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Comparative chemistry of η^3-oxaallyl and η^3-allyl rhodium(I) complexes in the hydrosilylation of cyclopropyl ketones: observation of an unprecedented rearrangement

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Abstract

Addition of η^3-oxaallyl bis(triphenylphosphine)rhodium(I) (**1**) or η^3-allyl bis(triphenylphosphine)rhodium(I) (**2**) to a mixture of cyclopropyl phenyl ketone and triethylsilane promotes two competitive catalytic reactions. Complex **1** gives high yields of the silyl ether **13**, while complex **2** favors an unprecedented cyclopropyl carbinyl ring-opening reaction providing good yields of enol silane (*Z*)- and (*E*)-**14** (4.1 *Z*/*E* ratio). Studies of catalyst turnover provide evidence that two monomeric rhodium complexes account for the competing reactions. The cyclopropyl carbinyl catalysis occurs under a narrow reaction regime with a specific set of ketone substrates suitable for the reaction. Chemicals such as triethylsilane activate the catalysis leading to **13**, while triphenylphosphine strongly inhibits the formation of **14**. A mechanism involving a polar transition state for the cyclopropyl carbinyl rearrangement is proposed.

Keywords: Kinetics of hydrosilylation; Cyclopropyl carbinyl rearrangement; η^3-Allyl rhodium; η^3-Oxaallyl rhodium

1. Introduction

The development of an homogeneous catalyst for selective organic transformations is a major objective of chemical research. The hydrosilylation of organic carbonyls is an interesting case study that illustrates many of these goals. The quest for selective and efficient hydrosilylation catalysts remains open, and recent studies have taken two different approaches [1]. One approach examined the influence of ancillary phosphine ligand basicity on catalyst activity, while the second approach began investigating the affect of σ-bound ligands on rhodium(I) catalysts. Wrighton [2] demonstrated that oxidation of the 1,1′-bis(diphenylphosphino)cobaltocene ancillary ligand enhanced the catalytic properties of rhodium(I) complexes towards the reductive hydrosilylation of ketones. This result fits into a larger class of reactions in which the donicity of 'electronically tuned' ligands affects the reactivity and selectivity of catalyzed reactions [3].

The effect of σ-bound ligands on rhodium catalysts is only beginning to emerge. Wilkinson's catalyst ($(PPh_3)_3RhCl$) and bis(phosphine)rhodium cations are classic catalysts for the hydrosilylation of organic carbonyls, recently however, hydrido rhodium(I) complexes were shown to be very active catalysts in the same reaction [4]. Particularly noteworthy is the observations of Itoh, that organosilanes having two tethered Si–H groups react with Wilkinson's catalyst giving a Rh(V) trihydrido-bis(silyl) complex [4c]. Itoh proposed that the σ-bound chloro ligand exchanges during catalyst activation, and that the resulting hydrido rhodium material is orders of magnitude more reactive. Furthermore, both putative mechanisms suggested in Itoh's paper involve bis(hydrido)-silyl rhodium(III) reaction intermediates.

Taken together, these new catalyses revolve around the exchange of an Rh–Cl bond for an Rh–H bond, with the hydrido–rhodium complex being a more active catalyst. We proposed that the Cl for H-ligand exchange can be circumvented through the use of η^3-allyl or η^3-oxaallyl rhodium complexes as catalyst precur-

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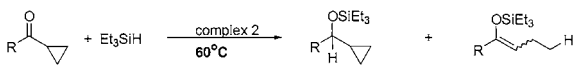
sors. Marder recently demonstrated that allylrhodium complexes were highly selective catalyst precursors in the mechanistically related hydroboration of alkenes [5]. Work in our laboratory showed that a variety of η^3-oxaallyl rhodium(I) complexes (**1**) reacted under a wide range of conditions, including organosilane, and that a rhodium(I) hydride (**4**) is available for catalysis [6]. We reasoned that η^3-ligand elimination could be probed by conducting parallel experiments with the isoelectronic η^3-allyl rhodium complex (**2**) [7]. Electronic features of the η^3-allyl ligand relative to the η^3-oxaallyl ligand would alter the reaction with organosilanes, and the production of a trialkylsilylrhodium(I) (**3**) catalyst would be anticipated. Work by Milstein [8], Thorn [9], and Wrighton [10], strongly supported this plan, in that, Group VIII alkyl–metal complexes reacted with organosilane preferentially eliminating alkane (R–H) relative to tetraalkylsilane (R–Si).

We wish to report that isoelectronic η^3-oxaallyl and η^3-allyl rhodium(I) complexes react with triethylsilane and act as catalyst precursors for the hydrosilylation of phenyl cyclopropyl ketone. The incipient rhodium complex from η^3-allyl bis(triphenylphosphine)rhodium(I) catalyzes an unprecedented reductive arrangement of cyclopropyl ketones [11,12], while the η^3-oxaallyl complex favors 1,2-carbonyl reduction.

2. Results and discussion

Addition of the η^3-oxaallyl rhodium complex **1** (2.5×10^{-3} mmol) to a concentrated solution of cyclopropyl phenyl ketone (3.5 M) and triethylsilane (3.5 M) resulted in consumption of cyclopropyl phenyl ketone when heated to 60.0°C. The reaction mixture showed formation of the expected triethylsilyl ether (**13**) and a combined 3% yield of *E*- and *Z*-enol silane ((*E*)-**14**, (*Z*)-**14**) ([13,14], Fig. 1). The same reaction conducted with the η^3-allyl rhodium complex **2** (2.5×10^{-3} mmol) significantly enhanced the production of **14** (*Z*/*E* ratio 4:1) to ca. 53% of the mixture.



Ketone	R	Ether	Yield %	Enol Silane	Yield %
9	Ph	**13**	47 (GC)	**14**	53 (GC)
	Silane addition 135 μL h^{-1}		15 (GC)		81 (GC)
10	p-CH_3OPh	**15**	24 (GC)	**16**	43 (GC)
11	p-CF_3Ph	**17**	66	**18**	<3 (GC)
12	CH_3	**19**	17 (GC)	**20**	<1 (GC)

These data indicate that two active catalysts formed in the initial phase of the reaction (see Scheme 1). Polarization of the oxaallyl ligand kinetically favored the elimination of enolsilane, **7**, while complex **2** gave a higher fraction of propene. To test these competing processes we examined the reaction of rhodium complexes **1** and **2** with triethylsilane. In each experiment

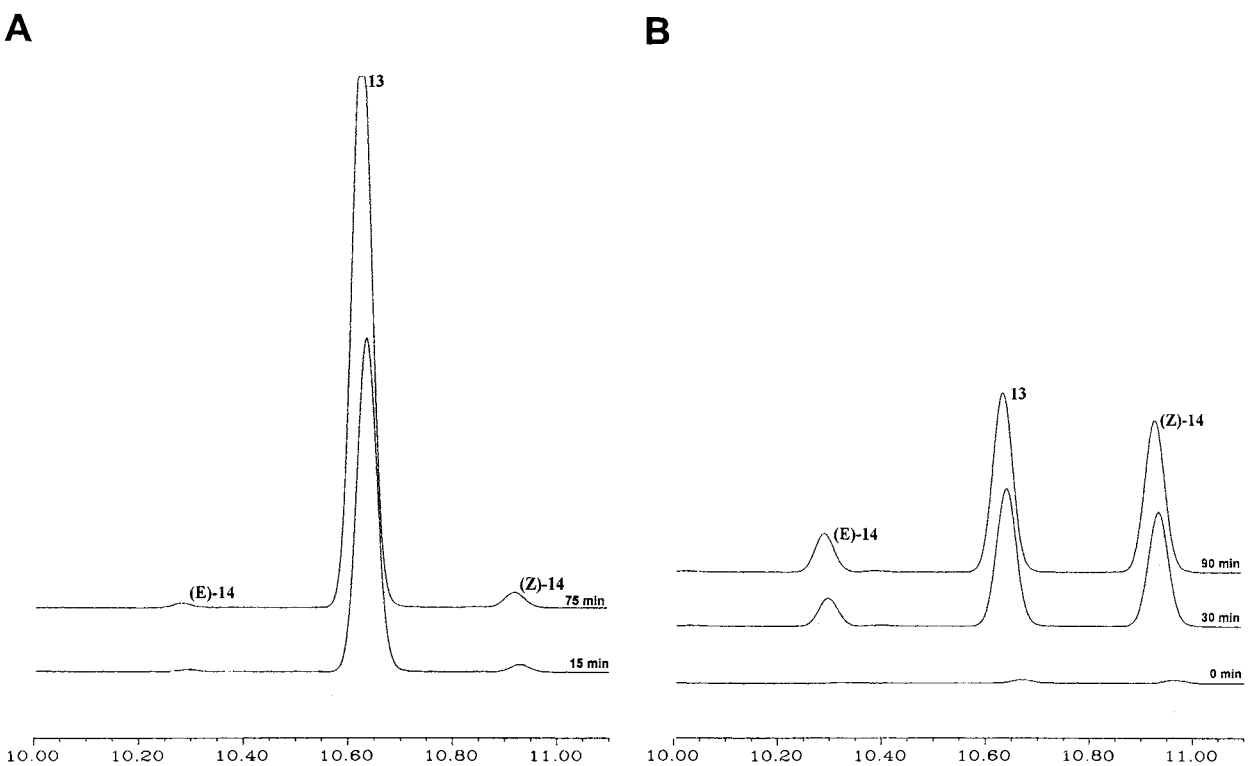
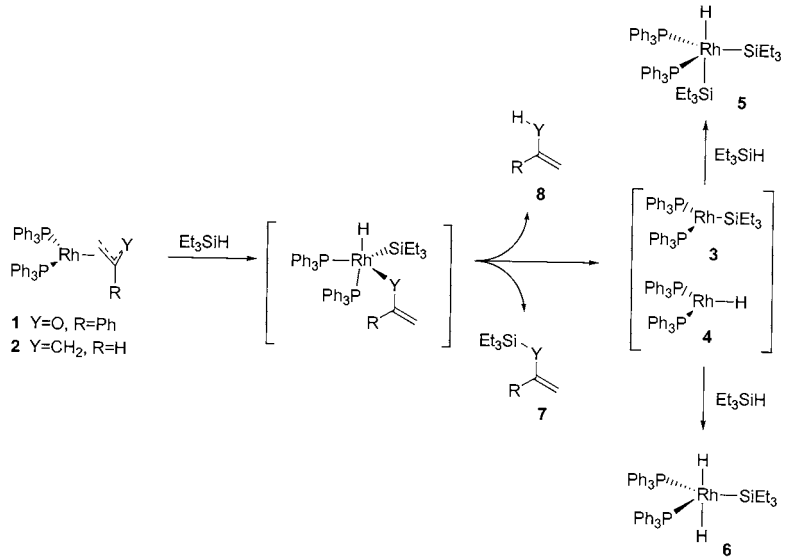


Fig. 1. The hydrosilylation of cyclopropyl phenyl ketone catalyzed by complex **1** (chromatogram A) and complex **2** (chromatogram B), respectively. Both chromatograms show ca. 20% of the catalyzed reaction.



Scheme 1.

we analyzed the organic products [15]. Treatment of **1** with two equivalents of triethylsilane in C_6D_6 followed by heating to 60°C produced two sets of signals in the ^{1}H-NMR. The major set, integrating to 73% of the mixture, was a pair of olefinic doublets ($J = 1.6$ Hz) at 4.87 and 4.45 ppm. These NMR signals matched enol silane **7**. The second organic product showed a diagnostic quartet centered at 4.78 ppm. The chemical shift and multiplicity of this signal were not anticipated; however, the reductive elimination of acetophenone generated a carbonyl substrate suitable for hydrosilylation reduction. Reduction of the acetophenone under the ambient conditions resulted in 1-phenyl-1-triethylsiloxyethane [16]. The reaction of complex **2** with triethylsilane (two equivalents) under the same conditions produced both propene and allyltriethylsilane. Gas–liquid partitioning made GC–MS analyses quite variable, however, we concluded that similar amounts of each chemical arose in the reaction. This conclusion is supported by evidence found in the reaction of tris(trimethylphosphine)(methyl)rhodium(I) and triethylsilane in which nearly equal amounts of methane and methyltriethylsilane were generated [9]. Taken together, complex **1** proceeded through complex **4** selectively, while complex **2** gave similar quantities of **3** and **4**.

3. Catalysis study

To further characterize the difference in catalyses brought about by complexes **1** and **2**, we examined the pseudo-zero order turnover rates for the reaction at 60.0°C. At high ketone concentration (3.5 M) [17], the maximal initial turnover rate for the total production of **14** was linear. Competitive production of silyl ether **13** in each reaction never showed linearity (see Fig. 2), therefore its production can only be described qualitatively.

Three sets of experiments were examined to evaluate the competing catalyses. First, we established that the production rate of **14** followed directly with the concentration of complex **2** (see entries 1–3 in Table 1). When normalized for complex **2** concentration, similar turnover rates were observed for each reaction. This observation implied that the active catalyst leading to **14** was monomeric. Low catalyst concentrations decrease the possibility of dimerization or oligomerization, yet the normalized turnover rate of each experiment remained constant. Linearity of the turnover rate decayed after consumption of the first 20% of ketone, and distinct curvature was observed [18]. Below 2.75 M ketone, the rhodium catalyst is no longer saturated and at least two catalytic steps affected the turnover rate. By looking at the total turnover numbers at any time, one can compare the relative rates of Path A and Path B. For example, in the experiment leading to Entry 1 in Table 1, the turnover number for the production of **13** was slightly smaller than that leading to **14** (see Fig. 2).

Similar results were observed with oxaallyl complex **1** as the catalyst precursor except that the production of silylether **13** was enhanced (see Fig. 1 and Entries 4,5 in Table 1). Analysis of enol silane data revealed that the production of **14** decreased ca. 13 times relative to reactions catalyzed by complex **2**. Two factors contributed to this decrease. First, the selective generation of hydridorhodium **4** led to an active five-coordinate catalyst, **6**, which promoted carbonyl reduction. The enhanced production of **13** efficiently drained cyclo-

propyl phenyl ketone away from Path B lowering its reaction rate. Since both factors contributed to the relative production of **13** and **14**, the amount of rhodium complexes **3** and **4** (subsequently **5** and **6**) present during catalysis could not be evaluated.

A second set of experiments focused on triethylsilane concentration effects. Prior studies demonstrated that silane concentration affected both reaction rates and partitioning of products in the catalyzed hydrosilylation of ketones [19]. It has been postulated that an associa-

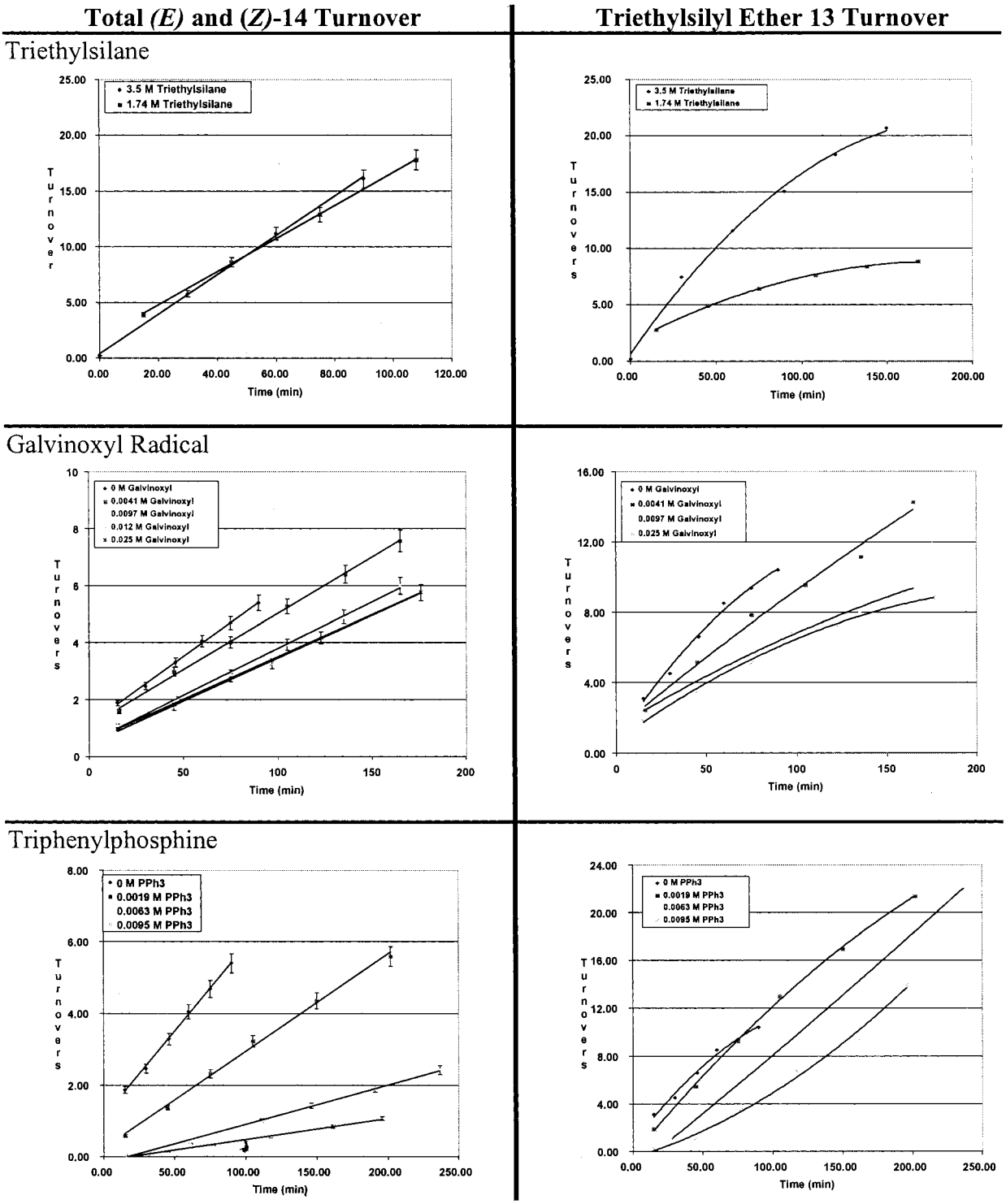


Fig. 2. Initial turnover rate studies for the reaction of ketone **9** with triethylsilane catalyzed by complex **2**. The reaction additive is highlighted for each set of experiments.

Table 1
Pseudo-zero-order turnover rates for the production of enol silane

Entry	Complex ($M \times 10^2$)	Ketone (M)	Triethylsilane (M)	Enol silane (**14**) turnover mmol (mmol cat.*min)$^{-1}$
1	**2** (2.50)	**9** (3.50)	(3.50)	0.177 ± 0.005
2	**2** (1.26)	**9** (3.50)	(3.50)	0.169 ± 0.005
3	**2** (0.63)	**9** (3.50)	(3.50)	0.178 ± 0.005
4	**1** (2.50)	**9** (3.50)	(3.50)	0.011 ± 0.003
5	**1** (1.27)	**9** (3.50)	(3.50)	0.014 ± 0.002
6	**2** (2.50)	**9** (3.50)	(1.74)	0.140 ± 0.011
7	**2** (2.50)	**10** (3.49)	(3.50)	0.060 ± 0.004

tive mechanism for the final reductive elimination step leading to trialkylsilyl ethers is important for proper catalyst function. Although the association of silane in the final step is not well understood, such a process prevents formation of a three-coordinate rhodium complex. In our study, we found that triethylsilane significantly favored the production of **13**, but negligibly impacted the formation of **14**. For example, decreasing the concentration of triethylsilane by one-half resulted in a turnover rate for **14** only slightly less than the maximal turnover (see Entry 6, Table 1). However, the same concentration change significantly slowed the production of **13**. For instance, the time required for the formation of 0.2 mmol of **13** increased from 60 to 138 min. These results indicated that triethylsilane was involved in the rate-limiting step leading to **13**, while the rate-limiting reaction producing **14** was independent of triethylsilane. We tested the synthetic importance of this observation by infusing triethylsilane into the reaction mixture with a syringe pump. Slow addition of triethylsilane increased the chromatographic yield of 14 to 81%.

Inhibition studies of the competing catalyses comprised the third aspect of our study. We reasoned that the cyclopropyl ring-opening reaction (Path B) occurred by either a free radical pathway or through a cyclopropyl carbinyl cation rearrangement. To distinguish these mechanistic alternatives, a radical trapping agent such as galvinoxyl radical should decrease the turnover rate of pathway B if the reaction operates by way of a free radical. An ionic reaction should be impervious to this agent. Conversely, a cationic rearrangement requires both a polar reaction media and a coordination site at the metal center to accommodate the incoming alkyl ligand. We anticipated that a less polar solvent such as benzene and a strong coordinating ligand such as triphenylphosphine might decrease the production of **14**. The solvent choice was fortuitous since both galvinoxyl radical and triphenylphosphine dissolved sparingly in the neat ketone/triethylsilane mixture. Benzene completely dissolved the catalytic mixture. The dilute reaction mixture was examined and the maximal turnover rate for the formation of **14** with no additives was linear through the first 5–6 turnovers (see Entry 1, Table 2). Interestingly, the turnover rate for the production of **13** in this modified reaction media decreased slightly, while the turnover rate for **14** decreased ca. 3.5 times.

Introduction of 0.0040 M galvinoxyl radical (0.33 equivalents relative to **2**) slowed the turnover rate leading to **14** by ca. 17%. Higher concentrations of galvinoxyl radical decreased the turnover rate marginally to a point such that at one equivalent, no further decrease was observed (see Entries 2–5, Table 2). At the two highest concentrations of galvinoxyl radical, the turnover rate remained ca. 60% of the original rate. The catalysis leading to **13** showed a similar galvinoxyl radical effect (see Fig. 2). For instance, the turnover rate decreased when 0.0040 M galvinoxyl radical was added and then decreased more until nearly a stoichiometric amount relative to **2** was

Table 2
Inhibition of the hydrosilylation reaction catalyzed by complex **2**

Entry	Complex ($M \times 10^2$)	Ketone (M)	Triethylsilane (M)	Additive ($M \times 10^2$)	Enol silane (**14**) turnover mmol (mmol cat.*min)$^{-1}$
1	**2** (1.25)	**9** (1.75)	(1.75)	–	0.048 ± 0.0002
2	**2** (1.25)	**9** (1.75)	(1.75)	Galvinoxyl (0.40)	0.040 ± 0.0003
3	**2** (1.25)	**9** (1.75)	(1.75)	Galvinoxyl (0.95)	0.033 ± 0.0002
4	**2** (1.25)	**9** (1.75)	(1.75)	Galvinoxyl (1.25)	0.030 ± 0.0003
5	**2** (1.25)	**9** (1.75)	(1.75)	Galvinoxyl (2.50)	0.030 ± 0.0002
6	**2** (1.25)	**9** (1.75)	(1.75)	PPh_3 (0.19)	0.027 ± 0.0003
7	**2** (1.25)	**9** (1.75)	(1.75)	PPh_3 (0.63)	0.011 ± 0.0002
8	**2** (1.25)	**9** (1.75)	(1.75)	PPh_3 (0.95)	0.0059 ± 0.0003

added. These results suggested that galvinoxyl radical reacted with rhodium complexes in the reaction mixture generating materials that were less efficient at catalyzing the reduction and ring-opening reactions. However, we cannot exclude the possibility that the galvinoxyl radical–rhodium complex interaction is reversible and that these experiments follow saturation kinetics. The latter explanation is appealing since the production of **13** and **14** continued even in the presence of radical trapping agent. It is surprising however that saturation occurs close to the stoichiometric balance. Nevertheless, galvinoxyl radical is not a strong inhibitor of either reaction Path A or B [20c,e].

By contrast, triphenylphosphine had a powerful inhibitory affect on the product of **14**. Addition of 1.0 mg of triphenylphosphine to a catalytic mixture decreased the turnover rate by ca. 44% (see Table 2). Adding 5.0 mg of the triphenylphosphine to a similar mixture decreased the catalytic turnover rate to ca. 12% of the maximal. Interestingly, triphenylphosphine showed little or no effect on the formation of **13**. At the highest phosphine concentration, there appeared to be a brief induction period followed by a rapid reaction (see Fig. 2). This behavior is similar to hydrosilylation reactions catalyzed by Wilkinson's catalyst and hydridotetrakis(triphenylphosphine)rhodium(I) in that dissociation of triphenylphosphine must occur to open a coordination site at the catalytic center [5,20a].

4. Substrates for competitive catalysis

Other cyclopropyl ketones were investigated using complex **2** as catalyst, however, aryl-cyclopropyl ketones occupied a unique niche in this catalytic scheme. Three aryl-cyclopropyl ketones were examined and all gave different results. For example, cyclopropyl *p*-methoxy-phenyl ketone (**10**) reacted slowly relative to ketone **9** but gave both ring-opening and reduction products (see Table 1). With ketone **10**, the silyl ether **16** yield was ca. half that of enol silane **15** (*Z*/*E* ratio 4:2). On the other hand, cyclopropyl *p*-trifluoromethylphenyl ketone reacted rapidly within 2 h and ultimately gave a 66% isolated yield of silyl ether **17**. A trace amount of the ring-opened enol silanes were observed in the gas chromatogram. These three aryl ketones followed a general trend in which electron-withdrawing groups on the ketone increased the rate of hydrosilylation [21].

Finally, cyclopropyl methyl ketone proved to be a very poor substrate for either catalysis. The aliphatic ketone reacted slowly, and after 10 h of heating only about 20% of the ketone was consumed. The dominant product, albeit in low yield, was silyl ether **18**. A trace amount of ring-opened enol silane was observed by gas chromatography.

5. Summary and conclusions

The competitive nature of reaction Paths A and B suggested that two similar catalytic species formed initially from complexes **1** and **2**. The strength of the Si–O (786 kJ mol^{-1}) bond facilitated the reductive elimination of 1-phenyl-1-triethylsilyloxyethene from complex **1**. When complex **1** was used, a high yield of silyl ether **13** resulted. We propose that a predominance of hydrido rhodium(I) (**4**) formed and this complex catalyzed the reduction of the ketone carbonyl [7a]. Reaction mixtures catalyzed by complex **2** generated nearly equal amounts of silyl ether **13** and **14** (*E* and *Z*) suggesting that a second catalytic species was responsible for the ring-opened products. We believe that the second catalytic species is a triethylsilyl rhodium(I) complex (**3**). The difference in size and electronic character of the hydride ligand and the triethylsilyl ligand accounts for the bifurcated catalytic behavior. Neither species remains coordinately unsaturated in the reaction mixture and rapidly converts to reactive rhodium(III)-bis(hydride)triethylsilyl complex or a rhodium(III)-hydride-bis(triethylsilyl) complex.

Once the two respective rhodium(III) species form, each inserts the ketone carbonyl through a silicon-first mechanism. Such an addition is believed to be the first step in the hydrosilylation reaction catalyzed by Wilkinson's catalyst, [20] and this step explains the rate effect observed with ketones **9**, **10** and **11**. Substituents in the *para* position of the phenyl group also influence the rhodium–carbon bond strength in the α-triethylsiloxy alkyl rhodium intermediates (**21** and **22**). This situation is manifest in the noted product ratios observed with cyclopropyl *p*-methoxyphenyl ketone and cyclopropyl phenyl ketone. The ring-opened product became dominant with ketone **10**. Other mechanisms such as direct rhodium insertion into the cyclopropane ring fail to account for the observed rate effects [11d].

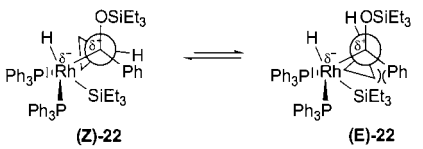
The differentiating step in the competing catalyses involves the transformation of α-triethylsiloxy alkyl rhodium intermediates **21** and **22**. As depicted in Scheme 2, reaction Path A transforms directly into the silyl ether **13**. High triethylsilane concentration facilitates loss of **13** by consuming coordination sites generated during the reductive elimination step [20c,22]. Since no coordinative unsaturation is exposed, this catalysis should not be inhibited by triphenylphosphine. Similarly, galvinoxyl radical may have a modest inhibitory effect since complex **6** is its most likely reaction partner. Complex **6** is competitively consumed in the carbonyl insertion reaction, therefore, saturation kinetics should be anticipated.

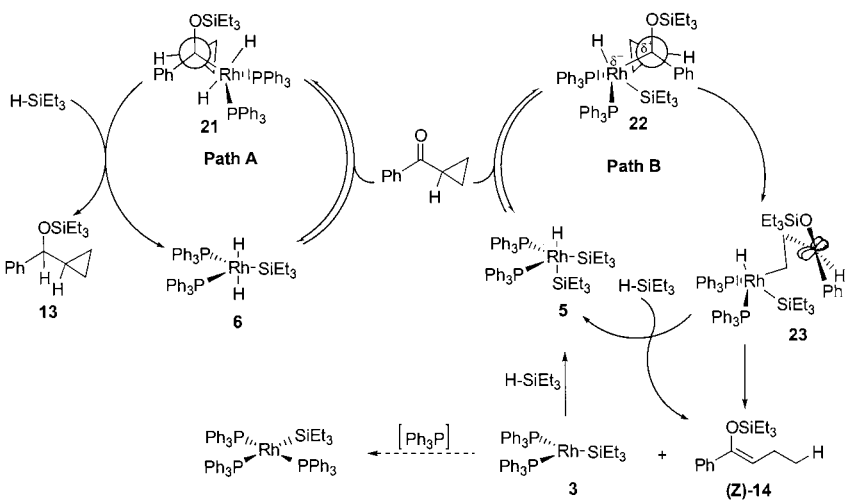
Reaction Path B, on the other hand, shows no triethylsilane dependence since the rate-determining step is presumably the molecular rearrangement. The key cyclopropyl carbinyl rearrangement has been observed in a cyclopropylmethylcobalamin, however, the mechanistic course could not be identified [23]. The cobalamin

complex rearranged at ca. the same rate in solvents of different dielectric constants, and the authors concluded that the reaction did not occur by an ionic pathway. In our case, there was a measurable solvent effect when benzene was added to the reaction mixture.

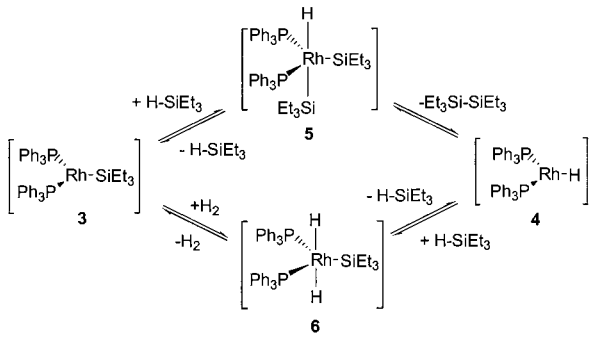
The experimental data are best accommodated by a reaction mechanism proceeding through a polar transition state. Two lines of argument in addition to the solvent effect lead us to this proposal. First, ketones capable of stabilizing positive charge promote the cyclopropyl carbinyl rearrangement, while ketones possessing weaker electron-donating groups such as methyl- and *p*-trifluoromethylphenyl ketones do not submit to the rearrangement. Second, intermediates **21** and **22** differ only in the nature of the hydride and triethylsilyl ligands. Differences between these ligands include (1) steric interactions in the α-triethylsiloxyalkyl intermediate (**22**), and (2) the influence of the Rh–silyl bond on an adjacent Rh–C bond. NMR data and MO calculations support this influence. For example in the *facial* isomer $[Ir(CH_3)H(SiR_3)(P(CH_3)_3)_3]$, the chemical shift of the methyl resonance shifts downfield 0.1 ppm as the silicon ligand, R, changes from ethyl to methoxy [8]. In the same iridium complexes the hydride resonance shifts only 0.03 ppm. Both changes in chemical shift are in the predicted direction, however, the silyl group has a greater influence on the polarizable methyl group. As for MO predictions, calculations on transition metal silyl derivatives suggest that the short M–Si bonds can be attributed to d_p–d_p bonding in which the metal donating electron density to an empty d-orbital on silicon [24]. Taken together, these data indicate that the Rh–C bond in complex **22** is polarized more toward rhodium than in complex **21**. Both the aryl-substituent effect and the Rh–Si effect work in concert shifting electron density from carbon to rhodium. We propose that the transformation of **22** to **23** occurs by either an asynchronous concerted reaction or an ion-pair mechanism. In each, charge develops at the transition state, and the reaction media imposes some influence on the reaction rate. Excess electron density at rhodium makes possible an internal nucleophilic attack at the γ-carbon of the cyclopropane ring [25,26]. As shown in Scheme 2, a conformer of the **22** brings a γ-carbon into proximity for nucleophilic attack. As the rearrangement occurs, steric interactions decrease by moving the bulky rhodium complex to a primary carbon and torsional strain in the cyclopropane ring is released. Despite the numerous advantages of the molecular rearrangement, this transformation is rate-determining. Recall that Path B is independent of triethylsilane concentration, is seems unlikely that the final C–H bond forming step would limit the turnover rate.

Scheme 2 also provides a sensible rationale for the production of excess *Z*-isomer in the ring-opening reaction path. Cyclopropane is a powerful stabilizing substituent for carbocations when a C–C bond of the ring can align with the vacant p-orbital on carbon [27]. Two conformations are possible for intermediate **22** such that a C–C bond in the cyclopropane is colinear with the Rh–C bond. (For simplicity Scheme 2 shows only the conformer leading to the *Z*-isomer.) Conformer (*E*)-**22** suffers from steric interactions with the phenyl group and is presumably less stable. Rearrangement by way of conformer (*Z*)-**22** places the alkyl group at C2 *syn* with respect to the triethylsiloxy group, while (*E*)-**22** delivers the alkyl group *syn* relative to the phenyl group. The relative ground-state population of (*Z*)- and (*E*)-**22** would account for the observed *Z*/*E* ratio in the enol silane products.





Scheme 2.



Scheme 3.

Our data can not unequivocally identify the source of profound triphenylphosphine inhibition. Green reported that trimethylphosphite inhibited triethylsilane addition to $[Rh(\eta^3\text{-}C_3H_5)(P(OCH_3)_3)]$ [7a], however, our catalytic system is different since complex **2** is doubly coordinately unsaturated and 2 mol of triphenylphosphine must add to **2** to prevent oxidative addition of triethylsilane. We suggest, on the other hand, that inhibition stems from phosphine addition to complex **3**. The conversion of **23** into **5** may occur by two routes: (1) triethylsilane assisted reductive elimination, or, (2) direct C–H reductive elimination. The latter route produces complex **3** during every turnover of catalyst thereby maintaining a level of **3** that could be trapped by triphenylphosphine. We cannot rule out an assisted reductive elimination process, however, this mechanism would generate an active catalyst that enters directly into the reaction stream. We anticipate that **5** exists in a steady-state concentration, and trapping with triphenylphosphine would be ineffective.

Finally, we are unable to address two issues associated with this unique bifurcated catalysis. Inspection of intermediate **22** reveals that it could eliminate **13** instead of rearrange to **23**. Formation of **13** from **22** could occur slowly compared to rearrangement yet be proportional to catalyst concentration and triethylsilane concentration. Our analytical method cannot distinguish the contribution of this alternative elimination. One method which we investigated involved preparing complex **3** in very high yield, thereby all reaction products would funnel through the same catalyst. Based on an observation of Thorn [9], addition of triphenylsilane to a benzene solution of **2** should generate complex **3** very selectively. After heating a mixture of **2** and triphenylsilane (two equivalents) for 10 min, ketone and triethylsilane were added but unfortunately the mixture showed no catalytic activity.

A second issue is concerned with the integrity of complexes **5** and **6** during the catalysis. We found compelling evidence in this study that complexes **5** and **6** remain active, competitive catalysts throughout the reaction. A simple reductive elimination/oxidative addition sequence can, however, interchange the triethylsilyl ligand in **5** with the hydride ligand in **6** (see Scheme 3). Reductive elimination of hexaethyldisilane from **5**, or loss of H_2 from **6**, interchanges the constituency of complexes **3** and **4**. Oxidative addition of triethylsilane to the reconstituted complexes completes the interchange of active catalysts. Eisenberg characterized a similar σ-bound ligand exchange in the complex [IrX(CO)(dppe)] (X = Br, CN) [28,29]. In the iridium series, ligand exchange was considered a secondary reaction with considerably longer reaction times than the initial oxidative addition. Since we observe no significant drift in the catalysis towards production of **13** or **14** over many hours, we conclude that σ-bound ligand exchange does not occur to an appreciable extent.

In conclusion, we have found a unique axis of reagents and reaction conditions that catalyzed an unprecedented cyclopropyl carbinyl rearrangement. Under all conditions the cyclopropyl carbinyl rearrangement competed against the expected 1,2-carbonyl addition reaction. The two catalyses showed different characteristics when exposed to excess triethylsilane and stoichiometric quantities of triphenylphosphine, thereby demonstrating that two rhodium catalysts are responsible for the product mixture.

6. Experimental

6.1. General considerations

All manipulations of air-sensitive materials were performed under nitrogen by vacuum-line techniques or in a Vacuum Atmosphere drybox equipped with an inert gas purifier. Air-sensitive compounds were exposed to benzene, or benzene-d_6 (C_6D_6) which were dried over sodium/benzophenone before use. Cyclopropyl phenyl ketone (Aldrich), cyclopropyl methyl ketone (Aldrich), and triethylsilane (Aldrich) were doubly distilled and degassed by freeze–pump–thaw cycles prior to use in a drybox. Oxaallyl complex $(Ph_3P)_2Rh(\eta^3\text{-}CH_2C(Ph)O)$ (**1**) was prepared by a previously reported method [6], while rhodium allyl complex $(Ph_3P)_2Rh(\eta^3\text{-}CH_2CH\text{-}CH_2)$ (**2**) was prepared by the method of Muetterties [30].

^{1}H-NMR spectra were acquired on either a Varian Unity 300 (300 MHz) or Jeol FX-90Q (90 MHz) spectrometer. Broadband decoupled and gated ^{13}C-NMR spectra were obtained on a JEOL FX-90Q (22.5 MHz) spectrometer, while proton decoupled $^{31}P\{^1H\}$-NMR spectra were obtained on a Jeol FX-90Q (36.3 MHz) spectrometer. Chemical shifts were recorded relative to the residual benzene signal in benzene-d_6 (δ 7.16) in the ^{1}H-NMR spectra and relative to the central carbon

resonance of benzene (δ 128.0) in the carbon spectra. All $^{31}P\{^{1}H\}$-NMR resonances were measured relative to an external standard of 85% H_3PO_4. IR spectra were measured on a Perkin–Elmer 16 (FTIR) spectrometer. Gas chromatographic analysis was conducted on a Hewlett Packard 5890 IIA gas chromatograph equipped with a flame ionization detector. All analyses were done with a 25 m OV-1 capillary column.

6.2. General catalytic study (complex **2** or complex **1** catalyst)

Cyclopropyl phenyl ketone was weighed (510.5 mg, 3.50 mmol) into an oven-dried 1.00 ml volumetric flask, and triethylsilane (405 μl, 3.50 mmol) was added by syringe. Solid complex **2** (16.8 mg, 0.025 mmol) was added in one portion. The volume was adjusted to 1.00 ml with benzene. The mixture was thoroughly mixed and the mixture was divided equally into six 1-ml ampules, each equipped with a small stir bar. All ampules were sealed with a septum cap. Outside the glovebox, the six ampules were set into a rack in a 60.0 ± 0.2°C oil bath. At appropriate times an ampule was withdrawn from the oil bath and frozen in N_2. After thawing, 5.0 μl of the mixture is removed by a syringe and placed in a 2.00 ml volumetric flask. The oil was diluted to 2.00 ml with benzene. A 1.0 μl injection volume was used for GC analysis. A second sample was prepared by the same dilution procedure and the sample was analyzed.

In the case of complex **1**, 18.8 mg of the orange solid was weighed and added to the reaction mixture.

Area counts for the remaining ketone and each reaction product were averaged for the two GC analyses. Using standard curves generated for cyclopropyl phenyl ketone, **13**, and (*Z*)-**14** the area counts were converted to molarity. The ketone (510.5 mg, 3.50 mmol), triethylsilane (10 μl) was added by syringe, and then solid complex molarities of **13** and the sum of $(Z+E)$-**14** were divided by the concentration of complex **2** (or **1**). These normalized values were plotted vs. time (min) to determine the initial turnover rate.

6.3. Syringe pump addition of triethylsilane

Cyclopropyl phenyl **2** was weighed (16.8 mg, 0.025 mmol) into an oven-dried 1.00 ml ampule, equipped with a small stir bar, and was added in one portion. The ampule was sealed with a septum cap. A 6 inch needle attached to a 0.5 ml syringe filled with triethylsilane (400 μl) was inserted through the septum cap. Outside the glovebox, the ampule was set into a rack in a 60.0 ± 0.5°C oil bath. The syringe was placed in a single stage syringe pump and the addition rate was adjusted to 135 μl h^{-1}. After 3.5 h the addition of triethylsilane was complete. The mixture was heated for an additional 10 h. An aliquot of reaction mixture (5.0 μl) was removed by a syringe and placed in a 2.00 ml volumetric flask. The oil was diluted to 2.00 ml with benzene. A 1.0 μl injection volume was used for GC analysis. The total integration of enol silane products ((*E*)10.29 min, (*Z*) 10.94 min) and silyl ether (10.64 min) were measured and the yield of each product based on standard curve data was 81:15%, respectively.

6.4. Inhibition studies with galvinoxyl radical (or triphenylphosphine)

Because of solubility issues the general reaction method was modified. Into an oven-dried 2.00 ml volumetric flask cyclopropyl phenyl ketone was weighed (510.5 mg, 3.50 mmol) and triethylsilane (405 μl, 3.50 mmol) was added by syringe. Solid galvinoxyl radical (each of the following weights were used 3.5, 8.2, 10.4 and 20.8 mg) was weighed and added to the volumetric flask. Finally, solid complex **2** (16.8 mg, 0.025 mmol) was added in one portion. The volume was adjusted to 2.00 ml with benzene. The mixture was thoroughly mixed, and the mixture was divided equally into six 1 ml ampules, each equipped with a small stir bar. All ampules were sealed with a septum cap. Outside the glovebox, the six ampules were set into a rack in a 60.0 ± 0.2°C oil bath. At appropriate times an ampule was withdrawn from the oil bath and frozen in $N_{2(1)}$. After thawing, 5.0 μl of the mixture is removed by a syringe and placed in a 2.00 ml volumetric flask. The oil was diluted to 2.00 ml with benzene. A 1.0 μl injection volume was used for GC analysis. Each sample was analyzed in duplicate.

In the case of triphenylphosphine, the following weights were used: 1.0 mg, 3.3 mg, 5.0 mg.

6.5. Preparation of silyl ether **17**

Into an oven-dried 1.00 ml ampule, equipped with a small stir bar, cyclopropyl *p*-trifluoromethylphenyl ketone was weighed (510.5 mg, 3.50 mmol). Triethylsilane (405 μl, 3.50 mmol) was added by syringe, and then solid complex **2** (16.8 mg, 0.025 mmol) was added in one portion. The ampule was sealed with a septum cap. Outside the glovebox, the ampule was set into a rack in a 60.0 ± 0.5°C oil bath. The mixture was heated for 10 h. The septum cap was removed and red/orange solution was added to a 25 ml pear flask. Approximately 5 μl of the mixture was removed and used for GC analysis. The remaining solution was concentrated in vacuo. The residue was separated by flash chromatography using 10:1 hexane: ethyl acetate as eluant ($R_f = 0.88$). Compound **17** (762 mg,

66%) was isolated as a faint yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.57 (d, $J = 9.0$ Hz, H-Ar), 7.47 (d, $J = 9.0$ Hz, 1H, H-Ar), 4.25 (d, $J = 6.0$ Hz, 1H, H–C–O), 1.09 (m, 1H, cyclopropyl), 0.92 (dt, $J = 2.9$, 8.0 Hz, 9H, CH_3), 0.55 (m, 10H, Si–CH_2 and cyclopropyl), 0.46 (m, 2H, cyclopropyl), 0.37 (m, 1H, cyclopropyl). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.6 (Ar), 129.2 (q, $J_{C-F} = 31.2$ Hz, Ar), 126.1 (Ar), 125.0 (Ar), 125.0 (Ar), 76.8 (C-O), 20.1 (cyclopropyl), 6.7 (CH_3), 4.9 (Si–C), 3.2 (cyclopropyl), 2.5 (cyclopropyl). IR (neat): 3084(m), 3009(m), 2957(s), 1619(m), 1321(vs), 1164(s), 1128(vs).

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