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Heterogenizing Homogeneous Catalysis Using Molecular Self-Assembly of Long Alkane Chain Phosphines Bound to Rh(I) Complexes

Maria G. L. Petrucci and Ashok K. Kakkar*

Department of Chemistry, McGill University, 801 Sherbrooke St. West,
Montreal, Quebec, Canada

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Long alkane chain hydrocarbons terminated with OH and PPh_2 groups, $HO-(CH_2)_n-PPh_2$ ($n = 10-12$) were self-assembled on inorganic oxide surfaces via acid−base hydrolysis of surface-anchored $[Si]-NEt_2$ groups with terminal OH moieties and subsequently used to covalently anchor Rh(I) complexes. Similar thin films can also be prepared from $[Si]-NEt_2$ and $RhCl(1,5\text{-}C_8H_{12})[PPh_2(CH_2)_nOH]$. The functionalized surfaces were characterized using solid-state NMR, contact angle goniometry, ellipsometry, X-ray photoelectron spectroscopy, and FT-IR. The self-assembled organometallic thin films were found to be highly active in catalyzing hydrogenation of tolan. Surface-bound Rh(I) catalyst is stable and can be recycled, while the homogeneous analogue decomposes under similar catalytic reaction conditions.

Introduction

Supported metal catalysis continues to be a topical area of research due to its potential in establishing links between solution and solid-phase catalysts.[1] Immobilization of transition metal complexes offers obvious advantages by combining useful properties of homogeneous catalysts stemming from their molecular nature with the ease of separation of heterogeneous analogues. The traditional supports for immobilizing transition metal catalysts include organic polymers[2] and inorganic oxides such as silica,[3] with the latter being the most commonly employed anchor. We have recently developed[4] a new inorganic oxide surface modification route that uses easily accessible starting materials and avoids some of the common problems of the trialkoxysilane grafting methodology on silica, including the presence of substantial amounts of surface-bound phosphorus oxide.[5] The latter does not bind transition metals tightly and may be responsible for the leaching process that remains a key issue in catalysis.[1]

One may further enhance the potential of heterogenized homogeneous catalysis by constructing organometallic surfaces of controlled structure and functionality.[6] Thus, building supports which have a large number density of organized and advantageously oriented active catalytic sites with known structures is a tantalizing and highly fruitful task. In this regard, molecular self-assembly is a promising approach to build robust and ordered interfaces.[7] Much of the work in the area of molecular self-assembly has been devoted to building long chain alkane thin films, and it has been demonstrated that such supramolecular structures are tightly packed due to strong interchain van der Waals forces of attraction.[7] We were intrigued by the possibility of creating similar organic/organometallic interfaces by using PPh_2-terminated long alkane chain chromophores which can subsequently bind organometallic centers. We report herein the synthesis of two-dimensional thin film assemblies of functionalized long alkane chain donor ligands, $HO-(CH_2)_n-PPh_2$ ($n = 10-12$), on inorganic oxide surfaces using our new acid−base hydrolytic approach.[4,8] These donor thin films were then used to introduce Rh(I) metal centers by bridge-splitting reactions. The metal centers were also bound to the long alkane chain donor molecules prior to their self-assembly on flat surfaces to evaluate packing in organometallic assemblies. The characterization of the newly formed organic and organometallic phases was carried out using solid-state NMR, contact angle goniometry, ellipsometry, FT-IR-ATR, and XPS. The self-assembled organometallic thin films, $[Si]-O-(CH_2)_n-PPh_2[RhCl(1,5\text{-}C_8H_{12})]$, were found to be highly active in catalyzing hydrogenation of diphenylacetylene with a product distribution different than that from the catalyst in solution. The Rh(I) complex in solution decomposes during the catalytic process, while the self-assembled

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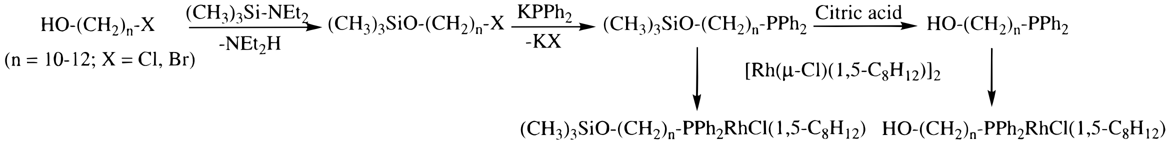
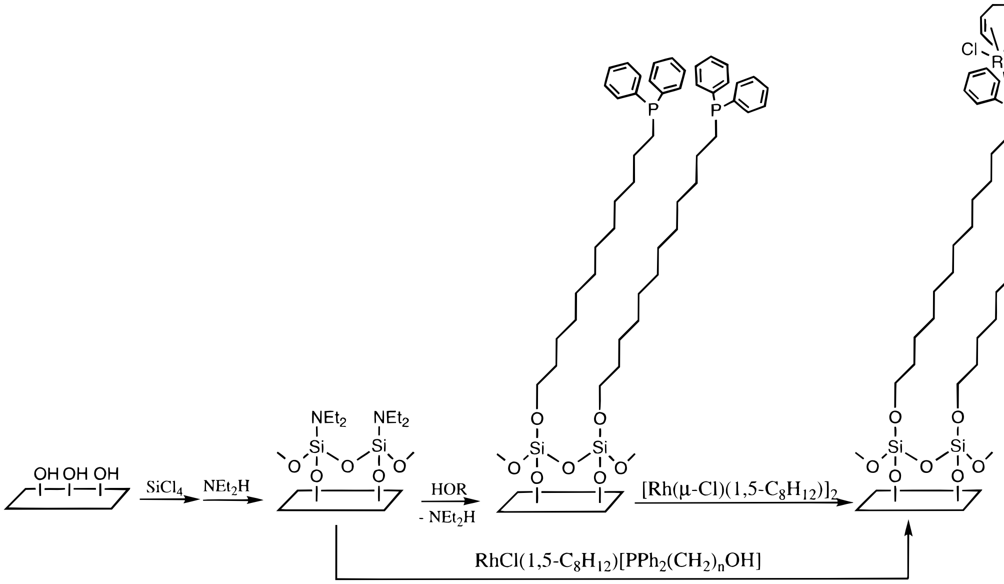
Scheme 1



Scheme 2



organometallic catalyst is stable and can be recycled with good reproducibility.

Results and Discussion

Solution Chemistry. The required long alkane chain donor molecules HO$-$(CH$_2$)$_n-$PPh$_2$ (n = 10$-$12) were easily prepared in very good yields from the commercially available alcohols, HO$-$(CH$_2$)$_n-$X (X = Cl, Br), by first protecting the alcohol group with a Me$_3$Si group and reacting the resulting Me$_3$SiO$-$(CH$_2$)$_n-$X compound with KPPh$_2$, followed by desilylation with citric acid (Scheme 1). The solution analogues of the surface-bound organometallic complexes were prepared via bridge-splitting reactions[9] of μ-chloro-(1,5-cyclooctadiene)rhodium(I) dimer with 2 equiv of Me$_3$SiO$-$(CH$_2$)$_n-$PPh$_2$ or HO$-$(CH$_2$)$_n-$PPh$_2$. The identity and purity of all the new compounds were established by routine characterization methods, including elemental analysis.

Surface Chemistry and Characterization. The construction of thin film assemblies is based on the hydrolysis of inorganic oxide surface anchored [Si]$-$NEt$_2$ groups with the terminal hydroxyl groups of HO$-$(CH$_2$)$_n-$PPh$_2$.[4,8] Glass, quartz, single-crystal Si(100) substrates and ground glass silica were cleaned[10] by (i) washings with a soap solution and sonication for 0.5 h, (ii) soaking in a mixture of 70% H$_2$SO$_4$ and 30% H$_2$O$_2$ (the piranha solution) at 100 °C for 1 h (**Caution**: The piranha solution is highly corrosive and explosive. Care should be taken while using this mixture!), (iii) repeated washings with deionized water at room temperature, and (iv) finally drying over a stream of nitrogen. The surfaces of inorganic oxide substrates contain Si$-$OH groups with a packing density of 4.70 OH/100 Å^{2}[11] and offer extensive chemistry. The surface functionalization was achieved by placing the clean substrates in toluene solutions of (i) SiCl$_4$, (ii) dry NEt$_2$H, and finally (iii) the appropriate donor ligand. An idealized functionalized surface is shown in Scheme 2. The latter donor thin films were then used to introduce Rh(I) centers by bridge-splitting reactions of μ-chloro-(1,5-cyclooctadiene)rhodium(I) dimer, [Rh(μ-Cl)(C$_8$H$_{12}$)]$_2$, as described above for the solution analogues. In a similar procedure, surface-functionalized [Si]$-$NEt$_2$ moieties were reacted with HO$-$(CH$_2$)$_n-$PPh$_2$[RhCl(1,5-C$_8$H$_{12}$)] to prepare thin films directly from the phosphine-bound Rh(I) metal centers.

Solid-state ^{31}P{^{1}H} NMR spectroscopy is a useful technique in the surface characterization of functionalized ground glass silica.[5] The results of cross-polarized ^{31}P{^{1}H} NMR spectral measurements of {Si}-O$-$(CH$_2$)$_n$-PPh$_2$ ({Si} = ground glass silica; n = 10$-$12) and their Rh(I) complexes {Si}-O$-$(CH$_2$)$_n$PPh$_2$RhCl(1,5-C$_8$H$_{12}$) are given in Table 1. The high-resolution solution ^{31}P{^{1}H} NMR data for Me$_3$Si$-$O$-$(CH$_2$)$_n$PPh$_2$, HO$-$(CH$_2$)$_n$PPh$_2$, Me$_3$SiO$-$(CH$_2$)$_n$PPh$_2$RhCl(1,5-C$_8$H$_{12}$), and HO$-$(CH$_2$)$_n$-PPh$_2$RhCl(1,5-C$_8$H$_{12}$), are also included for comparison. The thin films of {Si}$-$O$-$(CH$_2$)$_n$PPh$_2$ showed a single resonance each at ca. $-$16 ppm, which is very close in value to the high-resolution ^{31}P{^{1}H} NMR of their solution analogues. Similarly, the peak positions in the CP/MAS ^{31}P{^{1}H} NMR spectra of thin films of [Si]$-$O$-$

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Table 1. High-Resolution Solution (C_6D_6) and Solid-State Cross-Polarized/Magic Angle Spinning (CP/MAS) $^{31}P\{^1H\}$ NMR Data for Long Chain Phosphine Donor Ligands and Their Rh(I) Complexes

compound	$^{31}P\{^1H\}$ δ (ppm)	thin film (silica)	$^{31}P\{^1H\}$ CP/MAS δ (ppm)
$(CH_3)_3SiO(CH_2)_{10}PPh_2$	−15.8	$\{Si\}-O(CH_2)_{10}PPh_2$	−15.9
$HO(CH_2)_{10}PPh_2$	−15.7		
$(CH_3)_3SiO(CH_2)_{11}PPh_2$	−15.8	$\{Si\}-O(CH_2)_{11}PPh_2$	−16.3
$HO(CH_2)_{11}PPh_2$	−15.9		
$(CH_3)_3SiO(CH_2)_{12}PPh_2$	−15.7	$\{Si\}-O(CH_2)_{12}PPh_2$	−16.2
$HO(CH_2)_{12}PPh_2$	−15.7		
$(CH_3)_3SiO(CH_2)_{10}PPh_2-RhCl(1,5\text{-}C_8H_{12})$	27.3 (d)	$\{Si\}-O(CH_2)_{10}PPh_2-RhCl(1,5\text{-}C_8H_{12})$	27.7 (br)
$HO(CH_2)_{10}PPh_2-RhCl(1,5\text{-}C_8H_{12})$	27.2 (d)	$\{Si\}-O(CH_2)_{10}PPh_2-RhCl(1,5\text{-}C_8H_{12})$[a]	27.4 (br)
$(CH_3)_3SiO(CH_2)_{11}PPh_2-RhCl(1,5\text{-}C_8H_{12})$	27.3 (d)	$\{Si\}-O(CH_2)_{11}PPh_2-RhCl(1,5\text{-}C_8H_{12})$	28.0 (br)
$HO(CH_2)_{11}PPh_2-RhCl(1,5\text{-}C_8H_{12})$	27.3 (d)	$\{Si\}-O(CH_2)_{11}PPh_2-RhCl(1,5\text{-}C_8H_{12})$[a]	27.4 (br)
$(CH_3)_3SiO(CH_2)_{12}PPh_2-RhCl(1,5\text{-}C_8H_{12})$	27.1 (d)	$\{Si\}-O(CH_2)_{12}PPh_2-RhCl(1,5\text{-}C_8H_{12})$	29.5 (br)
$HO(CH_2)_{12}PPh_2-RhCl(1,5\text{-}C_8H_{12})$	27.4 (d)	$\{Si\}-O(CH_2)_{12}PPh_2-RhCl(1,5\text{-}C_8H_{12})$[a]	28.8 (br)

[a] Prepared from surface anchored $[Si]-NEt_2$ and $RhCl(1,5\text{-}C_8H_{12})[PPh_2(CH_2)_nOH]$ (Procedure B).

Table 2. FT-IR-ATR and Ellipsometric Data for Thin Films of Long Alkane Chain Phosphines and Their Rh(I) Complexes on Single Crystal Silicon Wafers

	FT-IR-ATR		thickness (Å)	
thin film	ν_s (CH_2), cm^{-1}	ν_a (CH_2), cm^{-1}	ellipsometric	theoretical
$[Si]-O-(CH_2)_{10}-PPh_2$	2851.0	2923.0	26	28
$[Si]-O-(CH_2)_{11}-PPh_2$	2850.7	2920.8	28	30
$[Si]-O-(CH_2)_{12}-PPh_2$	2850.2	2922.0	32	31
$[Si]-O-(CH_2)_{10}-PPh_2-RhCl(1,5\text{-}COD)$	2850.0	2923.0	35	34
$[Si]-O-(CH_2)_{11}-PPh_2-RhCl(1,5\text{-}COD)$	2851.0	2921.0	38	36
$[Si]-O-(CH_2)_{12}-PPh_2-RhCl(1,5\text{-}COD)$	2851.5	2922.4	40	37
$[Si]-O-(CH_2)_{10}-PPh_2-RhCl(1,5\text{-}COD)$[a]	2852.3	2925.4	33	34
$[Si]-O-(CH_2)_{11}-PPh_2-RhCl(1,5\text{-}COD)$[a]	2852.9	2925.9	35	36
$[Si]-O-(CH_2)_{12}-PPh_2-RhCl(1,5\text{-}COD)$[a]	2852.7	2925.3	37	38

[a] Prepared from surface anchored $[Si]-NEt_2$ and $RhCl(1,5\text{-}C_8H_{12})[PPh_2(CH_2)_nOH]$ (Procedure B).

$(CH_2)_nPPh_2RhCl(1,5\text{-}C_8H_{12})$ are identical to those for their solution analogues, except for the broadening of the peaks on the surface. No peaks for any residual unbound phosphine were observed in the CP/MAS $^{31}P\{^1H\}$ NMR spectra of the organometallic thin films. These results suggest that the acid−base hydrolytic route is highly effective in the construction of thin films of donor ligands and their subsequent high-yield bridge-splitting reaction with the Rh(I) dimer.

A detailed characterization of the newly formed thin film assemblies was achieved by a combination of techniques such as contact angle goniometry, FT-IR both in the transmission and attenuated total reflection (ATR) modes, ellipsometry, and X-ray photoelectron spectroscopy. Contact angle goniometry has been widely used to study the wetting characteristics of the molecularly self-assembled thin films and provides a rough estimate of the packing behavior of the films.[7] Water and hexadecane are two commonly used liquids for such measurements. The thin films of $HO-(CH_2)_n-PPh_2$ ($n = 10-12$) displayed contact angles of ~90° with water and ~20° with hexadecane. These values are typical of close-packed thin films with phenyl groups exposed to the surface.[12]

Ellipsometry is routinely used to measure thicknesses of the newly formed self-assembled thin films and can help establish surface characteristics of molecules at interfaces. For calculating the thickness, one compares data from the same substrate before and after functionalization and makes an assumption for the refractive index of the organic phase. For long alkane chain hydrocarbon interfaces, a typical value of 1.45−1.50 is usually employed.[7] We used a value of 1.46 for our calculations, and the ellipsometric data for the thin films on single-crystal silicon of $HO-(CH_2)_n-PPh_2$ ($n = 10-12$) and their Rh(I) complexes are shown in Table 2. The ellipsometric thicknesses for the thin films are well in accord with the theoretical model thicknesses and suggest that the self-assembled thin films are one layer thick.

X-ray photoelectron spectroscopy is a useful technique to evaluate the surface composition of the covalently anchored species. We used this technique for analytical evaluation of our self-assembled thin films on silicon wafers. The binding energies for the surface bound donor ligands and their Rh(I) complexes are presented in Tables 3 and 4. The binding energies for the complexes that are the solution analogues to the surface species are also given in Tables 3 and 4. The data confirms the composition of the thin film structures, and the binding energies for the surface bound species are consistent with those of their analogues in the solid state. There is a slight shift in the $Si_{2p1/2}$ binding energy on the surface as compared to its solid-state analogues, and this shift is consistent with the expected value for SiO_2. Charging effects of the glass may be responsible for the increase in binding energies for the surface-immobilized species. In addition, coordination of the ligands to the metal may also result in an increase in binding energies.

Fourier transform infrared spectroscopy (FT-IR) is a commonly used technique to characterize long alkane chain self-organized thin films.[7] In particular, FT-IR in the attenuated total reflection mode (ATR) is extremely

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Table 3. Binding Energies (eV) for Surface Bound Long Chain Phosphorus Donor Ligands and Rh(I) Complexes on Single Crystal Si Wafers

	Si		O		C		P		Cl		Rh	
	$2p_{1/2}$	fwhm	$1s_{1/2}$	fwhm	$1s_{1/2}$	fwhm	$2s_{1/2}$	fwhm	$2s_{1/2}$	fwhm	$3d_{5/2}$	fwhm
Thin Film												
$[Si]-O(CH_2)_{10}PPh_2$	102	8.00	533	9.00	285	6.00	189	8.00				
$[Si]-O(CH_2)_{11}PPh_2$	103	8.00	533	9.00	286	7.00	190	8.00				
$[Si]-O(CH_2)_{12}PPh_2$	103	8.00	533	8.00	286	7.00	189	9.00				
$[Si]-O(CH_2)_{10}PPh_2RhCl(1,5\text{-}C_8H_{12})$	103	9.00	535	7.00	286	7.00	197	8.00	269	7.00	312	9.00
$[Si]-O(CH_2)_{11}PPh_2RhCl(1,5\text{-}C_8H_{12})$	104	8.00	534	7.00	285	6.00	196	8.00	269	7.00	311	10.00
$[Si]-O(CH_2)_{12}PPh_2RhCl(1,5\text{-}C_8H_{12})$	102	8.00	534	7.00	287	6.00	196	8.00	271	8.00	311	11.00
Complex												
$Me_3Si-O(CH_2)_{10}PPh_2RhCl(1,5\text{-}C_8H_{12})$	99	3.00	532	2.00	286	3.00	192	6.00	270	4.00	311	8.00
$Me_3Si-O(CH_2)_{11}PPh_2RhCl(1,5\text{-}C_8H_{12})$	98	3.00	532	2.00	285	2.00	194	5.00	272	4.00	312	7.00
$Me_3Si-O(CH_2)_{10}PPh_2RhCl(1,5\text{-}C_8H_{12})$	98	3.00	532	3.00	285	2.50	193	5.00	270	4.50	309	8.00

Table 4. Binding Energies (eV) for Surface Bound and Solution Analogs of Long Chain Anchored Phosphorus Donor Ligands and Rh(I) Complexes on Single Crystal Si Wafers

	Si		O		C		P		Cl		Rh	
	$2p_{1/2}$	fwhm	$1s_{1/2}$	fwhm	$1s_{1/2}$	fwhm	$2s_{1/2}$	fwhm	$2s_{1/2}$	fwhm	$3d_{5/2}$	fwhm
Complex												
$HO-(CH_2)_{10}PPh_2Rh-COD(Cl)$			535	2.50	287	2.00	192	5.00	271	4.00	310	7.50
$HO-(CH_2)_{11}PPh_2Rh-COD(Cl)$			532	3.00	285	3.00	194	6.00	270	6.50	309	8.00
$HO-(CH_2)_{12}PPh_2Rh-COD(Cl)$			534	3.00	285	3.00	193	5.00	270	6.00	309	9.00
Thin Film[a]												
$[Si]-O-(CH_2)_{10}PPh_2Rh-COD(Cl)$	105	9.00	535	6.50	287	5.00	197	8.00	270	7.00	311	9.50
$[Si--O-(CH_2)_{11}PPh_2Rh-COD(Cl)$	104	8.00	534	6.00	285	6.00	199	9.00	270	7.00	312	10.00
$[Si]-O-(CH_2)_{12}PPh_2Rh-COD(Cl)$	104	8.00	534	6.00	285	6.00	198	9.00	271	8.00	312	10.00

[a] Prepared from surface anchored $[Si]-NEt_2$ and $HO-(CH_2)_nPPh_2Rh-COD(Cl)$ ($n = 10-12$).

valuable in evaluating uniformity and packing density of such thin film assemblies. For example, in an FT-IR-ATR spectrum of highly ordered long chain hydrocarbons, the symmetric $\nu_s(CH_2)$ and asymmetric $\nu_a(CH_2)$ modes are typically observed at 2850 and 2920 cm^{-1}, respectively.[7b] These values are characteristic of a densely packed hydrocarbon surface environment.[7] Higher frequencies of the peak positions for $\nu_s(CH_2)$ and $\nu_a(CH_2)$ at 2856 and 2928 cm^{-1} are indicative of a disordered and liquidlike chain structure in the self-assembled thin films. The thin films on single-crystal silicon wafers of $HO-(CH_2)_n-PPh_2$ ($n = 10-12$) showed $\nu_s(CH_2)$ and $\nu_a(CH_2)$ peaks at ~2851 and 2922 cm^{-1} (Table 2). The data suggests that these thin film assemblies are relatively tightly packed. Upon binding the Rh(I) complex to these monolayers (Scheme 2), no significant change in the $\nu_s(CH_2)$ and $\nu_a(CH_2)$ frequencies (~2851 and 2922 cm^{-1}) was observed (Table 2). The $\nu_s(CH_2)$ (~2853 cm^{-1}) and $\nu_a(CH_2)$ (~2925 cm^{-1}) peak positions for the thin films prepared from $HO-(CH_2)_n-PPh_2[RhCl(1,5\text{-}C_8H_{12})]$ and surface bound $[Si]-NEt_2$ moieties (Scheme 2, Table 2) were found to be at higher frequencies than those prepared from $HO-(CH_2)_nPPh_2$. These results suggest a disorder in the alkane chains in the thin films prepared from long alkane phosphines bound to Rh(I) centers, which can be explained by considering the steric effects of the ligands around the metal center that might push the alkane chains apart.

Catalysis. Rh(I) complexes are well-known to catalyze hydrogenation of a variety of unsaturated hydrocarbons, including alkynes.[13] We chose to investigate catalytic hydrogenation of tolan (diphenylacetylene) using $Me_3SiO-(CH_2)_n-PPh_2RhCl(1,5\text{-}C_8H_{12})$ in solution and molecularly self-assembled on glass, $[Si]-O-(CH_2)_n-PPh_2RhCl(1,5\text{-}C_8H_{12})$. This catalytic reaction can yield three products, *cis*-stilbene, *trans*-stilbene, and bibenzyl in different ratios. The results of the hydrogenation under 5−20 bar H_2 pressure and using Rh(I) catalysts in the homogeneous and heterogenized homogeneous phases are shown in Table 5.

Catalysis in Solution. The compounds $Me_3SiO-(CH_2)_n-PPh_2RhCl(1,5\text{-}C_8H_{12})$ ($n = 10-12$) were found to be active catalysts for the hydrogenation of tolan. The number of CH_2 groups in the alkane chains did not have much effect on the product distribution. At 5 bar of H_2 pressure, ~60% *cis*-stilbene, 35−37% *trans*-stilbene, and 4% bibenzyl were obtained (Table 5). As the hydrogen pressure was increased to 10 bar, almost all of *cis*-stilbene was converted to bibenzyl: 3% *cis*-stilbene, 33−39% *trans*-stilbene, and 60−64% bibenzyl. Upon further increasing the H_2 pressure to 20 bar, the amount of bibenzyl increased to 72−75%, and 1% *cis*-stilbene and 24−27% *trans*-stilbene were obtained.

Catalysis Using Self-Assembled Rh(I) Thin Films on Glass. The thin films of Rh(I) complexes on flat glass, $[Si]-O-(CH_2)_n-PPh_2RhCl(1,5\text{-}C_8H_{12})$ ($n = 10-12$), were also found to be highly active in the catalytic hydrogenation of tolan (Table 5). At 5 bar of H_2 pressure, the percent product distribution was found to be ~85% *cis*-stilbene, 5% *trans*-stilbene, and 10% bibenzyl. The latter product distribution is different than that in solution and suggests that there is strong preference for *cis*-stilbene when a thin film of the catalyst is employed under similar conditions. When the H_2 pressure was increased to 10 bar, equal percent amounts of *cis*-stilbene and bibenzyl (~40%) were formed, and the amount of *trans*-stilbene increased to 17−20%. Finally, when the pressure was increased to 20 bar, there was almost an exclusive formation of bibenzyl (up to 100%) while the reaction in solution under similar conditions gave ~75% bibenzyl and ~25% *trans*-stilbene (Table 5).

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Table 5. Hydrogenation of Diphenylacetylene (30 min, 25 °C) Using Surface Bound Rh(I) Complexes on Glass and Their Solution Analogs

complex/thin film	H_2 pressure (bar)	*cis*-stilbene (%)	*trans*-stilbene (%)	bibenzyl (%)
$(CH_3)_3Si-O-(CH_2)_{10}-PPh_2RhCl(1,5\text{-}COD)$	5	61	35	4
	10	3	38	59
	20	1	24	75
$(CH_3)_3Si-O-(CH_2)_{11}-PPh_2RhCl(1,5\text{-}COD)$	5	59	37	4
	10	3	33	64
	20	1	27	72
$(CH_3)_3Si-O-(CH_2)_{12}-PPh_2RhCl(1,5\text{-}COD)$	5	60	37	4
	10	-	40	60
	20	-	25	75
$[Si]-O-(CH_2)_{10}-PPh_2RhCl(1,5\text{-}COD)$	5	86	5	9
	10	37	17	46
	20	-	5	95
$[Si]-O-(CH_2)_{11}-PPh_2RhCl(1,5\text{-}COD)$	5	84	6	10
	10	40	16	44
	20	-	1	99
$[Si]\text{-}O-(CH_2)_{12}-PPh_2RhCl(1,5\text{-}COD)$	5	83	5	12
	10	37	21	41
	20	-	-	100

Table 6. Recycling of the Catalysts (30 min, room temperature)

complex/thin film on a glass slide	H_2 pressure (bar)	*cis*-stilbene (%)	*trans*-stilbene (%)	bibenzyl (%)
$(CH_3)_3Si-O-(CH_2)_{10}-PPh_2RhCl(1,5\text{-}COD)$ first run, decomposition	10	3	38	59
$[Si]-O-(CH_2)_{10}-PPh_2RhCl(1,5\text{-}COD)$ first run	10	37	17	46
$[Si]-O-(CH_2)_{10}-PPh_2RhCl(1,5\text{-}COD)$ recycle[a]	10	34	12	43

[a] Based on GC−MS results, overall ∼90% conversion to products and 10% diphenylacetylene was recovered unreacted.

Stability of the Catalyst and Reproducibility. The Rh(I) complex, $(CH_3)_3Si-O-(CH_2)_n-PPh_2RhCl(1,5\text{-}C_8H_{12})$, decomposed during catalytic hydrogenation of tolan in solution. However, upon covalent anchoring on flat surfaces, no decomposition of the catalyst was observed. A thin film of $[Si]-O-(CH_2)_{10}-PPh_2RhCl(1,5\text{-}C_8H_{12})$ on glass, after one cycle of hydrogenation for 30 min at 10 bar H_2 pressure, was removed and washed with toluene. It was then reintroduced into the reactor, a fresh batch of diphenylacetylene was added, and hydrogenation was repeated with 10 bar of H_2 pressure for 30 min at room temperature (Table 6). The catalyst was found to be still active and produced a similar product distribution as in the first run, except for the lower conversion (about 10% of unreacted diphenylacetylene was recovered from the reaction mixture).

The issue of leaching of Rh from the surface during tolan hydrogenation was addressed by undertaking a quantitative evaluation of the thin films of $[Si]-O-(CH_2)_{12}PPh_2Rh(1,5\text{-}C_8H_{12})Cl$ before and after catalysis using XPS. The Rh $3d_{5/2}$, Cl $2s_{1/2}$, $P2s_{1/2}$, and $C1s_{1/2}$ peaks showed a decrease in atomic concentration by approximately 5%, 22%, 17%, and 1.5%, respectively. The O 1s and Si 2p atomic concentrations showed an increase of 10%. In addition to the metal complex leaching from the surface, we should also take into account varying degrees of radiation damage. The shift in Rh and P peak positions to higher binding energies by approximately 1 eV also suggests that the elements may be in a different environment upon the onset of the catalytic cycle. In the hydrogenation of tolan, the cyclooctadiene ligand dissociates to form an active catalyst. The latter leads to the modification of the electronics at the metal center.

Conclusions

Using simple acid−base hydrolytic chemistry, long hydrocarbon chains terminated with PPh_2 groups have been self-assembled on glass, quartz, and single-crystal Si and subsequently used to covalently anchor Rh(I) complexes. Application of a combination of numerous surface characterization techniques to flat surfaces indicates that these thin films are relatively tightly packed. The organometallic thin films of Rh(I), $[Si]-O-(CH_2)_nPPh_2RhCl(1,5\text{-}C_8H_{12})$ ($n = 10-12$), on glass are highly active in catalytic hydrogenation of tolan (diphenylacetylene). The catalyst is stable on the surface and can be recycled while it decomposes in a similar reaction in solution. The role of molecularly self-assembled organometallic interfaces in tailoring catalytic activity and selectivity is currently being further explored by using phosphines containing longer alkane chains and variable headgroups, $[Si]-O-(CH_2)_nPR_2\text{-}MLn$ ($n = 18-20$; R = CH_3, C_2H_5).

Experimental Section

Materials and Measurements. All manipulations were carried out under a nitrogen atmosphere using either standard Schlenk line techniques or in an Innovative Technology (Braun) Labmaster MB-150-M drybox. Thin film deposition was performed in a self-assembly apparatus. Toluene, benzene, and THF were stored under nitrogen after being distilled over sodium. Diethylamine was dried and distilled over KOH and degassed prior to use. Methanol was distilled over Mg/iodine before use. Unless otherwise specified, all other reagents were obtained from the usual commercial suppliers and used as received. NMR spectra were measured on a JEOL 270 MHz spectrometer at ambient temperature. All NMR samples were prepared under a nitrogen atmosphere in C_6D_6. Chemical shifts (ppm) reported are relative to tetramethylsilane as an internal standard for ^1H NMR spectra and to H_3PO_4 for $^{31}P\{^1H\}$ NMR spectra. Coupling constants (J) are given in hertz. Mass spectra were obtained using a low-resolution KRATOS MS25RSA spectrometer with xenon as the ionizing gas or on a Hewlett-Packard 5973 mass spectrometer. MALDI-TOF mass spectra were obtained on a Kratos Kompact Maldi 3 v.4.0.0 spectrometer using LiBr/didronel or LiBr/gentisic acid as the matrix. Infrared spectra were recorded on a Bruker IFS-48 Fourier transform infrared spectrometer using a standard resolution of 4 cm^{-1} for transmission. Elemental analyses were performed by the Guelph Chemical Laboratory, Guelph, Ontario, Canada. HO$-$(CH$_2$)$_n$$-$X ($n$ = 10$-$12; X = Cl, Br) and [Rh(μ-Cl)(1,5-C$_8$H$_{12}$)]$_2$ were purchased from Aldrich and Pressure Chemicals and used as received.

Static contact angles were measured with a Rame-Hart NRL100 goniometer using deionized water and hexadecane. At least 5 drops were used for the reported contact angle readings. A Gaertner ellipsometer was used for thickness measurements with He$-$Ne laser (632.8 nm) light incident at 70° on the sample and reflected into the analyzer. A refractive index of 1.458 was assumed for thickness calculations. A Graseby Specac variable angle ATR in conjunction with a Bruker IFS-48 Fourier transform infrared spectrometer was used for attenuated total reflectance spectroscopy. The thin films were studied using FT-IR in the transmission (resolution of 4 cm^{-1}) and ATR modes (resolution of 2 cm^{-1}), and in the latter case, a KRS crystal was positioned between the reflective sides of $\langle 100 \rangle$ Si wafers. A miniature pressure device was employed in order to maximize optical contact. A critical incidence angle of $\theta = 45°$ was used, affording a maximum signal of 6000 counts/s. X-ray photoelectron spectra were measured either on a INRS 220i XL spectrometer (Varenne, Quebec, Canada) or on a VG Escalab MKII instrument, (École Polytechnique, Université de Montreal). Binding energies, peak intensities, and peak widths at half-height were recorded using Mg Kα radiation to produce the photoemission of electrons from the core levels of the surface atoms. About 60 Å of depth was probed for a detector perpendicular to the surface. The analyzed surface was 2 × 3 mm. All peak positions were corrected for carbon at 285.0 eV in binding energy to adjust for charging effects. The power of the source was 300 W and at a pressure of 1×10^{-9} Torr. Lines were measured for Si 2p$_{1/2}$, O 1s, C 1s, P 2s, Cl 2s, and Rh 3d$_{5/2}$. The solid-state ^{31}P{^{1}H} NMR spectra were recorded on a Chemagnetics CMX-300 MHz spectrometer using ammonium phosphate as an internal standard and operating at 121.279 MHz, with high-power decoupling, using a recycle time of 6 s and a contact time of 2 ms. Different spinning rates, ranging from 2.5 to 4.0 kHz, were used to identify the isotropic peaks.

$(CH_3)_3SiO(CH_2)_{10}Cl$ (1). A solution of 1-chloro-10-decanol (5.4 mL, 0.0267 mol) in 5 mL of benzene was added to *N,N′*-diethyltrimethylsilylamine (5.1 mL, 0.0267 mol). The cloudy mixture was allowed to stir at 55 °C for 14 h. Benzene and diethylamine were distilled off, and the pale yellow liquid was filtered through glass wool to yield 7.28 mL, 98%. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 0.11 (9H, s, CH_3), 0.97$-$1.56 (16H, m, $-$(CH_2)$_8$$-$), 3.13 (2H, t, J_{H-H} = 6.9 Hz, CH_2Cl), 3.54 (2H, t, J_{H-H} = 6.3 Hz, CH_2O) ppm. CI-MS: *m/z* 265. Anal. Calcd for C$_{13}$H$_{29}$OSiCl (264.91): C, 58.94; H, 11.03. Found: C, 58.90; H, 11.30.

$(CH_3)_3SiO(CH_2)_{10}PPh_2$ (2). Potassium diphenylphosphide (53.4 mL, 0.0267 mol) was added dropwise to a solution of (CH$_3$)$_3$SiO(CH$_2$)$_{10}$Cl (7 g, 0.0267 mol) in 15 mL of THF at 0 °C. The orange solution was allowed to stir overnight. KCl was filtered off and THF was removed under vacuum, affording a viscous orange/brown liquid. The product was extracted in benzene and filtered to remove any residual KCl. Benzene was distilled off to afford a pale yellow liquid; yield, 10.8 g, 99%. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 0.13 (9H, s, CH_3), 1.13$-$1.62 (16H, m, $-$(CH_2)$_8$$-$), 1.98 (2H, br t, J_{H-H} = 7.7 Hz, CH_2P), 3.55 (2H, t, J_{H-H} = 6.3 Hz, CH_2O), 7.08, 7.47 (10H, m, C$_6$$H_5$) ppm. ^{31}P{^{1}H} NMR (109 MHz, C$_6$D$_6$): δ $-$15.75 (s) ppm. FT-IR (neat): ν_s (CH$_2$) 2853.4, ν_a (CH$_2$) 2926.3 cm^{-1}. CI-MS: *m/z* 415. Anal. Calcd for C$_{25}$H$_{39}$OSiP (414.64): C, 72.42; H, 9.48. Found: C, 72.15; H, 9.23.

$HO(CH_2)_{10}PPh_2$ (3). Anhydrous citric acid (5.13 g, 0.0267 mol) was dissolved in 17 mL of methanol and the solution was transferred via syringe into a Schlenk flask containing (CH$_3$)$_3$SiO(CH$_2$)$_{10}$PPh$_2$ (11 g, 0.0267 mol), resulting in a cloudy mixture. The solvent was removed under vacuum and 15 mL of benzene was added to extract the product. The solution was filtered several times through glass wool until a clear filtrate was observed. Benzene and any residual methanol were distilled off, affording a pale yellow, viscous liquid; yield, 6.8 g, 75%. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 1.11$-$1.55 (16H, m, $-$(CH_2)$_8$$-$), 1.99 (2H, t, J_{H-H} = 7.9 Hz, CH_2P), 3.46 (2H, br t, J_{H-H} = 6.6 Hz, CH_2O), 7.09, 7.47 (10H, m, C$_6$$H_5$) ppm. ^{31}P{^{1}H} NMR (109 MHz, C$_6$D$_6$): δ $-$15.73 (s) ppm. FT-IR (neat): ν_s (CH$_2$) 2852.4 ν_a, (CH$_2$) 2925.5 cm^{-1}. EI-MS: *m/z* 342. Anal. Calcd for C$_{22}$H$_{31}$OP (342.46): C, 77.15; H, 9.12. Found: C, 76.90; H, 8.80.

$(CH_3)_3SiO(CH_2)_{11}Br$ (4). *N,N′*-Diethyltrimethylsilylamine (3.02 mL, 0.016 mol) was added to a 15 mL benzene solution containing 4.01 g of 1-bromo-11-undecanol (0.016 mol). The mixture was stirred at 40 °C for 15 h, after which benzene and diethylamine were distilled off, and the red liquid was filtered through glass wool; yield, 5 g, 97%. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 0.09 (9H, s, CH_3), 0.99$-$1.53 (18H, m, $-$(CH_2)$_9$$-$), 3.01 (2H, t, J_{H-H} = 6.9 Hz, CH_2Br), 3.50 (2H, t, J_{H-H} = 6.3 Hz, CH_2O) ppm. CI-MS: *m/z* 323. Anal. Calcd for C$_{14}$H$_{30}$OSiBr (323.39): C, 51.99; H, 9.35. Found: C, 54.80; H, 10.20.

$(CH_3)_3SiO(CH_2)_{11}PPh_2$ (5). A 2.61 g portion of (CH$_3$)$_3$SiO(CH$_2$)$_{11}$Br (8.09 mmol) in 10 mL of THF was cooled to 0 °C. KPPh$_2$ (16.17 mL, 8.09 mmol) was added dropwise to the above solution. The reaction was slowly brought to room temperature and left to stir for 18 h. The mixture was filtered by suction inside a glovebox, and the solvent evaporated was under vacuum to afford an orange gel. The compound was extracted in benzene and the solvent distilled off to result in a yellow oil; yield, 3.20 g, 92%. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 0.13 (9H, s, CH_3), 1.02$-$1.55 (18H, m, $-$(CH_2)$_9$$-$), 1.98 (2H, br t, J_{H-H} = 7.2 Hz, CH_2P), 3.55 (2H, t, J_{H-H} = 6.3 Hz, CH_2O), 7.08, 7.47 (10H, m, C$_6$$H_5$) ppm. ^{31}P{^{1}H} NMR (109 MHz, C$_6$D$_6$): δ $-$15.83 (s) ppm. FT-IR (neat): ν_s (CH$_2$) 2853.4, ν_a (CH$_2$) 2925.5 cm^{-1}. EI-MS: *m/z* 428. Anal. Calcd for C$_{26}$H$_{41}$OSiP (428.67): C, 72.85; H, 9.64. Found: C, 73.13; H, 9.52.

$HO(CH_2)_{11}PPh_2$ (6). A solution of anhydrous citric acid (1.26 g, 6.55 mmol) in 3 mL of methanol was syringed into a flask containing 2.81 g of (CH$_3$)$_3$SiO(CH$_2$)$_{11}$PPh$_2$ (6.55 mmol), resulting in a cloudy mixture which was allowed to stir at room temperature for 15 min. The solvent was removed in vacuo and the product was extracted into benzene and filtered several times through glass wool. The benzene was distilled off, resulting in a clear and colorless oil; yield, 2.25 g, 96.3%. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 1.19$-$1.54 (18H, m, $-$(CH_2)$_9$$-$), 1.98 (2H, br t, J_{H-H} = 7.3 Hz, CH_2P), 3.57 (2H, t, J_{H-H} = 6.6 Hz, CH_2O), 7.08, 7.44 (10H, m, C$_6$$H_5$) ppm. ^{31}P{^{1}H} NMR (109 MHz, C$_6$D$_6$): δ $-$15.85 (s) ppm. FT-IR (neat): ν_s (CH$_2$) 2851.4, ν_a (CH$_2$) 2924 cm^{-1}. EI-MS: *m/z* 356. Anal. Calcd for C$_{23}$H$_{33}$OP (356.49): C, 77.49; H, 9.33. Found: C, 77.14; H, 9.04.

$(CH_3)_3SiO(CH_2)_{12}Br$ (7). A 10 g sample of 1-bromo-12-dodecanol (0.038 mol) was added to a 20 mL benzene solution containing *N,N′*-diethyltrimethylsilylamine (3.02 mL, 0.016 mol). The mixture was stirred at 30 °C for 20 h, after which benzene and diethylamine were distilled off and the yellow liquid was filtered through glass wool; yield, 11.6 g, 91%. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 0.13 (9H, s, CH_3), 1.09$-$1.59 (20H, m, $-$(CH_2)$_{10}$$-$), 2.98 (2H, t, J_{H-H} = 6.9 Hz, CH_2Br), 3.55 (2H, t, J_{H-H} = 6.3 Hz, CH_2O) ppm. CI-MS: *m/z* 337. Anal. Calcd for C$_{15}$H$_{32}$OSiBr (336.41): C, 53.56; H, 9.59. Found: C, 53.72; H, 9.47.

$(CH_3)_3SiO(CH_2)_{12}PPh_2$ (8). A 7 g sample of (CH$_3$)$_3$SiO(CH$_2$)$_{12}$Br (0.021 mol) in 15 mL of THF was cooled to 0 °C, followed by the dropwise addition of KPPh$_2$ (41.54 mL, 0.021 mol). The reaction was slowly brought to room temperature and left to stir for 30 h. The solvent was evaporated under vacuum to afford an orange/red gel. The compound was extracted in benzene and filtered through glass wool, and the solvent was distilled off to result in an orange oil; yield, 8.6 g, 93.5%. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 0.11 (9H, s, CH_3), 1.10$-$1.57 (20H, m, $-$(CH_2)$_{10}$$-$), 1.98 (2H, br t, J_{H-H} = 7.3 Hz, CH_2P), 3.55 (2H, t, J_{H-H} = 6.3 Hz, CH_2O), 7.06, 7.44 (10H, m, C$_6$$H_5$)

ppm. $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ −15.73 (s) ppm. FT-IR (neat): ν_s (CH_2) 2853.1, ν_a (CH_2) 2925.6 cm^{-1}. EI-MS: *m/z* 443. Anal. Calcd for $C_{27}H_{43}OSiP$ (442.69): C, 73.26; H, 9.79. Found: C, 72.89; H, 9.25.

$HO(CH_2)_{12}PPh_2$ (9). Anhydrous citric acid (1.97 g, 0.010 mol) in 10 mL of methanol was added to 4.55 g of $PPh_2(CH_2)_{12}OSi(CH_3)_3$ (0.010 mol). The cloudy white mixture was allowed to stir at room temperature for 15 min. The solvent was evaporated under vacuum and the product extracted with 35 mL of benzene. The solvent was distilled off and the product was filtered through glass wool to afford a pale yellow oil; yield, 3.55 g, 93.3%. ^1H NMR (270 MHz, C_6D_6): δ 1.11−1.51 (20H, m, $-(CH_2)_{10}-$), 1.99 (2H, br t, $J_{H-H} = 7.6$ Hz, CH_2P), 3.46 (2H, t, $J_{H-H} = 6.6$ Hz, CH_2O), 7.06, 7.45 (10H, m, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ −15.65 (s) ppm. FT-IR (neat): ν_s (CH_2) 2852.8, ν_a (CH_2) 2924.8 cm^{-1}. EI-MS: *m/z* 370. Anal. Calcd for $C_{24}H_{35}OP$ (370.51): C, 77.8; H, 9.52. Found: C, 79.28; H, 8.70.

$RhCl(1,5\text{-}C_8H_{12})[PPh_2(CH_2)_{10}OSi(CH_3)_3]$ (10). A 86 mg (0.174 mmol) portion of μ-chloro(1,5-cyclooctadiene)rhodium(I) dimer was dissolved in 10 mL of benzene, and a solution of $PPh_2(CH_2)_{10}OSi(CH_3)_3$ (144 mg, 0.35 mmol) in 10 mL of benzene was added dropwise. The mixture was left to stir at room temperature for 30 min, and then the solvent was removed under vacuum. Recrystallization of the product from a toluene/hexane mixture gave a red powder; yield, 195 mg, 85%. ^1H NMR (270 MHz, C_6D_6): δ 0.11 (9H, s, CH_3), 1.01−1.70 (16H, m, $-(CH_2)_8-$), 2.11 (8H, m, CH_2CH_2), 2.57 (2H, m, CH_2P), 3.54 (2H, t, $J_{H-H} = 5.9$ Hz, CH_2O), 4.28, 5.81 (4H, br s, $CH{=}CH$), 7.06, 7.67 (10H, m, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ 27.3 (d, $J_{Rh-P} = 148.8$ Hz) ppm. FT-IR (KBr): ν_s (CH_2) 2852.0, ν_a (CH_2) 2926.1 cm^{-1}. MALDI-TOF (LiBr/Didronel): 661.3 *m/z*. Anal. Calcd for $C_{33}H_{51}OSiPClRh$ (660.52): C, 60.01; H, 7.78. Found: C, 58.24; H, 7.49. XPS (Mg Kα): Si ($2p_{1/2}$, 99 eV), O ($1s_{1/2}$, 532 eV), C ($1s_{1/2}$, 286 eV), P ($2s_{1/2}$, 192 eV), Cl ($2s_{1/2}$, 270 eV), Rh ($3d_{5/2}$, 311 eV).

$RhCl(1,5\text{-}C_8H_{12})[PPh_2(CH_2)_{10}OH]$ (11). Reaction of μ-chloro-(1,5-cyclooctadiene)rhodium(I) dimer (284 mg, 0.58 mmol) and $PPh_2(CH_2)_{10}OH$ (394 mg, 1.15 mmol) using a procedure analogous to the preparation of **10** led to the isolation of **11**. Recrystallization of the product from a toluene/hexanes mixture gave a dark red solid; yield, 650 mg, 95%. ^1H NMR (270 MHz, C_6D_6): δ 1.11−1.66 (16H, m, $-(CH_2)_8-$), 2.12 (8H, m, CH_2CH_2), 2.53 (2H, m, CH_2P), 3.57 (2H, t, $J_{H-H} = 6.6$ Hz, CH_2O), 4.26, 5.73 (4H, br s, $CH{=}CH$), 4.55 (1H, br s, OH), 7.09, 7.66 (10H, m, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ 27.2 (d, $J_{Rh-P} = 148.8$ Hz) ppm. FT-IR (KBr): ν_s (CH_2) 2852.0, ν_a (CH_2) 2924.5 cm^{-1}. MALDI-TOF (LiBr/gentisic acid): 588.1 *m/z*. Anal. Calcd for $C_{30}H_{43}OPClRh$ (589.0): C, 61.18; H, 7.36. Found: C, 60.11; H, 7.24. XPS (Mg Kα): O ($1s_{1/2}$, 535 eV), C ($1s_{1/2}$, 287 eV), P ($2s_{1/2}$, 192 eV), Cl ($2s_{1/2}$, 271 eV), Rh ($3d_{5/2}$, 310 eV).

$RhCl(1,5\text{-}C_8H_{12})[PPh_2(CH_2)_{11}OSi(CH_3)_3]$ (12). Reaction of μ-chloro(1,5-cyclooctadiene)rhodium(I) dimer (107 mg, 0.22 mmol) and $PPh_2(CH_2)_{11}OSi(CH_3)_3$ (185 mg, 0.432 mmol) using a procedure analogous to the preparation of **10** led to the isolation of **12**. The product was recrystallized from a toluene/hexanes mixture to afford a purple solid; yield, 280 mg, 96%. ^1H NMR (270 MHz, C_6D_6): δ 0.11 (3H, s, $Si(CH_3)_3$), 1.10−1.70 (18H, m, $-(CH_2)_9-$), 2.13 (8H, m, CH_2CH_2), 2.56 (2H, m, CH_2P), 3.52 (2H, t, $J_{H-H} = 6.8$ Hz, CH_2O), 4.28, 5.80 (4H, br s, $CH{=}CH$), 7.06, 7.67 (10H, m, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ 27.3 (d, $J_{Rh-P} = 149$ Hz) ppm. FT-IR (KBr): ν_s (CH_2) 2852.8, ν_a (CH_2) 2924.2 cm^{-1}. MALDI-TOF (LiBr/gentisic acid): 674.5 *m/z*. Anal. Calcd for $C_{34}H_{53}OSiPClRh$ (675.21): C, 60.48; H, 7.91. Found: C, 59.87; H, 7.95. XPS (Mg Kα): Si ($2p_{1/2}$, 98 eV), O ($1s_{1/2}$, 532 eV), C ($1s_{1/2}$, 285 eV), P ($2s_{1/2}$, 194 eV), Cl ($2s_{1/2}$, 272 eV), Rh ($3d_{5/2}$, 312 eV).

$RhCl(1,5\text{-}C_8H_{12})[PPh_2(CH_2)_{11}OH]$ (13). Reaction of μ-chloro-(1,5-cyclooctadiene)rhodium(I) dimer (88 mg, 0.176 mmol) and $PPh_2(CH_2)_{11}OH$ (125 mg, 0.35 mmol) using a procedure analogous to the preparation of **10** led to the isolation of **13**. The product was recrystallized from a toluene/hexanes mixture to afford a dark red solid; yield, 195 mg, 92%. ^1H NMR (270 MHz, C_6D_6): δ 1.17−1.70 (18H, m, $-(CH_2)_9-$), 2.14 (8H, m, CH_2CH_2), 2.57 (2H, m, CH_2P), 3.06 (1H, br s, OH), 3.51 (2H, t, $J_{H-H} = 6.5$ Hz, CH_2O), 4.31, 5.81 (4H, br s, $CH{=}CH$), 7.07, 7.68 (10H, m, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ 27.3 (d, $J_{Rh-P} = 149$ Hz) ppm. FT-IR (KBr): ν_s (CH_2) 2853.0, ν_a (CH_2) 2925.0 cm^{-1}. MALDI-TOF (LiBr/didronel): *m/z* 609.1 (M+Li). Anal. Calcd for $C_{31}H_{45}OPClRh$ (603.03): C, 61.75; H, 7.52. Found: C, 61.56; H, 7.51. XPS (Mg Kα): O ($1s_{1/2}$, 532 eV), C ($1s_{1/2}$, 285 eV), P ($2s_{1/2}$, 194 eV), Cl ($2s_{1/2}$, 270 eV), Rh ($3d_{5/2}$, 309 eV).

$RhCl(1,5\text{-}C_8H_{12})[PPh_2(CH_2)_{12}OSi(CH_3)_3]$ (14). Reaction of μ-chloro(1,5-cyclooctadiene)rhodium(I) dimer (177 mg, 0.359 mmol) and $PPh_2(CH_2)_{12}OSi(CH_3)_3$ (318 mg, 0.717 mmol) using a procedure analogous to the preparation of **10** led to the isolation of **14**. The product was recrystallized from a toluene/hexanes mixture to afford a deep purple solid. Yield, 465 mg (94%). ^1H NMR (270 MHz, C_6D_6): δ 0.09 (3H, s, $Si(CH_3)_3$), 1.15−1.71 (20H, m, $-(CH_2)_{10}-$), 2.11 (8H, m, CH_2CH_2), 2.57 (2H, m, CH_2P), 3.52 (2H, t, $J_{H-H} = 6.6$ Hz, CH_2O), 4.27, 5.77 (4H, br s, $CH{=}CH$), 7.07, 7.65 (10H, m, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ 27.1 (d, $J_{Rh-P} = 148.8$ Hz) ppm. FT-IR (KBr): ν_s (CH_2) 2852.2, ν_a (CH_2) 2923.6 cm^{-1}. MALDI-TOF (LiBr/gentisic acid): 689.6 *m/z*. Anal. Calcd for $C_{35}H_{55}OSiPClRh$ (689.23): C, 60.99; H, 8.04. Found: C, 60.54; H, 8.12. XPS (Mg Kα): Si ($2p_{1/2}$, 98 eV), O ($1s_{1/2}$, 532 eV), C ($1s_{1/2}$, 285 eV), P ($2s_{1/2}$, 193 eV), Cl ($2s_{1/2}$, 270 eV), Rh ($3d_{5/2}$, 309 eV).

$RhCl(1,5\text{-}C_8H_{12})[PPh_2(CH_2)_{12}OH]$ (15). Reaction of μ-chloro-(1,5-cyclooctadiene)rhodium(I) dimer (75 mg, 0.15 mmol) and $PPh_2(CH_2)_{12}OH$ (113 mg, 0.30 mmol) using a procedure analogous to the preparation of **10** led to the isolation of **15**. Recrystallization from a toluene/hexanes mixture gave a dark red solid; yield, 180 mg, 96%. ^1H NMR (270 MHz, C_6D_6): δ 1.09−1.71 (20H, m, $-(CH_2)_{10}-$), 2.13 (8H, m, CH_2CH_2), 2.58 (2H, m, CH_2P), 3.07 (1H, br s, OH), 3.49 (2H, t, $J_{H-H} = 6.3$ Hz, CH_2O), 4.30, 5.81 (4H, br s, $CH{=}CH$), 7.06, 7.68 (10H, m, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ 27.4 (d, $J_{Rh-P} = 148.8$ Hz) ppm. FT-IR (KBr): ν_s (CH_2) 2853.0, ν_a (CH_2) 2924.0 cm^{-1}. MALDI-TOF (LiBr/didronel): *m/z* 616.8. Anal. Calcd for $C_{32}H_{47}OPClRh$ (617.05): C, 62.29; H, 7.68. Found: C, 61.48; H, 7.49. XPS (Mg Kα): O ($1s_{1/2}$, 534 eV), C ($1s_{1/2}$, 285 eV), P ($2s_{1/2}$, 193 eV), Cl ($2s_{1/2}$, 270 eV), Rh ($3d_{5/2}$, 309 eV).

Surface Reactions and Characterization. General Procedure: Thin Films of Long Hydrocarbon Chain Donor Ligands. Clean substrates of glass, quartz, single-crystal silicon, and ground glass silica were first treated with a toluene solution of $SiCl_4$ (10% *v/v*) at room temperature for 18 h. They were then washed with copious amounts of dry toluene, placed in a solution of fresh toluene containing 5% v/v $HN(C_2H_5)_2$, and left to stir at 70 °C for 14 h. The substrates were washed with toluene and then immersed in a toluene solution containing appropriate ligands ($HO(CH_2)_nPPh_2$, $n = 10-12$) and left to react at room temperature for 24 h.

$\{Si\}-O-(CH_2)_{10}-PPh_2$ ($\{Si\}$ = ground glass silica). Solid-state $^{31}P\{^1H\}$ NMR cross polarization with xmtr blanking: δ −15.9 ppm.

$[Si]-O-(CH_2)_{10}-PPh_2$ ($[Si]$ = glass, quartz or single-crystal silicon). Contact angles were measured on the thin films deposited on 1 in. × 1 in. glass slides, UV−vis data were measured on quartz, and the ellipsometeric thickness, FT-IR-ATR, and XPS data were obtained from samples prepared on single-crystal silicon wafers. Contact angles: θ_{water}, 89°; $\theta_{hexadecane}$, 19°. Ellipsometric thickness: 26 Å. FT-IR-ATR (KRS): ν_s (CH_2) 2851.0; ν_a (CH_2) 2923.0. XPS (Mg, Kα) (eV): Si ($2p_{1/2}$, 103), O ($1s_{1/2}$, 533), C ($1s_{1/2}$, 285), P ($2s_{1/2}$, 189).

$\{Si\}-O-(CH_2)_{11}-PPh_2$. $^{31}P\{^1H\}$ NMR cross polarization with xmtr blanking. δ −16.3 ppm.

$[Si]-O-(CH_2)_{11}-PPh_2$. Contact angles: θ_{water}, 90°; $\theta_{hexadecane}$, 19°. Ellipsometric thickness: 28 Å. FT-IR-ATR (KRS): ν_s (CH_2) 2850.7, ν_a (CH_2) 2920.8. XPS (Mg, Kα) (eV): Si ($2p_{1/2}$, 103), O ($1s_{1/2}$, 533), C ($1s_{1/2}$, 286), P ($2s_{1/2}$, 190).

$\{Si\}-O-(CH_2)_{12}-PPh_2$. $^{31}P\{^1H\}$ NMR cross polarization with xmtr blanking. δ −16.2 ppm.

$[Si]-O-(CH_2)_{12}-PPh_2$: Contact angles: θ_{water}, 87°; $\theta_{hexadecane}$, 22°. Ellipsometric thickness: 32 Å. FT-IR-ATR (KRS): ν_s (CH_2) 2850.2, ν_a (CH_2) 2922.0. XPS (Mg, Kα) (eV): Si ($2p_{1/2}$, 103), O ($1s_{1/2}$, 533), C ($1s_{1/2}$, 286), P ($2s_{1/2}$, 190).

Organometallic Thin Films. A general procedure for functionalizing inorganic oxide surfaces such as ground glass silica, glass, quartz and single-crystal silicon with a rhodium(I) complex is described below.

Ground Glass Silica. $[\mathrm{Rh}(\mu\text{-Cl})(1,5\text{-C}_8\mathrm{H}_{12})]_2$ (50 mg) was dissolved in 20 mL of toluene. Ground glass silica functionalized with **3**, **6**, or **9** was added, and the mixture was stirred at ambient temperature for 2 h. It was then filtered and washed with copious amounts of toluene and dried in vacuo.

{Si}−O−(CH$_2$)$_{10}$PPh$_2$RhCl(1,5-C$_8$H$_{12}$). Solid-state $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (cross polarization with transmitter blanking): δ 27.7 (br) ppm. FT-IR (KBr): $\nu_s(\mathrm{CH}_2)$ 2852.5, $\nu_a(\mathrm{CH}_2)$ 2924.1 cm^{-1}.

{Si}−O−(CH$_2$)$_{11}$PPh$_2$RhCl(COD). Solid-state $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (cross polarization with transmitter blanking): δ 27.4 (br s) ppm. FT-IR (KBr): $\nu_s(\mathrm{CH}_2)$ 2852.7, $\nu_a(\mathrm{CH}_2)$ 2926 cm^{-1}.

{Si}−O−(CH$_2$)$_{12}$PPh$_2$RhCl(COD): Solid-state $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (cross polarization with transmitter blanking): δ 28.0 (br s) ppm. FT-IR (KBr): $\nu_s(\mathrm{CH}_2)$ 2852.8, $\nu_a(\mathrm{CH}_2)$ 2924.7 cm^{-1}.

Flat Glass/Quartz/Single-Crystal Si: Procedure A. $[\mathrm{Rh}(\mathrm{Cl})(\eta^2\text{-C}_8\mathrm{H}_{12})]_2$ (50 mg) was dissolved in 25 mL of toluene in a self-assembly apparatus containing a glass slide or ground glass silica functionalized with **3**, **6**, or **9**. The solution was stirred for 1 h at room temperature, followed by washing the glass slide or silica with toluene (3 × 30 mL) and drying under a nitrogen atmosphere. **[Si]−O−(CH$_2$)$_{10}$PPh$_2$RhCl(1,5-C$_8$H$_{12}$)**. Ellipsometric thickness (Si wafer): 35 Å. FT-IR-ATR (KRS) (Si wafer): ν_s (CH$_2$) 2850, ν_a (CH$_2$) 2923 cm^{-1}. XPS (Si wafer) (Mg Kα): Si (2p$_{1/2}$, 103 eV), O (1s$_{1/2}$, 535 eV), C (1s$_{1/2}$, 286 eV), P (2s$_{1/2}$, 197 eV), Cl (2s$_{1/2}$, 269 eV), Rh (3d$_{5/2}$, 312 eV). UV−vis (quartz): monolayer coverage 1.7503×10^{-8} mol/cm^2.

[Si]−O−(CH$_2$)$_{11}$PPh$_2$RhCl(COD). Ellipsometric thickness (Si wafer): 38 Å. FT-IR-ATR (KRS) (Si wafer): ν_s (CH$_2$) 2851, ν_a (CH$_2$) 2921 cm^{-1}. XPS (Mg Kα) (Si wafer): Si (2p$_{1/2}$, 104 eV), O (1s$_{1/2}$, 534 eV), C (1s$_{1/2}$, 285 eV), P (2s$_{1/2}$, 196 eV), Cl (2s$_{1/2}$, 269 eV), Rh (3d$_{5/2}$, 311 eV).

[Si]−O−(CH$_2$)$_{12}$PPh$_2$RhCl(COD): Ellipsometric thickness (Si wafer): 40 Å. FT-IR-ATR (KRS) (Si wafer): ν_s (CH$_2$) 2851.5, ν_a (CH$_2$) 2922.4 cm^{-1}. XPS (Si wafer) (Mg Kα): Si (2p$_{1/2}$, 102 eV), O (1s$_{1/2}$, 534 eV), C (1s$_{1/2}$, 287 eV), P (2s$_{1/2}$, 196 eV), Cl (2s$_{1/2}$, 271 eV), Rh (3d$_{5/2}$, 311 eV).

Procedure B. RhCl(1,5-C$_8$H$_{12}$)([PPh$_2$(CH$_2$)$_n$OH] (n = 10−12; 50 mg) was dissolved in 25 mL of toluene in a self-assembly apparatus containing a glass slide or ground glass silica functionalized with tetrakis(diethylamino)silane. The solution was stirred for 16 h at room temperature, followed by washing the glass slide or silica with toluene (3 × 30 mL) and drying under a nitrogen atmosphere.

[Si]−O−(CH$_2$)$_{10}$PPh$_2$RhCl(1,5-C$_8$H$_{12}$). Ground Glass Silica. Solid-state $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (cross polarization with transmitter blanking): δ 27.4 (br) ppm. FT-IR (KBr): ν_s (CH$_2$) 2852.5, ν_a (CH$_2$) 2924.5 cm^{-1}. **Flat Surface** (Si wafer). Ellipsometric thickness: 33 Å. FT-IR-ATR (KRS): ν_s (CH$_2$) 2852.3, ν_a (CH$_2$) 2925.4 cm^{-1}. XPS (Mg Kα): Si (2p$_{1/2}$, 105 eV), O (1s$_{1/2}$, 535 eV), C (1s$_{1/2}$, 287 eV), P (2s$_{1/2}$, 197 eV), Cl (2s$_{1/2}$, 270 eV), Rh (3d$_{5/2}$, 311 eV).

[Si]−O−(CH$_2$)$_{11}$PPh$_2$RhCl(COD): **Ground Glass Silica**. Solid-state $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (cross polarization with transmitter blanking): δ 29.5 (br s) ppm. FT-IR (KBr): ν_s (CH$_2$) 2853, ν_a (CH$_2$) 2926 cm^{-1}. **Flat Surface** (Si wafer). Ellipsometric thickness: 35 Å. FT-IR-ATR (KRS): ν_s (CH$_2$) 2852.9, ν_a (CH$_2$) 2925.9 cm^{-1}. XPS (Mg Kα): Si (2p$_{1/2}$, 104 eV), O (1s$_{1/2}$, 534 eV), C (1s$_{1/2}$, 285 eV), P (2s$_{1/2}$, 199 eV), Cl (2s$_{1/2}$, 270 eV), Rh (3d$_{5/2}$, 312 eV).

[Si]−O−(CH$_2$)$_{12}$PPh$_2$RhCl(COD): **Ground Glass Silica**. Solid-state $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (cross polarization with transmitter blanking): δ 28.8 (br s) ppm. FT-IR (KBr): ν_s (CH$_2$) 2853, ν_a (CH$_2$) 2924 cm^{-1}. **Flat Surface** (Si wafer). Ellipsometric thickness: 38 Å. FT-IR-ATR (KRS): ν_s (CH$_2$) 2852.7, ν_a (CH$_2$) 2925.3 cm^{-1}. XPS (Mg Kα): Si (2p$_{1/2}$, 104 eV), O (1s$_{1/2}$, 534 eV), C (1s$_{1/2}$, 285 eV), P (2s$_{1/2}$, 198 eV), Cl (2s$_{1/2}$, 271 eV), Rh (3d$_{5/2}$, 312 eV).

Hydrogenation of Diphenylacetylene Using (CH$_3$)$_3$Si−O(CH$_2$)$_{10}$PPh$_2$RhCl(1,5-C$_8$H$_{12}$) in a Catalyst to Monomer Ratio of 1:155. RhCl(1,5-C$_8$H$_{12}$)[PPh$_2$(CH$_2$)$_{10}$OSi(CH$_3$)$_3$] (100 mg, 0.151 mmol) was dissolved in 25 mL of C$_6$H$_6$ containing 4.18 g (0.023 mol) of diphenylacetylene. The mixture was pressurized with 5, 10, or 20 bar of hydrogen and allowed to stir at ambient temperature for 30 min each. The resulting solution was distilled to remove benzene, resulting in an off-white viscous solid characterized by ^{1}H NMR, FT-IR, UV−vis, melting point, and GC−MS. The *cis*- and *trans*-stilbene had different retention times. Total product yield: 4 g, 95%. Turnover number (mol$_{\mathrm{sub}}$ mol$_{\mathrm{cat}}$$^{-1}$): 140. Turnover frequency (mol$_{\mathrm{sub}}$ mol$_{\mathrm{cat}}$$^{-1}$ h^{-1}) h^{-1}: 279.

Bibenzyl. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 2.74 (4H, br s, C*H*$_2$C*H*$_2$), 6.97, 7.11 (10H, m, 2C$_6$*H*$_5$) ppm. FT-IR (KBr): ν 3080.1, 3057.6, 3024.5, 2928.1, 1599.0, 1492.9, 757.8, 697.3 cm^{-1}. Mp: 53 °C. UV−vis (C$_6$H$_{12}$): $\lambda_{\max}$ 216, 287 nm.

***trans*-Stilbene**. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 7.16 (C*H*=C*H*), 7.22, 7.32 (10H, m, 2C$_6$*H*$_5$) ppm. FT-IR (KBr): ν 2928.1, 2854.5, 1650.7, 1450.0, 965.4, 770.4 cm^{-1}. Mp: 121 °C. UV−vis (C$_6$H$_{12}$): $\lambda_{\max}$ 207, 289 nm.

***cis*-Stilbene**. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 6.46 (C*H*=C*H*), 7.10, 7.17 (10H, m, 2C$_6$*H*$_5$) ppm. FT-IR (KBr): ν 3078.9, 3058.9, 3021.9, 2940.8, 1598.9, 1492.3, 754.0, 688.3 cm^{-1}. UV−vis (C$_6$H$_{12}$): $\lambda_{\max}$ 266, 298 nm.

Hydrogenation of Diphenylacetylene Using a Supported Rh(I) Complex. [Si]−O−(CH$_2$)$_{10}$PPh$_2$RhCl(1,5-C$_8$H$_{12}$). The catalytic reaction was performed using the Rh(I) complex [Si]−O−(CH$_2$)$_{10}$PPh$_2$RhCl(COD) surface immobilized on a 1 in. × 1 in. glass slide. The slide was placed in a 20 mL beaker equipped with a stir bar, 15 mL of dry benzene, and 100 mg of diphenylacetylene. The beaker was transferred into a reactor and the system was pressurized with 5, 10, or 20 bar of hydrogen and was allowed to stir at room temperature for 30 min. The resulting solution was distilled to remove benzene, resulting in a white viscous solid characterized by ^{1}H NMR, FT-IR, UV−vis, melting point, and GC−MS.

The percentage of the products is based on GC−MS results. Pressure: 10 Bar. Total yield: 86.2 mg, 85.23%.

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