

transition-state geometry for the reaction involving the intramolecular attack of hydroxide ion on a coordinated phosphate derivative (vide supra). In contrast to this expectation, a suitable transition-state geometry for the corresponding Co(III) complex would be closer to 78–80°, based on the geometry in the product ground state.^{6,32} Large energy increases per unit angle compression are expected when the O–M–O bond is required to achieve such a configuration. The greater compression required in the case of the Ir(III) complex is therefore expected to markedly increase the energy required to reach the transition state in this reaction.

In conclusion, this work attests the efficiency of OH⁻ bound to the metal ion as an intramolecular nucleophile for phosphate ester hydrolysis via the four-membered ring metal ion–phosphorane chelate. However, the rate is apparently modulated by the size of the metal ion and the ease of formation of the four-membered chelate ring. Given that Mg²⁺, Zn²⁺, and Mn²⁺ are the ions likely to be involved in biological systems and that they are larger than Ir³⁺,³¹ it does not seem likely that these ions will act efficiently in this way. They can, of course, still function as both a source of nucleophiles (M–OH⁻) and as electrophilic activators of the phosphate ester, although these functions may be carried out by different metal ions. The enzyme cleft can, of course, arrange

the intramolecularity of the reaction. Presumptions of this kind are supported by the proximity of the metal ions in the refined alkaline phosphatase structure³⁵ and the frequency with which multiple metal ions appear to be required in phosphate-utilizing enzymes.¹

Finally, this study has shown conclusively that a four-membered ring chelate phosphate ester will not hydrolyze with loss of the exocyclic esterifying group even when the metal ion ligand bonds are inert.

Acknowledgment. We thank the ANU NMR service for their help and the Analytical Service Unit for the microanalyses.

Supplementary Material Available: Table of rate constants for the hydrolysis of *cis*-[(en)₂Ir(OH₂)OP(O)(OC₂H₅)-(OC₆H₄NO₂)]²⁺ (1 page). Ordering information is given on any current masthead page.

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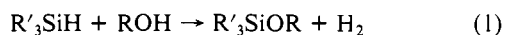
Homogeneous Catalysis of Silane Alcoholysis via Nucleophilic Attack by the Alcohol on an Ir(η^2 -HSiR₃) Intermediate Catalyzed by [IrH₂S₂(PPh₃)₂]SbF₆ (S = Solvent)

Xiao-Liang Luo and Robert H. Crabtree*

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511. Received August 22, 1988

Abstract: [IrH₂S₂L₂]SbF₆ (**1**, L = PPh₃; S = THF, **a**; CH₃OH, **b**; H₂O, **c**; Me₂CO, **d**) is found to be a very active and highly selective catalyst for silane alcoholysis. A hydroxyl group can be selectively silylated even in the presence of another potentially reactive C=C or C=O group. The homogeneity of the catalytic system has been established by DCT (dibenzo[*a,e*]cyclooctatetraene) and Hg tests. Rather than the "oxidative addition" mechanism commonly postulated, the results of kinetic and mechanistic studies are more consistent with a mechanism in which the silane is activated through binding to the metal via the Si–H bond in an η^2 fashion without oxidative addition and then undergoes nucleophilic attack by the alcohol. The order of relative reactivities of different alcohol isomers is secondary alcohol > primary alcohol > tertiary alcohol. The origin of this anomalous reactivity pattern is discussed with reference to the proposed mechanism. Some silane adducts (e.g., with Et₃SiH and Et₂HSiSiHEt₂) related to the intermediate species proposed in the catalytic cycle can be detected spectroscopically at low temperatures, but they are too reactive for isolation. In particular, they react rapidly with nucleophiles such as water and alcohols. The proposed "adduct formation" mechanism cannot apply to simple alkenes, which are insufficiently nucleophilic to attack even an activated η^2 -bound silane. Consistent with this picture, alkene hydrosilylation is not catalyzed by **1**.

The alcoholysis of hydrosilanes, or the O-silylation of alcohols (eq 1), has important applications in the synthesis of silyl ethers and in the protection of reactive OH groups in organic syntheses.¹



Since alcohols are normally insufficiently nucleophilic to attack silanes in the absence of a catalyst, most silanes undergo alcoholysis only in the presence of either strongly nucleophilic or electrophilic catalysts. These are often unsuitable for use in organic substrates with sensitive functional groups. Only a very limited number of homogeneous transition-metal complexes have been reported as catalysts for the reaction. At room temperature the majority of these catalysts fail to catalyze the alcoholysis of trialkylsilanes such as triethylsilane. For example, CoH₃(PPh₃)₃,² CoH(N₂)-

(PPh₃)₃,² FeH₂(PMePh₂)₄, and FeH₂(N₂)(PEtPh₂)₃³ are active for (EtO)₃SiH but inactive for Et₃SiH. Rh(PPh₃)₃Cl (Wilkinson's catalyst) is active for Et₃SiH only in refluxing benzene.⁴ Co₂(CO)₈,⁵ IrX(CO)L₂ and [IrCl(C₈H₁₄)₂]₂,⁶ and Ru(PMe₃)₂(CO)₂Cl₂⁷ are the most active catalysts reported to date. They

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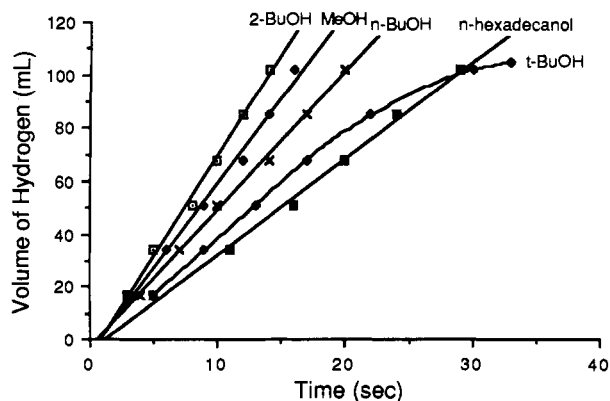


Figure 1. Hydrogen evolution curves for the reaction of Et_3SiH (5.0 mmol) with a variety of alcohols (5.0 mmol) in CH_2Cl_2 at 25°C catalyzed by $[\text{IrH}_2(\text{THF})_2(\text{PPh}_3)_2]\text{SbF}_6$ (**1a**, 0.020 mmol except for 2-BuOH where only 0.010 mmol was used). The total volume of the solution was 20 mL.

operate at room temperature, but rates are modest and the activity declines drastically with the elongation and branching of the alkyl group of the alcohol.

We now report on the unusually high catalytic activity of $[\text{IrH}_2\text{S}_2\text{L}_2]\text{SbF}_6$ (**1**, $\text{L} = \text{PPh}_3$; $\text{S} = \text{THF}$, **a**; CH_3OH , **b**; H_2O , **c**; Me_2CO , **d**)⁸ for the reaction of eq 1. Kinetic and mechanistic studies have led us to propose a new mechanism for silane alcoholysis, which involves the activation of the silane through η^2 -bonding of the Si-H group to the metal center without oxidative addition and subsequent nucleophilic attack on the η^2 - HSiR_3 by the alcohol. We have spectroscopically detected some silane adducts, which are analogous to agostic C-H...M systems^{9a} and dihydrogen complexes.^{9b,c}

Results and Discussion

Silane Alcoholysis Catalyzed by 1. We have previously found that the solvent complexes of the type *cis,cis,trans*- $[\text{IrH}_2\text{S}_2\text{L}_2]\text{SbF}_6$ (**1**),^{8a,b} which can lose the S groups very readily to generate two vacant coordination sites, are very useful for alkane activation under mild thermal conditions.^{8b-h} In relation to the C-H activation, we wondered whether the same complexes could also show interesting Si-H activation chemistry in the catalytic reactions of silanes. This has led to the discovery that **1** is an extremely active catalyst for silane alcoholysis at room temperature.

When a silane was added to a mixture of $[\text{IrH}_2(\text{THF})_2(\text{PPh}_3)_2]\text{SbF}_6$ (**1a**) and an alcohol in CH_2Cl_2 at room temperature, vigorous evolution of hydrogen occurred at once. Cooling was necessary to keep the exothermic reaction under control. The complexes **1b-d** were equally active catalysts. Among various silanes, we studied only Et_3SiH in detail, but others (e.g., Et_2SiH_2 , Ph_2SiH_2 , Ph_3SiH , Ph_2MeSiH , PhMe_2SiH , $(\text{MeO})_3\text{SiH}$, or $(\text{EtO})_3\text{SiH}$) also reacted. Figure 1 shows some typical hydrogen evolution curves with Et_3SiH and a variety of alcohols as substrates. There was no obvious induction period. The reaction of a primary or secondary alcohol with Et_3SiH went to completion in less than 1 min using a $\text{ROH}/\text{Et}_3\text{SiH}/\mathbf{1a}$ molar ratio of 250:250:1. The resulting silyl ethers were isolated in good yields generally greater than 90%. With 2 equiv of Et_3SiH , both hydroxyl groups of a diol such as ethylene glycol or 1,15-pentadecanediol were silylated.

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Table I. Comparative Rates of Alcoholysis of Et_3SiH Catalyzed by $[\text{IrH}_2(\text{THF})_2(\text{PPh}_3)_2]\text{SbF}_6$ (**1a**) and $\text{Ru}(\text{PMe}_3)_2(\text{CO})_2\text{Cl}_2$

alcohol	rate, turnovers h^{-1} per mol of catalyst	
	$[\text{IrH}_2(\text{THF})_2(\text{PPh}_3)_2]\text{SbF}_6$ (1a) ^a	$\text{Ru}(\text{PMe}_3)_2(\text{CO})_2\text{Cl}_2$ ^b
MeOH	53 000	2500
EtOH	47 000	1500
<i>n</i> -PrOH	47 000	710
<i>n</i> -BuOH	41 000	490
<i>n</i> -pentanol	39 000	230
<i>n</i> -hexanol	38 000	170
<i>i</i> -PrOH	130 000 ^c	580
2-BuOH	110 000 ^c	70
<i>t</i> -BuOH	24 000	6
cyclohexanol	2 500	15
$\text{CH}_3\text{COCH}_2\text{OH}$	560	250
$\text{ClCH}_2\text{CH}_2\text{OH}$	30 000	12
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$	1 463	56
PhOH	520 ^d	no reaction
$\text{CCl}_3\text{CH}_2\text{OH}$	340 ^e	no reaction

^aIn CH_2Cl_2 at 25°C , 5.0 mmol of ROH, 5.0 mmol of Et_3SiH , 0.020 mmol of **1a** (unless otherwise noted). ^bIn THF at 18°C , 6.28 mmol of ROH, 6.28 mmol of Et_3SiH , 0.026 mmol of $\text{Ru}(\text{PMe}_3)_2(\text{CO})_2\text{Cl}_2$.⁷ ^cOnly 0.010 mmol of **1a** used for the secondary alcohol, which is extremely reactive. ^d96 turnovers (38% conversion) achieved in 11 min after which the reaction is very slow. ^e57 turnovers (23% conversion) achieved in 10 min after which the reaction is very slow.

For comparison, some rates of alcoholysis of Et_3SiH catalyzed by **1a** and $\text{Ru}(\text{PMe}_3)_2(\text{CO})_2\text{Cl}_2$ ⁷ are listed in Table I. It can be seen that **1a** is more active, especially when a long-chain alcohol or a secondary or tertiary alcohol (more representative of the type of alcohol that might be encountered in organic syntheses) is used as the substrate.

The deactivation of the catalyst occurred slowly in the presence of substrate and more rapidly when the alcohol had been consumed. In most cases, the yellow catalyst residue recovered after the reaction was shown to be mainly the known hydride-bridged dinuclear complex $[\text{Ir}_2(\mu\text{-H})_3\text{H}_2(\text{PPh}_3)_4]\text{SbF}_6$ (**2**)¹⁰ identified by comparison of its ^1H NMR and IR spectra to those of the authentic compound. No silicon-containing metal complex was isolated. This dinuclear species (**2**) was shown to be much less active than **1**. For example, the methanolysis of Et_3SiH was slow at room temperature in the presence of **2**. However, **2** was moderately active for the methanolysis of dialkylsilanes such as Et_2SiH_2 .

The choice of the counterion is important since we have found that the activity of the catalyst strongly depends on the counterion used. When SbF_6^- was the counterion, the deactivation of the catalyst occurred much slower than with BF_4^- or PF_6^- . A similar counterion dependence has previously been observed in thermal alkane dehydrogenation studies.^{8g,h} This may be due to the fact that BF_4^- and PF_6^- are less stable and more susceptible to F⁻ abstraction (vide infra) under the reaction conditions.

Like $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ ^{4a} and $\text{Ru}(\text{PMe}_3)_2(\text{CO})_2\text{Cl}_2$,⁷ **1** is a remarkably selective catalyst for silane alcoholysis. A hydroxyl group can be preferentially silylated even when another functional group, which could potentially be hydrosilylated, is present in the same molecule. For example, silyl ethers were formed and isolated as products from the reactions of hydroxyacetone, 4-hydroxy-2-butanone, and terpineol with Et_3SiH without appreciable formation of byproducts from the hydrosilylation of the carbonyl group or C=C bond. However, in some cases such as terpinen-4-ol and 9-decen-1-ol, O-silylation was accompanied by C=C bond isomerization.

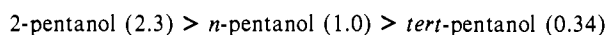
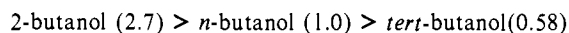
We also separately examined the catalytic activity of **1** for the hydrosilylation of simple olefins and ketones lacking other functional groups. Under the conditions used for silane alcoholysis, **1** showed no catalytic activity for the hydrosilylation of olefins. However, it did catalyze the slow hydrosilylation of ketones. For example,

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with 10 mmol of CH_3COCH_3 and 10 mmol of Et_3SiH as substrates and 0.050 mmol of **1a** as the catalyst, the yield of the hydrosilation product was ca. 35% in 3.5 h at room temperature. Since the catalytic activity of **1** for ketone hydrosilation was lower than that of $\text{RhCl}(\text{PPh}_3)_3$ ¹¹ and $\text{RuCl}_2(\text{PPh}_3)_3$,¹² it was not further investigated.

An interesting feature of the present catalytic system is that, in contrast with the known catalysts, the reactivity of acyclic alcohols with Et_3SiH declines only very slowly with the elongation of the alkyl chain of the alcohol. No reactivity difference between EtOH and *n*-propanol could be observed. Even the reaction of Et_3SiH with 2-nonadecanol (2- $\text{C}_{19}\text{H}_{39}\text{OH}$) was completed in only 22 s. By comparison, $\text{CoH}_3(\text{PPh}_3)_3$ or $\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$ catalyzed the reaction of $(\text{EtO})_3\text{SiH}$ with MeOH and EtOH , but no reaction was observed with *n*- BuOH .²

A study of the effect of changes in alcohol structure on the reactivity has revealed another striking feature of **1**. An irregular change in rates was observed upon change in the branching of alcohols: secondary alcohols are more reactive than primary alcohols, which in turn react faster than tertiary alcohols. For example, it was found that the reactivity (relative to the *n*-alcohol) of different isomers of butanol and pentanol in the reaction with Et_3SiH was as follows:



This result is unexpected and unprecedented since all catalysts reported to date show the greatest activity with primary alcohols. We will discuss the origin of this unusual reactivity pattern of our catalytic system in a later section.

A comparison of the rates obtained for the reaction with Et_3SiH of *i*- PrOH (1.3×10^5 turnovers h^{-1} per mol of catalyst) and CH_3OH (5.3×10^4 turnovers h^{-1} per mol of catalyst) in two separate experiments gave a rate ratio of ca. 2.4:1. In a competitive experiment, the reaction of a mixture of 10 mmol of *i*- PrOH and 10 mmol of MeOH with only 10 mmol of Et_3SiH resulted in a mixture of *i*- PrOSiEt_3 (57%) and MeOSiEt_3 (43%) in a ratio of 1.3:1, as determined by GC and ^1H NMR. This product ratio is only about half of the rate obtained in separate experiments.

Kinetics and Mechanism of Silane Alcoholysis Catalyzed by 1. The mechanism of silane alcoholysis catalyzed by homogeneous transition-metal complexes has been thought to involve the formation of a metal silyl hydride intermediate via the oxidative addition of Si-H to a metal center as a necessary step followed by nucleophilic attack of the alcohol on the bound silyl group. Unfortunately, in only a few cases, i.e., $\text{RhCl}(\text{PPh}_3)_3$,^{11a,13} $\text{CoH}_3(\text{PPh}_3)_3$ or $\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$,² and $\text{Co}_2(\text{CO})_8$,¹⁴ has the oxidative addition step been well established.

In many cases the homogeneity of the catalytic system has not been unambiguously established, the exact nature of the active catalytic species being uncertain. The active form of a supposedly homogeneous catalytic system with a soluble metal complex as the catalyst precursor may actually be heterogeneous. For example, it has been suggested^{15a} and recently proven^{15b} that the

Table II. Rates of the $[\text{IrH}_2(\text{THF})_2(\text{PPh}_3)_2]\text{SbF}_6$ -Catalyzed Reaction of Et_3SiH with MeOH in CH_2Cl_2 at 25 °C in the Presence of a Potential Inhibitor^a

potential inhibitor	rate, ^b turnovers h^{-1} mol cata. ⁻¹
none	51000
DCT (1.0 mol equiv/Ir)	0
2,2'-bipyridyl (1 mol equiv/Ir)	0
MeCN (2.0 mol equiv/Ir)	0
liquid mercury (excess)	51000

^a 5.0 mmol of CH_3OH , 5.0 mmol of Et_3SiH , 0.010 mmol of **1a**.

^b Mean values of three runs.

catalytic system of H_2PtCl_6 (Speier's catalyst), the best known catalyst for hydrosilation of olefins¹⁶ and ketones¹⁷ and alcoholysis of silanes,¹⁸ is heterogeneous with colloidal platinum particles formed by reduction of the precatalyst under the reaction conditions being the true catalyst. It has been reported^{6a} that, in $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ -catalyzed alcoholysis of silanes, the yellow reaction mixture turned dark brown, and a fine brown precipitate, presumably iridium metal, was recovered after the reaction. Thus, the observed catalytic activity seems very likely to have a heterogeneous origin.

For these reasons, the homogeneity of the catalytic system of **1** was examined by the DCT (dibenzo[*a,e*]cyclooctatetraene) and Hg tests.¹⁹ We found that the presence of liquid mercury, a well-known selective poison for heterogeneous catalysts, had no appreciable effect on the rate of reaction, whereas the reaction was drastically inhibited by strongly binding ligands such as DCT, 2,2'-dipyridyl, and CH_3CN (Table II). These results suggest that the catalytic system is indeed homogeneous.

In the case of **1** as the catalyst, the oxidative addition of SiH to the Ir(III) center to form a cationic Ir(V) species seems unlikely. Although a few neutral organometallic Ir(V) complexes, e.g., $\text{IrH}_5(\text{PR}_3)_2$,^{10,20} Cp^*IrH_4 ,²¹ $\text{Cp}^*\text{IrH}_3(\text{SiMe}_3)$,^{21b} $\text{Cp}^*\text{IrH}_2(\text{SiR}_3)_2$,²² and Cp^*IrMe_4 ,²³ have been reported, no example of a cationic Ir(V) has ever been well established. Bergman et al.²⁴ reported that protonation of $\text{Cp}^*\text{Ir}(\text{PMe}_3)_2\text{H}_2$ with $\text{HBF}_4 \cdot \text{OEt}_2$ gave $[\text{Cp}^*\text{Ir}(\text{PMe}_3)_3\text{H}]^+\text{BF}_4^-$, which they proposed as the first example of a cationic Ir(V) complex. Nevertheless, their low-temperature ^1H NMR studies revealed an anomalously large H-H coupling, which is not usually observed with classical metal hydrides, and so the Ir(V) formulation may not apply. Recent studies²⁵ by other groups on some analogous systems favor a different formulation of the compound either as a trihydrogen or as a dihydrogen hydride complex. Alternatively, the addition of SiH to **1** may lead to an Ir(III) dihydrogen silyl hydride complex. This possibility tends

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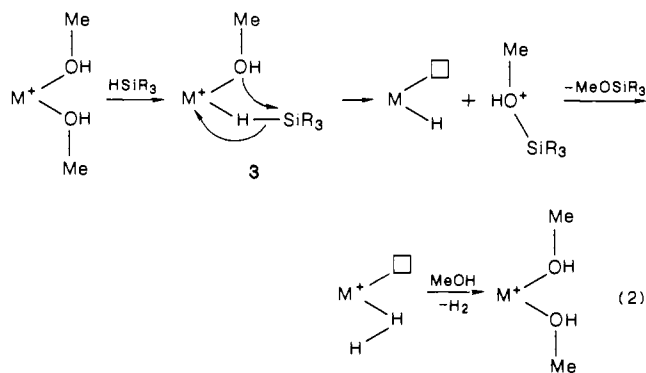
Table III. Kinetic Data for the Reaction of Et₃SiH with MeOH in CH₂Cl₂ at 25 °C Catalyzed by [IrH₂(THF)₂(PPh₃)₂]SbF₆ (**1a**)

[1a], M	[Et ₃ SiH], M	[MeOH], M	initial rate, ^a M s ⁻¹	k _{obsd} , ^{b,c} s ⁻¹
7.5 × 10 ⁻⁴	0.25	0.25	1.1 × 10 ⁻²	15
5.0 × 10 ⁻⁴	0.25	0.25	7.0 × 10 ⁻³	14
2.5 × 10 ⁻⁴	0.25	0.25	3.4 × 10 ⁻³	14
5.0 × 10 ⁻⁴	0.25	0.50	3.2 × 10 ⁻³	13
5.0 × 10 ⁻⁴	0.25	0.75	2.2 × 10 ⁻³	13
5.0 × 10 ⁻⁴	0.25	1.00	1.7 × 10 ⁻³	14
5.0 × 10 ⁻⁴	0.125	0.25	3.0 × 10 ⁻³	12
5.0 × 10 ⁻⁴	0.375	0.25	9.5 × 10 ⁻³	13
5.0 × 10 ⁻⁴	0.50	0.25	1.4 × 10 ⁻²	14

^a Mean values of three runs and calculated from initial rate = (P_{H₂}/RTV_{soln})(dV_{H₂}/dt) where V_{H₂} and P_{H₂} are the volume and pressure, respectively, of the evolved hydrogen, R is the ideal gas constant, T is the temperature (298 K), and V_{soln} is the volume of the solution (20 mL). ^b Calculated from k_{obsd} = initial rate × [CH₃OH]/([Et₃SiH][**1a**]). ^c (k_{obsd})_{mean} = 14.

to be ruled out by the work described below and will be addressed in detail in a later section.

We have previously shown that a number of unconventional ligands (e.g., H₂,²⁶ MeI,²⁷ agostic CH²⁸) can bind in the system IrH₂S₂L₂⁺ (L = PAr₃ or PCy₃) without oxidative addition. This reluctance to undergo oxidative addition may perhaps be ascribed to the electrophilic character of the cationic Ir(III) center and the greater stability of d⁶ Ir(III) relative to d⁴ Ir(V). For the present discussion, the case of MeI coordination is particularly relevant. This ligand binds via the iodine atom to the cationic Ir(III) center. The coordinated MeI is ca. 10⁴–10⁵ times more susceptible to nucleophilic attack by NEt₃ than is free MeI. The oxidative addition of the coordinated MeI cannot occur unless the metal center is first reduced from Ir(III) to Ir(I) by abstraction of the hydride ligands with the hydrogen acceptor *t*-BuCH=CH₂.^{27b} These results suggest a working hypothesis for the alcoholysis of silanes by **1**, as shown in eq 2. It involves the dissociation of S from **1** and formation of an intermediate η²-H-SiR₃ complex of type 3 which then undergoes nucleophilic attack by MeOH.



□ = open site or solvent

Two-electron three-center Si–H...M interaction has been proposed in compounds of the type CpMn(CO)LHSiR₃ (L = phosphine or CO) by several groups and supported by X-ray and neutron diffraction studies^{29–31} and theoretical calculations,³² but

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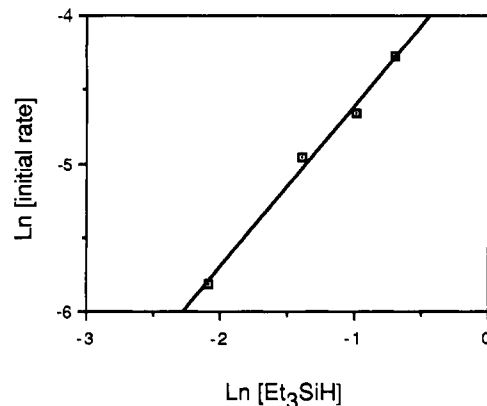


Figure 2. Plot of ln [initial rate] vs ln [Et₃SiH] for the reaction of Et₃SiH with MeOH catalyzed by **1a**. [**1a**] = 5.0 × 10⁻⁴ M, [MeOH] = 0.25 M. Reaction conditions as described in Table III. The slope (1.08) of the plot shows a first-order rate dependence on the concentration of Et₃SiH.

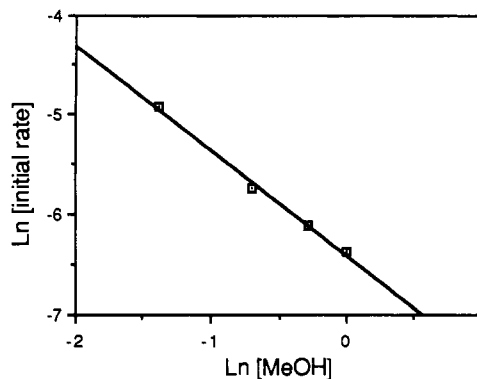


Figure 3. Plot of ln [initial rate] vs ln [MeOH] for the reaction of Et₃SiH with MeOH catalyzed by **1a**. [**1a**] = 5.0 × 10⁻⁴ M, [Et₃SiH] = 0.25 M. Reaction conditions as described in Table III. The negative slope (-1.04) of the plot shows an inverse first-order rate dependence on the concentration of MeOH.

its relation to the problem of Si–H bond activation in the catalytic reactions of silanes has not been considered. As a result of the higher electronegativity of H than Si, the Si–H bond in free R₃SiH is already polar in the sense Si^{δ+}–H^{δ-}. The Lewis acidic metal center of the present catalytic system would render the bound Si–H group more polarized in an adduct of type **3** and significantly increase its electrophilic character, thus making it much more susceptible to nucleophilic attack by an alcohol.

Kinetic studies were carried out using MeOH and Et₃SiH as substrates and [IrH₂(THF)₂L₂]SbF₆ (**1a**) as the catalyst. The rates were measured by monitoring the volume of the evolved hydrogen. The initial rates were calculated to derive the rate law. The kinetic data are summarized in Table III. The reaction was shown to be first order on the concentration of the catalyst and of Et₃SiH (Figure 2) but inverse first order on the concentration of MeOH (Figure 3). This experimental rate law (eq 3) is consistent with the observation that the rate of hydrogen evolution remained constant over the course of the reaction when 1:1 ratio of Et₃SiH to MeOH was used (see Figure 1).

$$\text{obsd rate} = k_{\text{obsd}}[\text{catalyst}][\text{Et}_3\text{SiH}]/[\text{MeOH}] \quad (3)$$

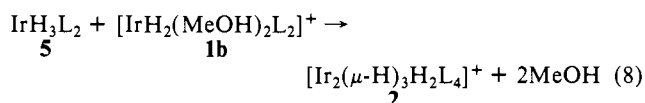
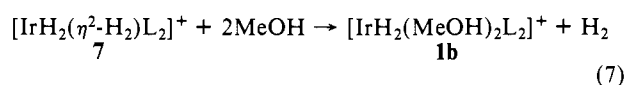
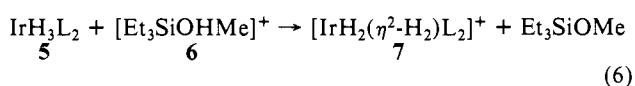
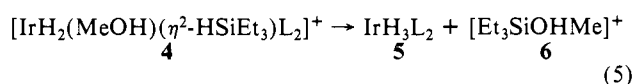
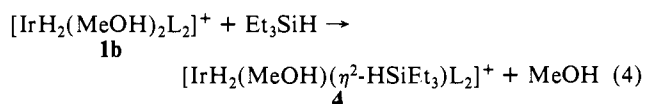
(30) (a) Schubert, U.; Ackermann, K.; Worle, B. *J. Am. Chem. Soc.* **1982**, *104*, 7378. (b) Kraft, G.; Kabas, C.; Schubert, U. *J. Organomet. Chem.* **1985**, *289*, 247. (c) Schubert, U.; Scholz, G.; Müller, J.; Ackermann, K.; Worle, B. *J. Organomet. Chem.* **1986**, *306*, 303 and references therein. (d) Schubert, U.; Müller, J.; Alt, H. G. *Organometallics* **1987**, *6*, 469.

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The kinetic isotope effects were determined for isotopic substitution in Et_3SiH and MeOH . The methanolysis of Et_3SiH with MeOH and MeOD separately revealed a relatively large isotope effect ($k_{\text{O-H}}/k_{\text{O-D}} = 1.8$), whereas a very small isotope effect ($k_{\text{Si-H}}/k_{\text{Si-D}} = 1.1$) was found for the O-silylation of MeOH with Et_3SiH versus Et_3SiD . The large value for $k_{\text{O-H}}/k_{\text{O-D}}$ suggests that the O-H bond cleavage may be directly involved in the rate-determining step of the catalytic cycle. On the other hand, the small $k_{\text{Si-H}}/k_{\text{Si-D}}$ may be due to a secondary isotope effect, implying that the Si-H bond is not broken in the rate-determining step.

In light of the kinetic studies and the arguments discussed above, we propose a mechanism (eq 4-9) for silane alcoholysis catalyzed by **1**. In the presence of the substrate MeOH , which has a high



binding constant,^{8b} the solvent complex **1b** would be the resting state of the catalyst. Et_3SiH may displace one MeOH from **1b** to form **4** (eq 4). The $\eta^2\text{-HSiR}_3$ group bound to the electrophilic Ir(III) center in **4** would be highly activated toward nucleophilic attack by MeOH (eq 5). In eq 6 the initially protonated form of the silyl ether could protonate the neutral trihydride to give a dihydrogen hydride complex. A close analogy for such a step comes from the facile protonation of $[\text{IrH}_2(\text{bq})\text{L}_2]$ to give $[\text{IrH}(\text{H}_2)(\text{bq})\text{L}_2]^+$ ($\text{bq} = 7,8\text{-benzoquinolate}$, $\text{L} = \text{PPh}_3$).^{26b,c} Displacement of the labile dihydrogen ligand in $[\text{IrH}_2(\eta^2\text{-H}_2)\text{L}_2]^+$ by MeOH would regenerate **1b** (eq 7), just as $[\text{IrH}(\text{H}_2)(\text{bq})\text{L}_2]^+$ reacts rapidly with water to give $[\text{IrH}(\text{H}_2\text{O})(\text{bq})\text{L}_2]^+$.^{26b,c} Equation 8 would lead to deactivation of the catalyst. The isolation of $[\text{Ir}_2(\mu\text{-H})_3\text{H}_2(\text{PPh}_3)_4]\text{SbF}_6^-$ (**2**) as the major deactivation product supports this step of the mechanism.

An important feature of **1** is that it can generate two cis vacant coordination sites to bind the alcohol and the silane simultaneously. Thus, the second step of the proposed mechanism (eq 5) involves an internal or intramolecular nucleophilic attack, i.e., the bound CH_3OH attacks, from within the coordination sphere, the $\eta^2\text{-HSiEt}_3$ coordinated to the same metal center. This attack is made possible by the availability of two lone pairs on the oxygen atom of CH_3OH . We found that $[\text{IrH}(\text{OH}_2)(\text{bq})\text{L}_2]\text{SbF}_6^-$ was ca. 90 times less active than **1** for the reaction of Et_3SiH with MeOH under similar conditions. This closely related catalyst differs in that it can produce only one empty coordination site. Thus, MeOH presumably attacks from outside the coordination sphere, the catalyst being much less efficient.

The rate equation of the catalytic reaction can be derived from the proposed mechanism with the aid of a few simplifying assumptions: (a) Equation 4 is a rapid preliminary equilibrium with a small equilibrium constant ($K_4 \ll 1$), which is supported by our previous observation that the exchange of S groups in $\text{IrH}_2\text{S}_2\text{L}_2^+$ is fast on the ^1H NMR time scale.^{8b} (b) Since eq 5 is unlikely rate determining in view of the very small $k_{\text{Si-H}}/k_{\text{Si-D}}$, we assume that it is also a fast preliminary equilibrium with a small equilibrium constant ($k_5 \ll 1$). (c) Equation 7 is a fast step, as supported by our previous studies.²⁶ (d) Equation 6 is the slow and therefore rate-determining step as implied by the relatively

large $k_{\text{O-H}}/k_{\text{O-D}}$. These assumptions lead to the rate law shown in eq 12 which is in agreement with the experimentally observed kinetics (eq 3).

$$\text{rate} = k_6[\mathbf{5}][\mathbf{6}] \quad (9)$$

$$K_5 = [\mathbf{5}][\mathbf{6}]/[\mathbf{4}] \quad (10)$$

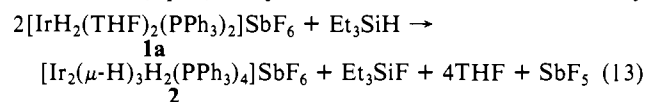
$$K_4 = [\mathbf{4}][\text{MeOH}]/([\mathbf{1b}][\text{Et}_3\text{SiH}]) \quad (11)$$

$$\text{rate} = k_6 K_4 K_5 [\mathbf{1b}][\text{Et}_3\text{SiH}]/[\text{MeOH}] = k[\text{catalyst}][\text{R}_3\text{SiH}]/[\text{MeOH}] \quad (12)$$

In our mechanism, the effect of changes in the alcohol structure on the observed rate constant k is the result of changes in K_4 , K_5 , and k_6 . Changing from a 1° to a 2° alcohol should lead to a decrease in k_6 by making the silyl ether more basic. K_4 , on the other hand, should increase because the 2° alcohol is a poorer ligand^{8b} and so more easily displaced by Et_3SiH . K_5 probably changes little. The observation that 2° alcohols react faster suggests the increase in K_4 dominates. 3° alcohols perhaps show a falloff in rate because their bulk leads to a drastic fall in k_6 .

The proposed mechanism also explains the results of the competitive experiment mentioned earlier. Although $i\text{-PrOH}$ is more reactive than MeOH when run separately, the poorer ligating ability of $i\text{-PrOH}$ makes it the loser in competition with MeOH for the active site in a competitive experiment in which both alcohols are present. As a result, the product ratio in such an experiment is significantly lower than the rate ratio obtained in separate experiments.

Spectroscopic Observation of Species Related to the Proposed Catalytic Cycle. If the mechanism described above is correct, we may be able to observe silane adducts of type **3** under carefully controlled conditions. This led us to examine the reaction of **1** with Et_3SiH in the absence of ROH . When the reaction was run with **1a** and Et_3SiH in dry CH_2Cl_2 at room temperature, the hydride-bridged dimer $[\text{Ir}_2(\mu\text{-H})_3\text{H}_2(\text{PPh}_3)_4]\text{SbF}_6^-$ (**2**) was formed and isolated (eq 13). Et_3SiF was also formed and detected by



comparison of ^{19}F NMR and GC data to those of the authentic sample. Similar results were obtained in the reactions of **1b-d** with Et_3SiH at room temperature except that O-silylation or hydrosilylation of the coordinated S groups also took place in these cases. By analogy to the reaction of Et_3SiH with $[\text{Ph}_3\text{C}]\text{SbF}_6^-$,³³ the reaction of eq 13 may occur via hydride transfer from Et_3SiH to **1a** to form a neutral iridium trihydride, which subsequently combines with another molecule of **1a** to afford the dimer **2**. Et_3SiF may arise from rapid abstraction of one F^- from the SbF_6^- counterion by the unstable triethylsilyl fragment generated in the hydride transfer step.

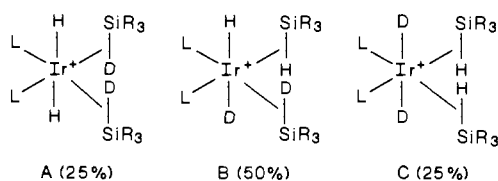
We thought that it might be possible to observe binding of Et_3SiH to **1** spectroscopically at low temperature. Addition of an excess of Et_3SiH (ca. 4 equiv) to $[\text{IrH}_2(\text{CH}_3\text{OH})_2\text{L}_2]\text{SbF}_6^-$ (**1b**) in CD_2Cl_2 at -80°C in an NMR tube under argon resulted in hydrogen evolution and concomitant formation of Et_3SiOMe . ^1H NMR showed that the hydride resonance of **1b** at $\delta -29.4$ disappeared, and a new species **8** was formed as the major organometallic product. The subsequent introduction of an excess of MeOH to the resulting mixture led once again to hydrogen evolution and formation of Et_3SiOMe , and **1b** was regenerated. The cycle could be repeated by successive additions of Et_3SiH and MeOH . **8** was more conveniently formed from the reaction of $[\text{IrH}_2(\text{THF})_2(\text{PPh}_3)_2]\text{SbF}_6^-$ (**1a**) with 2 equiv of Et_3SiH under the same conditions. In this case resonances due to free THF were also observed. **8** was stable only in solution at low temperature and extremely sensitive to nucleophiles. Attempted isolation under a variety of conditions led to decomposition to the known $[\text{Ir}_2(\mu\text{-H})_3\text{H}_2(\text{PPh}_3)_4]\text{SbF}_6^-$ (**2**).¹⁰

By analogy both to the known $\text{IrH}_2\text{S}_2\text{L}_2^+$ species ($\text{S} = \text{H}_2$,²⁶ MeI ,²⁷ agostic CH ;²⁸ $\text{L} = \text{PPh}_3$ or PCy_3) and to the crystallographically characterized silane adducts such as $\text{CpMn}(\text{CO})_2(\eta^2\text{-HSiPh}_3)$,^{29a} $(\text{MeCp})\text{Mn}(\text{CO})_2(\eta^2\text{-HSiPh}_2\text{F})$,^{30a} or $\text{C}_6\text{Me}_6\text{Cr}(\text{CO})_2(\eta^2\text{-HSiHPh}_2)$,^{30d} we propose the formulation of **8** as the bis(triethylsilane) complex $[\text{IrH}_2(\eta^2\text{-HSiEt}_3)_2(\text{PPh}_3)_2]\text{-SbF}_6$. **8** is closely related to the key intermediate species $[\text{IrH}_2(\text{MeOH})(\eta^2\text{-HSiEt}_3)_2\text{L}]^+$ (**4**) in the proposed catalytic cycle that we have not been able to observe directly, presumably due to its transient existence and low concentration in the presence of CH_3OH .

The stereochemistry of **8** can be derived from ^1H NMR. The hydride resonance region of its ^1H NMR spectra is temperature dependent, indicating the existence of a dynamic exchange process fast on the NMR time scale. The low-temperature limiting spectrum at 193 K exhibits two hydride resonances of equal intensity at δ -9.85 and -12.75, each corresponding to two protons. Homonuclear ^1H decoupling experiments ruled out any coupling between the two hydride resonances since irradiation of one hydride resonance caused no change in the appearance of the other. The triplet resonance at δ -9.85 shows typical cis coupling to the two phosphorus nuclei ($^2J(\text{PH}) = 16$ Hz). The other hydride resonance centered at δ -12.75 is a complex pattern characteristic of an AA'XX' spin system in which the two mutually cis hydrides are trans coupled to the two phosphines, which are chemically but not magnetically equivalent. Thus, the two PPh_3 ligands in **8** must be mutually cis. Although most bis(triphenylphosphine) complexes of 6-coordinate Ir(III) adopt an octahedral structure in which the two phosphine ligands are trans to each other, a few examples containing two mutually cis PPh_3 ligands are known.³⁴ Computer simulation of the HH'PP' system gave $^2J(\text{HH}')_{\text{cis}} = 0$ Hz, $^2J(\text{HP})_{\text{cis}} = -14$ Hz, $^2J(\text{HP}')_{\text{trans}} = 85$ Hz, and $^2J(\text{PP}')_{\text{cis}} = 18$ Hz. The trans H-P coupling constant of 85 Hz is somewhat smaller than is usually found for trans $^2J(\text{HP})$. Nonclassical ligands, such as $\eta^2\text{-H}_2$, often show reduced coupling constants compared to their classical analogues,⁹ and so the value observed here is consistent with the proposed nonclassical structure. Accordingly, we assign the hydride resonance at δ -9.85 to the two mutually trans IrH groups and the other centered at δ -12.75 to the two $\eta^2\text{-HSiEt}_3$ ligands cis to each other.

When the temperature is raised from 193 K, the two types of hydride resonances of **8** broaden and then coalesce at ca. 250 K into a single broad resonance at δ -11.2 with an intensity corresponding to four protons. **8** begins to decompose to $[\text{Ir}_2(\mu\text{-H})_3(\text{PPh}_3)_4]\text{SbF}_6$ (**2**)¹⁰ above ca. 280 K.

We have previously looked at isotopic trans effects in metal hydrides.³⁵ To further confirm the stereochemistry of **8**, we decided to apply this technique to the problem. The reaction of $[\text{IrH}_2(\text{THF})_2\text{L}_2]\text{SbF}_6$ (**1a**) with 2 equiv of Et_3SiD gave **8-d₂**; the same product was formed from $[\text{IrD}_2(\text{THF})_2(\text{PPh}_3)_2]\text{SbF}_6$ (**1a-d₂**) and 2 equiv of Et_3SiH . In the ^1H NMR spectrum at 193 K, the IrH resonance appears as two triplets separated by $\Delta\delta = 0.064$ ppm (16 Hz at 250 MHz), but the position of the $\text{Ir}(\eta^2\text{-HSi})$ resonance remains unchanged. It will be seen that this result is in agreement with the assigned stereochemistry of **8** with two trans IrH groups if we consider three different arrangements (A-C)



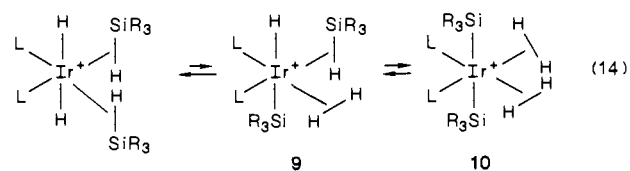
for **8-d₂**. We assume that the isotopic fractionation between the IrH and $\text{Ir}(\eta^2\text{-HSi})$ positions is small, as is expected as a result

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of the similar values for the two stretching frequencies involved. The hydrides and deuterides should therefore be statistically distributed over the two IrH and two $\text{Ir}(\eta^2\text{-HSi})$ positions. Only A and B will appear in the IrH resonance region, and they are expected to have significantly different chemical shifts due to the relatively large differential isotopic trans influence of H and D. Similarly, only B and C will appear in the $\text{Ir}(\eta^2\text{-HSi})$ resonance region. Going from B to C, we simply exchange the H of the IrH with the D of the $\text{Ir}(\eta^2\text{-DSi})$. This would be expected to have a negligibly small effect on the chemical shift of the $\text{Ir}(\eta^2\text{-HSi})$ proton in B and C because the $\text{Ir}(\eta^2\text{-H(D)Si})$ group is cis to the IrH(D). The result of the isotopic trans effect studies is therefore consistent with the proposed structure.

The rapid fluxionality of **8** is reminiscent of that of the related $\text{L}_n\text{MH}_x(\eta^2\text{-H}_2)$ species. We have considered two mechanisms to account for the dynamic exchange process between the classical hydride site and the nonclassical dihydrogen site in $[\text{IrH}(\eta^2\text{-H}_2)(\text{bq})\text{L}_2]^+$ ^{26b,c} one via a classical trihydride tautomer and the other via a trihydrogen complex of the sort recently proposed by Chaudret et al. and Heinekey et al.²⁵ The analogous mechanisms for **8** would involve, in the first case, a classical trihydride silyl complex, and, in the second, an $(\eta^3\text{-H}_2\text{SiR}_3)$ species. In either case, **8** should be capable of equilibrating with the silyl dihydrogen species **9** and **10** (eq 14). However, at low temperature (193 K)



only **8** was detected spectroscopically. The intermediates **9** and **10**, if present at all, must be in very low concentration. The thermochemical implication of this is interesting. The preferred ground-state structure indicates that the IrH and $\text{Ir}(\eta^2\text{-HSi})$ groups of **8** are favored over the IrSiR_3 and $\text{Ir}(\eta^2\text{-H}_2)$ groups present in **9** and **10**. At first glance, **9** and **10** might have been thought to be the preferred structure because of the general perception of the great weakness of Si-H bonds relative to H-H. Recent advances³⁶ in the determination of Si-H bond dissociation energies have shown that Si-H bonds are not as weak as once thought. In fact, they appear to be only slightly weaker than analogous C-H bonds. For example, $D_{\text{Si-H}}$ of Me_3SiH (90.3 kcal mol⁻¹) is very close to $D_{\text{C-H}}$ of Me_3CH (92 kcal mol⁻¹).³⁶ This is still ca. 14 kcal mol⁻¹ weaker than the H-H bond, however, and so we must postulate either that Si-H is a much better ligand than H-H or that Ir-H is considerably stronger than Ir-Si in this system. Both factors may well contribute but cannot yet be quantified.

The question remained as to whether **9** and **10** might be intermediates in the fluxional process or might be present only at higher temperatures. We felt that variable-temperature T_1 measurements would offer useful information in this respect. Other work in our laboratory has shown that the T_1 of an $\eta^2\text{-H}_2$ ligand is very short as a result of dipole-dipole relaxation between the two H nuclei.²⁶ H-H distances can even be obtained from variable-temperature T_1 data in some cases.³⁷ T_1 measurements on the hydride resonances of **8** showed that the slopes of the $\ln T_1$ vs $1/T$ curve below and above the coalescence temperature are almost the same but have the opposite signs and that the value of the minimum T_1 (212 ms at 253 K and 250 MHz in CD_2Cl_2 , see the Experimental Section) is consistent with the proposed ground-state structure of **8**, with no significant amount of any $\text{Ir}(\eta^2\text{-H}_2)$ species such as **9** or **10** present. However, trace amounts (<1%) of **9** or **10** would escape detection but could still be sufficient for the fluxional process to operate.

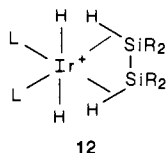
8 shows no satellite peaks due to coupling to ^{29}Si ($I = 1/2$, natural abundance = 4.7%). We ascribe this to the multiplicity and width of the $\eta^2\text{-HSiEt}_3$ resonance in the AA'XX' spin system

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at low temperature together with solubility limitation on the intensity of the signal. In addition, above the coalescence temperature, we expect only one-fourth of the splitting, because each H will be bound to ^{29}Si only one-fourth of the time in the fluxional system; this would bring the satellites into the wings of the broad resonance and thus make them undetectable.

We naturally tried to find a more stable silane complex in our catalytic system, which one we might be able to isolate and characterize crystallographically. Other work in our laboratory has made 1,1,2,2-tetraethyldisilane, $\text{Et}_2\text{HSiSiHEt}_2$ (**11**), available directly from Et_2SiH_2 by mercury-photosensitized dehydrodimerization.³⁸ We therefore looked at this potentially chelating disilane. Reaction of **1a** with **11** in CD_2Cl_2 in an NMR tube at room temperature led to displacement of THF and formation of a new complex, which appeared to be the disilane complex $[\text{IrH}_2(\eta^4\text{-Et}_2\text{HSiSiHEt}_2)(\text{PPh}_3)_2]\text{SbF}_6$ (**12**). Like **8**, **12** was stable at low temperature but slowly decomposed to $[\text{Ir}_2(\mu\text{-H})_3\text{H}_2\text{-}(\text{PPh}_3)_4]\text{SbF}_6$ (**2**) at room temperature, and so isolation of **12** was no more successful than in the case of **8**.

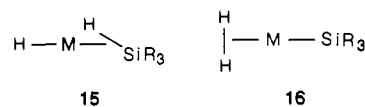


The variable-temperature ^1H NMR spectra of **12** resemble those of **8**, but lower temperature was required to freeze the fluxionality. The slow limit spectrum was observed at 180 K in $\text{CD}_2\text{Cl}_2/\text{CF}_3\text{Cl}$. The triplet resonance at $\delta -9.84$ is assigned to the two IrH groups cis split by the two phosphorus nuclei ($^2J(\text{HP}) = 15$ Hz), while the broad resonance at $\delta -12.6$ to -12.9 characteristic of an AA'XX' spin system is assigned to the two $\text{Ir}(\eta^2\text{-HSi})$ groups trans coupled to the two phosphorus atoms ($^2J(\text{SiHP})_{\text{trans}} = \text{ca. } 79$ Hz). When the temperature is raised, the two hydride resonances broaden and coalesce at 203 K. At 298 K only an averaged triplet hydride resonance of intensity 4 is present at $\delta -11.0$ ($J(\text{HP}) = 10.2$ Hz). The fluxional process may operate by the same mechanisms as discussed for **8**. Again no satellite peak due to coupling to ^{29}Si was observed throughout the whole temperature range for the same reasons cited above for **8**.

We found that $[\text{IrH}_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]\text{PhC}(\text{O}_2\text{SCF}_3)_2$ (**13**) generated by protonation of $\text{IrH}_3(\text{PCy}_3)_2$ with $\text{PhCH}(\text{O}_2\text{SCF}_3)_2$ ^{26a,b} was also very active for silane alcoholysis. Although no species analogous to **8** could be observed upon addition of Et_3SiH to **13** probably due to the great bulk of PCy_3 , reaction of **13** with $\text{Et}_2\text{HSiSiHEt}_2$ (**11**) in CD_2Cl_2 resulted in hydrogen evolution and formation of a new complex (**14**), which seemed to be the PCy_3 analogue of **12**. The variable-temperature ^1H NMR of **14** suggests that it has a different stereochemistry than **12**. At 193 K, the hydride region shows a triplet at $\delta -11.7$ ($^2J(\text{HP})_{\text{cis}} = 17.4$ Hz) and a broad singlet at $\delta -11.2$ assignable to IrH and $\text{Ir}(\eta^2\text{-HSi})$, respectively. Since no large H-P coupling is present, the two phosphorus ligands must be mutually trans, probably as a result of the large cone angle of PCy_3 . The two hydride resonances coalesce at ca. 253 K into a single broad resonance at $\delta -11.4$. Attempted isolation of **14** was not successful.

“Oxidative Addition” versus “Adduct Formation” Mechanisms for Silane Alcoholysis Catalyzed by 1. We now turn to the reasons that lead us to prefer the adduct formation (AF) mechanism described above over the oxidative addition (OA) mechanism commonly proposed for silane alcoholysis.

In our catalytic system the two mechanisms differ from one another in that nucleophilic attack of the alcohol can take place either on $\text{HM}(\eta^2\text{-HSiR}_3)$ (**15**) (AF mechanism) or on $(\eta^2\text{-H}_2)\text{-MSiR}_3$ (**16**) (OA mechanism). In either case we would not exceed the preferred oxidation state of III for iridium, and similar rate



equations would be obtained. The spectroscopic evidence in our system suggests that the adducts of type **15** are preferred over the ones of type **16**. However, the catalytic cycle could still go via tautomer **16** since it could be kinetically accessible through a fast equilibrium with **15**, as suggested by the rapid fluxionality we have observed. There are, we feel, several arguments in favor of the AF mechanism over the OA mechanism.

We have studied not only silanes but also a very wide variety of other ligands coordinated in cationic $\text{Ir}(\text{III})$ complexes. In each case, the adduct shows pronounced electrophilic properties but not the oxidative addition product. For example, we have shown that in $[\text{Ir}(\eta^2\text{-H}_2)\text{H}(\text{bq})\text{L}_2]^+$ it is the $\eta^2\text{-H}_2$ ligand, not the terminal H, that is the stronger kinetic acid.^{26b,c} In $[\text{IrH}_2(\text{IME})_2\text{L}_2]^+$, a complex in which MeI binds via the iodine atom and retains the Me-I bond, the bound MeI is ca. $10^4\text{-}10^5$ times more sensitive to attack by a nucleophile than is free MeI ; the oxidative addition product, on the other hand, is entirely unreactive toward nucleophiles.²⁷

We would have seen an inverse kinetic isotope effect (i.e., $k_{\text{Si-H}}/k_{\text{Si-D}} < 1$) for $\text{R}_3\text{SiH}(\text{D})$ in the OA mechanism. Since D would show a strong tendency to prefer the nonclassical H_2 site of **16** over the terminal or bridging sites of **15**, D substitution should shift the equilibrium between **15** and **16** toward **16** and so increase its concentration. This equilibrium isotope effect would appear in the observed kinetic isotope effect. As a result, if the OA mechanism is operating, the deuterated substrate, Et_3SiD , should react faster than Et_3SiH , which is contrary to the actually observed $k_{\text{Si-H}}/k_{\text{Si-D}}$ (ca. 1.1).

Of the three types of catalytic reactions most frequently observed for silanes (e.g., silane alcoholysis, ketone and aldehyde hydrosilation, and alkene hydrosilation), silane alcoholysis is most likely to involve the AF mechanism since an alcohol is a stronger nucleophile than is a carbonyl compound or an alkene. Simple alkenes are probably insufficiently nucleophilic to attack even an activated η^2 -bound silane and so the AF mechanism cannot apply. The classical OA mechanism involving cleavage of the Si-H bond and concomitant formation of a metal silyl hydride intermediate is therefore appropriate for thermal or photoinduced homogeneous alkene hydrosilation.^{16,39} Nevertheless, the actual mechanism may be more complex than the commonly proposed one; e.g., recent reinvestigations⁴⁰ on $\text{RhCl}(\text{PPh}_3)_3$ -catalyzed alkene hydrosilation reactions have revealed that the reactions are initiated by O_2 or $t\text{-BuOOH}$. In the case of the hydrosilation of carbonyl compounds, although the OA mechanism has been generally postulated,^{11,41} the mechanistic situation may need further clarification.

Most catalysts reported to date for silane alcoholysis are also active for alkene hydrosilation. The OA mechanism is therefore

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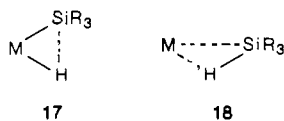
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likely to operate in these cases for both types of reactions. In contrast, **1** is not only unusually active for silane alcoholysis (36 turnovers/s for the reaction of *i*-PrOH with Et₃SiH as shown in Table I) but also highly selective; in particular, alkene hydrosilation is not catalyzed by **1** even with more reactive dialkylsilanes such as Et₂SiH₂ and Ph₂SiH₂. These observations are more easily understood in terms of the AF mechanism. Further work will be required to test our suggestion, but we believe that the evidence in its favor is sufficiently cogent that it cannot be ignored.

Comparison with Agostic C-H...M Systems and Previous Silane Complexes. Agostic C-H...M interactions^{9d} occur between coordinatively unsaturated metal centers and a C-H bond of a ligand that is already bound to the metal. The entropic advantage of intramolecular C-H bond chelation allows the complex to be isolated even if the C-H...M interaction itself is relatively weak. As a consequence, structural data are available for a wide range of cases. The M-C and M-H distances can go all the way from only slightly longer than the normal covalent bond lengths in the cases where the C-H bond interacts very strongly with the metal right up to 70% longer than the normal bond distances in the weakly interacting cases. On the other hand, the C-H bond length is only slightly elongated. From a Burgi-Dunitz analysis⁴² of the structural parameters, we²⁸ have been able to construct a kinetic trajectory for the CH + M → CMH reaction pathway. Lichtenberger and Kellogg⁴³ have studied the relatively weak agostic C-H...M interaction in Mn(CO)₃(η³-C₆H₉) by photoelectron spectroscopy and concluded that the donation of electron density from the C-H(σ) bonding orbital to the empty metal d_σ orbitals dominates over the M(d_π) to C-H(σ*) back-donation. This is consistent with the accepted theoretical picture of the oxidative addition of H₂ and CH₄ to transition-metal complexes, in which X-H(σ) (X = H or C) to M(d_σ) donation dominates at an early stage of the reaction, whereas M(d_π) to X-H(σ*) back-donation becomes more important at a late stage.⁴⁴

A series of compounds of the type CpMn(CO)LHSiR₃ (L = CO or phosphine) have been previously proposed²⁹⁻³² to contain an η²-HSiR₃ bound via a two-electron three-center bond analogous to that in agostic C-H...M systems and η²-H₂ complexes.⁹ Recent photoelectron spectroscopic data and Fenske-Hall calculations by Lichtenberger et al.⁴⁵ suggest that the M(d_π) to Si-H(σ*) back-donation is more important than the Si-H(σ) to M(d_σ) donation in these cases and that the complexes may be very close to the true oxidative addition products, as shown in **17**. They



ascribe the short distance between the Si and H atoms to the small angle between the two metal hybrid d orbitals involved in the Mn-H and Mn-Si bonding. We have examined the metrical data for these complexes and found that the M-Si and M-H distances are always close to the normal covalent bond lengths (never more than 12% longer), as would be expected if the oxidative addition of the Si-H bond is close to completion. Furthermore, in contrast to the normally slight change in the C-H bond length in agostic C-H...M cases, the Si-H distance in CpMn(CO)LHSiR₃ seems to be significantly longer (by ca. 0.28-0.32 Å) than the normal Si-H covalent bond length (1.48 Å). It therefore appears that the interaction between the silane and the metal fragment in CpMn(CO)LHSiR₃ is similar to the very strong agostic C-H...M interactions both electronically and structurally. The dominant M(d_π) to Si-H(σ*) back-donation in these complexes may tend to lower their reactivity toward nucleophiles.

A key feature of our catalytic system is that the Ir(III) center carries a positive charge making the metal electrophilic. The

electrophilicity of the metal center would tend to disfavor the oxidative addition of the Si-H bond. It is likely that in our system the Si-H(σ) to Ir(d_σ) donation outweighs the Ir(d_π) to Si-H(σ*) back-donation, as opposed to the situation in CpMn(CO)LHSiR₃. If so, the interaction between R₃SiH and the Ir center would resemble the weak type of agostic C-H...M interactions, as illustrated in **18**. Binding of type **18** should lead to a depletion of electron density from the Si-H σ bond to the electrophilic metal center and therefore activation of the silane toward nucleophilic attack, which is consistent with the chemistry we have observed.

Conclusion

The results of this study show that Lewis acidic metal complexes, particularly **1a-d**, are very efficient and highly selective catalysts for silane alcoholysis. These catalysts may find application in the protection of reactive hydroxyl groups in organic syntheses involving multifunctional compounds. We have established the homogeneity of our catalytic system by DCT and Hg tests.

In contrast to the classical oxidative addition mechanism commonly proposed, kinetic and mechanistic studies, which we have described, appear to support a mechanism in which the silane is activated through coordination of the Si-H bond to the metal in an η² fashion without oxidative addition and subsequently undergoes nucleophilic attack by the alcohol. Some silane adducts related to the proposed catalytic cycle can be detected at low temperatures by NMR spectroscopy but cannot be isolated because of decomposition and high reactivity toward nucleophiles such as water, alcohols, and even the counterion. The same mechanism may well operate for other Lewis acid catalysts, which are active for silane alcoholysis, such as ZnCl₂.⁴⁶ However, the adduct formation mechanism seems not to work for the hydrosilation of alkenes, which are insufficiently nucleophilic.

Experimental Section

General. All manipulations were performed under a dry N₂ or Ar atmosphere by standard Schlenk-tube techniques. NMR spectra were recorded on Bruker WM 250 and HX 490 instruments and IR spectra on a Nicolet 5-SX FT-IR. GC analyses were performed on a Varian Model 3700 gas chromatograph equipped with a flame ionization detector and a Varian 4270 integrator and using a 50-m SE 30 capillary column. Mass spectra were obtained with a Hewlett-Packard Model 5985 GC/MS spectrometer.

Reagents were purchased from Aldrich Chemical Co., Petrarch Systems, Inc., Columbia Organic Chemical Co., Wiley Organics, and Pfaltz & Bauer, Inc. Solvents, alcohols, and silanes were purified by standard techniques and stored under N₂ over 4-Å molecular sieves. [IrH₂S₂(PPh₃)₂]SbF₆ (S = solvent) was synthesized according to the literature method.^{9a,b}

O-Silylation of Alcohols. The O-silylation reactions were generally conducted with 5.0 mmol of alcohol, 5.0 mmol of R₃SiH, and 0.020 mmol of [IrH₂(THF)₂(PPh₃)₂]SbF₆ (**1a**) in CH₂Cl₂ with magnetic stirring in a Schlenk tube fitted with a pressure-equilibrating addition funnel and immersed in a 25 °C water bath. The apparatus was connected to a gas buret. A CH₂Cl₂ (10 mL) solution of the Ir catalyst and alcohol was prepared in the Schlenk tube, and another CH₂Cl₂ (10 mL) solution of the silane was placed in the addition funnel. The system was allowed to equilibrate for 5 min. The silane solution was added quickly from the addition funnel to the Schlenk tube containing the solution of the catalyst and the alcohol. The rate of reaction was measured by monitoring the volume of the evolved hydrogen with time until hydrogen evolution stopped. The dichloromethane was then evaporated. The residue was extracted with hexane or diethyl ether (2 × 10 mL) and filtered through Celite to remove the precipitated catalyst residue. Removal of the solvent gave the silyl ether. The product was analyzed by GC, ¹H NMR, IR, and MS. The identity of the product was established by its physical properties and spectroscopic data.

DCT and Hg Tests for Homogeneity. The experiments were carried out with the same apparatus as described above. A CH₂Cl₂ (10 mL) solution of **1a** (0.010 mmol) and CH₃OH (5.0 mmol) was stirred in the Schlenk tube with a potential inhibitor such as DCT (1.0 mol equiv) or

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liquid mercury (excess) for 30 min. Another CH_2Cl_2 (10 mL) solution of Et_3SiH (5.0 mmol) was then added from the addition funnel. The rate of reaction, determined by following hydrogen evolution, was compared with the rate obtained in the absence of an inhibitor (Table II). In the Hg test, the rate of reaction was not affected by the presence of excess liquid mercury, and the surface of the mercury bead remained shiny at the end of the reaction. In the DCT test, a complete inhibition of catalysis was observed using 1 mol equiv of DCT.

Observation of Intermediates Related to the Catalytic Cycle. A typical experiment for the observation of **8** is described as follows. $[\text{IrH}_2\text{S}_2(\text{PPh}_3)_2]\text{SbF}_6$ ($\text{S} = \text{THF}$; **1a**; 40 mg, 0.036 mmol) was dissolved in rigorously dry CD_2Cl_2 (0.5 mL) in an NMR tube. The sample was cooled to -80°C (dry ice/acetone). Et_3SiH (10.8 μL , 0.072 mmol) was added via a microsyringe under Ar. The sample was shaken and then

introduced into an NMR probe precooled to -80°C . The solution gave the variable-temperature ^1H NMR spectra as described in the text.

T_1 Experiments. The variable-temperature T_1 measurements for the hydride resonances of **8** were carried out at 250 MHz in CD_2Cl_2 at 193–273 K by the method of ref 37. The data obtained are reported as the following: temperature (K), T_1 (ms, of the IrH resonance), T_1 (ms, of the $\text{Ir}(\eta^2\text{-H}_2\text{SiEt}_3)$). Only one average T_1 can be measured above the coalescence temperature: 193, 653, 519; 203, 352, 315; 213, 267, 251; 223, 215, 212; 253, 212; 263, 326; 273, 454.

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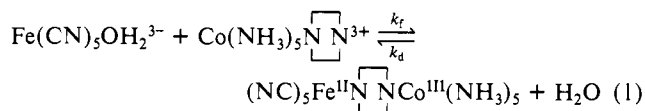
Intramolecular Electron Transfer from Pentacyanoferrate(II) to Pentaamminecobalt(III) with 3,3'-Dimethyl-4,4'-bipyridine, 4,4'-Bipyridylacetylene, 1,4-Bis(4-pyridyl)butadiyne, 2,7-Diazapyrene, and 3,8-Phenanthroline as Bridging Ligands: Adiabaticity and the Role of Distance

Gyu-Hwan Lee, Leopoldo Della Ciana, and Albert Haim*

Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11794-3400. Received August 1, 1988

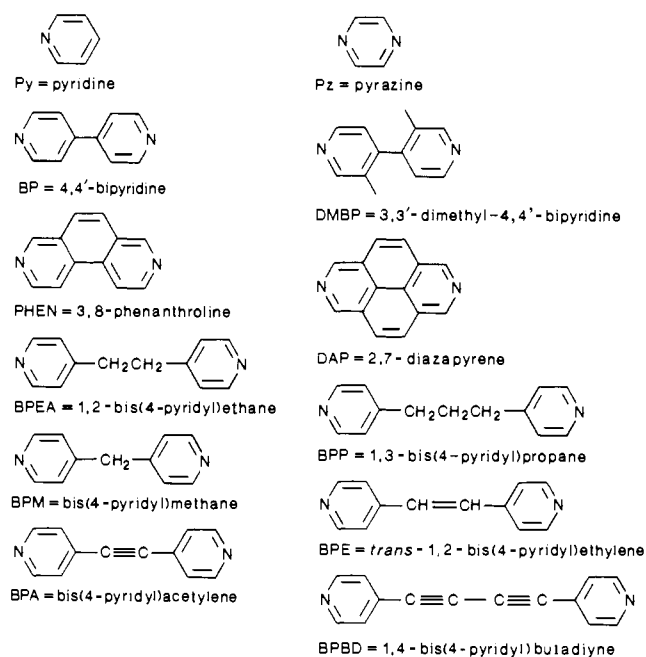
Abstract: Rate constants for intramolecular electron transfer from iron to cobalt in $(\text{NH}_3)_5\text{Co}^{\text{III}}\text{LFe}^{\text{II}}(\text{CN})_5$ ($\text{L} = 3,3'$ -dimethyl-4,4'-bipyridine, 4,4'-bipyridylacetylene, 1,4-bis(4-pyridyl)butadiyne, 2,7-diazapyrene, and 3,8-phenanthroline) have been measured at 25°C and ionic strength 0.10 M. The values of the rate constants (in the same order as the ligands above) are 2.3×10^{-3} , 1.7×10^{-3} , 0.69×10^{-3} , 4.2×10^{-3} , and $9.3 \times 10^{-3} \text{ s}^{-1}$. The activation free energies for electron transfer display an inverse dependence with respect to the Fe-Co distance in the binuclear complexes. When these free energies are corrected for the solvent reorganization energies, the resulting corrected values are independent of distance and cover the narrow range $13.5 \pm 0.5 \text{ kcal/mol}$. The metal to ligand charge-transfer bands of $\text{Fe}^{\text{II}}(\text{CN})_5\text{L}^{3-}$ complexes are shifted to higher energies when the remote N of L is coordinated to $\text{Co}(\text{NH}_3)_5^{3+}$. The shifts in energy are (in the same order as the ligands above) 4.0, 4.3, 1.7, 8.9, and 6.9 kcal/mol. On the basis of the observed trends, it is concluded that the intramolecular electron-transfer reactions proceed in the limiting adiabatic regime.

The measurement of intramolecular rather than intermolecular electron-transfer rates offers distinct advantages for investigating the details of the mechanism of electron transfer.¹ Complications involved in assembling the reactants are absent, and the transition state has a relatively well-defined geometry. Unfortunately, the search for systems feasible for intramolecular electron-transfer studies is beset by many difficulties.¹ It is not surprising, therefore, that there is only one type of system for which a wide range of precursor complexes that undergo intramolecular electron transfer can be prepared in high concentration by simply mixing two redox reagents.² In this type of system the lability of water in $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ and the affinity of the $\text{Fe}(\text{CN})_5^{3-}$ moiety for aromatic nitrogen heterocycles ($\text{N} \cdots \text{N}$)^{3,4} are exploited to generate precursor complexes $(\text{NC})_5\text{Fe}^{\text{II}}\text{N} \cdots \text{NCo}^{\text{III}}(\text{NH}_3)_5$ in near quantitative yields from reaction 1. Once formed (k_f pathway), the precursor



complexes generally disappear via intramolecular electron transfer

Chart I



from $\text{Fe}(\text{II})$ to $\text{Co}(\text{III})$, eq 2 (k_{et} pathway), as well as dissociation into the reactants (k_d pathway).²

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