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Addition of Water Across Si−Ir Bonds in Iridium Complexes with κ-*P*,*P*,*Si* (biPSi) Pincer Ligands

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Electrophiles such as Me^+, Ag^+, or protons react with the five-coordinate Ir(III) complex [IrClH(biPSi)] (biPSi = κ-*P*,*P*,*Si*-Si(Me){$(CH_2)_3PPh_2$}$_2$) by abstracting its chloride ligand. The resulting species can be stabilized by a variety of L ligands to give the cationic complexes $[IrH(biPSi)L_2]^+$. The derivative $[IrH(biPSi)(NCMe)_2]^+$ has been subjected to a kinetic study regarding the facile dissociations of its acetonitrile ligands. The presence of water changes the course of the reaction producing dihydride complexes that contain the silanol ligand κ-*O*,*P*,*P*-HOSi(Me){$(CH_2)_3PPh_2$}$_2$ (biPSiOH). The water activation product $[IrH_2(biPSiOH)(NCMe)](CF_3SO_3)$ undergoes insertion reactions with ethylene and phenylacetylene. The use of hydrolyzable fluorinated counterions such as PF_6^- or BF_4^- further modifies the reaction by provoking the incorporation of fluoride at the silicon atom of the former biPSi ligand. The dihydride resulting after such a process, $[IrH_2(biPSiF)(NCMe)_2]BF_4$ (biPSiF = κ-P^2-FSi(Me){$(CH_2)_3PPh_2$}$_2$), displays a *trans*-chelating diphosphine ligand. When dehydrogenating the Ir center, spontaneously or using ethylene as hydrogen acceptor, the diphosphine backbone undergoes a Si−C bond cleavage leading to a new Ir(III) species with κ-*P*,*Si* and κ-*C*,*P* chelate ligands.

Introduction

The addition of water to transition metal complexes is a key process for challenges such as the catalytic production of hydrogen[1] or the anti-Markovnikov hydration of alkenes.[2] Despite its importance, the reported examples of this reaction are scarce:[3] a noteworthy fact when considering the ubiquity of the water molecule and its easy activation by deprotonation. The lack of examples is attributable, at least in part, to the exigent thermodynamics of the O−H bond cleavage: difficult to balance only on the basis of weaker M−H and M−OH bonds. Probably as a result, some of the successful water additions to metal complexes involve extra thermodynamic contributions whose origin is the polynuclear nature of the reaction products or the participation of non-innocent functional ligands. In the first case, the resulting OH fragment can bridge metals, forming two bonds instead of one.[3,4] In the second, in addition to enabling alternative pathways for O−H bond splitting, the ligand environment facilitates the formation of strong new bonds such as C−H.[3,5]

The present work describes a water addition reaction that formally benefits from both aforementioned thermodynamic advantages, since the OH fragment ends up as a bridge between an iridium center and the silicon atom of a κ-*P*,*P*,*Si* pincer ligand, which therefore contributes with a strong Si−O bond.[6] This reaction, facile for complex [IrClH(biPSi)] (biPSi = κ-*P*,*P*,*Si*-Si(Me){$(CH_2)_3PPh_2$}$_2$) in the presence of electrophilic reagents, might limit the practical application in catalysis of silicon-donor pincers: ligands capable of stabilizing very reactive unsaturated complexes[7] with distinctive structures.[8] On the other hand, the reaction leads to new iridium derivatives with rare silanol pincers or *trans*-chelating

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disphosphines.[9] Moreover, this water addition is not a dead end, since any of its resulting fragments can undergo subsequent reaction under favorable thermodynamics.

Results and Discussion

In a previous work,[8] we described the behavior of the five-coordinate complex [IrClH(biPSi)] (**1**). The compound forms an equilibrium mixture of two isomers (*anti* and *syn*, attending to the relative orientation of the hydride and the methyl substituent at silicon) that interconvert very slowly. The isomers display rather similar structures but a noticeably different behavior as Lewis acids. Less expectedly given its coordinative unsaturation, we have now found that **1** also reacts with electrophiles such as the proton, Me^+ or Ag^+. The final result of these reactions is independent of the electrophile but depends on the presence of water or hydrolizable anions, as explained below.

Reactions with Electrophiles. The simplest and cleanest observed reactions between **1** and electrophilic reagents have been those with methyl triflate in chlorinated solvents. Out of the two likely targets for the electrophile in complex **1**, the hydride or the halide ligand,[10] the methyl selectively attacks the chloride to release methyl chloride. The in situ reaction at 250 K in $CDCl_3$ has permitted the NMR observation of the two coordination compounds resulting from this attack: tentatively formulated as the *syn* and *anti* isomers of the complex [Ir(O_3SCF_3)H(biPSi)] (**2**) (eq 1). The NMR data clearly establish the *syn* or *anti* structure of each isomer (^{1}H NOE) but not the triflate coordination. Both the ^{19}F and $^{13}C\{^1H\}$ NMR signals corresponding to this anion are slightly shifted with respect to those typical of non-coordinated triflates: δ −76.71 versus −78 ppm and 119.85 versus 122 ppm, respectively (for the major isomer **2**-*syn*). With regard to some precedents,[11] such small chemical shift differences might support the coordination of the triflate in **2**, although the coordination mode (chelate or monodentate) remains unclear. Actually, this aspect could be difficult to ascertain even with the help of X-ray data, as already discussed for the reported complex [Ir(O_2CMe)H(biPSi)], an analogue of **2** with acetate instead of triflate.[8]

Even though the clean generation of **2** is difficult and its isolation has not been possible, a variety of its cationic derivatives has been prepared by replacing the triflate by other ligands: acetonitrile, carbon monoxide, and bipyridine in eq 1. These cationic complexes, $[IrH(biPSi)(L)_2]^+$ (L = NCMe (**3**), CO (**4**); L_2 = bipy (**5**)), can also be conveniently prepared using silver salts or HBF_4 diethyl ether solutions as electrophiles, provided these hygroscopic reagents are dry.

Starting from equilibrium mixtures of **1** (*anti*/*syn* = 83/17),[8] both the neutral complex **2** and the cationic derivatives in eq 1 have been obtained as *anti*/*syn* mixtures of approximate composition 15/85, irrespective of the electrophilic reagent.

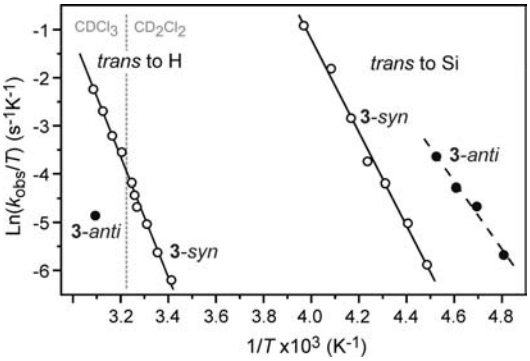
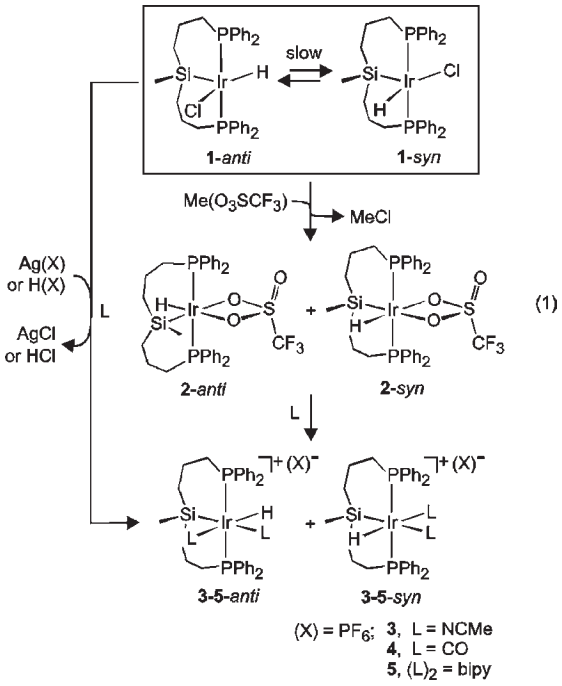


Figure 1. Eyring representations of the rate constants for acetonitrile dissociations from isomers **3**. Activation parameters for **3**-*syn*: *trans* to silicon: $\Delta H^{\ddagger}$ = 19 (±1) kcal mol^{-1}, $\Delta S^{\ddagger}$ = 27 (±1) cal K^{-1} mol^{-1}; *trans* to hydride: $\Delta H^{\ddagger}$ = 25 (±1) kcal mol^{-1}, $\Delta S^{\ddagger}$ = 25 (±1) cal mol^{-1} K^{-1}.

For cations **3**−**5**, this composition has been found to persist with time and even when the acetonitrile ligands of **3** are replaced in situ by CO or bipy. This suggests that the observed distribution of isomers has a kinetic origin. On the one hand, it would indicate that the reactions of **1** with electrophiles proceed with inversion of the stereochemistry around iridium, thus suggesting that the actions of the electrophile and incoming ligands are somehow concerted. On the other hand, it would imply that isomerizations (*anti* to *syn*) are more difficult for these cationic biPSi derivatives than for their neutral counterparts.[8]



The easy dissociation of acetonitrile ligands in complex **3** has been subjected to a kinetic study. Pseudo-first order rate constants (k_{obs}) have been obtained for the exchanges between free acetonitrile and each of the acetonitrile ligands of isomers **3**, using ^{1}H NMR spin saturation transfer and line-width methods (see Experimental Section). These k_{obs} have been found independent of the concentration of free acetonitrile, as expected for first order dissociation processes. The kinetic information collected for the major isomer **3**-*syn*, summarized in Figure 1, indicates that the

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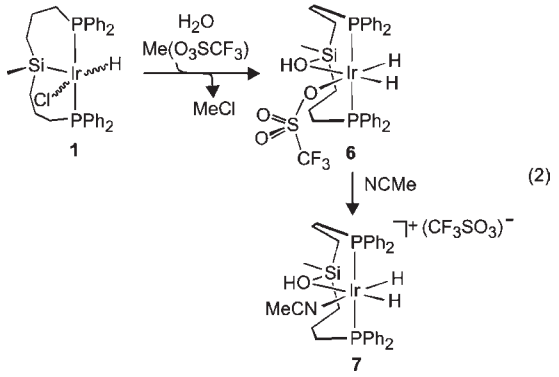
generation of a coordination vacancy *trans* to silicon is about 6 kcal mol^{-1} easier than *trans* to hydride, in agreement with the expected trend of *trans* effects.[12] For the minor isomer, **3**-*anti*, the experimental determinations could not be extended over temperature intervals wide enough to support Eyring analyses. Nevertheless, the rate constants indicate that the difference in lability between the two acetonitriles is greater for this isomer, since the ligand *trans* to silicon dissociates faster than in **3**-*syn* while than *trans* to hydride does it slower.

Water. The presence of adventitious water has been observed to modify the course of the reactions in eq 1, since the species resulting from chloride loss, readily activate this reagent. Again, the cleanest products have been obtained using methyl triflate, in this case together with 1 equiv of water. This procedure has allowed the preparation of complex $[Ir(O_3SCF_3)H_2(biPSiOH)]$ (**6**) (biPSiOH = κ-*O*,*P*,*P*-$HOSi(Me)\{(CH_2)_3PPh_2\}_2$) in excellent yield, as a pale yellow solid insoluble in diethyl ether (eq 2).



In spite of starting from an *anti*/*syn* mixture of **1**, complex **6** has been obtained as a single isomer. Its ^1H NMR spectrum shows two high-field signals corresponding to non-equivalent hydride ligands, both doublets of triplets, with a mutual J_{HH} coupling constant of 8.8 Hz and clear mutual NOE effects in the NOESY spectrum. The latter experiment also shows the spatial proximity of the methyl substituent at silicon and the OH hydrogen, in agreement with their proposed *syn* relative orientation. Just as for complex **2**, the NMR data of **6** are ambiguous when considering triflate coordination. In fact, the ^{19}F and $^{13}C\{^1H\}$ NMR chemical shifts of the signals corresponding to the proposed κ-*O* triflate are virtually those typical of the free anion. Yet, the in situ treatment of **6** with acetonitrile has been observed by NMR to produce the compound $[IrH_2(biPSiOH)(NCMe)](CF_3SO_3)$ (**7**) without additional signals suggesting the release of water or ligands other than triflate. This cationic complex has also been conveniently prepared starting from **1**, water, and acetonitrile, using triflic acid as the electrophile.

Complex **7** displays spectroscopic features similar to those already mentioned for its neutral precursor **6** and shows the solid state structure represented in Figure 2. The relevant bond distances and angles of this structure are collected in Table 1.The structure of **7** exhibits a tridentate *mer*-coordinating κ-*O*,*P*,*P* silanol ligand constructed from the biPSi and the OH of a water molecule. The silanol function displays conventional structural parameters and forms an $O-H\cdots OSO_2CF_3$ hydrogen bond with the triflate anion ($d(H\cdots O)$ = 1.957(14) Å). This latter interaction, very common for silanol functions in solid state,[13] has been removed from the representation of Figure 2 for clarity, although its details are available in the Supporting Information. As expected for a coordination position *trans* to hydride, the Ir−O bond distance is long, 2.254(2) Å, close to the upper limit of the Ir−O bond lengths distribution obtained from the CCDC.[14] This suggest that the silanol arm of this pincer might be readily dissociable, a fact that would imply that the observed *syn* relative orientation along the Me−Si−O−H bonds is the thermodynamically preferred one, not a kinetic result.

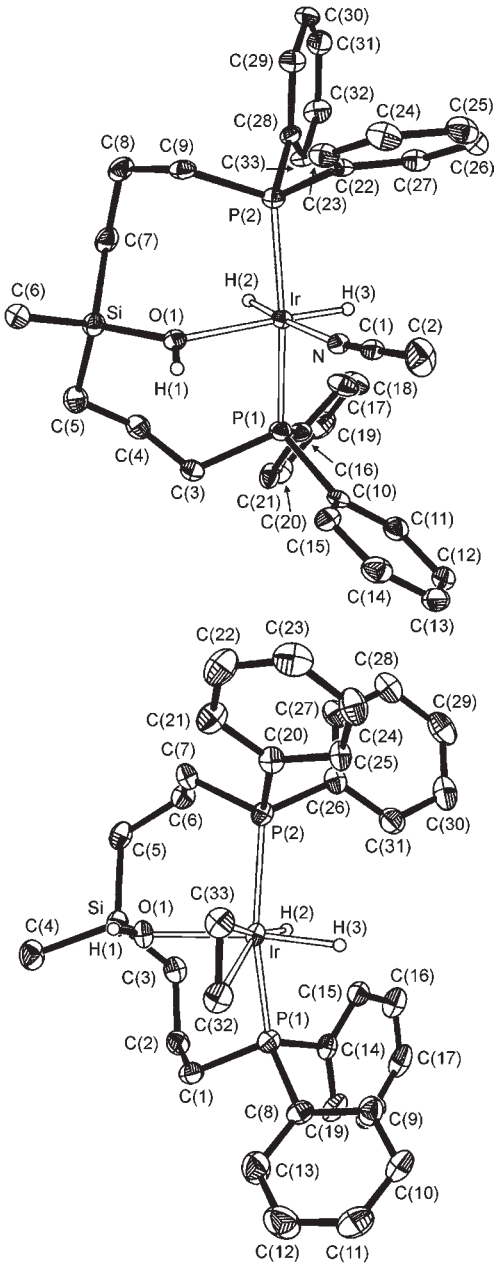


Figure 2. X-ray structures of the cations of complexes **7** (above) and **8** (below).

The formation of Si−O bonds by silane hydrolysis or alcoholysis has been the subject of investigation because

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Table 1. Bond Distances (Å) and Angles (deg) for Complexes **7** and **8**

	7		8
Ir−P(1)	2.2908(9)		2.3077(18)
Ir−P(2)	2.2999(9)		2.3032(17)
Ir−N	2.084(3)	Ir−C(32)	2.245(6)
		Ir−C(33)	2.241(6)
Ir−O	2.254(2)		2.241(4)
Ir−H(2)	1.471(10)		1.4739
Ir−H(3)	1.471(10)		1.6396
Si−O	1.674(3)		1.689(5)
P(1)−Ir−P(2)	171.66(3)		155.10(6)
P(1)−Ir−N	97.72(8)	P(1)−Ir−C(32)	84.63(18)
		P(1)−Ir−(C33)	120.66(18)
P(1)−Ir−O	91.21(6)		90.41(13)
P(1)−Ir−H(2)	83.8(12)		68.9
P(1)−Ir−H(3)	86.2(12)		82.9
P(2)−Ir−N	90.60(8)	P(2)−Ir−C(32)	120.19(18)
		P(2)−Ir−C(33)	84.08(18)
P(2)−Ir−O	92.08(7)		93.37(13)
P(2)−Ir−H(2)	87.9(12)		86.2
P(2)−Ir−H(3)	93.9(12)		93.5
		C(32)−Ir−C(33)	36.1(2)
N−Ir−O	87.48(10)	C(32)−Ir−O	85.5(2)
N−Ir−H(2)	176.6(13)	C(32)−Ir−H(2)	153.0
N−Ir−H(3)	93.9(14)	C(32)−Ir−H(3)	92.2
		C(33)−Ir−O	88.3(2)
		C(33)−Ir−H(2)	167.9
		C(33)−Ir−H(3)	93.6
O−Ir−H(2)	95.6(13)		99.5
O−Ir−H(3)	177.2(12)		173.1
H(2)−Ir−H(3)	83.1(18)		79.7

of the importance of silanols as bulding blocks in organic synthesis and in the polymer industry,[13] and because of the generalized use of silyl ethers as protecting groups for the hydroxyl function.[15] These reactions can be catalyzed by a variety of soluble metal complexes,[16] some of them of iridium.[17] The prevalent mechanistic description for Si−O bond formation during such processes involves the nucleophilic attack of water or alcohol to a previously activated silane at the metal coordination sphere,[16,17] a step fully consistent with the reaction in eq 2. The closest precedent for this reaction was described for the coordinatively saturated ruthenium complex [RuH(biPSi)$(CO)_2$], which was found capable of incorporating the oxygen atom of water, in the presence of bases, to form *κ-O,P,P* siloxide complexes.[18] In that system, the use of isotopically labeled water confirmed the source of oxygen atoms but did not offer further mechanistic information about the water splitting process. Our experiments using ^{2}H-labeled water in eq 2 have also failed to extract mechanistic information because of the Brønsted acidity of both the silanol and the hydrides of products **6** and **7**. These three hydrogen atoms have been found to rapidly exchange with the protons of free water

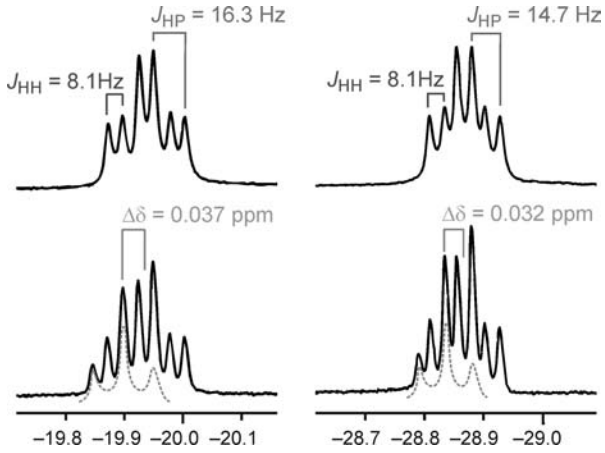
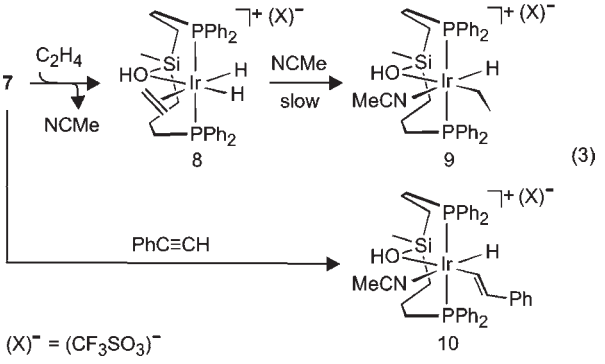


Figure 3. Hydride ^{1}H NMR signals of complex **7** (top) and a mixture of partially deuterated isotopomers (bottom).

provoking the fast redistribution of the label among all these acidic sites. The experiments have confirmed the thermodynamic preference of ^{2}H for the silanol position and its similar affinity for both hydride sites. Figure 3 illustrates the shift provoked by the ^{2}H isotopic substitution at the hydride site in the ^{1}H NMR signal of the neighboring hydride. In addition, each hydride isotopic substitution has been found to shift the $^{31}P\{^1H\}$ NMR signal of the complex by +0.10 ppm. These isotopic shifts are of the same sign and magnitude as those previously observed in related Ir(III) compounds.[19]

As expected from its long Ir−N bond distance, 2.084(3) Å,[20] the acetonitrile ligand of complex **7** can be readily substituted by a variety of other ligands. Equation 3 depicts the substitution by ethylene, which has led to the dihydride-ethylene complex [IrH_2(biPSiOH)(η^2-C_2H_4)]-(CF_3SO_3) (**8**). The NMR spectroscopic observation of the reaction has confirmed that acetonitrile substitution is nearly immediate, while the possible replacement of the silanol arm of the pincer has not been detected with a moderate excess of ethylene (e.g., $CDCl_3$ saturated solutions at room temperature).



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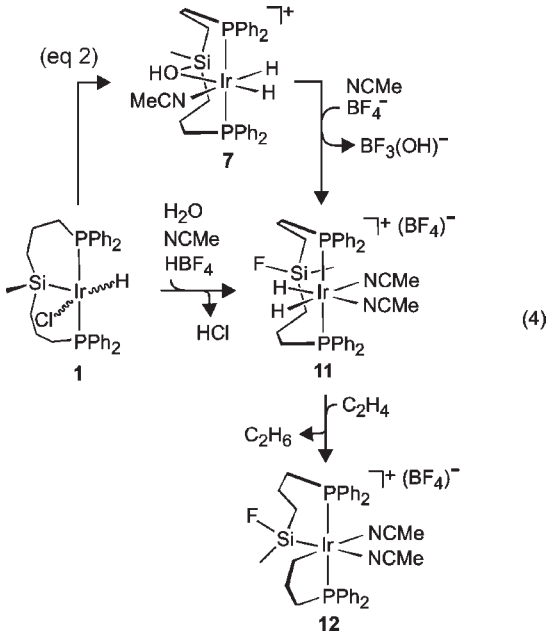
The X-ray structure of the cation of complex **8** is shown in Figure 2. Its main bond distances and angles are collected in Table 1. The structure shows various similarities with that of its precursor **7**, including a hydrogen bond with the triflate anion (also removed for clarity in Figure 2, H···O distance 1.92(7) Å). The most noteworthy structural detail of **8** concerns the orientation of the ethylene ligand, almost parallel to the P−Ir−P axis. This orientation does not seem the sterically preferred one, as it causes a clear distortion in the angle between the two phosphorus atoms, from 172° in **7** to 155° in **8**. More likely, according to the Chatt−Dewar−Duncanson bonding model,[21] the observed orientation is that maximizing the back-bonding from metal filled orbitals to the π^* olefin orbital. The magnitude of this bond contribution seems to be significant because the elongation of the C=C bond is notable (1.391(4) vs 1.339 Å in free ethylene)[22] in spite of the unusually long Ir−C distances (2.245(6) and 2.241(6) Å).[14,23] The ^{1}H NMR spectrum of **8** at room temperature displays a single signal attributable to the ethylene ligand, a poorly resolved multiplet at δ 2.66 containing a J_{HP} coupling constant of about 2.1 Hz. The VT NMR spectra in CD_2Cl_2 have not shown any significant broadening of this signal above 213 K, nor its decoalescence at the lowest temperature attained, 183 K. This behavior is consistent with a low barrier for ethylene rotation.

Insertion of the ethylene ligand into the neighboring Ir−H is a very slow process. In the presence of acetonitrile, this insertion has been found to afford the ethylhydride complex [Ir(Et)H(biPSiOH)(NCMe)](CF_3SO_3) (**9**). As shown in eq 3, this latter complex is the stable product of the reaction between **7** and ethylene, whereas the above-described dihydride-ethylene complex **8** is just an intermediate. Yet, the formation of **9** is so slow that it has not caused any problem in the characterization of **8** or its crystallization. In fact, the complete formation of **9** has not been observed, so that its characterization was accomplished in solution by NMR once it became the major product in the reaction mixture, after approximately 2 weeks of reaction at room temperature. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **9** display characteristic resonances for the ethyl ligand, and the ^{1}H NOESY spectrum reveals the *cis* position of this ligand relative to the hydride.

A second insertion product, analogous to **9**, has been obtained after the treatment of **7** with phenylacetylene (eq 3). This alkyne insertion is also relatively slow, although it has been completed in a few hours at room temperature. The reaction product, [Ir(*E*-CH=CHPh)H(biPSiOH)(NCMe)](CF_3SO_3) (**10**), has been isolated and characterized as a single isomer containing an *E* alkenyl ligand, as indicated by the J_{HH} coupling constant of 15.6 Hz present in both alkenyl hydrogen ^{1}H NMR signals. The mutually *cis* hydride and alkenyl ligands have not been seen to undergo spontaneous reductive elimination in solution. Nevertheless, the complex has been found to slowly decompose when heating to form several species that could not be identified.

Hydrolyzable Fluorinated Anions. If, besides water, the reactions of **1** with electrophiles contain anions susceptible to hydrolysis, such as hexafluorophosphate or tetrafluoroborate,[24] the final products are not those of eq 2 but species that incorporate fluoride at the silicon atom of the former biPSi ligand (eq 4). The treatment of **1** with 2 equiv of a wet diethyl ether solution of HBF_4 in the presence of acetonitrile has led to the cationic dihydride complex [IrH_2(biPSiF)$(NCMe)_2$]BF_4 (**11**) (biPSiF = κ-P^2-FSi(Me){$(CH_2)_3PPh_2$}$_2$). The compound has also been prepared from **7** and acetonitrile, via treatment with sodium fluoride or sodium tetrafluoroborate. Along this latter reaction, the ^{19}F NMR spectra have confirmed the formation of BF_4^- hydrolysis byproducts ($BF_3(OH)^-$, etc.).



Most likely, this reaction is thermodynamically driven by the formation of the very strong Si−F bond (above 150 kcal mol^{-1}). Evidence for this new bond is provided by the NMR spectra of **11**, in the form of a J_{SiF} coupling constant of 287.6 Hz in the ^{29}Si{^{1}H} spectrum (Figure 4), a new signal at δ −167.02 in the ^{19}F spectrum displaying ^{29}Si satellites, and a J_{CF} coupling constant of 14.1 Hz in the ^{13}C{^{1}H} NMR signal corresponding to the methyl substituent at silicon. The NMR spectra also indicate the equivalence of the phosphorus atoms and non-equivalence of acetonitriles and hydrides. The ^{1}H NMR signals of the latter show a J_{HH} mutual coupling constant of 6.3 Hz, in agreement with their *cis* relative position. This structural information implies that the new diphosphine generated after silicon fluorination coordinates via two

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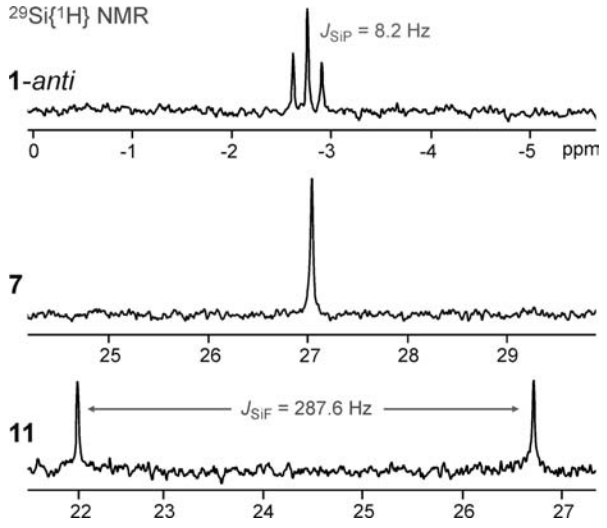

Figure 4. $^{29}Si\{^1H\}$ NMR spectra of complexes **1**-*anti*, **7**, and **11**.

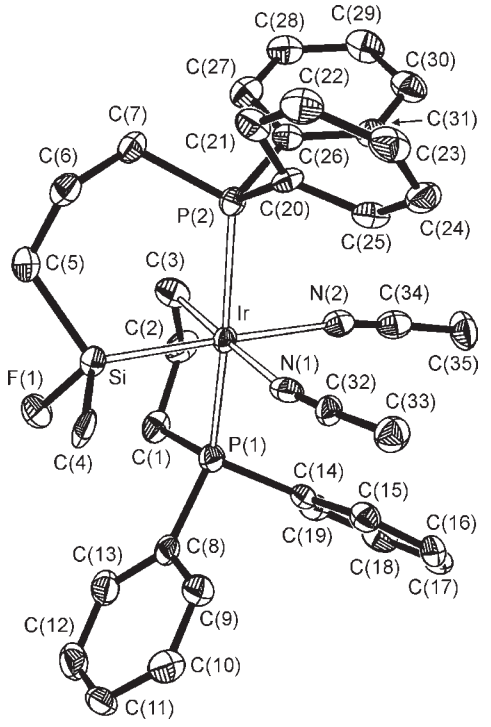

Figure 5. X-ray structure of the cation of complex **12**.

mutually *trans* positions of an assumed octahedron. Although relatively unusual, such *trans*-chelating coordination is known for diphosphines[9] and other ligands[25] with long chains connecting the donor atoms. Apart from the backbone connecting the two phosphorus, the coordination sphere of iridium in **11** is that of the known complex $[IrH_2(PR_3)_2(NCMe)_2]BF_4$.[26]

The attempts to confirm the proposed structure of **11** by X-ray diffraction have led to the characterization of a derivative, the complex $[Ir\{\kappa\text{-}P,Si\text{-}Si(F)(Me)CH_2CH_2CH_2PPh_2\}(\kappa\text{-}C,P\text{-}CH_2CH_2CH_2PPh_2)(NCMe)_2]BF_4$ (**12**). One of the enantiomers of this compound is shown in Figure 5; its main bond distances and angles are collected in Table 2. The slow development of this complex at room temperature has been monitored by NMR in $CDCl_3$ solutions of **11**, from which it has been crystallized in low yield. Mechanistically, the formation of **12** from **11** can be rationalized in two steps, namely, H_2 loss and Si−C bond activation; most likely in that order. An example of the second step has recently been reported for Ni(0) and Pd(0) species with closely related κ-*P*,*P*,*Si* pincer ligands.[27] Given the difficulties inherent for the reductive elimination of H_2 from Ir(III) dihydrides,[28] this step is most likely rate limiting in the formation of **12**. This mechanistic rationalization has been implemented by introducing a hydrogen acceptor such as ethylene in the reaction (eq 4), which has rendered reaction times of a few hours instead of weeks. Nevertheless, this procedure seems to favor the formation of several byproducts that could not be conveniently separated from **12**. The monitoring of this reaction by NMR has shown the formation of several dihydride and monohydride reaction intermediates, probably in route to Ir(I) species, although they have not been investigated in more detail.

Table 2. Bond Distances (Å) and Angles (deg) for Complex **12**

Ir−P(1)	2.3108(16)	Ir−P(2)	2.3541(17)
Ir−Si	2.3233(18)	Ir−C(3)	2.097(6)
Ir−N(1)	2.064(5)	Ir−N(2)	2.155(5)
P(1)−Ir−P(2)	170.51(6)		
P(1)−Ir−Si	88.44(6)	P(2)−Ir−Si	93.02(6)
P(1)−Ir−C(3)	83.10(18)	P(2)−Ir−C(3)	87.54(18)
P(1)−Ir−N(1)	96.17(14)	P(2)−Ir−N(1)	93.10(14)
P(1)−Ir−N(2)	88.53(14)	P(2)−Ir−N(2)	89.59(14)
Si−Ir−N(1)	93.63(15)	Si−Ir−N(2)	176.17(14)
C−Ir−N(1)	177.1(2)	C−Ir−N(2)	88.1(2)
Si−Ir−C	89.20(19)	N(1)−Ir−N(2)	89.0(2)

Conclusion

The simple reactions and mild conditions necessary to transform the complex [IrClH(biPSi)] (**1**) into radically different derivatives such as **11** and **12** highlight that, despite its integration into a polydentate ligand, the silicon atom of the biPSi remains a reactive site. The sequence of reactions unraveled throughout this study most likely starts at the labile Ir(III) coordination sphere generated after the removal of chloride by an electrophile, and is driven by the strength of single bonds such as Si−O or Si−F. These reactions indicate that certain experimental conditions should be avoided when searching for catalytic applications of **1** and related species. Nevertheless, each of these reactions constitutes a route for the transformation of **1** into a new type of complex with potential application in catalysis. These include cationic dihydride-solvato complexes containing either silanol pincers or *trans*-chelating diphosphines generated from the silanol templates. In particular, compounds such as **7** and **8**, which incorporate the H and OH fragments of a split water molecule and offer readily accessible coordination sites, merit further examination within the contexts of hydrogen production and catalytic hydration.

Experimental Section

Equipment. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry (MALDI-TOF-MS)

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data were obtained in a Bruker Microflex mass spectrometer using DIT (1,8,9-trihydroxy-anthracene) as matrix. Infrared spectra were recorded in KBr using a FTIR Perkin-Elmer Spectrum One spectrometer. NMR spectra were recorded on Bruker Avance 400 or 300 MHz spectrometers. ^{1}H (400.13 or 300.13 MHz) and ^{13}C (100.6 or 75.5 MHz) NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in parts per million (ppm) relative to TMS. ^{19}F (376.5 or 288.3 MHz), ^{31}P (162.0 or 121.5 MHz), and ^{29}Si (59.6 or 79.5 MHz) NMR chemical shifts were measured relative to $CFCl_3$, H_3PO_4 (85%), and TMS, respectively. In general, NMR spectral assignments were achieved through ^{1}H COSY, ^{1}H NOESY, ^{13}C APT, and $^{1}H/^{13}C$-HSQC experiments. Spectroscopic data are given at room temperature unless otherwise indicated.

Synthesis. All manipulations were carried out under argon by standard Schlenk techniques. Solvents were obtained from an Innovative Technology solvent purification system. Deuterated solvents were dried with appropriate drying agents and degassed with argon prior to use. The starting complex [IrClH(biPSi)] (**1**) was prepared by known procedures.[29] All commercial reagents were used as received without further purification. All new complexes described below are air sensitive in solution.

[Ir(O_3SCF_3)H(biPSi)] (2). To a 0.5 mL $CDCl_3$ solution of **1** (25.0 mg, 0.03 mmol) in a NMR tube was added methyl triflate (3.9 μL, 0.03 mmol). The resulting mixture was cooled down to 253 K and analyzed by NMR. Methyl chloride, and the *anti* and *syn* isomers of **2** in relative proportion 15:85, respectively, were the only detectable reaction products. Partial data for **2**-*anti*: ^{1}H NMR ($CDCl_3$, 253 K): δ −28.25 (t, J_{HP} = 16.0, 1H, IrH). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 253 K): δ 14.90 (s). Partial data for **2**-*syn*: ^{1}H NMR ($CDCl_3$, 253 K): δ 7.95 (m, 4H, CH), 7.58 (m, 8H, CH), 7.25 (m, 8H, CH), 3.36, 2.86, 2.19, 1.54, 1.43, 0.60 (all m, 2H each, CH_2), −0.10 (s, 3H, CH_3), −27.19 (t, J_{HP} = 12.6, 1H, IrH). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 253 K): δ 13.88 (s). ^{19}F NMR ($CDCl_3$, 253 K): δ −76.71 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 253 K): δ 134.75, 132.58 (both t, J_{CP} = 6.1, CH), 129.99, 129.71 (both s, CH), 128.29, 127.99 (both t, J_{CP} = 5.4, CH), 119.85 (q, J_{CF} = 318.9, CF_3), 28.87 (t, J_{CP} = 16.9, PCH_2), 18.30, 17.62 (both s, CH_2), 6.38 (s, CH_3).

Preparation of [IrH(biPSi)($NCMe)_2$]PF_6 (3). To a 5 mL acetone solution of **1** (148 mg, 0.20 mmol) were added acetonitrile (31 μL, 0.60 mmol) and silver hexafluorophosphate (51 mg, 0.20 mmol). The mixture was protected from the daylight and stirred for 45 min, after which it was filtered through Celite to remove the insoluble silver chloride. The resulting solution was concentrated to about 0.5 mL and treated with diethyl ether to give a white solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 130 mg (71%). Anal. Calcd (%) for $C_{35}H_{42}N_2F_6IrP_3Si$: C, 45.79; H, 4.61; N, 3.05. Found: C, 46.21; H, 4.74; N, 2.72. IR (cm^{-1}): 2250 ν(IrH). Partial data for **3**-*anti*: ^{1}H NMR ($CDCl_3$): δ 7.98 (m, 4H, CH), 7.45 (m, 16H, CH), 2.91, 2.75 (both m, 2H each, CH_2), 2.46 (s, 3H, $NCCH_3$), 2.43, 1.79 (both m, 2H each, CH_2), 1.47 (s, 3H, $NCCH_3$), 0.79, 0.67 (both m, 2H each, CH_2), −0.26 (s, 3H, CH_3), −18.83 (t, J_{HP} = 15.2, 1H, IrH). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ −5.28 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 135.18 (t, J_{CP} = 27.1, C), 132.93 (t, J_{CP} = 5.8, CH), 132.38 (t, J_{CP} = 4.9, CH), 130.47, 130.02 (both s, CH), 128.84 (t, J_{CP} = 4.2, CH), 128.17 (t, J_{CP} = 5.1, CH), 120.93 (s, $NCCH_3$), 30.75 (t, J_{CP} = 19.7, PCH_2), 22.64 (s, CH_2), 17.84 (t, J_{CP} = 3.9, CH_2), 3.28 (s, $NCCH_3$), 0.75 (s, CH_3). Partial data for **3**-*syn*: ^{1}H NMR ($CDCl_3$): δ 7.98 (m, 4H, CH), 7.45 (m, 16H, CH), 2.91, 2.75 (both m, 2H each, CH_2), 2.56 (s, 3H, $NCCH_3$), 2.43, 1.79 (both m, 2H each, CH_2), 0.79, 0.67 (both m, 2H each, CH_2), −0.11 (s, 3H, CH_3), −19.41 (t, J_{HP} = 14.0, 1H, IrH). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ −3.28 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 134.56 (t, J_{CP} = 23.2, C), 134.21 (t, J_{CP} = 5.6, CH), 131.16 (t, J_{CP} = 5.0, CH), 131.0, 129.87 (both s, CH), 128.76 (t, J_{CP} = 4.5, CH), 128.58 (t, J_{CP} = 5.1, CH), 121.02 (s, $NCCH_3$), 27.37 (t, J_{CP} = 18.2, PCH_2), 19.81 (s, CH_2), 15.42 (t, J_{CP} = 5.4, CH_2), 3.47 (s, $NCCH_3$), 2.82 (s, CH_3).

Preparation of [IrH(biPSi)($CO)_2$]PF_6 (4). A 5 mL CH_2Cl_2 solution of **3** (80 mg, 0.08 mmol) was stirred under a CO atmosphere (ca. 1 bar) for 15 min at room temperature. The resulting solution was concentrated to about 0.5 mL and treated with diethyl ether to give a pale yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried: yield 59 mg (83%). Anal. Calcd (%) for $C_{33}H_{36}F_6IrO_2P_3Si$: C, 44.44; H, 4.07. Found: C, 44.75; H, 4.02. MS (m/z): 719 [M^+ − CO]. IR (cm^{-1}): 2091, 2033 ν(CO). Partial data for **4**-*anti*: ^{1}H NMR ($CDCl_3$): δ 8.16−7.4 (m, 20H, Ph), 3.16, 2.81, 2.48, 1.90, 1.32, 0.93 (all m, 2H each, CH_2), 0.53 (s, 3H, CH_3), −9.03 (t, J_{HP} = 14.5, 1H, IrH). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ −22.51 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 131.33, 130.78 (both t, J_{CP} = 5.2, CH), 132.32, 131.75 (both s, CH), 129.54 (t, J_{CP} = 5.5, CH), 129.41 (t, J_{CP} = 5.4, CH), 28.45 (t, J_{CP} = 21.1, PCH_2), 18.93 (s, CH_2), 15.09 (t, J_{CP} = 5.7, CH_2), 3.93 (s, CH_3). Partial data for **4**-*syn*: ^{1}H NMR ($CDCl_3$): δ 8.16−7.4 (m, 20H, Ph), 3.38, 2.89, 2.69, 1.95, 1.43, 1.02 (all m, 2H each, CH_2), 0.34 (s, 3H, CH_3), −8.74 (t, J_{HP} = 12.5, 1H, IrH). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ −23.20 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 171.64 (t, J_{CP} = 5.8, CO), 161.06 (t, J_{CP} = 8.2, CO), 136.41 (t, J_{CP} = 28.5, C), 133.70 (t, J_{CP} = 6.0, CH), 132.13 (t, J_{CP} = 6.0, CH), 133.02, 131.75 (both s, CH), 129.91 (t, J_{CP} = 5.5, CH), 129.76 (t, J_{CP} = 5.0, CH), 126.05 (t, J_{CP} = 32.4, C), 28.77 (t, J_{CP} = 19.8, PCH_2), 19.15 (s, CH_2), 15.92 (t, J_{CP} = 4.6, CH_2), 4.05 (s, CH_3).

Preparation of [IrH(biPSi)(κ^2-*N*-bipy)]PF_6 (5). To a 5 mL CH_2Cl_2 solution of **3** (100 mg, 0.11 mmol) was added 2,2′-bipyridine (16 mg, 0.11 mmol). The reaction mixture was stirred at room temperature for 15 min, after which it was concentrated to about 0.5 mL. The addition of diethyl ether produced a pale yellow solid, which was separated by decantation, washed with diethyl ether, and dried: yield 81 mg (81%). Anal. Calcd (%) for $C_{41}H_{44}F_6IrN_2P_3Si$: C, 49.64; H, 4.47; N, 2.82. Found: C, 49.74; H, 4.34; N, 2.63. Partial data for **5**-*anti*: ^{1}H NMR (acetone-d_6): δ 0.13 (s, 3H, CH_3), −19.60 (t, J_{HP} = 13.1, 1H, IrH). $^{31}P\{^{1}H\}$ NMR (acetone-d_6): δ −5.00 (s). Partial data for **25**-*syn*: ^{1}H NMR (acetone-d_6): δ 9.59(d, J_{HH} = 5.3, 2H, CH), 8.87(d, J_{HH} = 5.0, 2H, CH), 8.30 (m, 6H, CH), 8.03 (td, J_{HH} = 1.3, 5.5, 2H, CH), 7.52 (d, J_{HH} = 1.2, 6.8, 2H, CH), 7.54 (m, 6H, CH), 7.34, 7.19 (both m, 4H, CH), 2.71, 2.51, 2.27, 1.54, 1.57, 0.79 (all m, 2H each, CH_2), 0.32 (s, 3H, CH_3),−18.90 (t, J_{HP} = 12.8, 1H, IrH). $^{31}P\{^{1}H\}$ NMR (acetone-d_6): δ −2.00 (s). $^{13}C\{^{1}H\}$ NMR (acetone-d_6): δ 158.27(s, C), 155.42, 139.33 (both s, CH), 135.91 (t, J_{CP} = 6.3, CH), 132.43 (s, CH), 129.86 (t, J_{CP} = 4.3, CH), 129.75 (t, J_{CP} = 5.3, CH), 129.29 (s, CH), 128.56 (t, J_{CP} = 4, CH), 124.55, 121.83 (both s, CH), 27.24 (t, J_{CP} = 18.6, PCH_2), 20.53 (s, CH_2), 17.41 (t, J_{CP} = 4.2, CH_2), 8.64 (s, CH_3).

Preparation of [Ir(O_3SCF_3)H_2(biPSiOH)] (6). To a 5 mL CH_2Cl_2 solution of **1** (125 mg, 0.17 mmol) were added water (3.5 μL, 0.2 mmol) and methyl triflate (19 μL, 0.17 mmol). The reaction mixture was stirred at room temperature for 15 min, after which it was concentrated to about 0.5 mL. The addition of diethyl ether produced a pale yellow solid, which was separated by decantation, washed with diethyl ether, and dried: yield 168 mg (98%). Anal. Calcd (%) for $C_{32}H_{38}F_3IrO_4P_2SSi$: C, 44.80; H, 4.46; S, 3.74. Found: C, 44.97; H, 4.80; S, 3.76. MS (m/z): 707 [$M^+ - O_3SCF_3$ − 2H]. ^{1}H NMR ($CDCl_3$): δ 7.89 (m, 4H, CH), 7.47 (m, 6H, CH), 7.27 (m, 2H, CH), 7.14 (m, 6H, CH), 7.05 (m, 2H, CH), 6.76 (s, 1H, OH), 2.94, 2.56, 1.89, 1.56, 1.14, 0.52 (all m, 2H each, CH_2), 0.47 (s, 3H, CH_3), −27.31 (td, J_{HP} = 16.0, J_{HH} = 8.8, 1H, IrH), −29.09 (td, J_{HP} = 14.4, J_{HH} = 8.8, 1H, IrH). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 23.34 (s). ^{19}F NMR ($CDCl_3$): δ −77.98 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 135.62 (t, J_{CP} = 6.5, CH), 135.36 (t, J_{CP} = 17.2, C), 131.27 (s, CH), 131.09

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(t, J_{CP} = 5.1, CH), 130.97 (t, J_{CP} = 29.6, C), 129.06 (s, CH), 128.63 (t, J_{CP} = 5.3, CH), 128.32 (t, J_{CP} = 4.0, CH), 122.29 (q, J_{CF} = 318.3, CF_3), 24.88 (t, J_{CP} = 15.1, PCH_2), 17.41, 16.39 (both s, CH_2), −2.02 (s, CH_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 22.74 (s).

Preparation of [IrH_2(biPSiOH)(NCMe)](CF_3SO_3) (7). To a 5 mL CH_2Cl_2 solution of **1** (312 mg, 0.43 mmol) were sequentially added water (8 μL, 0.44 mmol), triflic acid (38 μL, 0.43 mmol), and acetonitrile (30 μL, 0.58 mmol). The resulting solution was stirred at room temperature for 15 min, after which it was concentrated to about 0.5 mL. The addition of diethyl ether produced a pale yellow solid, which was separated by decantation, washed with diethyl ether, and dried: yield 371 mg (93%). Anal. Calcd (%) for $C_{34}H_{41}NF_3IrO_4P_2SSi$: C, 45.42; H, 4.60; N, 1.56; S, 3.57. Found: C, 45.09; H, 4.65; N, 2.04; S, 3.29. MS (*m*/*z*): 748 [$M^+ - H_2$]. IR (cm^{-1}): 2204 ν(IrH). ^1H NMR ($CDCl_3$): δ 8.07 (m, 2H, CH), 7.44 (m, 18H, CH), 6.72 (s, 1H, OH), 2.96, 2.77, 2.05, 1.75 (all m, 2H each, CH_2), 1.56 (s, 3H, $NCCH_3$), 1.33, 0.65 (both m, 2H each, CH_2), 0.55 (s, 3H, CH_3), −19.81 (td, J_{HP} = 16.0, J_{HH} = 7.4, 1H, IrH), −28.75 (td, J_{HP} = 13.8, J_{HH} = 7.4, 1H, IrH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.56 (s). ^{19}F NMR ($CDCl_3$): δ −78.11 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$,): δ 135.54 (t, J_{CP} = 22.9, C), 135.39 (t, J_{CP} = 6.5, CH), 131.59 (t, J_{CP} = 28.9, C), 131.13 (t, J_{CP} = 5.2, CH), 128.74, 128.70 (both s, CH), 128.45 (t, J_{CP} = 5.3, CH), 122.35 (q, J_{CF} = 319.9, CF_3), 118.90 (s, N*C*CH_3), 25.10 (t, J_{CP} = 15.4, CH_2), 17.19, 16.21 (both s, CH_2), 2.36 (s, NC*C*H_3), −2.09 (s, CH_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 22.99 (s). The crystals used in the X-ray experiment were obtained from a CH_2Cl_2 solution layered with diethyl ether, at room temperature.

Preparation of [IrH_2(biPSiOH)(η²-C_2H_4)](CF_3SO_3) (8). A 5 mL CH_2Cl_2 solution of **7** (101 mg, 0.11 mmol) was stirred under ethylene atmosphere (ca. 1 bar) for 15 min at room temperature. The resulting solution was concentrated to about 0.5 mL and treated with diethyl ether to give a pale yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried: yield 88 mg (90%). Anal. Calcd (%) for $C_{34}H_{42}F_3IrO_4P_2SSi$: C, 46.09; H, 4.78; S, 3.62. Found: C, 45.93; H, 5.02; S, 3.46. IR (cm^{-1}): 2232, 2176 ν(IrH). ^1H NMR ($CDCl_3$): δ 7.88 (m, 2H, CH), 7.45 (m, 8H, CH), 7.27 (m, 2H, CH), 7.18 (m, 8H, CH), 5.68 (s, 1H, OH), 2.78 (m, 4H, CH_2), 2.66 (m, 4H, C_2H_4), 1.94, 1.51, 0.97, 0.43 (all m, 2H each, CH_2), 0.30 (s, 3H, CH_3), −9.64 (td, J_{HP} = 16.8, J_{HH} = 6.4, 1H, IrH), −30.68 (td, J_{HP} = 13.6, J_{HH} = 6.4, 1H, IrH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.73 (s). ^{19}F NMR ($CDCl_3$): δ −78.05 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 136.28 (t, J_{CP} = 26.3, C), 134.94 (t, J_{CP} = 6.0, CH), 132.25 (t, J_{CP} = 31.1, C), 129.63 (s, CH), 130.53 (t, J_{CP} = 4.6, CH), 129.63 (s, CH), 128.48 (t, J_{CP} = 5.3, CH), 128.33 (t, J_{CP} = 4.5, CH), 122.01 (q, J_{CF} = 319.5, CF_3), 65.81 (s, C_2H_4), 24.42 (t, J_{CP} = 15.9, PCH_2), 16.97, 15.24 (both s, CH_2), −2.49 (s, CH_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 24.91 (s). The crystals used in the X-ray experiment were obtained from a CH_2Cl_2 solution layered with diethyl ether, at room temperature.

[Ir(Et)H(biPSiOH)(NCMe)](CF_3SO_3) (9). Ethylene was bubbled during 1 min through a 0.5 mL $CDCl_3$ solution of **7** (30 mg, 0.03 mmol) in a NMR tube. The resulting solution was periodically monitored by NMR. The initial reaction product **8** was slowly transformed into **9**, which became the major reaction product after about 2 weeks at room temperature. ^1H NMR ($CDCl_3$): δ 7.97 (m, 4H, CH), 7.39 (m, 16H, CH), 6.21 (s, 1H, OH), 2.99, 2.32, 1.85 (all m, 2H each, CH_2), 1.65 (s, 3H, $NCCH_3$), 1.55 (m, 2H, CH_2), 1.46 (m, 2H, $IrCH_2CH_3$), 1.21, 0.51 (both m, 2H each, CH_2), 0.42 (s, 3H, CH_3), −0.11 (t, J_{HH} = 7.2, 3H, $IrCH_2CH_3$), −19.18 (t, J_{HP} = 14.8, 1H, IrH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 14.40 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.99 (t, J_{CP} = 5.5, CH), 134.35 (t, J_{CP} = 21.4, C), 131.44 (t, J_{CP} = 4.8, CH), 129.07, 128.61 (both s, CH), 128.40 (t, J_{CP} = 5.5, CH), 127.79 (t, J_{CP} = 4.1, CH), 122.33 (q, J_{CF} = 320.1, CF_3), 116.45 (s, N*C*CH_3), 27.55 (t, J_{CP} = 16.5, PCH_2), 18.89 (s, $IrCH_2CH_3$), 17.13, 14.98 (both s, CH_2), 2.81 (s, NC*C*H_3), −2.75 (s, CH_3), −27.86 (t, J_{CP} = 4.8, $IrCH_2$).

Preparation of [Ir(*E*-CH=CHPh)H(biPSiOH)(NCMe)](CF_3SO_3) (10). To a 5 mL CH_2Cl_2 solution of **7** (180 mg, 0.20 mmol) was added phenylacetylene (33 μL, 0.30 mmol). The resulting solution was stirred at room temperature for 48 h and concentrated to about 0.5 mL. The addition of diethyl ether produced a yellow solid, which was separated by decantation, washed with diethyl ether, and dried: yield 156 mg (78%). Anal. Calcd (%) for $C_{42}H_{47}NF_3IrO_4P_2SSi$: C, 50.39; H, 4.73; N, 1.40; S, 3.20. Found: C, 50.70; H, 4.91; N, 1.35; S, 3.36. ^1H NMR ($CDCl_3$): δ 7.8−6.8 (m, 20H, CH), 7.76 (brd, J_{HH} = 15.6, 1H, IrC*H*CHPh), 6.48 (s, 1H, OH), 5.28 (d, J_{HH} = 15.6, 1H, IrCHC*H*Ph), 2.85, 2.29, 1.84, 1.53 (all m, 2H each, CH_2), 1.49 (s, 3H, $NCCH_3$), 1.27, 0.45 (both m, 2H each, CH_2), 0.38 (s, 3H, CH_3), −18.53 (t, J_{HP} = 14.0, 1H, IrH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.99 (s). ^{19}F NMR ($CDCl_3$): δ −80.33 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.53 (t, J_{CP} = 6.0, CH), 132.91 (s, IrC*C*H), 132.76 (t, J_{CP} = 23.4, C), 131.78 (t, J_{CP} = 4.7, CH), 130.94, 129.30 (both s, CH), 128.60 (t, J_{CP} = 5.1, CH), 127.29 (t, J_{CP} = 4.2, CH), 122.29 (q, J_{CF} = 320.0, CF_3), 117.96 (br, N*C*CH_3), 106.66 (t, J_{CP} = 9.3, Ir*C*H), 25.85 (t, J_{CP} = 15.9, PCH_2), 17.03, 15.17 (both s, CH_2), 2.41 (s, NC*C*H_3), −2.59 (s, CH_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 24.66 (s).

Preparation of [IrH_2(biPSiF)($NCMe)_2$]BF_4 (11). To a 5 mL CH_2Cl_2 solution of **1** (100 mg, 0.14 mmol) were sequentially added water (3 μL, 0.17 mmol), tetrafluoroboric acid diethyl ether complex (41 μL, 0.30 mmol), and acetonitrile (15 μL, 0.29 mmol). The resulting solution was stirred at room temperature for 30 min, after which it was concentrated to about 0.5 mL. The addition of diethyl ether produced a pale yellow solid, which was separated by decantation, washed with diethyl ether, and dried: yield 94 mg (76%). Anal. Calcd (%) for $C_{35}H_{43}N_2BF_5IrP_2Si$: C, 47.78; H, 4.93; N, 3.18. Found: C, 47.55; H, 4.90; N, 2.98. MS (*m*/*z*): 709 [$M^+ - 2H - 2NCMe$]. IR (cm^{-1}): 2197 ν(IrH). ^1H NMR ($CDCl_3$): δ 7.48 (m, 20H, CH), 2.54 (m, 4H, CH_2), 1.87, 1.70 (both s, 3H each, $NCCH_3$), 1.69, 1.08 (both m, 4H each, CH_2), 1.65 (d, J_{HF} = 7.5, 3H, CH_3), −21.12 (td, J_{HP} = 16.8, J_{HH} = 6.3, 1H, IrH), −21.38 (td, J_{HP} = 17.7, J_{HH} = 6.3, 1H, IrH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.92 (s). ^{19}F NMR ($CDCl_3$): δ −155.08 (br, BF_4), −167.02 (m, J_{FH} = 7.5, SiF). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.05 (t, J_{CP} = 23.7, C), 132.79 (t, J_{CP} = 6.0, CH), 132.45 (t, J_{CP} = 5.7, CH), 130.41, 130.24 (both s, CH), 128.58 (t, J_{CP} = 4.7 CH), 128.55 (t, J_{CP} = 4.7, CH), 120.14, 119.56 (both s, N*C*CH_3), 34.81 (t, J_{CP} = 20.3, PCH_2), 17.17 (s, CH_2), 16.54 (dt, J_{CF} = 13.2, J_{CP} = 3.3, CH_2), 2.43, 2.24 (both s, NC*C*H_3), −1.97 (d, J_{CF} = 14.1, CH_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 25.59 (d, J_{SiF} = 287.6).

[Ir{κ-*P*,*Si*-Si(F)(Me)$CH_2CH_2CH_2PPh_2$}(κ-*C*,*P*-$CH_2CH_2CH_2PPh_2$)($NCMe)_2$]BF_4 (12). The evolution of a NMR sample of **11** (15 mg, 0.02 mmol) in 0.5 mL of $CDCl_3$ was monitored over a period of 2 weeks. After this period, **11** was mostly transformed into **12**. Partial data for **12**: ^1H NMR ($CDCl_3$): 7.16 (m, 20H, CH), 2.91, 2.43 (both m, 1H, CH_2), 2.19 (s, 3H, $NCCH_3$), 2.15, 2.07 (both m, 1H, CH_2), 1.92 (s, 3H, $NCCH_3$), 1.87, 1.84, 1.82, 1.54, 1.46, 1.33, 0.85, 0.21 (all m, 1H, CH_2), −0.51 (d, J_{HF} = 8.1, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.41 (AB spin system), δ_A = 27.9, δ_B = −9.4, J_{AB} = 314.8). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 122.22, 122.09 (both s, N*C*CH_3), 27.66 (d, J_{CP} = 35.5, CH_2), 27.69 (d, J_{CP} = 38.6, CH_2), 18.57 (s, CH_2), 17.52 (m, CH_2), 3.78 (s, NC*C*H_3), 3.45 (d, J_{CF} = 15.1, CH_3), 3.02 (s, NC*C*H_3), 0.08 (m, CH_2), −2.00 (br, $IrCH_2$). The crystals used in the X-ray diffraction experiment were obtained upon cooling this NMR sample.

Kinetic Studies. The exchange between free acetonitrile and the acetonitrile ligands of isomers **3** was studied by ^1H NMR in solutions of **3** (approximately 0.06 M) containing acetonitrile excess. Experiments were carried out in CD_2Cl_2 solution with the exception of those at 312 K and above, which used $CDCl_3$ as solvent. The NMR sample temperature was calibrated using the temperature dependence of the chemical shifts of methanol and

Table 3. Rate Constants (k_{obs}, s^{-1}) for the Exchange between the Acetonitrile Ligands of Isomers **3** and Free Acetonitrile

		3-*syn*		**3**-*anti*	
T (K)	[NCMe]/[Ir]	*trans* to Si[b]	*trans* to H	*trans* to Si[b]	*trans* to H
208	1			0.71	
213	1			2.0	
217	1			3.0	
221	1			5.8	
221	10			5.6	
223	1	0.62			
227	1	1.5			
232	1	3.5			
236	1	5.6			
236	10	5.7			
240	1	14[a]			
245	1	40[a]			
252	1	101[a]			
293	1		0.61		
298	1		1.1		
302	1		2.0		
306	1		2.9		
306	3		2.4		
306	10		2.6		
307	1		3.7		
308	1		4.8		
312	1		9.1		
316	1		13[a]		
320	1		22[a]		
324	1		35[a]		2.5

[a] From line width. [b] The ^{1}H NMR signals corresponding to acetonitriles *trans* to Si are not observable in the room temperature spectrum: δ (208 K): **3**-*syn*, 0.99 (s); **3**-*anti*, 1.26 (s).

ethylenglycol. Pseudo-first order rate constants (k_{obs}) for each individual exchange process were obtained by spin saturation transfer following the Forsén−Hoffman method.[30] The presaturation pulse was applied on the ^{1}H NMR signal of free acetonitrile, and its effect was measured in the intensity of each of the signals corresponding to coordinated acetonitrile ligands. For some of the acetonitrile ligands (Table 3), the temperature range of the kinetic determinations could be extended using rate constants derived from the line-width of their ^{1}H NMR signals. After verifying that rate constants were independent upon acetonitrile concentration (first-order), they were used to estimate the activation parameters for the various acetonitrile dissociations via $\mathrm{Ln}(k_{obs}/T)$ versus $1/T$ regressions (Eyring representations). Errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were estimated through conventional error propagation formulas,[31] assuming 1 K error in the temperature and a 10% error in the rate constant.

Crystallography. X-ray data were collected at 100.0(2) K on a Bruker SMART APEX CCD with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected over the complete sphere by a combination of four sets. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[32] The structures were solved by the Patterson method and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL program package,[33] including isotropic and subsequently anisotropic displacement parameters. Weighted R factors (R_w) and goodness of fit (S) are based on F^2, and conventional R factors are based on F. The OH hydrogen and the hydride ligands of **7** and **8** were located in the difference Fourier maps but did not refined properly. Restrained geometries (**7** and **8**) and restrained thermal parameters (**8**) were used in the last cycles of refinement. The rest of the hydrogen atoms were calculated using a restricted riding model on their respective carbon atoms with the thermal parameter related to the bonded atom. Disordered CH_2Cl_2 and diethyl ether molecules were observed for **8**. These molecules were refined with restraints in both the geometry and the thermal parameters. All the highest electronic residuals were observed in close proximity of the Ir centers and make no chemical sense.

Data for 7. $C_{34}H_{41}F_3IrNO_4P_2SSi$, M = 898.97; colorless irregular block, 0.10 × 0.06 × 0.06 mm^3; monoclinic, $P2_1/n$; a = 10.8199(5), b = 10.1125(5), c = 32.9470(16) Å; β = 90.8420(10); Z = 4; V = 3604.5(3) Å^3; D_c = 1.657 g cm^{-3}; μ = 3.938 mm^{-1}, minimum and maximum transmission factors 0.719 and 0.805; $2\theta_{max}$ = 58.16°; 44435 reflections collected, 9043 unique [R(int) = 0.0583]; number of data/restraints/parameters 9043/3/435; final GoF 0.794, $R1$ = 0.0304 [6808 reflections $I > 2\sigma(I)$], $wR2$ = 0.0448 for all data; largest difference peak 1.676 e Å^{-3}.

Data for 8. $C_{34}H_{42}F_3IrO_4P_2SSi\cdot 0.5OEt_2\cdot 0.4CH_2Cl_2$, M = 955.48; colorless irregular block, 0.07 × 0.04 × 0.01 mm^3; triclinic, $P\bar{1}$; a = 8.8088(12), b = 12.3483(17), c = 18.596(3) Å; α = 81.914(2), β = 80.057(2), γ = 87.371(2); Z = 2; V = 1972.1(5) Å^3; D_c = 1.609 g cm^{-3}; μ = 3.656 mm^{-1}, minimum and maximum transmission factors 0.705 and 0.898; $2\theta_{max}$ = 57.50°; 17650 reflections collected, 9277 unique [R(int) = 0.0512]; number of data/restraints/parameters 9277/76/518; final GoF 0.962, $R1$ = 0.0538 [7452 reflections $I > 2\sigma(I)$], $wR2$ = 0.1050 for all data; largest difference peak 1.764 e Å^{-3}.

Data for 12. $C_{35}H_{41}BF_5IrN_2P_2Si$, M = 877.74; colorless irregular block, 0.08 × 0.06 × 0.04 mm^3; monoclinic, $P2_1/n$; a = 11.1805(8), b = 9.5246(7), c = 33.037(2) Å; β = 95.9480(10); Z = 4; V = 3499.1(4) Å^3; D_c = 1.666 g cm^{-3}; μ = 3.997 mm^{-1}, minimum and maximum transmission factors 0.661 and 0.837; $2\theta_{max}$ = 58.10°; 42818 reflections collected, 8723 unique [R(int) = 0.0919]; number of data/restraints/parameters 8723/6/428; final GoF 0.883, $R1$ = 0.0447 [5685 reflections $I > 2\sigma(I)$], $wR2$ = 0.0740 for all data; largest difference peak 2.179 e Å^{-3}.

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Supporting Information Available: X-ray crystallographic file for the complexes **7**, **8**, and **12** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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