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A study of the silanolysis of triphenylsilane and *p*-methoxyphenol catalysed by $(PMe_3)_4RuH_2$ and the stoichiometric reactions of $(PMe_3)_4Ru(H)(OC_6H_4$-*p*-X) (X = Me, OMe) with Ph_3SiH *

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Abstract

The ruthenium dihydride *cis*-$(PMe_3)_4Ru(H)_2$ (**1**) catalytically converts Ph_3SiH and HOC_6H_4-*p*-OMe to the alcoholysis products $Ph_3SiOC_6H_4$-*p*-OMe and H_2. This reaction was studied kinetically and the rate was found to be first-order in [**1**], first-order in [HOC_6H_4-*p*-OMe], and independent of [Ph_3SiH]. The stoichiometric reactions of *cis*-$(PMe_3)_4Ru(H)(OC_6H_4$-*p*-X) (X = Me, **2**; OMe, **3**) with Ph_3SiH were also studied in the presence of varying amounts of free *para*-substituted phenol. In the absence of the free phenol, compounds **2** and **3** reacted with Ph_3SiH to give $Ph_3SiOC_6H_4$-*p*-X and a compound we believe to be $(PMe_3)_3Ru(H)_3(SiPh_3)$ (**4**). In the presence of large amounts of phenol (> 10 equiv.), $(PMe_3)_4Ru(H)_2$ (**1**) was formed. However, at intermediate concentrations of free phenol, compounds **2** and **3** exhibited divergent behavior. Complex **2** gave dihydride **1** in a reaction whose rate was found to be first-order in the concentration of the starting aryloxy hydride **2**, first-order in phenol and independent of [Ph_3SiH]. In contrast, complex **3** reacted with less than 0.5 equiv. of *p*-methoxyphenol to form **1**, but when approximately 1 equiv. of *p*-methoxyphenol was added to the solution of **3** and Ph_3SiH a mixture of trihydride **4** and dihydride **1** were formed. The mechanisms of these complicated transformations, and their potential relationship to the dihydride-catalyzed silanolysis reaction, are discussed.

Key words: Silicon; Ruthenium; Silanolysis; Silane; Phenol

1. Introduction

The reaction of hydrosilanes and alcohols to form alkoxysilanes and dihydrogen (silane alcoholysis) has been an area of extensive interest due to potential applications to the synthesis of silyl ethers and to the protection of hydroxy groups in organic synthesis [1–4].

$$HSiR_3 + HOR' \xrightarrow{\text{catalyst}} R_3SiOR' + H_2$$

These reactions are typically run in the presence of either a nucleophilic or electrophilic catalyst. There are many known transition metal complexes that catalyze the alcoholysis reaction and a variety of mechanisms have been proposed for these processes.

Although primary alcohols react very quickly with catalysts such as $(PMe_3)_2Ru(CO)_2(Cl)_2$, reactivity decreases as the substitution on the alcohol increases. Rates are typically very slow for phenols [3–9] and, as a result, this reaction has not been studied extensively. We have now found that silane phenolysis is smoothly catalyzed by $(PMe_3)_4Ru(H)_2$ (**1**). Although the reaction is not rapid, it proceeds at reasonable temperatures and is quite clean, and the catalyst is robust. In an attempt to obtain information about individual steps expected to be involved in the mechanism of the catalytic silanolysis, we have prepared and studied the stoichiometric transformations of ruthenium phenolate hydride complexes $(PMe_3)_4Ru(H)(OC_6H_4$-*p*-Me) (**2**) and $(PMe_3)_4Ru(H)(OC_6H_4$-*p*-OMe) (**3**) that are potential intermediates in the catalytic reaction. This has led to some unexpected results. The phenolate hydrides react with silanes *via* two competitive pathways to form either a complex we believe to be the ruthenium silyl

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* Dedicated to Prof. Dr. Helmut Werner on the occasion of his 60th birthday.

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trihydride $(PMe_3)_3RuH_3(SiPh_3)$ (**4**), or a ruthenium dihydride, *cis*-$(PMe_3)_4RuH_2$ (**1**). The product mixture depends on both the nature of the phenolate ring and on the presence of free phenol.

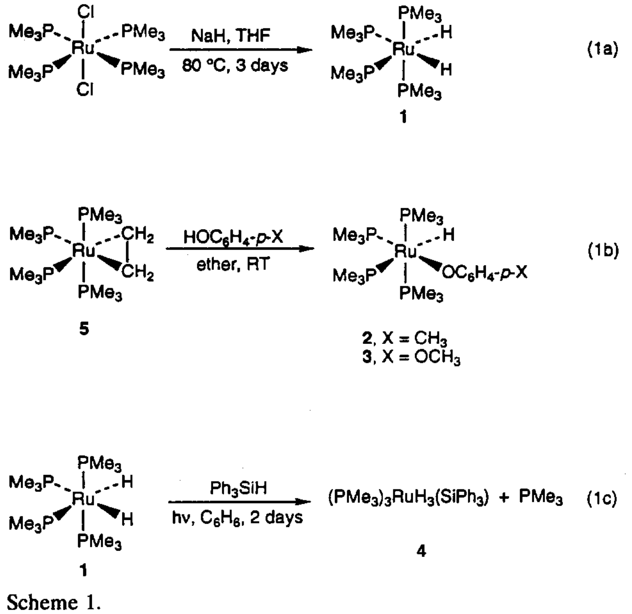
$$\begin{array}{lr} \underset{(1)}{L_4RuH_2} \xleftarrow{HOAr} L_4Ru(H)(OAr) + Ph_3SiH & \\ \qquad\qquad Ar = \text{-}C_6H_4\text{-}p\text{-}Me & (2) \\ \qquad\qquad\quad = \text{-}C_6H_4\text{-}p\text{-}OMe & (3) \\ \qquad\qquad L\ = PMe_3 & \\ \qquad\qquad\qquad\qquad \longrightarrow \underset{(4)}{L_3RuH_3(SiPh_3)} & \end{array}$$

Because our results are relatively complicated, we have chosen to organize the paper in the following way. We first present the following experimental results: (a) synthesis of the ruthenium hydride catalyst, as well as the hydride products and potential hydride intermediates; (b) kinetic study of the catalytic silanolysis, (c) studies of the reactions of potential intermediate phenolate hydrides with triphenylsilane. This is followed by a discussion of the catalytic and stoichiometric reactions and a summary of how they might be related.

2. Results

2.1. Synthesis of ruthenium hydrides

The dihydride catalyst *cis*-$(PMe_3)_4Ru(H)_2$ (**1**) has been prepared by a variety of methods [10]. The reaction of *trans*-$(PMe_3)_4RuCl_2$ with excess NaH at 90°C in THF forms **1** in high yield (Scheme 1, eqn. (1a)) [11]. The dihydride **1** is easily identified by its diagnostic $^{31}P\{^1H\}$ and ^1H NMR spectra [10,11].



Scheme 1.

The aryloxy hydride *cis*-$(PMe_3)_4Ru(H)(OC_6H_4$-*p*-Me) (**2**) can be prepared by a variety of routes [12,13] but we have found that it is most conveniently prepared in 45% yield from the room temperature reaction of *p*-cresol with $(PMe_3)_4Ru(C_2H_4)$ (**5**) (Scheme 1, eqn. (1b)). Compound **3**, *cis*-$(PMe_3)_4Ru(H)(OC_6H_4$-*p*-OMe), was prepared in an analogous reaction of the ethylene complex **5** with one equivalent of *p*-methoxyphenol at room temperature in pentane (Scheme 1, eqn. (1b)). The *p*-methoxy complex **3** was characterized by NMR spectrometry. The $^{31}P\{^1H\}$ NMR spectrum exhibits an A_2MX splitting pattern characteristic of an unsymmetrical *cis*-compound. The mutually *trans* phosphine ligands (P_A) appear as a doublet of doublets at δ 1.63 ($J_{AM} = 26.7$ Hz, $J_{AX} = 32.3$ Hz). The phosphine ligand *trans* to the hydride (the ligand with the strongest *trans* influence [14]) resonates furthest upfield at δ -12.5 (m) and the phosphine *trans* to the phenolate ligand resonates at δ 15.2 (dt, $J_{MX} = 16.4$ Hz). The distinctive hydride resonance at δ -7.69 (ddt, $J(HPx) = 102$ Hz, $J(HPm) = J(HPa) = 27.3$ Hz) in the ^1H NMR spectrum verifies the presence of the metal-bound hydride. The phenolate ligand displays a singlet at δ 3.39 for the *p*-methoxy group on the ring and an AA′XX′ quartet at δ 7.12 (d, $J = 9.0$ Hz) and 7.04 (d, $J = 9.0$ Hz) for the aryl protons. The methyl protons on the phosphine ligands show a pattern indicative of a *cis* arrangement of the four phosphine groups: a virtual triplet at δ 1.20 ($J = 2.6$ Hz) for the methyl protons on P_A and doublets at δ 1.16 (d, $J = 5.6$ Hz) and at δ 0.99 (d, $J = 7.4$ Hz) for the methyl protons on P_M and P_X, respectively. The $^{13}C\{^1H\}$ NMR spectrum confirms eight magnetically distinct carbon resonances. The aryl resonances establish that the aryl ring is rotating rapidly on the NMR time scale because both sides of the ring are equivalent.

Complex **4**, $(PMe_3)_3Ru(H)_3(SiPh_3)$, was prepared by the photochemical reaction of $(PMe_3)_4Ru(H)_2$ and Ph_3SiH in benzene (Scheme 1, eqn. (1c)). Although it could be recrystallized from pentane in 67% yield, we were not able to obtain successful elemental analyses on this material and so it was characterized primarily by NMR spectrometry. It appears to be analogous to the complex $(PMe_3)_3Ru(H)_3(SiMe_3)$, which was recently prepared in a similar manner by Procopio and Berry [15]. Like Berry's complex, the three phosphines in compound **4** appear as a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ -5.70 and the ^1H NMR spectrum displays complicated multiplets for both the hydride and the PMe_3 methyl proton signals. However, the aromatic region of the carbon spectrum is more complicated than one would expect for a simple freely rotating $SiPh_3$ group. It appears from these observations that the material either contains aromatic impurities or it is undergoing hindered aryl rotation on the NMR timescale at room temperature. The identification of this complex should therefore be considered tentative.

2.2. *Alcoholysis of Ph_3SiH and HOC_6H_4-p-OMe catalyzed by $(PMe_3)_4RuH_2$ (1)*

When catalytic amounts (< 0.1 mol%) of the ruthenium dihydride **1** were heated to 30.0 ± 1.5°C in the presence of triphenylsilane and *p*-methoxyphenol, the alcoholysis products, $Ph_3Si(OC_6H_4\text{-}p\text{-}OMe)$ (**6**) and dihydrogen, were catalytically formed. No reaction was observed between triphenylsilane and *p*-methoxyphenol in the absence of **1**.

$$Ph_3SiH + HOC_6H_4\text{-}p\text{-}OMe \xrightarrow[31°C,\ C_6D_6]{(PMe_3)_4RuH_2\ (1)} Ph_3SiOC_6H_4\text{-}p\text{-}OMe + H_2$$

Because of the relatively rapid rate of the reaction with *p*-methoxyphenol compared with other phenols (see below), this process was chosen for kinetic investigation. At 30°C, the catalytic formation of the silyl ether **6**, with 1 equiv. of catalyst **1** (4.36×10^{-7} mol, 0.00233 M), 100 equiv. of silane (4.36×10^{-5} mol, 0.217 M), and 10 equiv. of *p*-methoxyphenol (4.36×10^{-6} mol, 0.0218 M) required 4 days to completely consume the *p*-methoxyphenol. However, the catalyst is very stable to the reaction conditions; no decomposition of **1** was observed after 3 weeks at 30°C. Kinetic studies at 30.0 ± 1.5°C were carried out by NMR spectroscopy for the alcoholysis of triphenylsilane and *p*-methoxyphenol in C_6D_6. The rate was determined by monitoring the disappearance of free *p*-methoxyphenol and the appearance of the silylether product **6** *vs.* an internal standard (Table 1). Pseudo-first order conditions were maintained by using a constant concentration of $HOC_6H_4\text{-}p\text{-}OMe$ (0.0218 M) and varying the catalyst concentration (5.83×10^{-4} to 2.33×10^{-3} M, runs 1–4, Table 1) and the silane concentration (0.217 to 0.542 M, runs 5–9, Table 1).

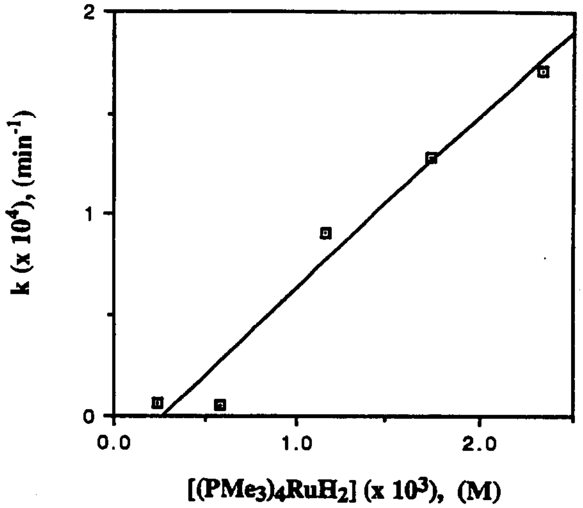


Fig. 1. Plot of first order rate constants for the catalytic silanolysis reaction *vs.* $[(PMe_3)_4RuH_2]$ (**1**).

TABLE 1. Initial concentrations and rate constants [a] for reaction of Ph_3SiH and $HOC_6H_4\text{-}p\text{-}OMe$ catalysed by $(PMe_3)_4RuH_2$ (**1**)

Exp. no	$[Ph_3SiH]$ M	[**1**] M	$[HOC_6H_4\text{-}p\text{-}OMe]$	k_{obs} ($\times 10^{-4}$) (min^{-1})
1	0.217	0.00233	0.0218	1.71
2	0.217	0.00175	0.0218	1.28
3	0.217	0.00117	0.0218	0.906
4	0.217	0.000583	0.0218	0.0540
5	0.217	0.000233	0.0218	0.0680
6	0.434	0.00233	0.0218	1.21
7	0.325	0.00233	0.0218	1.22
8	0.542	0.00233	0.0218	1.11
9	0.499	0.00233	0.0218	1.28

[a] Error in overall determination of $k \pm 5\%$ ($\approx \pm 0.05 \times 10^{-4}$ M min^{-1}).

For a particular concentration of silane and catalyst, a plot of the natural log of *p*-methoxyphenol *vs.* time was linear, indicating a first-order dependence on the phenol. Linear first-order plots of k_{obs} *vs.* [**1**] and k_{obs} *vs.* [silane] were obtained and are shown in Figs. 1 and 2. These data are consistent with a first-order dependence on the catalyst **1** and a zero order dependence on silane. The reaction was also run in the presence of varying amounts of added PMe_3. No rate dependence on $[PMe_3]$ was observed for the catalytic reaction.

Dihydride **1** catalyzes the silanolysis reaction of Ph_3SiH and $HOC_6H_4\text{-}p\text{-}Me$ to form $Ph_3SiOC_6H_4\text{-}p\text{-}$

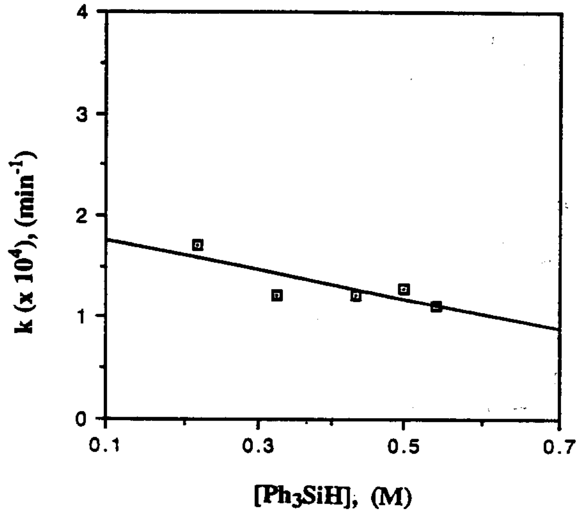
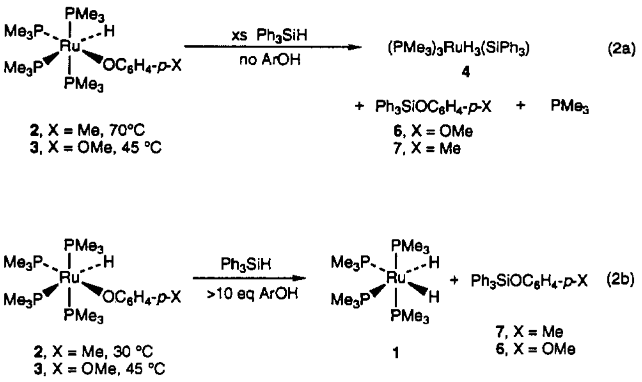


Fig. 2. Plot of first order rate constants for the catalytic silanolysis reaction *vs.* $[Ph_3SiH]$.



Scheme 2.

Me and H_2, but the rate is much slower. No reaction occurred at room temperature; at $T > 90$°C, slow silanolysis was observed. Because of its slow rate, full kinetic studies were not attempted on this reaction.

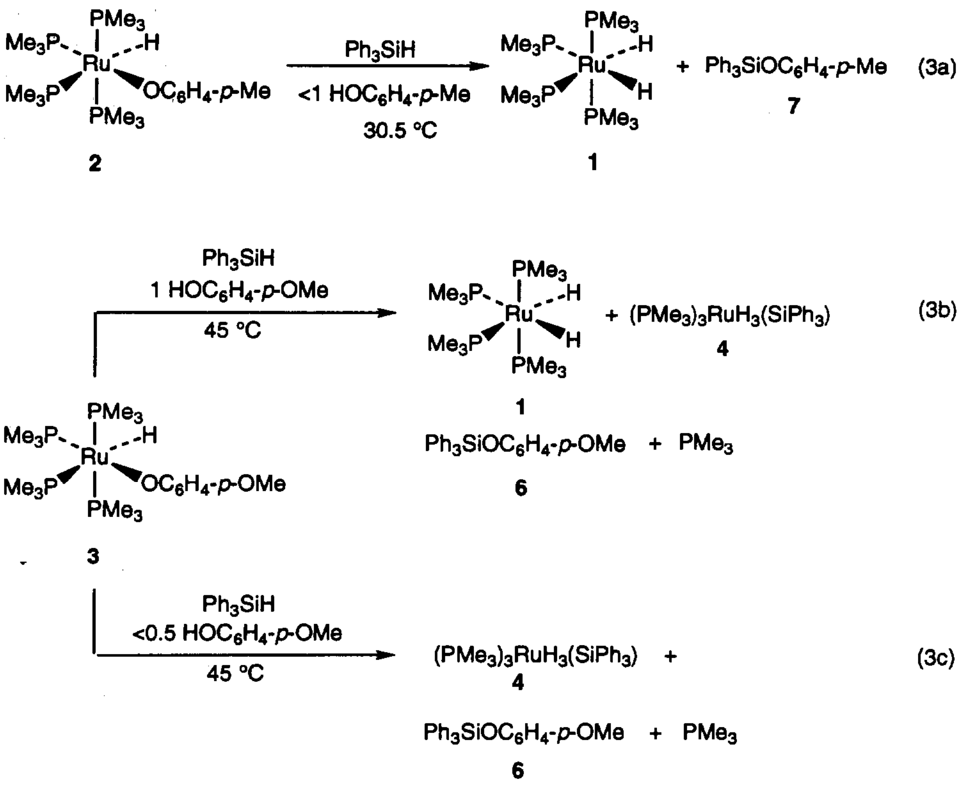
2.3. Stoichiometric reactivity of complexes 2 and 3 with triphenylsilane

The products formed from the reaction of triphenylsilane and the ruthenium phenolate hydrides **2** and **3** were influenced by both the amount of free *para*-substituted phenol present and by the nature of the *para*-substituent on the phenolate ring (Schemes 2 and 3). In all cases, complex **3** did not react with silane at room temperature but required a temperature of 45°C to undergo reaction.

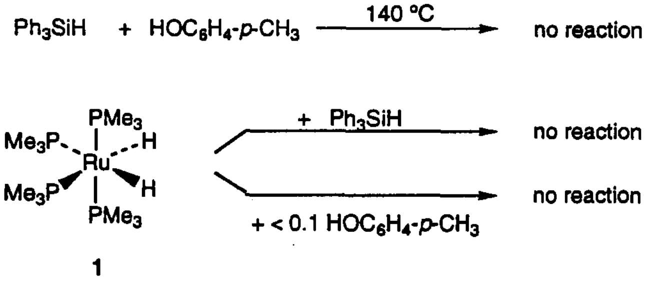
(a) *No added para-substituted phenol.* Treatment of **2** or **3** with excess triphenylsilane formed $(PMe_3)_3RuH_3(SiPh_3)$ (**4**), free PMe_3 and the alkoxysilane, $Ph_3SiOC_6H_4$-*p*-X (Scheme 2, eqn. (2a)). Although the reaction of **2** requires more vigorous conditions, both **2** and **3** formed the trihydride in high yields. The identity of **4** was confirmed by independent synthesis (Scheme 1).

(b) *Large amounts (> 10 equiv.) added para-substituted phenol.* In the presence of large amounts (> 10 equiv.) of the corresponding ArOH, both **2** and **3** reacted similarly with triphenylsilane to form $(PMe_3)_4RuH_2$ (**1**) and aryloxysilane (Scheme 2, eqn. (2b)). The rate of reaction of the *p*-methoxy complex is not strongly perturbed by the added phenol. However, the rate of the *p*-cresol reaction is dramatically catalyzed by free *p*-cresol, and proceeds at a convenient rate at 30°C rather than the 70°C required in the absence of the additive.

(c) *Small amounts (≤ 1 equiv.) added para-substituted phenol.* The reactions of complexes **2** and **3** with triphenylsilane differed drastically (Scheme 3) in



Scheme 3.



Scheme 4.

the presence of small amounts of free *para*-substituted phenol. Complex **2** reacted under these conditions to form $(PMe_3)_4RuH_2$ (**1**) and $Ph_3SiOC_6H_4$-*p*-Me (**7**) (Scheme 3, eqn. (3a)). When complex **3** was treated with approx. 1 equiv. of HOC_6H_4-*p*-OMe, both dihydride **1** and trihydride **4** were formed (Scheme 3, eqn. (3b)). However, if 0.5 equiv. or less of the phenol was added to a solution of complex **3** and silane the only ruthenium product observed was $(PMe_3)_3RuH_3(SiPh_3)$ (**4**) (Scheme 3, eqn. (3c)).

2.4. *Kinetic analysis of reactions 3a and 3c*

To help understand these peculiar observations, kinetic studies were performed on the reactions of **2** and **3** with Ph_3SiH in the presence of small amounts of free phenol.

(a) *$(PMe_3)_4Ru(H)(OC_6H_4$-p-Me)*. The reaction of $(PMe_3)_4Ru(H)(OC_6H_4$-*p*-Me) (**2**) with Ph_3SiH in the presence of small amounts of *p*-cresol (0.057 to 0.190 equiv. with respect to Ru) was studied by NMR spectrometry. Prior to the kinetic study a number of control experiments were run. These are summarized in Scheme 4. No reaction occurred between triphenylsilane and *p*-cresol at temperatures as high as 140°C. The ruthenium product of reaction, $(PMe_3)_4RuH_2$ (**1**), was treated separately with both triphenylsilane and small amounts of *p*-cresol. No reaction occurred in either case. It was also established that the organic silyl ether product **7** is unreactive towards *p*-cresol, complex **2**, and trihydride complex **4**. As mentioned previously, dihydride **1** does not catalyze the silanolysis of Ph_3SiH and HOC_6H_4-*p*-Me at 30°C.

TABLE 2. Initial concentrations and rate constants [a] for the alcoholysis reaction of **2** and Ph_3SiH in the presence of catalytic amounts of cresol

Exp. no.	[**2**] (M)	[*p*-cresol] (M)	[Ph_3SiH] (M)	k_{obs} (min^{-1})
1	2.25×10^{-2}	4.29×10^{-3}	2.17×10^{-1}	5.16×10^{-4}
2	2.25×10^{-2}	3.00×10^{-3}	2.17×10^{-1}	4.59×10^{-4}
3	2.25×10^{-2}	2.14×10^{-3}	2.17×10^{-1}	4.48×10^{-4}
4	2.25×10^{-2}	1.29×10^{-3}	2.17×10^{-1}	4.10×10^{-4}
5	2.26×10^{-2}	4.29×10^{-3}	4.34×10^{-1}	5.93×10^{-4}
6	2.26×10^{-2}	4.29×10^{-3}	4.77×10^{-1}	5.90×10^{-4}
7	2.26×10^{-2}	4.29×10^{-3}	3.69×10^{-1}	5.55×10^{-4}
8	2.26×10^{-2}	4.29×10^{-3}	6.51×10^{-1}	5.45×10^{-4}
9	2.26×10^{-2}	4.29×10^{-3}	7.59×10^{-1}	5.97×10^{-4}

[a] Error in overall determination of $k \pm 5\%$ ($\approx \pm 0.25\times10^{-4}$ min^{-1}).

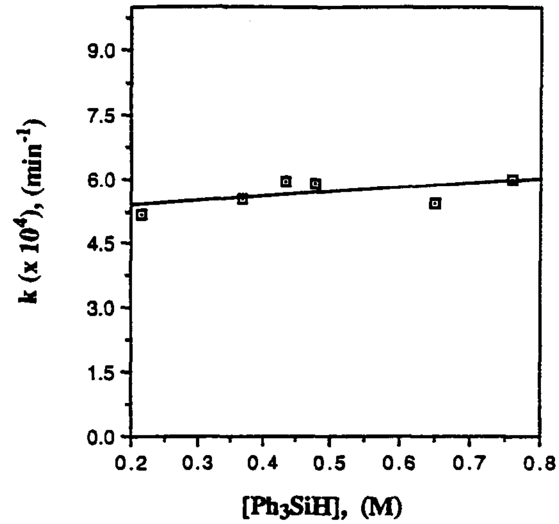


Fig. 3. Plot of first order rate constants for the alcoholysis reaction of **2** and Ph_3SiH in the presence of catalytic amounts of cresol *vs.* [Ph_3SiH].

In the presence of *p*-cresol, reaction of **2** with Ph_3SiH (Scheme 3, eqn. (3a)) proceeds readily at 30.5 ± 1.5°C and is accelerated by increasing the amount of the phenol. To establish the rate law for the silanolysis, the rate of disappearance of **2** was monitored by ^1H NMR spectrometry in the presence of catalytic amounts of *p*-cresol and excess triphenylsilane. These experiments established a clean pseudo-first-order disappearance of the ruthenium aryloxide **2**. The concentrations of catalyst and silane were varied systematically (Table 2); plots of k_{obs} *vs.* [ArOH] and k_{obs} *vs.* [Ph_3SiH] are

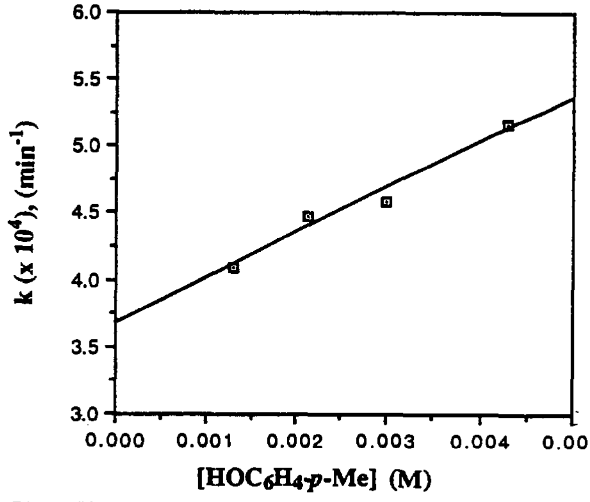
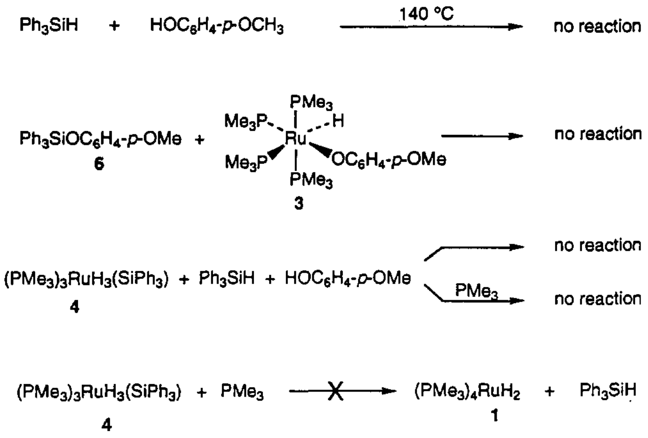


Fig. 4. Plot of first order rate constants for the alcoholysis reaction of **2** and Ph_3SiH in the presence of catalytic amounts of cresol *vs.* [HOC_6H_4-*p*-Me].



Scheme 5.

shown in Figs. 3 and 4. The cresol data are consistent with a first-order dependence of the rate on the cresol concentration. We observe a negligible dependence of the rate on the silane concentration, and believe that the data are most consistent with the conclusion that the rate law is essentially zero order in silane.

Addition of added PMe_3 to the reaction solution diverted the course of the alcoholysis reaction from alcoholysis product **7** to the formation of a phosphine salt **8a**. Compound **8a** has been observed and characterized as $[(PMe_3)_5Ru(H)][OC_6H_4$-p-Me $\cdot$ HOC_6H_4-p-Me] in a related hydrogenolysis study [16].

(b) *$(PMe_3)_4Ru(H)(OC_6H_4$-p-OMe)*. In contrast to the reaction of triphenylsilane with **2**, complex **3** reacted with Ph_3SiH at 45°C to form either a mixture of dihydride and trihydride or when less than 0.5 equiv. of *p*-methoxyphenol were present, just the trihydride **4** (Scheme 3, eqns. (3b) and (3c)). This reaction was monitored at 45°C in cyclohexane-d_{12} by ^1H and $^{31}P\{^1H\}$ NMR spectrometry and by UV spectroscopy, and was found to proceed cleanly to the products over the course of 12 h.

TABLE 3. Initial concentrations and rate constants [a] for the reaction of **3** and Ph_3SiH with decreasing amounts of *p*-methoxyphenol

Exp. no.	$[Ph_3SiH]$ $(\times 10^{-2}$ M)	[Ru] $(\times 10^{-4}$ M)	$[HOC_6H_4$-p-OMe] (M)	$(\times 10^{-5}$ $s^{-1})$
1	1.51	1.21	5.41×10^{-4}	6.09
2	1.51	1.21	1.08×10^{-3}	6.03
3	1.51	1.21	1.62×10^{-3}	6.09
4	1.51	1.21	2.17×10^{-3}	5.70
5	1.51	1.21	2.71×10^{-3}	4.97
6	1.51	1.21	1.62×10^{-3}	5.79
7	1.51	1.21	5.41×10^{-5}	6.36
8	1.51	1.21	1.08×10^{-5}	6.49
9	1.51	1.21	3.25×10^{-5}	6.77
10	1.51	1.21	1.08×10^{-4}	6.42
11	1.51	1.21	1.03×10^{-7}	10.7
12	1.51	1.21	6.17×10^{-8}	11.2
13	1.51	1.21	2.06×10^{-8}	12.1
14	1.51	1.21	2.06×10^{-9}	11.6
15	1.51	1.21	2.06×10^{-10}	15.2

[a] Error in overall determination of k $\pm 5\%$ $(\pm 0.05\times10^{-5}$ $s^{-1})$.

A number of control experiments were performed and are summarized in Scheme 5. No reaction occurred between triphenylsilane and *p*-methoxyphenol at temperatures as high as 140°C. The organic silylether product, $Ph_3SiOC_6H_4$-p-OMe (**6**), was unreactive towards the ruthenium complex **3**. When the ruthenium trihydride product **4** was dissolved in benzene in the presence of both triphenylsilane and *p*-methoxyphenol, no change in concentration of any of the components, with respect to an internal standard, was observed. In addition, complex **4** did not react with free PMe_3 to generate the dihydride **1**. When triphenylsilane and *p*-methoxyphenol were added to a solution containing complex **4** and PMe_3, no reaction was observed.

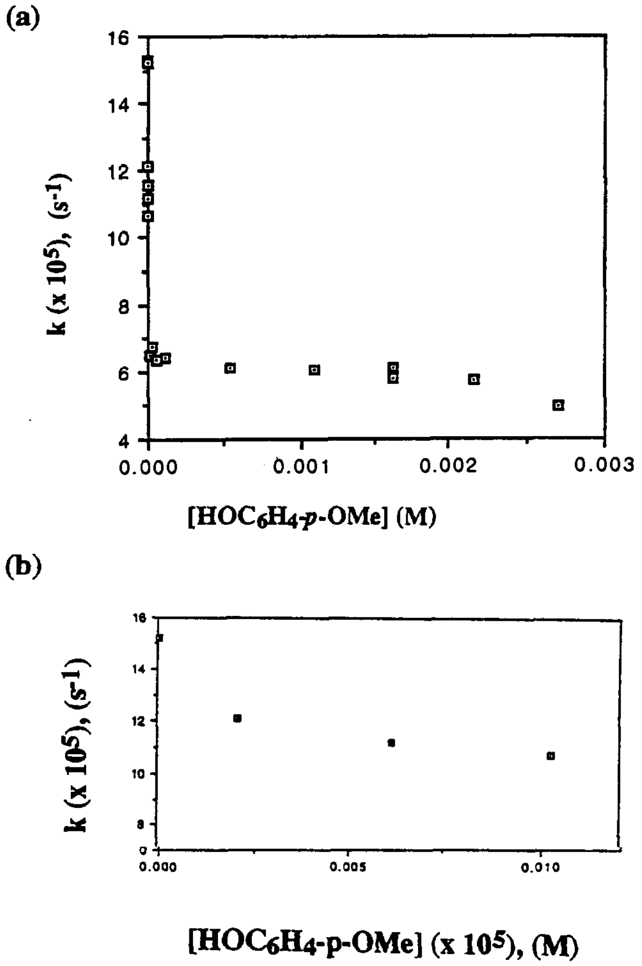


Fig. 5. (a) Plot of first order rate constants for the reaction of **3** and Ph_3SiH in the presence of small amounts of *p*-methoxyphenol *vs.* $[HOC_6H_4$-p-OMe]. (b) Expansion showing the first four (low concentration) points in the plot in (a).

We attempted to study the mechanism of this reaction. Compound **3** has a distinct absorbance in the UV-vis spectrum at 327 nm, and so the reaction of **3** with Ph_3SiH could be followed by monitoring the decrease in this absorbance at 45°C over the course of the reaction. The reaction was studied over a wide range of concentrations of added free*p*-methoxyphenol. The initial concentrations of silane and *p*-methoxyphenol were varied systematically, maintaining pseudo-first-order conditions in **3** by using excess silane (Table 3). In runs 1–15, the concentrations of **3** and silane were kept constant, and the concentration of cresol was varied from 2.71×10^{-3} to 2.06×10^{-10} M. A plot of k_{obs} *vs.* [ArOH] (Fig. 5) shows a very unusual dependence on *p*-methoxyphenol.

The effect of added phosphine on the overall reaction of **3** and silane was examined in an attempt to clarify the reaction mechanism. Two parallel NMR tube experiments were set up, one containing only silane, *p*-methoxyphenol and **3**, and one containing silane, *p*-methoxyphenol, **3**, and 180 equiv. of PMe_3 with respect to ruthenium. It was found that the added phosphine inhibited the reaction. No reaction occurred in the PMe_3-containing sample after 5 days at 45°C and $[(PMe_3)_5RuH]^+[OC_6H_4\text{-}p\text{-}OMe \cdot HOC_6H_4\text{-}p\text{-}OMe]^-$ (**8b**, analogous to salt **8a**) was not observed.

3. Discussion

3.1. Catalytic reaction of triphenylsilane and p-methoxyphenol by $(PMe_3)_4RuH_2$

The reaction of triphenylsilane and *p*-methoxyphenol is catalyzed by $(PMe_3)_4RuH_2$ at 30°C [3]. The alcoholysis reaction is thermodynamically driven. The bond dissociation energies for the bonds formed, a dihydrogen bond (BDE = 104 kcal/mol) [17] and a silicon–oxygen bond (BDE = 108 kcal/mol) [18] exceeds the BDEs for the bonds broken, a silicon–hydrogen bond (BDE = 90 kcal/mol) [19] and an alcohol O–H bond (BDE = 86.5 kcal/mol) [20]. The difference in these energies of −35.4 kcal/mol predicts this to be an enthalpically favored reaction.

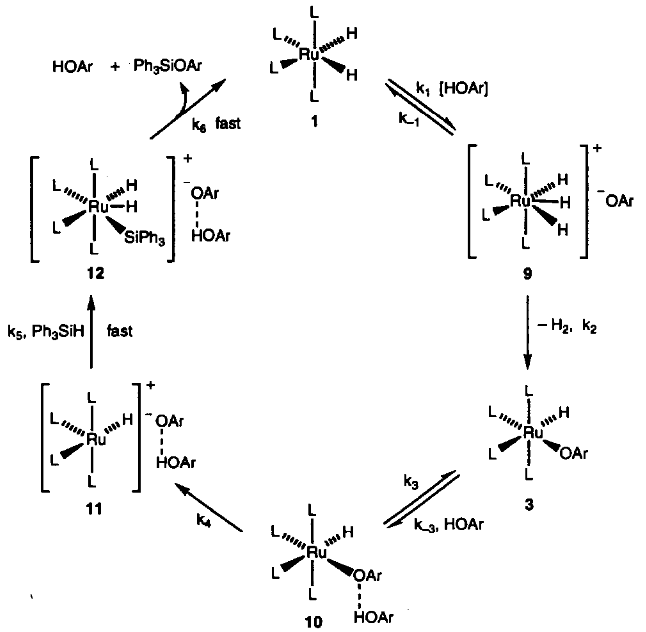
The alcoholysis reaction is first-order in [ArOH], first-order in [catalyst] and zero-order in $[Ph_3SiH]$. In the presence of excess ArOH, cresolate hydride **2** does not form trihydride **4**. We therefore propose that the mechanism for the catalytic cycle proceeds by a protonation mechanism (Scheme 6).

Protonation of the dihydride **1** by free ArOH, followed by irreversible loss of dihydrogen, generates the phenolate hydride complex **3** [13]. Complex **3** reacts with excess free phenol to form the hydrogen-bonded species **10** which can dissociate to the complex ion-pair **11**. Oxidative addition of silane to this species forms complex **12**. Irreversible nucleophilic attack of aryloxide at silicon and dissociation of the coordinated phenol regenerates the dihydride **1**. If we assume that the dihydrogen elimination step from **9** to **3** is irreversible (Scheme 6) and is slower than the preceding protonation step, the mechanism predicts a rate law that is first-order in **1**, first-order in $HOC_6H_4\text{-}p\text{-}OMe$ and zero-order in silane, as is observed. Assuming the k_2 step is effectively irreversible in the absence of added H_2, the steady-state derived rate law is shown below.

$$\text{rate} = k_{obs}[\text{ArOH}] = k[\mathbf{1}][\text{ArOH}],$$

$$k = (k_2 k_1)/(k_{-1} + k_2)$$

Studies done on the effect of added phosphine on the rate of the reaction have shown that the rate is phosphine-independent, ruling out an initial reversible phosphine dissociation mechanism. The presence of added PMe_3 should also divert the hydrogen-bonded intermediate, $[(PMe_3)_4Ru(H)]^+[ArOH \cdot OAr]^-$ (**11**), to form $[(PMe_3)_5Ru(H)]^+[OC_6H_4\text{-}p\text{-}OMe \cdot HOC_6H_4\text{-}p\text{-}OMe]$ (**8b**). To check this possibility, complex **8** was generated [16] and added to a solution containing catalyst **1**, Ph_3SiH and $HOC_6H_4\text{-}p\text{-}OMe$. Over the course of 12 h at 30.0 ± 1.5°C, it was observed that the silanolysis product **6** formed catalytically and complex **8b** disappeared during the course of the catalytic reaction. Although the presence of added PMe_3 should drive the intermediate **11** to form **8b**, we conclude from these experiments that the process is reversible and its



Scheme 6.

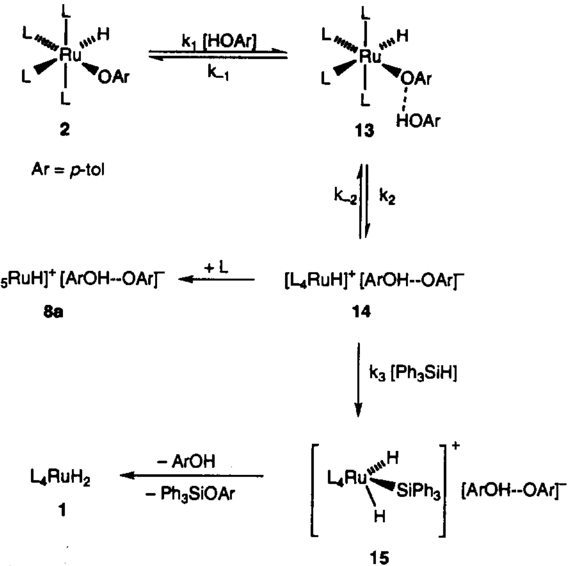
equilibrium concentration does not build up significantly under the catalytic conditions.

3.2. Stoichiometric reactions of $(PMe_3)_4Ru(H)(OC_6H_4$-p-X) with triphenylsilane

Reaction between $(PMe_3)_4Ru(H)(OC_6H_4$-*p*-X) (X = Me, **2**; OMe, **3**) and Ph_3SiH, in the presence of varying amounts of free ArOH, led to the formation of either $(PMe_3)_4Ru(H)_2$ (**1**) or $(PMe_3)_4Ru(H)_3(SiPh_3)$ (**4**).

(a) *No added para-substituted phenol.* In the absence of added free *para*-substituted phenol, both complexes **2** and **3** reacted with Ph_3SiH to form $(PMe_3)_3RuH_3(SiPh_3)$ (**4**) (Scheme 3, eqn. (3a)). This complex can be synthesized independently from the photochemical reaction of the dihydride and free silane in a manner analogous to the preparation of the known $(PMe_3)_3RuH_3(SiMe_3)$ [15]. The reaction of **2** required higher temperatures than **3** to form trihydride **4**. Although kinetic studies have not been performed on these reactions, the presence of excess free PMe_3 shut down the reaction of **3** to form **4** suggesting a dissociative mechanism.

(b) *Large amounts (> 10 equiv.) of added para-substituted phenol.* Addition of free phenol does not affect the rate of the *p*-methoxyphenoxide (**3**) reaction, but it dramatically catalyzes the rate of the *p*-methylphenoxide (**2**) reaction, lowering the reaction temperature from 70°C to 30°C (Scheme 2). In the presence of a large excess of free *para*-substituted phenol, for both **2** or **3** the observed product is dihydride **1**. Formation of dihydride **1** in the presence of Ph_3SiH and *p*-methoxyphenol at 30°C results in the onset of the silane phenolysis catalytic process. The corresponding catalytic cycle involving *p*-cresol is very slow at 30°C.



Scheme 7.

(c) *Small amounts of added para-substituted phenol (< 1 equiv.).* Treatment of **2** with Ph_3SiH and small amounts of *p*-cresol led to the quantitative formation of dihydride **1** (Scheme 3, eqn. (3a)). The reaction of **2** is first-order in [**2**], is catalyzed by added *p*-cresol, and shows a zero-order dependence on [Ph_3SiH]. Our combined observations are most consistent with the mechanism summarized in Scheme 7. Reaction of **2** with *p*-cresol results in assisted ionization of the cresolate ion (probably *via* the hydrogen-bonded intermediate **13** [5]) to give the ion pair **14**. The cationic ruthenium center then undergoes oxidative addition of Ph_3SiH to give **15**. Attack on **15** by aryloxide at the silicon atom then leads to dihydride **1** and silyl ether. Alternatively, **14** can be diverted by excess phosphine to pentakis(trimethylphosphine)ruthenium hydride **8a**. If one assumes that the rate of the back reaction from **14** (k_{-2}) is much slower than the rate of oxidative addition ($k_3[Ph_3SiH]$), this mechanism predicts a rate law that is first-order in **2** and *p*-cresol and zero-order in silane, as is observed. The steady-state derived rate law is shown below.

$$\text{rate} = k_{obs}[\mathbf{2}] = k[\mathbf{2}][\text{ArOH}],$$

$$k = (k_1 k_2)/(k_{-1} + k_2)$$

In contrast to the reaction of **2**, the reaction of the ruthenium phenolate hydride **3** with Ph_3SiH at 45°C varied greatly with the added amount of *p*-methoxyphenol. If less than 0.5 equiv. was added, the sole ruthenium containing product formed was trihydride **4** (Scheme 3, eqn. (3c)). However, if approximately 1 equiv. of *p*-methoxyphenol was added, a mixture of the dihydride and trihydride was formed. Under these conditions, dihydride **1** is an active catalyst for the silanolysis of *p*-methoxyphenol and triphenylsilane to form silyl ether **6**. We attempted to study the mechanism of this reaction but at present we do not understand the inhibition observed (Fig. 5) when free *p*-methoxyphenol is added to **3**. Further study will be necessary to elucidate the mechanism of this stoichiometric reaction.

We believe the difference in reactivity of **2** and **3** with triphenylsilane, in the presence of very small amounts of *para*-substituted phenol (< 0.5 equiv.), eqns. (3a) and (3c), respectively, is due to the difference in the acidity of *p*-cresol relative to *p*-methoxyphenol. The aqueous pK_a of the alcoholic proton in *p*-cresol is 18.2 and in *p*-methoxyphenol, it is 19.1 [21].

Although this difference is not large, it appears (if we assume that *p*-cresol is also the stronger of the two acids in benzene) to be sufficient to allow the more acidic *p*-cresol to react with the ruthenium complex **2** by protonating the ruthenium alkoxide to form a hydrogen-bonded ion pair (Scheme 7). This complex then reacts with silane to form the observed products. In the case of **3**, the acidity of *p*-methoxyphenol is not great enough to drive the protonation reaction of **3** before a competing reaction occurs to form trihydride **3**.

4. Summary and conclusions

We have observed that the ruthenium dihydride **1** is an effective catalyst for the silanolysis of Ph_3SiH and HOC_6H_4-*p*-OMe to form $Ph_3SiOC_6H_4$-*p*-OMe and dihydrogen. A strong substituent effect exists in this reaction; the corresponding *p*-methylphenol, HOC_6H_4-*p*-Me, also undergoes this reaction, but its rate is much slower. Stoichiometric reactions of ruthenium aryloxy hydrides **2** and **3**, potential intermediates in the catalytic reactions, with triphenylsilane were also investigated. Ruthenium trihydride **4** was the sole metal-containing product observed in the direct reaction of complex **2** or **3** with Ph_3SiH. As in the catalytic reaction, the *p*-methyl complex reacted more slowly than the *p*-methoxy complex. However, the presence of added phenol changes these reactions, dramatically accelerating the transformation of *p*-methyl complex **2** (but not **3**) and leading to polyhydrides **1** or **4**, depending on the substituents and reaction conditions. Our product and kinetic data are most consistent with a mechanism for these reactions that involves initial conversion of dihydride **1** and *p*-methoxyphenol to aryloxy hydride **3** by a protonation mechanism. The aryloxy hydrides can then undergo proton-assisted ionization of the aryloxide ligand leading to a hydrogen-bonded aryloxide and a coordinatively unsaturated cationic hydridoruthenium intermediate. This undergoes oxidative addition of silane, followed by reductive elimination to form silyl ether product and regenerate catalyst **1**.

5. Experimental details

5.1. General

Unless otherwise noted, all reactions and manipulations were carried out under a nitrogen atmosphere in a Vacuum Atmospheres 553-2 Dri-Lab with attached M6-40-1H Dri-Train or under argon using standard Schlenk and vacuum techniques and glassware dried in an oven at 150°C.

Reactions involving gaseous reagents were handled on a vacuum line equipped with a MKS Baratron gauge. A known pressure of volatile or gaseous reagents, calculated from the ideal gas law, was expanded into a bulb of known volume and then condensed at −196°C into a high pressure vessel consisting of a thick walled glass bomb attached to a Kontes vacuum stopcock. Benzene, toluene, tetrahydrofuran (THF), and diethyl ether were distilled from sodium-benzophenone ketyl. Pentane and hexane were distilled from lithium aluminum hydride. C_6D_6 and cyclohexane-d_{12} were obtained from Aldrich and were initially dried by alternatively freeze-pump-thawing, stirring over CaH_2 for 3 days, and then storing over Na/benzophenone ketyl. *p*-Methoxyphenol was obtained from Kodak and purified by sublimation. *p*-Cresol was obtained from Aldrich and purified by recrystallization from petroleum ether. 1,3,5-Trimethoxybenzene was obtained from Aldrich and purified by recrystallization from hexane. $(PMe_3)_4Ru(Cl)_2$ [22], $(PMe_3)_4Ru(C_2H_4)$ (**5**) [23], $(PMe_3)_4Ru(H)(OC_6H_4$-*p*-Me) (**2**) [12] and $(PMe_3)_4Ru(H)_2$ (**1**) [11] were prepared by literature methods. Unless otherwise noted, all other reagents were obtained from commercial suppliers and used without further purification.

UV kinetic experiments were monitored with a Hewlett-Packard 8450A instrument equipped with a 89100A temperature controller. Standard solutions were prepared in the drybox in volumetric flasks. Individual runs were prepared in the drybox by transferring aliquots of standard solutions using a gas-tight syringe, calibrated to be accurate to 1.0 μl by weight, into a quartz cuvette, which was then sealed with a Kontes high vacuum stopcock, removed from the box and placed in the spectrometer. The cuvette was allowed to reach temperature equilibrium with the cell holder before data were acquired. The solution in the cell was stirred with a micro-stir bar over the course of the reaction. Plots of absorbance versus time were fit using the IGOR graphics program (© Wavemetrics).

All ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were obtained at room temperature on a superconducting FT spectrometer incorporating Nicolet computers and cryomagnets assembled in the UC Berkeley NMR laboratory by Mr. Rudi Nunlist. The ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ spectra were determined at 300 MHz, 121 MHz and 75 MHz, respectively. Elemental analyses were conducted by the U.C. Berkeley Microanalysis Facility and FAB-MS was carried out on a VG-70SE instrument in the U.C. Berkeley Mass Spectrometry Facility.

5.2. $(PMe_3)_4Ru(H)(OC_6H_4$-p-OMe) (3)

To a pentane solution of $(PMe_3)_4Ru(C_2H_4)$ (**5**) (316 mg, 0.730 mmol in 5 ml of pentane) was added a solution of HOC_6H_4-*p*-OMe (9.17 mg, 0.740 mmol), in 2 ml pentane dropwise over 5 min. During the addition, the color of the solution turned from yellow to white. The mixture was allowed to stir for an additional 15 min at room temperature. Complex **3** is sparingly soluble in pentane and is easily purified by reduction of the volume of solution under vacuum to 0.5 ml followed by cooling at −30°C. Compound **3** crystallized as a white solid to yield 174.6 mg (45% yield). ^{1}H NMR (C_6D_6): δ 7.12 (d, 9.0 Hz); 7.04 (d, $J = 9.0$ Hz); 3.39 (s); 1.20 (t, $J = 2.59$ Hz); 1.16 (d, $J = 5.57$ Hz); 0.99(d, $J = 7.4$ Hz); −7.69(dq, $J = 27.3$ Hz, $J = 102$ Hz). ^{31}P NMR (C_6D_6): δ A_2MX 1.63 (dd, P_A, $J_{AX} = 26.7$ Hz, $J_{AM} = 32.3$ Hz); 15.2 (P_M, m, $J_{MX} = 16.4$ Hz); −12.5 (dt, P_X). ^{13}C{^{1}H} NMR (C_6D_6): δ 165.93 (s); 147.80 (s); 119.89 (s); 115.41 (s); 56.23 (s); 27.3 (d, $J = 26.6$ Hz); 22.96 (dt, $J = 3.81$ Hz, $J = 12.65$ Hz); 20.60 (d, $J = 12.0$ Hz). IR (C_6D_6): ν 3244, 2968, 2906, 2823, 1845 cm^{-1}. Anal. Found: C, 43.06; H, 8.12. $C_{19}H_{44}O_2P_4Ru$ calcd.: C, 43.10; H, 8.40%.

5.3. $(PMe_3)_3Ru(H)_3(SiPh_3)$ (4)

(a) *Independent synthesis*. $(PMe_3)_4RuH_2$ (42.7 mg, 0.105 mmol) and Ph_3SiH (35.1 mg, 0.135 mmol) were dissolved in 0.5 ml of benzene in a thick-walled NMR tube. The colorless solution was degassed three times and sealed under vacuum. The tube was placed in a constant temperature bath equipped with an external Hg photolysis lamp. The solution was photolyzed at room temperature for 48 h with periodic monitoring by NMR spectrometry. The solvent was removed under vacuum and compound **4** was recrystallized to yield 41.2 mg (67% yield) of pure product by dissolving the resulting white residue in a minimum amount of pentane and cooling the solution to −30°C. ^{1}H NMR (C_6D_6): δ 7.89 (d, $J = 7.57$ Hz); 7.30 (t, $J = 7.4$ Hz); 1.38 (m); 1.25 (d, $J = 4.68$ Hz); 1.0 (t, $J = 5.2$ Hz); 0.79 (d, $J = 2.28$ Hz); −9.5 (m). ^{31}P NMR (C_6D_6): δ −5.7 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 147.01 (s); 132.3 (s); 132.2 (s); 129.68 (s); 126.04 (s); 122.99 (s) 122.79 (s); 25.7 (t, $J = 13.35$ Hz); 23.7 (t, $J = 8.61$ Hz); 21.1 (t, $J = 14.0$ Hz). IR (CH_2Cl_2): ν 2956, 2904, 2140, 1919 cm^{-1}. FAB-MS (Sulfolane): *m/e* 591.1 (M^+). In spite of repeated attempts, a consistent elemental analysis could not be obtained.

(b) *From 2*. Treatment of **2** (12.7 mg, 0.0248 mmol) with excess Ph_3SiH (65.6 mg, 0.252 mmol) in C_6D_6 at 70°C led to the formation of trihydride **4** and $Ph_3SiOC_6H_4$-*p*-Me (**7**) after 12 h. The NMR yield of complex **4** was 85% versus an internal standard. Due to similar solubilities, complex **4** could not be isolated free from compound **7**. Identification of the products was based on comparison of NMR spectral data to authentic samples of **7** and **4**.

(c) *From 3*. To 0.7 ml of cyclohexane-d_{12} was added **3** (11.4 mg; 0.0216 mmol) and Ph_3SiH (117.3 mg, 0.451 mmol) in an NMR tube. The solution was degassed three times and sealed under vacuum. After heating at 45°C for 24 h, the only products observed by NMR spectroscopy were trihydride **4** and $Ph_3SiOC_6H_4$-*p*-OMe (**6**). By NMR integration versus an internal standard, complex **4** formed in quantitative yield but due to similar solubilities could not be separated from **6**.

5.4. $Ph_3SiOC_6H_4$-p-OMe (6)

Compound **6** was prepared independently from the reaction of Ph_3SiCl (556 mg, 1.89 mmol) and KOC_6H_4-*p*-OMe (301 mg, 1.86 mmol) in THF. The homogeneous solution was stirred at room temperature for 4 h. The solvent was then removed *in vacuo* and the product was extracted with benzene. Complex **6** was recrystallized from pentane at −30°C to give 426 mg pure product (60% yield). ^{1}H NMR (C_6D_6): δ 7.77 (m); 7.66 (d, $J = 7.23$ Hz); 7.13 (m); 6.89 (d, $J = 8.6$ Hz); 6.52 (d, $J = 8.6$ Hz); 3.55 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 136.2 (s); 134.3 (s); 130.5 (s); 154.9 (s); 149.2 (s); 128.3 (s); 120.9 (s); 114.8 (s); 54.96 (s). Anal. Found: C, 78.02; H, 5.97. $C_{25}H_{22}P_4O_2Si$ calcd. C, 78.50; H, 5.80%. FAB-MS (NBA): *m/e* 382.1 (M^+).

5.5. Reaction of 2 and Ph_3SiH in the presence of excess PMe_3

To a benzene solution (0.7 ml) of **2** (13.2 mg, 0.026 mmol), Ph_3SiH (33.4 mg, 0.129 mmol) and HOC_6H_4-*p*-Me (14.2 mg, 0.131 mmol) were added 26 μl PMe_3 (0.257 mmol). The solution was allowed to stand at room temperature for 1 day at which time the NMR spectra showed the formation of phosphine salt, $[(PMe_3)_5Ru(H)][OC_6H_4\text{-}p\text{-}Me \cdot HOC_6H_4\text{-}p\text{-}Me]$ (**8a**) [24].

5.6. Reaction of 3 and Ph_3SiH in the presence of excess PMe_3

To a benzene solution of **3** (8.0 mg, 0.0151 mmol) containing Ph_3SiH (12.7 mg, 0.0488 mmol) was added 60 μl of PMe_3 (0.591 mmol). The solution was heated at 45.0°C for 2 days during which time no reaction was observed by NMR spectroscopy.

5.7. Kinetic studies of the catalytic alcoholysis reaction with 1

^{1}H NMR spectrometry was used to study the catalytic formation of $Ph_3SiOC_6H_4$-*p*-OMe from Ph_3SiH and HOC_6H_4-*p*-OMe using the dihydride **1** as the catalyst and mesitylene as the internal standard. The disappearance of methoxyphenol and the appearance of product were monitored as the reaction progressed at 30.0 ± 1.5°C.

Four stock solutions were prepared. Stock solution no. 1 contained 1.9730 g (7.59×10^{-3} mol, 1.52 M) of

Ph_3SiH in 5 ml of C_6D_6 in a volumetric flask. Stock solution no. 2 contained 94.7 mg (7.64×10^{-4} mol, 0.0764 M) of HOC_6H_4-*p*-OMe in 10 ml of C_6D_6 in a volumetric flask. Stock solution no. 3 contained 16.6 mg (4.08×10^{-5} mol, 0.00816 M) of **1** in 5 ml of (C_6D_6). Stock solution no. 4 contained 36.5 mg (3.04×10^{-4} mol, 0.304 M) of 1,3,5-trimethylbenzene internal standard in 1 ml of C_6D_6. These solutions were prepared *in situ* for each set of kinetic runs.

In a typical run, a nine inch NMR tube was charged with 100 μl of stock solution no. 1, 200 μl of stock solution no. 2, 200 μl of stock solution no. 3, 50 μl of stock solution no. 4, and 150 μl of C_6D_6 to bring the total volume to 700 μl. Based on the volumes used, the calculated concentrations of the reactants were $[\mathbf{1}] = 2.33 \times 10^{-3}$ M, $[Ph_3SiH] = 2.17 \times 10^{-1}$ M, $[HOC_6H_4\text{-}p\text{-OMe}] = 2.18 \times 10^{-2}$ M. The samples were sealed with NMR tube septa and parafilm. The solutions were allowed to equilibrate at room temperature for 3 min and then a one-pulse ^1H NMR spectrum was taken. The scan was baseline corrected, Fourier transformed and plotted with integrals. The concentrations of both the phenol and the product were then determined by integration against the internal standard. The sample was then placed in a constant temperature bath at 30.0 ± 1.5°C. Periodically, the samples were removed from the temperature bath, cooled immediately to 0°C and the procedure described above was used to take spectra. The rate constant data are presented in Table 1. The reaction shows a first-order dependence on catalyst **1**, a first-order dependence on *p*-methoxyphenol and a negligible dependence on silane.

To test for a possible phosphine dependence on the catalytic reaction, a set of reactions were run systematically varying the $[PMe_3]$. Using the standard stock solutions from above, each nine inch NMR tube was charged with 100 μl of stock solution no. 1, 200 μl of stock solution no. 2, 200 μl of stock solution no. 3 and 50 μl of stock solution no. 4. PMe_3 and C_6D_6 were syringed into each tube using a gas-tight syringe, maintaining a constant overall solution volume of 810 μl. Based on the volumes used, the calculated concentrations of the reactants were $[\mathbf{1}] = 2.01 \times 10^{-3}$ M, $[Ph_3SiH] = 1.87 \times 10^{-1}$ M, $[HOC_6H_4\text{-}p\text{-OMe}] = 1.89 \times 10^{-2}$ M. The samples were sealed with NMR tube septa and parafilm. The solutions were allowed to equilibrate at room temperature for 3 min and then a one-pulse ^1H NMR spectrum was taken. The scan was baseline corrected, Fourier transformed and plotted with integrals. The concentrations of both the phenol and the product were then determined by integration against the internal standard. The sample was then placed in a constant temperature bath at 30.0 ± 1.5°C. Periodically, the samples were removed from the constant temperature bath, cooled immediately to 0°C and the procedure described above was used to take spectra. The solutions were kept at 0°C when not in the 30.0°C bath. Immediately prior to the NMR spectrum one-pulse acquisition, the solution was thawed and placed into the NMR probe. Within 1 min, the spectrum was acquired and the tube was replaced in the ice-bath. The phosphine concentration was varied from 0.617 M to 1.60 M. There was no rate dependence observed over this range.

To test the effect of added $[(PMe_3)_5Ru(H)]^+[OC_6H_4\text{-}p\text{-OMe} \cdot HOC_6H_4\text{-}p\text{-OMe}]$ (**8b**) on the catalytic cycle, complex **8b** (30.1 mg, 0.0412 mmol) was added to a C_6D_6 solution containing **1** (4.2 mg, 0.0103 mmol), Ph_3SiH (26.8 mg, 0.103 mmol) and HOC_6H_4-*p*-OMe (6.4 mg, 0.0516 mmol). The solution was heated at 30.0 ± 1.5°C and monitored by ^1H NMR spectrometry. Over the course of 12 h at 30.0°C, the silanolysis product **6** was formed catalytically and complex **8b** disappeared.

5.8. *Kinetic studies of the reaction of Ph_3SiH with 2*

^1H NMR spectrometry was used to study the formation of $Ph_3SiOC_6H_4$-*p*-Me and $(PMe_3)_4RuH_2$ from Ph_3SiH and **2** using HOC_6H_4-*p*-Me as the catalyst and 1,3,5 trimethoxybenzene as the internal standard. The disappearance of **2** was monitored as the reaction progressed at 30.0 ± 1.5°C.

Three stock solutions were prepared. Stock solution no. 1 contained 1.95 g (7.48×10^{-3} mol, 1.50 M) of Ph_3SiH in 5.00 ml of C_6D_6 in a volumetric flask. Stock solution no. 2 contained 16.0 mg (1.481×10^{-4} mol, 0.0296 M) of HOC_6H_4-*p*-Me in 5.00 ml of C_6D_6 in a volumetric flask. Stock solution no. 3 contained 40.1 mg (7.82×10^{-5} mol, 0.0782 M) of **2** and 4.2 mg of 1,3,5-trimethoxybenzene (2.50×10^{-5} mol, 0.025 M) in 1 ml C_6D_6.

In a typical run, a nine inch NMR tube was charged with 100 μl of stock solution no. 1, 110 μl of stock solution no. 2, 200 μl of stock solution no. 3, and 290 μl of C_6D_6 to bring the total volume to 700 μl. Based on the weights used, the calculated concentrations of the reactant were $[\mathbf{2}] = 2.25 \times 10^{-2}$ M, $[Ph_3SiH], = 2.169 \times 10^{-1}$ M, $[HOC_6H_4\text{-}p\text{-OMe}] = 4.29 \times 10^{-3}$ M. The samples were sealed with NMR tube septa and parafilm. The solutions were allowed to equilibrate at room temperature for 3 min and then a one-pulse ^1H NMR spectrum was taken. The scan was baseline corrected, Fourier transformed and plotted with integrals. The concentrations of both the phenol and the product were then determined by integration against the internal standard. Two NMR spectra were plotted for each run and an average of the two integrations was used to determine the rates. The sample was then placed in a constant temperature bath at 30.0 ± 1.5°C. Periodically the samples were removed from the temperature bath, cooled to 0°C and the spectra were obtained by the procedure described previously. The rate constant data are presented in Table 2.

5.9. *Kinetic studies of the reaction of 3 and Ph_3SiH*

UV-vis spectrometry was used to study the reaction of **3** and triphenylsilane. The reaction was monitored by observing the disappearance of an absorbance due to **3** over time. The temperature was maintained at 45.0 ± 0.5°C throughout the course of the reaction. Three stock solutions were prepared in the drybox. Stock solution no. 1 contained 2.61 g (0.201 M) of Ph_3SiH in 50.0 ml hexane. Stock solution no. 2 contained 25.8 mg (0.00416 M) of HOC_6H_4-*p*-OMe in 50.0 ml of hexane. Stock solution no. 3 contained 25.7 mg (9.73×10^{-4} M) of **3** in 50.0 ml hexane.

A typical run entailed delivering specific amounts of the three stock solutions into a quartz cuvette equipped with a Kontes stopcock. The total volume was kept constant at 4.0 ml by the addition of hexane. The three portions were added to the cuvette in the drybox and then placed in the UV-vis cell holder and the temperature allowed to equilibrate before the first absorbance measurement was taken. An absorbance measurement was taken every 10 min for 12 h or until the absorbance at 327 nm was no longer detectable. The rate constant data are presented in Table 3.

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