+$ mode ions were produced with the standard Cs$^+$ gun at *ca.* 30 eV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. Electron impact MS (operating at 70 eV) was used for PhC≡CSiEt$_3$ and PhC≡CSiPh$_3$. The catalytic reactions were followed by measuring the silane consumption as a function of time using cyclohexane as the internal standard with a 15% β,β'-oxobis(propionitrile) on Chromosorb W-HP 80/100-mesh column at 40 °C on a Perkin-Elmer 8500 gas chromatograph with a flame ionization detector. Silicon-containing products were analyzed using a FFAP on Chromosorb GHP 80/100-mesh column at 175 °C. The starting materials, Ir(C$_2$Ph)(CO)$_2$(PCy$_3$) (**1**) and Ir(C$_2$Ph)(TFB)(PCy$_3$) (**6**), were prepared by published methods.[13]

Reaction of 1 with HSiEt$_3$. Preparation of Ir(C$_2$Ph)(H)(SiEt$_3$)(CO)$_2$(PCy$_3$) (2). This reaction was carried out in an NMR tube (method a) and on preparative scale (method b).

Method a. HSiEt$_3$ (10 μL, 0.063 mmol) was added to a solution of **1** (40 mg, 0.063 mmol) in benzene-d_6 (0.5 mL) contained in a 5 mm NMR tube. After 1 h, ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR were recorded. IR (CH$_2$Cl$_2$, cm^{-1}): ν(Ir−H) 2140 (m); ν(C≡C) 2130 (m); ν(CO) 2045 (s), 1998 (s). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): δ 7.52−6.93 (m, 5H, Ph), 2.20−1.10 (m, 33H, PCy$_3$), 0.96−0.50 (m, 15H, −SiEt$_3$), −9.27 (d, 1H, J_{P-H} = 15.6 Hz, Ir−H). ^{13}C{^{1}H} NMR (75.429 MHz, C$_6$D$_6$): δ 174.52 (d, J_{P-C} = 4.1 Hz, CO), 173.23 (d, J_{P-C} = 5.0 Hz, CO), 131.36 (s, Ph), 131.33 (s, Ph), 129.18 (s, Ph), 129.14 (s, Ph), 125.63 (s, Ph), 106.94 (d, J_{P-C} = 4.1 Hz, C$_\beta$, C≡C), 75.05 (d, J_{P-C} = 16.1 Hz, C$_\alpha$, C≡C), 34.38 (d, J_{P-C} = 18.9 Hz, PCy$_3$), 29.96 (s, PCy$_3$), 29.63 (s, PCy$_3$), 27.73 (d, J_{P-C} = 10.5 Hz, PCy$_3$), 27.63 (d, J_{P-C} = 10.6 Hz, PCy$_3$), 26.72 (s, PCy$_3$), 10.81 (d, J_{P-C} = 4.1 Hz, Si*C*H$_2$CH$_3$), 9.60 (d, J_{P-C} = 1.0 Hz, SiCH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (121.421 MHz, C$_6$D$_6$): δ 8.2 (s with ^{29}Si satellites, $J_{P-^{29}Si}$ = 73 Hz).

Method b. HSiEt$_3$ (25 μL, 0.159 mmol) was added to a solution of **1** (100 mg, 0.159 mmol) in toluene (5 mL). The solution was stirred for 1 h at room temperature and concentrated to ca. 0.5 mL, and addition of methanol caused the precipitation of a pale yellow solid. The solution was decanted, and the solid was washed with methanol and dried in vacuo, yield 77 mg (65%). Anal. Calcd for C$_{34}$H$_{54}$IrO$_2$PSi: C, 54.73;

(25) See for example: (a) Echavarren, A. M.; López, J.; Santos, A.; Romero, A.; Hermoso, J. A.; Vegas, A. *Organometallics* **1991**, *10*, 2371. (b) Santos, A.; López, J.; Montoya, J.; Noheda, P.; Romero, A.; Echavarren, A. M. *Organometallics* **1994**, *13*, 3605. (c) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616.

(26) Chalk, A. J.; Harrod, F. G. *J. Am. Chem. Soc.* **1965**, *87*, 16.

H, 7.29. Found: C, 55.10; H, 6.43. IR (Nujol, cm^{-1}): ν(Ir−H), ν(C≡C) 2146 (m); ν(CO) 2046 (s), 2004 (s); ν(C═C, Ph) 1599 (m). MS (FAB): *m/e* 747 ($M^+ + 1$), 718 ($M^+ - CO$), 528 ($M^+ - SiEt_3 - H - C_2Ph$).

Reaction of 1 with $HSiPh_3$. Preparation of $Ir(C_2Ph)(H)(SiPh_3)(CO)_2(PCy_3)$ (3). This reaction was carried out analogously as described for **2**, by starting from **1** (40 mg, 0.063 mmol) and $HSiPh_3$ (16.5 mg, 0.063 mmol) (method a) and by starting from **1** (100 mg, 0.159 mmol) and $HSiPh_3$ (41.3 mg, 0.159 mmol) (method b).

Method a. IR (CH_2Cl_2, cm^{-1}): ν(Ir−H) 2140 (m), ν(C≡C) 2130 (m), ν(CO) 2055 (s), 2010 (s). ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 8.10−6.83 (m, 20H, Ph), 2.20−1.00 (m, 33H, PCy_3), −8.71 (d, 1H, J_{P-H} = 14.8 Hz, Ir−H). $^{13}C\{^1H\}$ NMR (75.429 MHz, C_6D_6): δ 173.39 (d, J_{P-C} = 4.7 Hz, CO), 171.73 (d, J_{P-C} = 5.1 Hz, CO), 142.74 (d, J_{P-C} = 4.1 Hz, $SiPh_3$), 136.93 (s, $SiPh_3$), 131.29 (s, Ph), 131.26 (s, Ph), 130.03 (s, $SiPh_3$), 128.68 (s, Ph), 128.64 (s, Ph), 127.55 (s, $SiPh_3$), 125.77 (s, Ph), 109.23 (d, J_{P-C} = 4.6 Hz, C_β, C≡C), 74.44 (d, J_{P-C} = 15.7 Hz, C_α, C≡C), 34.34 (d, J_{P-C} = 19.8 Hz, PCy_3), 29.79 (s, PCy_3), 29.62 (s, PCy_3), 27.70 (d, J_{P-C} = 9.6 Hz, PCy_3), 27.61 (d, J_{P-C} = 9.2 Hz, PCy_3), 26.63 (s, PCy_3). $^{31}P\{^1H\}$ NMR (121.421 MHz, C_6D_6): δ 9.7 (s with ^{29}Si satellites, $J_{P-^{29}Si}$ = 89 Hz).

Method b. Compound **3** was isolated as a pale yellow solid, yield 99 mg (70%). Anal. Calcd for $C_{46}H_{54}IrO_2PSi$: C, 62.06; H, 6.11. Found: C, 61.38; H, 5.41. IR (Nujol, cm^{-1}): ν(Ir−H), ν(C≡C) 2135 (m); ν(CO) 2054 (s), 2012 (s); ν(C═C, Ph) 1600 (m). MS (FAB): *m/e* 890 (M^+), 862 ($M^+ - CO$), 834 ($M^+ - 2$ CO), 527 ($M^+ - SiPh_3 - H - C_2Ph$).

Reaction of 1 with H_2SiPh_2. Preparation of $Ir(C_2Ph)(H)(SiHPh_2)(CO)_2(PCy_3)$ (4). This reaction was carried out analogously as described for **2**, by starting from **1** (40 mg, 0.063 mmol) and H_2SiPh_2 (12.5 μL, 0.063 mmol) (method a) and by starting from **1** (100 mg, 0.159 mmol) and H_2SiPh_2 (31 μL, 0.159 mmol) (method b).

Method a. IR (CH_2Cl_2, cm^{-1}): ν(Ir−H), ν(Si−H) 2140 (m), ν(C≡C) 2125 (m), ν(CO) 2060 (s), 2015 (s). ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 8.32−7.00 (m, 15H, Ph), 6.39 (d, 1H, J_{P-H} = 6.6 Hz, Si−H), 2.20−1.10 (m, 33H, PCy_3), −8.95 (d, 1H, J_{P-H} = 15.1 Hz, Ir−H). $^{13}C\{^1H\}$ NMR (75.429 MHz, C_6D_6): δ 172.14 (d, J_{P-C} = 5.1 Hz, CO), 171.69 (d, J_{P-C} = 5.0 Hz, CO), 141.66 (d, J_{P-C} = 3.2 Hz, $SiPh_2$), 141.22 (d, J_{P-C} = 3.6 Hz, $SiPh_2$), 136.23 (d, J_{P-C} = 1.4 Hz, $SiPh_2$), 136.15 (d, J_{P-C} = 0.9 Hz, $SiPh_2$), 131.52 (s, Ph), 131.49 (s, Ph), 128.77 (s, Ph), 128.74 (s, Ph), 128.57 (s, $SiPh_2$), 128.41 (s, $SiPh_2$), 128.16 (s, $SiPh_2$), 127.80 (s, $SiPh_2$), 125.85 (s, Ph), 108.28 (d, J_{P-C} = 4.1 Hz, C_β, C≡C), 72.87 (d, J_{P-C} = 15.6 Hz, C_α, C≡C), 34.47 (d, J_{P-C} = 20.2 Hz, PCy_3), 29.91 (s, PCy_3), 29.62 (s, PCy_3), 27.62 (d, J_{P-C} = 10.1 Hz, PCy_3), 27.53 (d, J_{P-C} = 11.1 Hz, PCy_3), 26.56 (s, PCy_3). $^{31}P\{^1H\}$ NMR (121.421 MHz, C_6D_6): δ 11.6 (s with ^{29}Si satellites, $J_{P-^{29}Si}$ = 87 Hz).

Method b. Compound **4** was isolated as a pale yellow solid, yield 88 mg (68%). Anal. Calcd for $C_{40}H_{50}IrO_2PSi$: C, 59.01; H, 6.19. Found: C, 59.14; H, 5.39. IR (Nujol, cm^{-1}): ν(Ir−H), ν(Si−H), ν(C≡C) 2125 (m), ν(CO) 2057 (s), 2015 (s); ν(C═C, Ph) 1599 (m). MS (FAB): *m/e* 814 (M^+).

Reaction of 1 with H_3SiPh. Preparation of $Ir(C_2Ph)(H)(SiH_2Ph)(CO)_2(PCy_3)$ (5). This reaction was carried out analogously as described for **2**, by starting from **1** (40 mg, 0.063 mmol) and H_3SiPh (8 μl, 0.063 mmol) (method a) and by starting from **1** (100 mg, 0.159 mmol) and H_3SiPh (19.5 μL, 0.159 mmol) (method b).

Method a. IR (CH_2Cl_2, cm^{-1}): ν(Ir−H), ν(Si−H) 2135 (m), ν(C≡C) 2120 (m), ν(CO) 2055 (s), 2010 (s). ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 8.15−6.94 (m, 10H, Ph), 5.43 (m, br, 2H, Si−H), 2.10−1.00 (m, 33H, PCy_3), −9.36 (d, 1H, J_{P-H} = 14.7 Hz, Ir−H). $^{13}C\{^1H\}$ NMR (75.429 MHz, C_6D_6): δ 171.45 (d, J_{P-C} = 4.6 Hz, CO), 171.39 (d, J_{P-C} = 5.5 Hz, CO), 139.49 (d, J_{P-C} = 2.7 Hz, SiPh), 135.74 (s, SiPh), 135.72 (s, SiPh), 131.71 (s, Ph), 131.68 (s, Ph), 128.81 (s, Ph), 128.77 (s, Ph), 128.60 (s, SiPh), 128.24 (s, SiPh), 127.89 (s, SiPh), 125.92 (s, Ph), 107.65 (d, J_{P-C} = 4.1 Hz, C_β, C≡C), 72.21 (d, J_{P-C} = 14.7 Hz, C_α, C≡C), 34.47 (d, J_{P-C} = 20.7 Hz, PCy_3), 29.96 (s, PCy_3), 29.55 (s, PCy_3), 27.61 (d, J_{P-C} = 10.1 Hz, PCy_3), 27.51 (d, J_{P-C} = 10.6 Hz, PCy_3), 26.51 (s, PCy_3). $^{31}P\{^1H\}$ NMR (121.421 MHz, C_6D_6): δ 12.2 (s with ^{29}Si satellites, $J_{P-^{29}Si}$ = 91 Hz).

Method b. Compound **5** was isolated as a yellow oil. MS (FAB): *m/e* 736 ($M^+ - 2$ H), 603 ($M^+ - SiH_2Ph - CO$).

Reaction of 6 with $HSiEt_3$: Formation of $IrH_2(SiEt_3)(TFB)(PCy_3)$ (7) and $PhC{\equiv}CSiEt_3$. $HSiEt_3$ (8 μL, 0.05 mmol) was added to a solution of **6** (40 mg, 0.05 mmol) in benzene-d_6 (0.5 mL) contained in a 5 mm NMR tube. After 1 h the ^1H and $^{31}P\{^1H\}$ NMR spectra show signals corresponding to the starting material (**6**, 50%) and **7** (50%). $^{31}P\{^1H\}$ NMR (121.421 MHz, C_6D_6): δ 23.2 (s, **6**), 8.9 (s with ^{29}Si satellites, $J_{P-^{29}Si}$ = 52 Hz, triplet in off-resonance; **7**). MS (EI) analysis of the mother liquors shows the presence of $PhC{\equiv}CSiEt_3$. Mass fragmentation pattern of $PhC{\equiv}CSiEt_3$ (*m/e*): 216 (M^+), 187 ($M^+ - Et$), 159 ($M^+ - 2Et$), 131 ($M^+ - 3Et$).

Reaction of 6 with $HSiPh_3$: Formation of $IrH_2(SiPh_3)(TFB)(PCy_3)$ (10), $PhC{\equiv}CSiPh_3$, and $Ir\{C(SiPh_3){=}CHPh\}(TFB)(PCy_3)$ (11). $HSiPh_3$ (13 mg, 0.05 mmol) was added to a solution of **6** (40 mg, 0.05 mmol) in benzene-d_6 (0.5 mL) contained in a 5 mm NMR tube. The reaction was monitored by ^1H and $^{31}P\{^1H\}$. After 30 min the ^1H and $^{31}P\{^1H\}$ show signals corresponding to **6** (60%) and **11** (40%). After 1 h 30 min the distribution is as follows: **6** (40%), **11** (52%), and **10** (8%). After 2 h 30 min the distribution is as follows: **6** (31%), **11** (50%), and **10** (19%). MS (EI) of the mother liquors shows the presence of $PhC{\equiv}CSiPh_3$. Mass fragmentation pattern of $PhC{\equiv}CSiPh_3$ (*m/e*): 360 (M^+), 283 ($M^+ - Ph$), 181 ($M^+ - Ph - C_2Ph$).

Spectroscopic data for $Ir\{C(SiPh_3){=}CHPh\}(TFB)(PCy_3)$ (**11**) are as follows. ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 7.99−6.93 (m, 20H, Ph), 6.50 (s, ═CH), 5.31 (br, 2H, −CH TFB), 3.45 (m, 2H, ═CH TFB), 2.74 (br, 2H, ═CH TFB), 2.00−0.90 (m, 33H, PCy_3). $^{13}C\{^1H\}$ NMR (APT, 75.429 MHz, C_6D_6): δ 146.16 (d, J_{P-C} = 2.7 Hz, J_{C-Si} = 35 Hz, C_α), 139.12 (s, $SiPh_3$), 136.29 (s, $SiPh_3$), 130.02 (s, Ph), 128.74 (s, Ph), 127.82 (s, $SiPh_3$), 127.59 (s, $SiPh_3$), 125.71 (s, Ph), 124.25 (s, C_β), 59.82 (d, J_{P-C} = 12.0 Hz, ═CH), 48.22 (s, ═CH), 40.73 (s, −CH), 40.70 (s, −CH), 36.09 (d, J_{P-C} = 23.9 Hz, PCy_3), 30.40 (s, PCy_3), 27.87 (d, J_{P-C} = 10.6 Hz, PCy_3), 26.77 (s, PCy_3). $^{31}P\{^1H\}$ NMR (121.421 MHz, C_6D_6): δ 17.7 (s).

Reaction of 6 with H_2SiPh_2. Preparation of $IrH_2\{Si(C_2Ph)Ph_2\}(TFB)(PCy_3)$ (12). This reaction was carried out in an NMR tube (method a) and on a preparative scale (method b).

Method a. H_2SiPh_2 (9.8 μL, 0.05 mmol) was added to a solution of **6** (40 mg, 0.05 mmol) in benzene-d_6 (0.5 mL) contained in a 5 mm NMR tube. After 1 h, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR were recorded. ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 8.22−6.98 (m, 15H, Ph), 5.30 (br, 2H, −CH), 3.40 (br, 4H, ═CH), 2.00−1.00 (m, 33H, PCy_3), −14.70 (br, 2H, Ir−H). ^1H NMR (300 MHz, C_7D_8, −60 °C): δ 5.90 (s, 1H, −CH), 4.78 (s, 1H, −CH), 3.59 (s, 2H, ═CH), 2.92 (s, 2H, ═CH), −14.80 (d, 2H, J_{P-H} = 19.9 Hz, Ir−H). $^{13}C\{^1H\}$ NMR (75.429 MHz, C_6D_6): δ 145.65 (s, $SiPh_2$), 135.31 (s, $SiPh_2$), 132.17 (s, Ph), 128.59 (s, $SiPh_2$), 128.54 (s, Ph), 128.19 (s, $SiPh_2$), 124.88 (s, Ph), 109.00 (s, C_β, C≡C), 99.53 (d, J_{P-C} = 4.6 Hz, C_α, C≡C), 39.60 (d, J_{P-C} = 22.1 Hz, PCy_3), 30.12 (s, PCy_3), 27.73 (d, J_{P-C} = 10.1 Hz, PCy_3), 26.82 (s, PCy_3). $^{31}P\{^1H\}$ NMR (121.421 MHz, C_6D_6): δ 10.7 (s with ^{29}Si satellites, $J_{P-^{29}Si}$ = 62 Hz, triplet in off-resonance).

Method b. H_2SiPh_2 (24 μL, 0.125 mmol) was added to a solution of **6** (100 mg, 0.125 mmol) in toluene (5 mL), and an immediate color change from red to pale yellow was observed. This solution was stirred for 5 min at room temperature. The solution was concentrated to ca. 0.5 mL, and addition of

methanol caused the precipitation of a white solid. The solution was decanted, and the solid was washed with methanol and dried in vacuo; yield 76 mg (62%). Anal. Calcd for $C_{50}H_{56}F_4IrPSi$: C, 61.01; H, 5.73. Found: C, 60.39; H, 5.36. IR (Nujol, cm^{-1}): ν(C≡C) 2148 (m), ν(Ir−H) 2140 (m), ν(C═C, Ph) 1596 (m). MS (FAB): *m/e* 983 ($M^+ - H$), 883 ($M^+ - C_8H_5$).

Catalytic Studies. The hydrosilylation reactions were performed under argon at 60 °C. The reactions were carried out in a two-necked flask fitted with a condenser and a magnetic stirring bar. The second neck was capped with a septum to allow periodical samples to be taken without opening the system.

The procedure was as follows: Each complex was dissolved in a 1,2-dichloroethane solution (8 mL) containing $HSiEt_3$, PhC≡CH, and C_6H_{12}. The reaction mixture was stirred at 60 °C and monitored by gas chromatography.

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