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A Silica-Supported Rhodium Hydroformylation Catalyst: Evidence for Dinuclear Elimination

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Abstract: Treatment of 3-(4-chlorophenoxy)-1,2-propanediol with MsCl and subsequently with $NaPPh_2$ gave the diphosphine **2**, which could be converted to the silylated phosphines **3** and **4** and attached to silica gel. It was determined experimentally that these ligands are distributed randomly on the silica surface. The synthesis of $(P_2)RhNBD^+BF_4^-$ (**14**) and $(P_2)RhC_3H_5$ (**16**) (P_2 = **4**) is described. Both **14** and **16** are precursors of monohydride catalysts for hydroformylation of styrene under mild conditions. When the silica-supported analogue of **14** was used as a catalyst precursor, the rate per rhodium was found to depend on the distribution of the catalyst on the silica surface. The role of dinuclear reductive elimination is discussed.

Although the hydroformylation reaction has been known for over 40 years, its mechanism is still the subject of controversy. Heck and Breslow[1] and Wilkinson et al.[2] carried out detailed mechanistic studies of the $Co_2(CO)_8$- and $RhHCO(PPh_3)_3$-catalyzed hydroformylations, respectively, in the 1960's. The results of these studies are widely accepted, although some questions remain unanswered. The mechanism of hydrogenolysis of the metal acyl in the rhodium-catalyzed hydroformylation reaction is one such question. It has been established that dinuclear reductive elimination occurs in several stoichiometric reactions[3] involving metal acyls and in the $Co_2(CO)_8$-catalyzed hydroformylation.[4]

The work described here provides evidence that dinuclear elimination is occurring in rhodium-catalyzed hydroformylation as well. The approach undertaken was to support a rhodium catalyst on silica gel and monitor the activity of the catalyst as a function of its distribution on the surface. If a unimolecular reaction were operative, catalysis should occur regardless of the catalyst distribution. If a step in the reaction cycle is bimolecular in rhodium, catalysis should cease when all catalyst sites are isolated from each other. Thus, this approach could detect a step in the catalytic cycle which is bimolecular in rhodium even in cases where the overall rate law in solution shows a first-order rhodium dependence.

This approach depends on the ability to isolate the catalyst sites from each other and to keep them isolated during the reaction. If catalyst were to be leached from the surface, other catalyst molecules on the surface that were previously isolated would no longer be so. Since rhodium systems attached to silica by the ubiquitous monodentate anchor $(EtO)_3SiCH_2CH_2PPh_2$ have been shown to undergo leaching,[5] it follows that a monophosphine-based attachment to silica would be unsuitable for this work. On the other hand, a chelating phosphine ligand would be expected to be less prone to catalyst leaching.[6]

Ligand Synthesis

Although several 1,2-bis(diphenylphosphino)alkanes are known,[7] there are none that also contain an alkoxy silane or other functionality suitable for attachment to silica.

The synthesis of the silylated diphosphines **3** and **4** is outlined in Figure 1. The precursor, (*p*-chlorophenoxy)-1,2-propanediol is readily converted to its ditosylate, **1a**, or dimesylate, **1b**. Treatment of **1a** or **1b** with lithium diphenylphosphide gave negligible yields of **2**. However, reaction of sodium diphenylphosphide with **1b** afforded a 63% yield of **2**; the ditosylate and sodium diphenylphosphide gave only an 8% yield of **2**.

Grignard formation from **2** could not be effected by using magnesium turnings, but it did proceed readily when the reactive powdered magnesium described by Rieke[8] was used. The Grignard reagent reacts with excess triethoxymethylsilane or diethoxydimethylsilane to give **3** or **4**, respectively, in high yield. The diethoxysilane **3** is a nondistillable viscous oil that could be freed of nonsilanized contaminants only with difficulty. The ethoxysilane **4**, on the other hand, was easily crystallized.

Distribution of Catalyst Sites on Silica

Little attention has been given to the question of site–site interactions on silica until recently, even though several instances are well-known.[9] Because site–site isolation is not guaranteed by immobilization of a species on silica, some calculations were carried out for the system described herein. Assuming a com-

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Table I. Loading Levels of Silicas 6a-i

	type of silica				loading level		
sample		area, m^2/g	av pore diameter	ligand	μmol/g	molecules/ 100 nm^2	anal., % P
6a	Grace 62	340	140	3	5.6	1.0	0.035
6b	Grace 62	340	140	3	2.9	0.52	0.018
6c	Grace 62	340	140	3	0.53	0.095	0.0033
6d	Grace 62	340	140	4	166	29.8	1.14
6e	Grace 62	340	140	4	6	1.1	0.04
6f	Porasil A	400	<100	4	129	19	0.74
6g	Porasil A	400	<100	4	16	2.5	0.10
6h	Porasil C	100	300	4	33	20	0.20
6i	Porasil C	100	300	4	5.0	3.0	0.031

Table II. Measurement of Ligand Concentration on Silica by UV/vis Spectroscopy

	ligand loading, μmol/g	
sample	determined by UV/vis, CH_2Cl_2 254 nm	determined by phosphorous analysis
6a	5.7	5.6
6b	3.0	2.9
6c	0.51	0.53

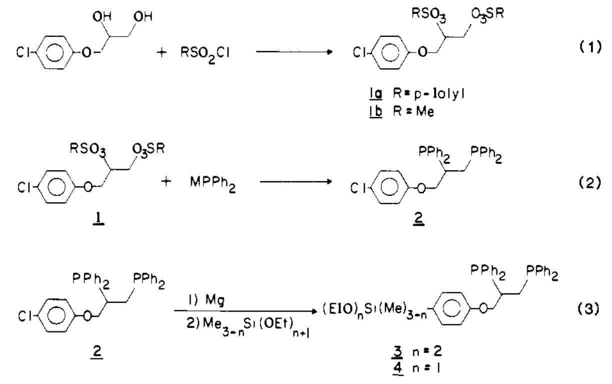


Figure 1. Ligand synthesis.

pletely random distribution, the probability that any surface species is able to interact with at least one other is given by

$$P = NX - \frac{N^2X^2}{2!} + \frac{N^3X^3}{3!} - \frac{N^4X^4}{4!} + \ldots$$

where N is the total number of surface-bound species, $X = \pi(r_2^2 - r_1^2)/A$, $r_1/2$ is the van der Waals radius of the base of the molecule at the surface, $r_2/2$ is the length of the molecule, and A is the total area of the surface.[10] The probabilities of interaction for various concentrations on 340 m^2/g of silica are plotted in Figure 2 as a function of r_1 and r_2. For ligand **4**, $r_1/2$ and $r_2/2$ were measured on CPK models as 10 and 19 Å, respectively, although it can be seen that the probabilities of isolation are relatively insensitive to changes in these values. These calculations

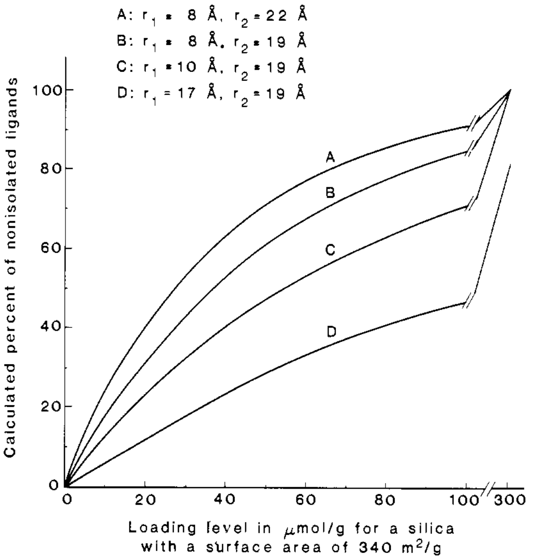


Figure 2. Calculated amount of site–site interaction for **4** on silica as a function of loading levels and the parameters r_1 and r_2.

could be experimentally verified by taking advantage of the reactions shown in eq 4–7 (COD = 1,5-cyclooctadiene, DPPE = 1,2-bis(diphenylphosphino)ethane).[11]

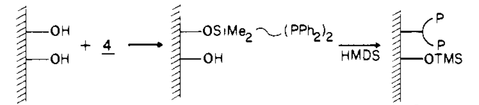
$$\underset{\mathbf{5a}}{[\mathrm{Rh(COD)(NCMe)_2}]\mathrm{BF_4}} + \mathrm{DPPE} \rightarrow [\mathrm{Rh(COD)(DPPE)}]\mathrm{BF_4} + [\mathrm{Rh(DPPE)_2}]\mathrm{BF_4} \quad (4)$$

$$[\mathrm{Rh(COD)(DPPE)}]\mathrm{BF_4} + 2\mathrm{MeCN} \rightleftharpoons [\mathrm{Rh(NCMe)_2(DPPE)}]\mathrm{BF_4} + \mathrm{COD} \quad (5)$$

$$\underset{\mathbf{5b}}{[\mathrm{Ir(COD)(NCMe)_2}]\mathrm{BF_4}} + \mathrm{DPPE} \rightarrow [\mathrm{Ir(COD)(DPPE)}]\mathrm{BF_4} + [\mathrm{Ir(DPPE)_2}]\mathrm{BF_4} \quad (6)$$

$$[\mathrm{Ir(COD)(DPPE)}]\mathrm{BF_4} + 2\mathrm{MeCN} \rightleftharpoons [\mathrm{Ir(NCMe)_2(DPPE)}]\mathrm{BF_4} + \mathrm{COD} \quad (7)$$

Silica gel was treated with various amounts of the silyldiphosphine **4** and then with hexamethyldisilazane (HMDS) to reduce the polarity of the surface (eq 8). The ligand-substituted



(8)

silicas, **6**, prepared by this method are listed in Table I. When these silicas were treated slowly with an excess of a dilute solution of **5a** in acetonitrile at 80 °C, bis-phosphine and tetrakis-phosphine rhodium complexes **7a** and **8a** were formed (eq 9), *in relative concentrations which depend on the distribution of the ligands*

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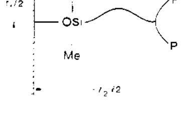
(10) Assuming that a molecule can interact with another only if it is between r_1 and r_2 of that molecule, the probability that it interacts is $X = \pi(r_2^2 - r_1^2)/A$, and the probability that it does not is $1 - X$. Then the probability that a given molecule has no interaction with any of the $N - 1$ molecules present is $(1 - X)^{N-1}$, and the probability of at least one interaction is:

$$\begin{aligned} P &= 1 - (1 - X)^{N-1} \\ &\approx 1 - (1 - X)^N \\ &\approx NX - \frac{N^2X^2}{2!} + \frac{N^3X^3}{3!} - \frac{N^4X^4}{4!} + \ldots \end{aligned}$$



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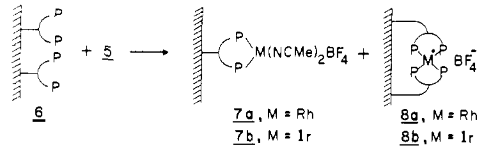
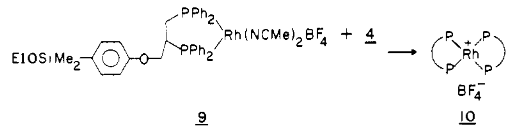


(9)

on the silica surface. When the related ligands are site isolated, **7a** is the product; when they are not, **8a** results. Analogous reactions occur for the iridium derivatives **5b**, **7b**, and **8b**.

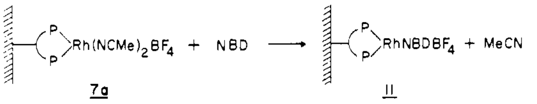
The products of these reactions are easily measured by UV/vis spectroscopy. Figure 3 shows the titration of a solution of **9** with **4** to give **10** (eq 10).



(10)

When silica gel is suspended in a mixture of solvents of the appropriate refractive index, a transparent mixture is obtained, and UV/vis spectra of silica-supported species are readily obtained. When **6** is suspended in CH_2Cl_2, the UV absorption of the ligand can be measured and the concentration of ligands on the surface determined. As shown in Table II, the results agree very well with those derived from phosphorus analysis of the same samples. However, when the loading level is too high, the resulting absorption becomes too large to measure. Dilution of the high loading level samples with unfunctionalized silica produced irreproducible results, probably because of nonuniform mixing.

When phosphinated silicas, **6**, treated with the soluble rhodium(I) complexes **5a** were suspended in 61/39 v/v anisole/acetonitrile, the relative proportions of the silica-bonded complexes, **7a** and **8a**, could be determined. An independent measurement of the relative concentrations of **8a** and **11a** was carried out by suspending the same sample in a different solvent system, 10/66/35 NBD/anisole/acetonitrile (eq 11, NBD = norbornadiene).



(11)

These experiments were carried out on three types of silica gel: Grace 62, a silica with a 340 m^2/g specific surface, and Porasils A and C, spherical silicas with specific areas of 400 and 100 m^2/g, respectively. The results of these experiments are shown in Figure 4 and agree well with the calculated values, regardless of the type of silica used. Repetition of these experiments using the iridium analogue **5b** provided comparable results for a silica with a high concentration of **4** (Table III), but poor base lines prevented interpretation of the results at lower **4** concentrations. It is known that $(DPPE)_2IrBF_4$ reacts with CO to form a five-coordinate CO adduct (eq 12).[12] Silica **6** was treated with $Ir(COD)(NCMe)_2BF_4$

$$(DPPE)_2IrBF_4 + CO \rightarrow (DPPE)_2Ir(CO)BF_4 \qquad (12)$$

and then with CO. Its IR spectrum was compared to those of standards prepared from solutions of various mixtures of the iridium complexes **12** and **13** that were treated with CO, precipitated, and run as Nujol mulls. These experiments yielded results close to those obtained by UV/vis spectroscopy (see Table III). This method provided an independent check of the concentration of the tetrakis-phosphine iridium complexes **12** and **13**.

Hydroformylation with Soluble Species

The preparation of the catalyst precursors **14–16** is shown in Figure 5. Treatment of Rh(NBD)(AcAc) (AcAc = 2,4-pentanedionato) with Ph_3CBF_4 and **4** gives **14** in high yield. The allyl **15** was prepared from $[Rh(DPPE)Cl]_2$ and allyl magnesium bromide; its analogue, **16**, was most conveniently prepared from **14**. Although the species **14** and **16a,b** were formed quantita-

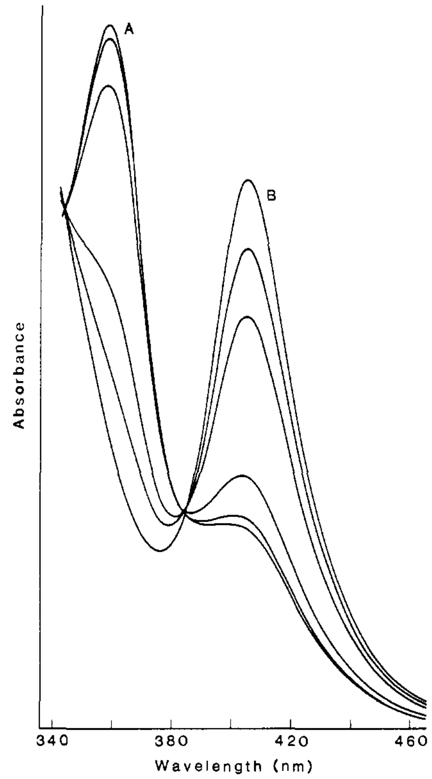


Figure 3. Titration of **9** (A) with **4** to give **10** (B) in 61/39 v/v anisole/acetonitrile solution.

Table III. Comparison of Methods for the Determination of the Amount of Site-Site Interaction of Species on Silica

method	sample	% *non*isolated ligands
Rh(I), UV/vis 61/39 PhOMe/MeCN	6h	83
Rh(I), UV/vis 10/55/35 NBD/PhOMe/MeCN	6h	84
Ir(I), UV/vis 61/39 PhOMe/MeCN	6h	73
Ir(I), then CO, IR	6h	81

Table IV. Loading Levels of Catalysts 17a-j

sample	anal., % P	anal., % Rh	loading level, μmol/g	calcd % isolation
17a	0.82		132	15
17b	0.59		95	24
17c	0.31		50	50
17d	0.16		26	71
17e	0.056		9.0	88
17f		0.92	103	27
17g		0.78	76	34
17h		0.37	39	61
17i		0.17	18	80
17j		0.041	4.2	95

Table V. Hydroformylation Catalyzed by 17[a]

catalyst	turnovers per Rh per h	calcd % isolation
17a	0.17, 0.21, 0.19, 0.22	15
17b	0.12	24
17c	0.097, 0.068	50
17d	0.054, 0.086	71
17e	0.031, 0.021	88

[a] Conditions: styrene, 0.92 M; 17 as needed to contain 0.004 mmol Rh; silica treated with hexamethyldisilazane added as needed to bring total silica to 0.5 g. Experiments run in anisole solution (8 mL) at ambient temperature with 19:1 H_2/CO at 50 psi.

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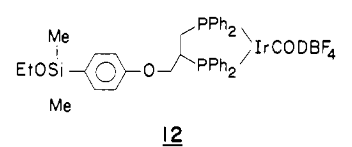
(12) Vaska, L.; Catrone, D. L. *J. Am. Chem. Soc.* **1966**, *88*, 5324.



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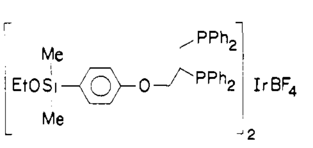

13

tively,[13] the isolated yields were low because of the extraction procedures.

The two isomers **16a,b** could be detected by ^{31}P and 300-MHz ^{1}H NMR spectroscopy, but no attempt was made to separate them or identify fluxionality that might allow their interconversion. All five protons of the π-allyl are inequivalent because of the lack of symmetry of the phosphine ligand, but their chemical shifts and coupling constants are consistent with the simpler pattern for **15**.

The cationic complex **14** was a catalyst precursor for the slow hydroformylation of styrene in anisole solution at ambient temperature with 50 psi of H_2/CO gas. The neutral allyls **15** and **16** are catalyst precursors that afford rates that are two orders of magnitude faster than those obtained from **14**. The alkyls would be expected to form a neutral monohydride on treatment with hydrogen (eq 13). However, the NBD complex **14** would be

$$\mathbf{16} + H_2 + CO \rightarrow L_n(CO)_mRhH \qquad (13)$$

expected to form several cationic species under hydroformylation conditions; some of these species can be expected to contain hydrogen and could be Brønsted acids (eq 14). It is conceivable

$$\mathbf{14} + H_2 + CO \rightarrow L_n(CO)_mRh(H_2)^+BF_4^- \qquad (14)$$

that the cationic species are not catalyst intermediates during hydroformylation but are merely related by an acid–base equilibrium to neutral species that are involved in the catalytic cycle (eq 15). In fact, addition of increasing amounts triethylamine

$$L_n(CO)_mRh(H)_2^+BF_4^- + \text{Base} \rightarrow L_n(CO)_mRhH + \text{H-Base}^+BF_4^- \qquad (15)$$

or trityl anion to a solution of **14** under CO and H_2 caused increasing hydroformylation rates until 1 equiv was added, at which point the rate was the same as was found for **15** and **16** (Figure 6). Addition of an excess of these bases had no further effect on the rate. However, addition of 2 equiv of the weaker bases pyridine or 2,4,6-collidine gave slower rates. Furthermore, the presence of 5 equiv of toluenesulfonic acid completely stopped catalysis.[14]

The rate of hydroformylation increased as the H_2:CO ratio increased. When 19:1 H_2:CO was used, the turnover rate was independent of the rhodium concentration.[15]

A modest rate increase was found on irradiation with UV light, although the reaction solution warmed significantly, so this effect is more likely to be of thermal origin. Addition of the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol had no effect and addition of *tert*-butyl hydroperoxide decreased the rate somewhat, so it is likely that a radical chain mechanism is not operative. Addition of benzoquinone had no effect, and dioxygen slows the catalysis.

Hydroformylation with Silica-Supported Catalysts

Catalysts **17** were prepared by treatment of silica gel with varying amounts of **14** and subsequently with excess hexa-

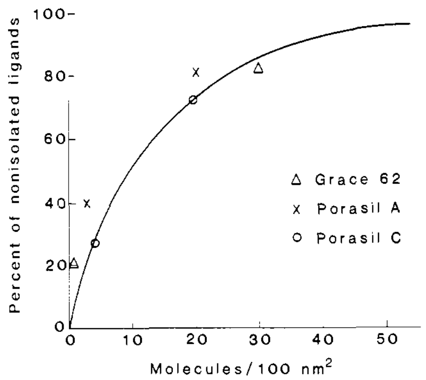

Figure 4. Experimentally determined amount of site–site interaction for **4** on various silica gels. The solid line represents calculated values.

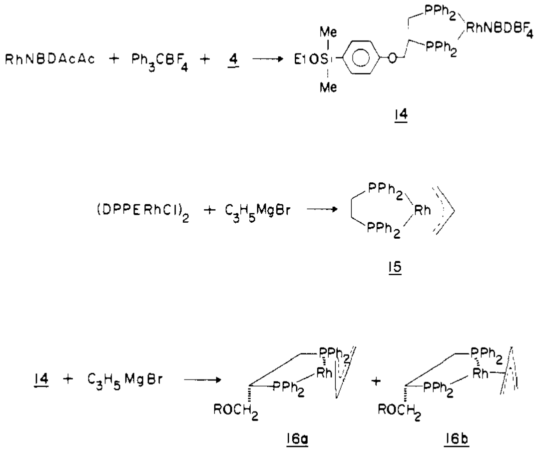

Figure 5. Preparation of catalyst precursors.

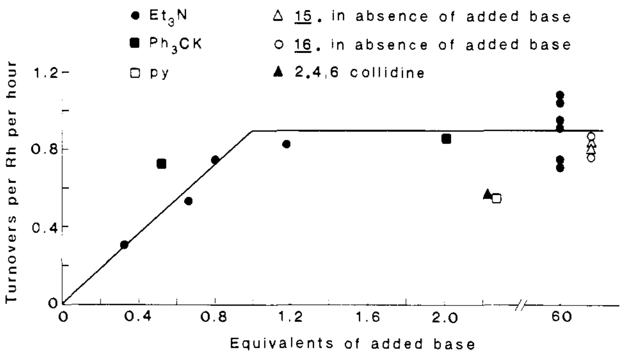

Figure 6. Effect of added base on the rate of hydroformylation using **14** as a catalyst precursor. Conditions: styrene, 0.74 M; **18**, 3.3 mM. Experiments run in anisole solution at ambient temperature with 50 psi 1:1 H_2/CO.

Table VI. Hydroformulation Catalyzed by 17/Et_3N Using 19:1 H_2/CO[a]

catalyst	turnovers per Rh per h	calcd % isolation
17f	9.9, 7.4, 7.0	27
17g	7.4, 7.4, 6.2	34
17h	5.8, 5.7, 7.1, 6.4	61
17i	3.6, 3.8, 5.3, 5.5	80
17j	0.95, 0.42	95

[a] Conditions: styrene, 0.74 M; Et_3N, 105 mM; 17 as needed to contain 0.001 to 0.004 mmol Rh. Experiments run in anisole solution (1–1.5 mL) at ambient temperature with 19:1 H_2/CO at 50 psi.

methyldisilazane (eq 16, Table IV). When **17a–e** were used as hydroformylation catalysts with 19:1 H_2:CO, the rate of the reaction per rhodium atom was found to depend on the concentration

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(13) As determined by ^{31}P NMR.

(14) A solution of **14** that had been deactivated by the addition of TsOH and subsequently treated with excess Et_3N showed the same catalytic behavior as the **14**/Et_3N system.

(15) When 1:1 H_2/CO was used, the turnover rate *decreased* slightly as the rhodium concentration increased.

Table VII. Hydroformylation Catalyzed by $17/Et_3N$ Using 1:1 H_2/CO^a

catalyst	turnovers per Rh per h	calcd % isolation
17f	0.60, 0.65, 0.71, 0.73, 0.70	27
17g	0.71, 0.72	34
17h	0.47, 0.56, 0.44, 0.49	61
17i	0.51, 0.47, 0.48	80
17j	0.32	95

[a] Conditions: styrene, 0.74 M; Et_3N, 105 mM; 17 as needed to contain 0.001 to 0.004 mmol Rh. Experiments run in anisole solution (1-1.5 mL) at ambient temperature with 1:1 H_2/CO at 50 psi.

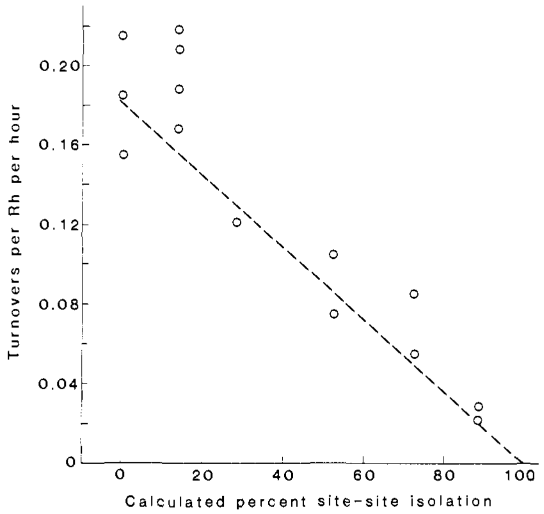
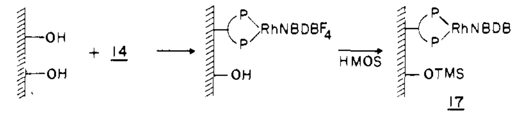


Figure 7. Hydroformylation catalyzed by 17 using 19:1 H_2/CO. Conditions shown in Table V. Data at zero isolation obtained with soluble catalyst.

of the catalyst on the silica surface (Table V). Addition of extra silica containing only Me_3Si groups did not affect the rate.

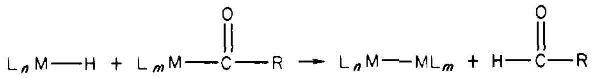


(16)

When styrene hydroformylation was run with 17 in the presence of excess triethylamine, the rates increased dramatically, as they did in the soluble case. The rates again depended on the concentration of the catalyst on the surface and on the ratio of hydrogen to carbon monoxide, but not on the presence of added silica containing only Me_3Si groups (Tables VI and VII).

The previously discussed calculations (Figure 2) allow a correlation between the concentration of ligands on the surface with the percentage of them that are site isolated. Here we make the assumption that the same correlation would hold for the surface-bound rhodium complex 17. In other words, we assume, for any given surface concentration, that *the percentage of catalyst sites that are isolated is the same as the percentage of surface bound bidentate ligands that fail to form tetracoordinate complexes.* With that assumption, the measured turnover rates per rhodium were plotted vs. the calculated percentage of isolated catalyst sites on the surface in Figures 7–9.

Figure 7 shows a near linear relationship between the catalytic activity and the calculated percentage of site-isolated catalysts. This behavior would result if the isolated species were catalytically inactive and if the nonisolated ones had an activity similar to that of their soluble analogue. These results are thus consistent with a dinuclear elimination step in the mechanism (eq 17).[16]



$$L_nM—H + L_mM—\overset{\displaystyle O}{\overset{\|}{C}}—R \rightarrow L_nM—ML_m + H—\overset{\displaystyle O}{\overset{\|}{C}}—R \quad (17)$$

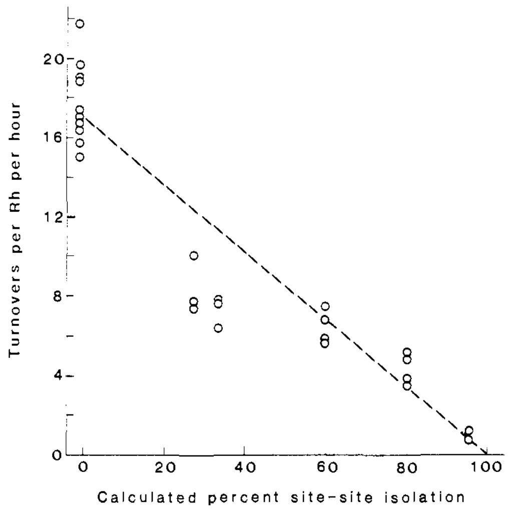


Figure 8. Hydroformylation catalyzed by $17/Et_3N$ using 19:1 H_2/CO. Conditions shown in Table VI. Data at zero isolation obtained with soluble catalyst.

Similar results are found when triethylamine is present. Figure 8 shows results for the $17/Et_3N$ system using 19:1 H_2:CO. Data corresponding to highly isolated catalysts are clearly consistent with the results in the absence of base. Catalysts with higher loading levels of rhodium had activities that were somewhat less than expected, but this could be attributed to mass transfer that is slow compared to the rate of the reaction.[17]

When 1:1 H_2:CO was used (Figure 9), activities with highly dispersed catalysts were higher than expected. However, a recycle experiment established that a small amount of catalyst leaching was taking place, and this may be responsible.[18] An identical experiment with 19:1 H_2:CO showed no evidence of leaching. Leaching in the former case and not in the latter may result from removal of rhodium from the chelate, induced by a higher CO partial pressure, or from desorption of some **14** that was not covalently attached to the surface over the course of the longer experiment.[19]

Attempts were made to increase the rate of catalysis by adding other metal complexes. Addition of $CpMo(CO)_3H$ or $HRe(CO)_5$ to a solution of **15**, styrene, and anisole before addition of synthesis gas produced a color change to orange-red. However, the rate of catalysis was decreased. The addition of $(CpFe(CO)_2)_2$ or $CH_3Mn(CO)_5$ had no effect.

Conclusions

A convenient route to an alkoxy silane containing a chelating phosphine has been developed. The distribution of this ligand on the surface of silica gel was found to be random and independent of the type of silica. Catalysts attached to silica at low loading levels with this ligand could be prepared with a low, but nonzero, amount of site–site interaction. Catalysts at high loading levels had significant amounts of site–site interaction. Hydroformylation with these catalysts showed that the turnover rate depended nearly linearly on the percentage of isolated catalysts, implying that a step in the catalytic cycle involves two rhodium centers. This step is probably the dinuclear elimination of aldehyde.

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(16) Although some authors may have been inclined to include here a detailed mechanism employing a dinuclear elimination step, we feel that there is presently insufficient evidence to warrant it.

(17) Pittman, C. U.; Smith, L. R.; Hanes, R. M. *J. Am. Chem. Soc.* **1975**, *67*, 1742.

(18) A reaction mixture containing catalyst **17b** was filtered under nitrogen. The filtrate was slightly colored and had about 5% of the activity of the mixture before filtration.

(19) An attempt at activating the isolated catalysts by the addition of soluble catalyst was unsuccessful, as observed rates with either 19:1 or 1:1 H_2/CO were approximately equal to the weighted mean of the solution and supported values. This may be due to slow diffusion of the homogeneous catalyst, which is larger than any of the substrates.

Experimental

Most of the compounds used are sensitive to oxygen and/or water and were handled under prepurified nitrogen or argon, using a Vacuum Atmospheres dry box or standard Schlenk techniques. THF and anisole were distilled under nitrogen from sodium/benzophenone ketyl. Toluene, hexanes, ethanol, and methanol were distilled under nitrogen from sodium, CaH_2, $Mg(OEt)_2$, and $Mg(OMe)_2$, respectively. Other solvents were reagent grade and were bubbled with nitrogen before use. Zinc chloride was sublimed before use. Silica gel used as a catalyst support was washed with 10% HCl and then with water until the washings were neutral. It was dried in vacuo at 185 °C. All other chemicals were used as received.

Proton NMR measurements were made on Varian T-60, XL-100, or Nicolet Technologies 300 spectrometers. ^{31}P NMR measurements were made on a Varian XL-100 spectrometer. IR spectra were recorded on a Nicolet Technologies 7000 FTIR instrument. UV/vis spectra were obtained with a Cary 219 spectrophotometer.

Microanalyses were performed by the Stanford microanalytical laboratory and by Galbraith Laboratories, Knoxville, TN.

3-(4-Chlorophenoxy)-1,2-propanediol Ditosylate (1a). A solution of 20.1 g (99 mmol) of 3-(4-chlorophenoxy)-1,2-propanediol in a minimum amount of pyridine was added slowly to an ice-cooled solution of 47.2 mg (0.248 mol) of tosyl chloride in 50 mL of pyridine and stirred overnight. Crushed ice was added. After 1 h the reaction mixture was acidified with concentrated HCl. The aqueous layer was discarded and the residue taken up in CH_2Cl_2 and extracted with dilute HCl and sodium bicarbonate and dried over $MgSO_4$. The solution was passed through a small silica gel plug and concentrated to give a viscous oil which solidified on standing. Yield 42.7 g (84%); mp 112–3 °C; ^1H NMR ($CDCl_3$) δ 2.5 (s, 6 H, CH_3), 4.1 (d, 2 H, $-CH_2OAr$), 4.3 (d, 2 H, $-CH_2OTs$), 4.8 (m, 1 H, CH), 6.6 (d, 2 H, ClC_6H_4O), 7.2 (d, 2 H, ClC_6H_4O), 7.3 (d, br, 4 H, $MeC_6H_4SO_2$), 7.75 (d, 2 H, $MeC_6H_4SO_2$), 7.80 (d, 2 H, $MeC_6H_4SO_2$).

Anal. Calcd for $C_{23}H_{23}ClO_7S_2$: C, 54.06; H, 4.54. Found: C, 53.70; H, 4.55.

3-(4-Chlorophenoxy)-1,2-propanediol Dimesylate (1b). The dimesylate **1b** was prepared in a manner similar to that of **1a**. Yield 89%; mp 67–69 °C; ^1H NMR ($CDCl_3$) δ 3.15 (s, 3 H, CH_3), 3.25 (s, 3 H, CH_3), 4.3 (d, 2 H, $-CH_2OAr$), 4.6 (d, 2 H, $-CH_2OMs$), 5.2 (m, 1 H, CH), 6.9 (d, 2 H, ClC_6H_4O), 7.4 (d, 2 H, ClC_6H_4O).

Anal. Calcd for $C_{11}H_{15}ClO_7S_2$: C, 36.82; H, 4.21. Found: C, 36.97; H, 4.24.

Reaction of 1a and 1b with Sodium Diphenylphosphide. Sodium diphenylphosphide was prepared by the addition of 0.71 mL (4.08 mmol) of PPh_2H to 190 mg (8.3 mmol) of Na and 10 mL of THF. The mixture was heated under reflux for 45 min. The excess Na was removed with forceps under a N_2 purge. The remaining solution was then cooled to −78 °C. A solution of **1a** (950 mg, 1.86 mmol) in 10 mL of THF was added via needlestock. The reaction solution was stirred for 2.5 h and then warmed to room temperature. The solvent was removed in vacuo. Degassed water (10 mL) was added; the resulting solution was shaken until the orange color of $NaPPh_2$ was gone and then extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried in vacuo, and stirred under MeOH overnight. Yield: 80 mg (8%) of **2**. Similar reaction of **1b** with $NaPPh_2$ gave 630 mg (63%) of **2**.

1,2-Bis(diphenylphosphino)-3-(4-chlorophenoxy)propane (2). Diphenylphosphine (172 g, 0.92 mol) was added in portions to a suspension of sodium (22 g, 0.96 mol) in 1 L of THF and heated at reflux for 5 h. After the mixture was cooled to −78 °C, a solution of **1b** (157 g, 0.44 mol) in 300 mL THF was added over 40 min. The solution was stirred for 30 min more at −78 °C and allowed to warm to room temperature over 1 h. Degassed water (0.5 mL) was added to discharge the orange color from $NaPPh_2$. The THF was distilled off. Methylene chloride (300 mL) was added, and the resulting suspension was extracted with 400-, 200-, and 100-mL portions of water. The CH_2Cl_2 was removed in vacuo and was replaced with 1 L of MeOH, which was heated and then cooled. The product was filtered off and recrystallized from EtOH. Yield 148 g (63%) of **2**; mp 106–108 °C; ^1H NMR ($CDCl_3$) δ 2.26, 2.48, 2.69 (each m, 1 H, $PPh_2CH_2CHPPh_2$), 3.88, 4.31 (each m, 1 H, $-OCH_2CHPPh_2$), 6.66 (d, 2 H, ClC_6H_4O), 7.15 (d, 2 H, ClC_6H_4O), 7.30 (m, 20 H, PPh_2); ^{31}P NMR ($CDCl_3$) δ −6.7 (d, J = 25 Hz), −20.2 (d, J = 25 Hz).

Anal. Calcd for $C_{33}H_{29}ClOP_2$: C, 73.54; H, 5.42. Found: C, 73.17, H, 5.59.

1,2-Bis(diphenylphosphino)-3-[4-(diethoxymethylsilyl)phenoxy]propane (3). Magnesium powder was prepared by the method of Rieke[8] from 11.6 g (62.9 mmol) of $MgBr_2$, 5.20 g (31.0 mmol) of KI, and 4.40 g (113 mmol) of K in 150 mL of THF. The aryl chloride **2** (15.3 g, 28.4 mmol) in 20 mL of THF was added, and the suspension was heated at reflux for 4.5 h. The flask was cooled to 0 °C and 13 mL (65 mmol) of $CH_3Si(OEt)_3$ was added rapidly; the suspension was stirred overnight. The THF was removed in vacuo, and the residue was extracted with 300 mL of toluene. Dimethylaminoethanol (12 g) containing 315 mg of $Me_2NCH_2CH_2ONa$ was added. The solution was then heated at reflux for 6 h and concentrated in vacuo to give a crude bis(dimethylaminoethoxy)silane. The residue was dissolved in 400 mL of Et_2O, and zinc chloride (9.9 g, 73 mol) in 50 mL of Et_2O was added to complex the amines. The resulting suspension was stirred for 1.5 h, filtered, and washed with Et_2O until the washings were free of unsilanized phosphines (by TLC). The residue was treated with stoichiometric NaOEt/EtOH to remove the dimethylaminoethoxy groups and bubbled with H_2S to precipitate the zinc salts. The resulting suspension was concentrated in vacuo and extracted with Et_2O. The Et_2O solution was treated with $ZnCl_2$ to trap any remaining amines, filtered, bubbled with H_2S to remove the zinc, and filtered again. The solution was then retreated with $ZnCl_2$ followed by H_2S and concentrated in vacuo. Ethanol was added, the solution filtered, and the solvent removed in vacuo to give **3** as a colorless, nondistillable oil.

^1H NMR ($CDCl_3$) δ 0.34 (s, 3 H, $SiCH_3$), 1.30 (t, 6 H, $-CH_2\mathit{CH}_3$), 2.26, 2.48, 2.69 (each m, 1 H, PCH_2CHP), 3.85 (q, 4 H, $O\mathit{CH}_2CH_3$), 3.88, 4.31 (each m, 1 H, $-O\mathit{CH}_2CHPPh_2$), 6.82 (d, 2 H, SiC_6H_4O), 7.3 (m, 20 H, PPh_2), 7.54 (d, 2 H, SiC_6H_4O); ^{31}P NMR ($CDCl_3$) δ −6.8 (d, J = 27 Hz), −20.3 (d, J = 27 Hz).

Anal. Calcd for $C_{38}H_{42}O_3P_2Si$: C, 71.68; H, 6.65. Found: C, 71.35; H, 6.70.

1,2-Bis(diphenylphosphino)-3-[4-(ethoxydimethylsilyl)phenoxy]propane (4). Magnesium powder was prepared by the method of Rieke[8] from 15.4 g (83.5 mmol) of $MgBr_2$, 6.2 g (370 mmol) of KI, and 6.00 g (153 mmol) of K in 225 mL of THF. The aryl chloride **2** (20.7 g, 38.3 mmol) in 25 mL of THF was added and the suspension was heated at reflux for 5 h. The flask was cooled to 0 °C and 9.9 mL (80 mmol) of $Me_2Si(OEt)_2$ was added rapidly and the suspension stirred overnight. The THF was removed in vacuo, and the residue was extracted with toluene. A few drops of EtOH were added to discharge the yellow color of $KPPh_2$. The solvent was removed in vacuo to give a viscous oil that could be crystallized from hexanes. Yield 15.1 g (65%); ^1H NMR ($CDCl_3$) δ 0.34 (s, 6 H, $SiCH_3$), 1.16 (t, 3 H, $OCH_2\mathit{CH}_3$), 2.22, 2.48, 2.67 (each m, 1 H, PCH_2CHP), 3.67 (q, 2 H, $O\mathit{CH}_2CH_3$), 3.92, 4.38 (each m, 1 H, $-O\mathit{CH}_2CHP$), 6.78 (d, 2 H, SiC_6H_4O), 7.25 (m, 20 H, PPh_2), 7.43 (d, 2 H, SiC_6H_4O); ^{31}P NMR ($CDCl_3$) δ −6.8 (d, J = 26 Hz), −20.3 (d, J = 26 Hz).

Anal. Calcd for $C_{37}H_{40}O_2P_2Si$: C, 73.24; H, 6.64. Found: C, 73.31; H, 6.88.

Reaction of 4 with Silica Gel. Silica gel was suspended in 10% HCl for approximately 2 h, filtered, resuspended in 10% HCl, and washed with water until neutral. It was dried at 120 °C and then dried at 185 °C in vacuo. In a typical preparation, 108 mg (0.178 mmol) in **4** in 5 mL of toluene was added to a stirred suspension of 6.3 g of Grace 62 silica gel in 50 mL of toluene. The suspension was heated at reflux overnight, cooled, filtered, washed with toluene, and dried in vacuo. After submission for phosphorous analysis, the silica was suspended in a solution of 5 mL of HMDS in 50 mL of toluene and allowed to stir for 90 min. It was filtered, washed with toluene, and dried in vacuo.

$[Rh(COD)(NCMe)_2]BF_4$ (5a). The complex **5a** was prepared by a simplification of the method of Green et al.[11] Methylene chloride (13 mL) was added to a mixture of 1.01 g (2.04 mmol) of $[Rh(COD)Cl]_2$ and 1.35 g (4.08 mmol) of Ph_3CBF_4. Acetonitrile (7.5 mL) was added and the resulting orange-brown solution was concentrated in vacuo to about 10 mL. Addition of 50 mL of Et_2O produced yellow crystals which were filtered and washed with Et_2O. Yield: 753 mg (49%). The NMR spectrum was identical with that previously reported.[11]

[1,2-Bis(diphenylphosphino)-3-(4-{ethoxydimethylsilyl}phenoxy)propane][bicyclo[2.2.1]hepta-2,5-diene]rhodium(I) Tetrafluoroborate (14). A solution of 3.19 g (9.67) of Ph_3CBF_4 in 25 mL of CH_2Cl_2 was added to a solution of 2.84 g (9.67 mmol) of Rh(NBD)(AcAc)[20] in 25 mL of CH_2Cl_2. The solution was cooled to −30 °C. A solution of 5.87 g (9.67 mmol) of **4** at −78 °C was added via needlestock in batches over a period of 1 h. The solution was allowed to warm to room temperature and was partially concentrated in vacuo. The product was precipitated with hexanes and then recrystallized from THF/hexanes.

^1H NMR ($CDCl_3$) δ 0.30 (s, 6 H, Si–CH_3), 1.14 (t, 3 H, $OCH_2\mathit{CH}_3$), 1.85 (br, 2 H, NBD methylene), 2.30 (m 1 H, CHP), 2.45 (m, 2 H, CH_2P), 3.61 (q, 2 H, $OCH_2\mathit{CH}_3$), 3.85, 4.02 (each m, 1 H, CH_2–OAr), 4.15, 4.32, 4.87, 5.38 (each br, 1 H, NBD vinyl), 5.46 (br 2 H, NBD methyne), 5.95 (d, 2 H, OC_6H_4Si), 7.0 (m, 22 H, aryl); ^{31}P NMR (THF) δ 45.5 (dd J_{PP} = 32 Hz, J_{PRh} = 155 Hz) 61.3 (dd, J_{PRh} = 159 Hz); UV/vis (10:35:55 NBD/MeCN/anisole) λ_{max} 474 nm.

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[20] (a) Neuberg, M. K. Ph.D. Thesis, Stanford University, Stanford CA, 1978. (b) Cramer, R. *Inorg. Synth.* **1974**, *15*, 16.

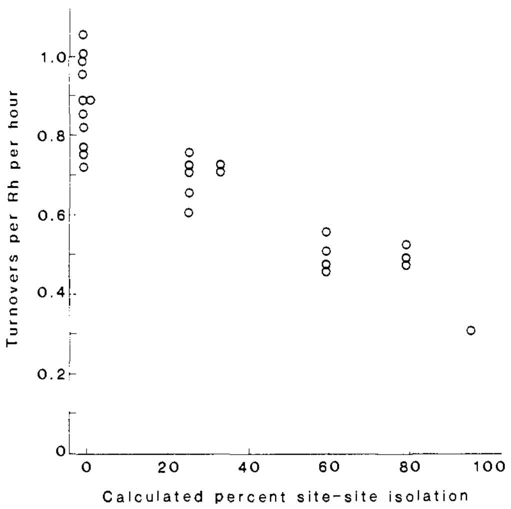

Figure 9. Hydroformylation catalyzed by **17**/Et_3N using 1:1 H_2/CO. Conditions shown in Table VII. Data at zero isolation obtained with soluble catalyst.

Anal. Calcd for $C_{44}H_{48}BF_4O_2P_2RhSi$: C, 59.47; H, 5.44. Found: C, 59.36; H, 5.60.

Bis(acetonitrile)[1,2-bis(diphenylphosphino)-3-(4-{ethoxydimethylsilyl}phenoxy)propane]rhodium(I) Tetrafluoroborate (9). Acetonitrile solutions of **9** could be generated from acetonitrile solutions of **14** by addition of hydrogen. A hexane solution of **9** could be generated by repeated extraction with hexane of an acetonitrile solution of **14**.

^{31}P NMR (CD_3CN) δ 62.58 (dd, J_{PP} = 46 Hz, J_{PRh} = 173 Hz), 77.24 (dd, J_{PP} = 46 Hz, J_{PRh} = 178 Hz); UV/vis (61:39 anisole/MeCN) λ_{max} 400 (sh), 359 nm.

Bis[1,2-bis(diphenylphosphino)-3-(4-{ethoxydimethylsilyl}phenoxy)propane]rhodium(I) Tetrafluoroborate (10). A mixture of 176 mg (0.198 mmol) of **14** and 120 mg (0.198 mmol) of **4** was dissolved in 1 mL of THF. After the solution was stirred for 15 min, hexanes were added. The product, an oil, separated from the solution. The solution was discarded, and the oil was solidified after washing with hexanes.

^1H NMR ($CDCl_3$) δ 0.34 (s, 12 H, $SiCH_3$), 1.17, 1.19 (each t, 3 H, $OCH_2\mathit{CH}_3$), 2.2 (br 5 H, OCH_2CHPCH_2P), 3.64, 3.66 (each q, 2 H, $O\mathit{CH}_2CH_3$), 6.30 (d, 4 H, OC_6H_4Si), 7.3 (m, 44 H, remaining aromatic H); ^{31}P NMR (CD_3CN), a 70-line pattern spanning the range of δ 40–65.

Anal. Calcd for $C_{74}H_{80}BF_4O_4P_4RhSi_2$: C, 63.34; H, 5.75. Found: C, 63.27; H, 5.76.

Reaction of 5a with Silica 6. A dilute solution of **5a** (about 0.3 mM) in CH_3CN was added dropwise to a rapidly stirred, boiling suspension of about 200 mg of **6** in a minimum amount of CH_3CN until a persistent yellow color was observed in the hot solution. The silica was filtered, washed with copious amounts of CH_3CN, diluted with silica treated with HMDS, as needed, and washed with 61:39 anisole/CH_3CN. UV/vis measurements in 61:39 anisole/MeCN were recorded as a difference between the sample treated with **5a** and a sample of **6** that was not treated with **5a**.

[1,2-Bis(diphenylphosphino)-3-(4-{ethoxydimethylsilyl}phenoxy)propane][1,5-cyclooctadiene]iridium Tetrafluoroborate (12). A solution of 67 mg (0.11 mmole of **4** in 1 mL of THF was added dropwise to a suspension of 52 mg (0.11 mmol) of **5b** in 50 mL of THF. The solution was partially concentrated and the product isolated by the addition of hexanes.

^1H NMR ($CDCl_3$) δ 0.35 (s, 6 H, MeSi), 1.20 (t, 3 H, $OCH_2\mathit{CH}_3$), 2 (m, 13 H, COD methylene, $PCHCH_2P$), 3.68 (q, 2 H, $O\mathit{CH}_2CH_3$), 3.75 (overlap with 3.68), 4.2, 4.9 (br, integration 1:2:1 vinyl), 6.4 d, 2 H, SiC_6H_4O), 7.6 (m, 22 H, aryl); ^{31}P NMR (CD_3CN) δ 29.09 (d, J = 15 Hz), 43.03 (d, J = 15 Hz); UV/vis (57:43 anisole/MeCN) λ_{max} 400 nm, 491 (sh), 506, 594.

Bis[1,2-bis(diphenylphosphino)-3-(4-{ethoxydimethylsilyl}phenoxy)propane]iridium(I) Tetrafluoroborate (13). A solution of 127 mg (0.21 mmol) of **4** in 1 mL of THF was added to a suspension of 50 mg (0.11 mmol) of **5b** in 5 mL of THF and warmed gently. The orange solution was partially concentrated and the product isolated by addition of hexanes. It was then crystallized from THF/hexanes.

^1H NMR ($CDCl_3$) δ 0.34, 0.35 (s, 6 H total, SiMe), 1.17, 1.18 (t, 3 H total $OCH_2\mathit{CH}_3$), 3 (very broad, 5 H, $O\mathit{CH}_2CH_3$, PCH_2CHP), 6.3 (d, 2 H, SiC_6H_4O), 7.4 (br. 22 H, remainder of aromatic); ^{31}P NMR (CD_3CN) δ 36 (t), 38 (t), 41 (t), 46 (t), 53 (t); UV/vis (57:43 anisole/MeCN) λ_{max} 382, 443, 525 nm.

Reaction of 5b with 6. Silicas **6** were treated with **5b** in the same manner as they were treated with **5a**. IR measurements were made by preparing Nujol mulls of silicas treated with **5b** and subsequently CO.

3^3-Allyl(1,2-bis(diphenylphosphino)ethane)rhodium(I) (15). Allylmagnesium bromide (2.28 mL of a 0.36 M solution in Et_2O) was added to a suspension of 438 mg (0.408 mmol) of $(DPPERhCl)_2$ in 15 mL of THF. The resulting yellow solution was concentrated to dryness in vacuo, extracted with toluene, filtered, reduced in vacuo, and re-extracted. The product was crystallized from THF/hexanes.

^1H NMR (C_6D_6) δ 2.0 (d, 4 H, PCH_2), 2.75 (dd, 2 H, allyl CH_2), 4.19 (d, 2 H, allyl CH_2), 5.25 (m, 1 H, CH), 7.0 (m, 12 H, aromatic H), 7.7 (m, 8 H, aromatic H); ^{31}P NMR (C_6D_6) δ 66.4 (d, J = 199).

Anal. Calcd for $C_{29}H_{29}P_2Ph$: C, 64.22; H, 5.39. Found: C, 63.91, H, 5.50.

3^3-Allyl[1,2-bis(diphenylphosphino)-3-[4-(ethoxydimethylsilyl)phenoxy]propane]rhodium(I) (16a, b). The cationic complex **14** (150 mg, 0.17 mmol) was dissolved in 1 mL of benzene. A solution of C_3H_5MgBr in Et_2O was added dropwise until the solution was yellow. The solution was decanted, filtered, and dried in vacuo. The residue was extracted with hexanes. This bright yellow solution was dried in vacuo, extracted with hexanes, and filtered; this entire process was done repeatedly.

^1H NMR (C_6D_6) δ 0.36 (s, 6 H, $SiCH_3$), 1.18 (t, 3 H, $OCH_2\mathit{CH}_3$), 2.25 (br, 1 H, CHP), 2.7 (m, 4 H, CH_2P, allyl CH_2), 3.5 (br, 2 H, $O\mathit{CH}_2CHP$), 4.00, 4.13, 4.19, 4.28 (each br, d, total 2 H, allyl CH_2), 5.12, 5.37 (m, total 1 H, allyl CH), 6.21, 6.25 (d, total 2 H, SiC_6H_4O), 7.1 (m, 12 H, aromatic), 7.9 (m, 10 H, aromatic); ^{31}P NMR (THF/C_6D_6) δ 60.3, 60.4 (dd, J_{PP} = 21 Hz, J_{PRh} = 197 Hz), 72.3, 72.1 (dd, J_{PP} = 21 Hz, J_{PRh} = 200 Hz).

Reaction of 14 with Silica Gel. Silica gel was treated with HCl and washed and dried as above. In a typical preparation, 103 mg (0.115 mmol) of **14** in 5 mL of anisole was added slowly to a stirred suspension of 2.3 g of Grace 62 silica gel in 20 mL of anisole. The mixture was heated at reflux for 4 h and cooled. Half of the solvent was decanted and 10 mL of HMDS was added. The suspension was heated at reflux for 1 h. The silica was separated by filtration, followed by washing with copious amounts of THF. Silicas **17f–j** were washed with DMF and acetonitrile and subjected to Soxhlet extraction with MeCN for 3 days.

Hydroformylation Procedure Using 17 as Catalyst. In a typical run, 31 mg of silica **17a** (0.005 mmol of Rh), 469 mg of silica that had been treated with HMDS, 728 mg of styrene, 108 mg of *n*-decane, and 7.25 mL of anisole were placed in a Fischer-Porter pressure bottle containing a magnetic stir bar. Next, 19:1 H_2/CO was added to reach 50 psig. The reaction was carried out at ambient temperature. The products were analyzed by GLC with use of a 10 ft. OV-101/Chromasorb W column.

Hydroformylation Using 14 as Catalyst. Solutions of **14**, styrene, *n*-decane, and anisole were prepared. In a given run, 7.5 g of such a solution was placed in a small pressure bottle containing a small stir bar. Next, 19:1 H_2/CO was added to reach 50 psig. The reaction was carried out at ambient temperature. The products were analyzed by GLC as above.

Hydroformylation Using 14/Base, 15, or 16 as Catalyst. Stock solutions of the catalyst, styrene, *n*-decane, and anisole were prepared. A stock solution of styrene, *n*-decane, and anisole (no catalyst), was prepared. An appropriate mixture of these solutions (1.0 to 1.5 g) was placed in a small vial containing a stir bar. The vial was placed in a pressure bottle and H_2/CO was added to 50 psig. The reactions were run at ambient temperature. The products were analyzed by GLC.

Hydroformylation Using 17/Et$_3$N as Catalyst. Silica **17** was weighed into a vial and 1.0–1.5 g of a stock solution of styrene, triethylamine, *n*-decane, and anisole was added. The vial was placed in a pressure bottle and H_2/CO was added to 50 psig. The reactions were run at ambient temperature. The produts were analyzed by GLC.

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Registry No. **1a**, 87481-86-5; **1b**, 87481-87-6; **2**, 87481-88-7; **3**, 87481-89-8; **4**, 87481-90-1; **5a**, 32679-02-0; **5b**, 32679-03-1; **9**, 87481-92-3; **10**, 87481-94-5; **12**, 87481-96-7; **13**, 87481-98-9; **14**, 87481-99-0; **15**, 87482-00-6; **16**, 87482-01-7; $CH_3Si(OEt)_3$, 2031-67-6; $Me_2Si(OEt)_2$, 78-62-6; $[Rh(COD)Cl]_2$, 12092-47-6; Ph_3CBF_4, 341-02-6; Rh(NBD)-(AcAc), 32354-50-0; $(DPPERhCl)_2$, 53204-14-1; 3-(4-chlorophenoxy)-1,2-propanediol ditosylate, 104-29-0; sodium diphenylphosphide, 4376-01-6; acetonitrile, 75-05-8; allyl bromide, 106-95-6; styrene, 100-42-5.