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THE PREPARATION AND CATALYTIC HYDROFORMYLATION ACTIVITY OF SOME HALOCARBONYLRHODIUM(I) COMPLEXES CONTAINING PHOSPHINOALKYLORGANOSILICON LIGANDS

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Summary

The synthesis and properties of a series of *trans*-halocarbonylrhodium(I) complexes containing the phosphinoalkylorganosilicon ligands $Me_3SiCH_2PPh_2$, $Me_3Si(CH_2)_3PPh_2$, and $PPh_2CH_2(Me)\overline{Si(OSiMe_2)_3O}$ have been investigated. The complexes could be prepared by an exchange reaction involving $RhCl(CO)(PPh_3)_2$ and the organosilicon ligands or in better yields by the reaction of $Rh_2Cl_2(CO)_4$ with the ligands. Iodorhodium derivatives were obtained as the exclusive products in the latter reaction if a small amount of LiI was present. The catalytic activity of $RhCl(CO)(PPh_2CH_2SiMe_3)_2$ was similar to that of $RhCl(CO)(PPh_3)_2$ in the hydroformylation of hex-1-ene at 100°C and 1000 psi pressure of H_2/CO. The catalytic properties of the iodo derivatives $RhI(CO)L_2$ [$L = Me_3SiCH_2PPh_2$, $Me_3Si(CH_2)_3PPh_2$, and $PPh_2CH_2(Me)\overline{Si(OSiMe_2)_3O}$] varied considerably, with $RhI(CO)(PPh_2CH_2SiMe_3)_2$ producing an unexpectedly low linear/branched aldehyde product ratio.

Introduction

Although transition-metal compounds that contain organosilicon groupings have been the subject of much investigation, relatively few studies have involved metal complexes that contain phosphinoalkylorganosilicon ligands [1—4]. The most systematically studied ligand in this class of transition-metal complexes is "silphos" $(Me_3SiCH_2)_3P$ [1,2]. In most cases, this ligand forms normal complexes with transition-metal systems. However, it is capable of undergoing an unusual transformation to $(Me_3SiCH_2)_2PCH_3$, and the chemistry of a "silphos" metal complex may be significantly different from that of an analogous triphenylphosphine derivative [1]. Surprisingly, little is known about the catalytic properties of simple phosphinoalkylorganosilicon-metal complexes, although information is available on various metal complexes bonded to phosphinoalkylated silica supports [5—7]. A few of the monomeric phosphinoalkyl complexes known have been evaluated as hydrosilylation catalysts [4] and phosphinated organosilicone polymers covering silica recently have been investigated as polymer supports for catalytic rhodium complexes [8,9]. The polymer-attached complexes derived from $Rh_2Cl_2(CO)_4$ are considerably more active toward olefin hydrogenation than their homogeneous analogs and other supported catalysts. The enhanced activity now appears to be due to the presence of metallic rhodium produced in an unexpected chemical reaction of the rhodium species coordinated to the phosphinoalkylorganosilicone polymer [9]. Completely different results are obtained when the polymer-coordinated rhodium(I) species contains triphenylphosphine ligands [9].

These observations point out that although phosphinated organosilicon compounds usually function as normal ligands in transition-metal complexes, they are capable of either undergoing or producing some unexpected chemical reactions. It remains to be established just how general this behavior will be. In the present project, we have studied the preparation of several *trans*-$RhX(CO)L_2$ (X = halogen, L = phosphinoalkylorganosilicon compound) complexes and have examined their performance as hydroformylation catalysts.

Discussion

The phosphinated organosilicon compounds that were investigated as ligands in rhodium(I) complexes in this work are $Me_3SiCH_2PPh_2$, $Me_3Si(CH_2)_3PPh_2$, and $PPh_2CH_2(Me)\overline{Si(OSiMe_2)_3O}$ *. The compounds could be prepared by the reaction of the appropriate chloromethyl derivative with $LiPPh_2$ in tetrahydrofuran. However, the reactions were smoother and yields were much better if the corresponding iodomethyl derivatives, prepared by refluxing the chloromethyl derivatives with NaI in acetone, were employed in the reaction. The compounds were sensitive to oxygen and were made and used in an oxygen-free environment to avoid forming the phosphine oxide. The phosphinated derivatives prepared by the iodide route normally were not isolated as pure compounds, but were used "in situ" after their extraction into benzene. Traces of LiI always remained in solution in this "in situ" preparation and became involved in certain subsequent reactions (vide infra). If this is to be avoided, the phosphinated silicon compound must be carefully distilled before further use.

The transition-metal complexes that were prepared with the above ligands have the general formula $RhX(CO)L_2$ where L is the phosphinated ligand and X a halogen (Cl or I). We were particularly interested in determining if a reactive transition-metal halogen-containing carbonyl entity could be incorporated into a relatively simple phosphinoalkylsiloxane without extensive cleavage of the silicon—oxygen bond. This bond is readily cleaved by a variety of covalent halides

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* This compound will be abbreviated as D_4—CH_2PPh_2 or PPh_2CH_2—D_4.

[10] and even the metal carbonyl $Cr(CO)_6$ has been shown to cause extensive degradation of the silicon—oxygen bond in certain silicone polymers under not too drastic conditions [11]. Thus, we avoided the common procedure of preparing phosphine complexes of this type by the addition of formaldehyde to a boiling ethanolic solution of rhodium(III) chloride containing the phosphine ligand [12].

Two general procedures were investigated as preparative routes for the desired metal derivatives. In the first, the complexes were prepared by an exchange reaction involving $RhCl(CO)(PPh_3)_2$ and the phosphinated organosilicon compound in benzene over a 12 h period. A similar exchange has been used to incorporate the rhodium carbonyl chloride entity onto polymer supports [13]. The phosphinated organosilicon compound can be prepared by the iodide route and used in the reaction without special purification. Trace amounts of iodide salts present did not cause any halogen exchange and the chlorocarbonyl derivative was the exclusive product.

$$2\ RPPh_2 + RhCl(CO)(PPh_3)_2 \rightleftharpoons RhCl(CO)(RPPh_2)_2 + 2\ PPh_3 \qquad (1)$$

$$(R = CH_2SiMe_3,\ CH_2(Me)\overline{Si(OSiMe_2)_3O})$$

Although the method was successful, the purification of the product proved to be very difficult due to the equilibrium nature of the reaction. The purification involved evaporating away the benzene solvent until the less soluble $RhCl(CO)(PPh_3)_2$ precipitated. This actually reversed the phosphine exchange away from the desired product and as a result the yield was low. Satisfactory yields of products could be obtained only when a large excess of the phosphinoalkylsilane was employed in the reaction. Thus, $RhCl(CO)(PPh_2CH_2SiMe_3)_2$ was obtained in 20% yield using a ligand/$RhCl(CO)(PPh_3)_2$ ratio of 5.2 while the yield of $RhCl(CO)(PPh_2CH_2{-}D_4)_2$ was 50% when the ligand/$RhCl(CO)(PPh_3)_2$ ratio was 10.3.

An attempt to substitute only one of the triphenylphosphine ligands on the starting rhodium complex by a phosphinated organosilicon ligand was not successful. The interaction of equimolar quantities of $PPh_2CH_2{-}D_4$ and $RhCl(CO)(PPh_3)_2$ produced only the disubstituted product $RhCl(CO)(PPh_2CH_2{-}D_4)_2$ in 10% yield.

The interaction of the $[Rh(CO)_2Cl]_2$ dimer with the phosphinated organosilicon compounds in benzene also was investigated as a preparative route to the desired compounds. This is a commonly used procedure for preparing various halocarbonylbis(phosphine) complexes [14]. The extent of the reaction can be conveniently monitored by following the evolution of CO. However, in the application of this method to our derivatives, we noted that unless great care was taken to remove all traces of LiI (formed in the preparation of the phosphinated organosilicon derivative), the final product of the reaction was exclusively the corresponding iodorhodium complex.

$$LiPPh_2 + ICH_2SiMe_3 \xrightarrow{\text{acetone}} Me_3SiCH_2PPh_2 + LiI \qquad (2)$$

$$4\ Me_3SiCH_2PPh_2 + [Rh(CO)_2Cl]_2 + 2\ I^- \xrightarrow{\text{benzene}}$$
$$2\ RhI(CO)(PPh_2CH_2SiMe_3)_2 + 2\ CO + 2\ Cl^- \qquad (3)$$

TABLE 1

PROPERTIES OF SOME *trans*-HALOCARBONYLBIS(PHOSPHINOALKYLORGANOSILANE)RHODIUM(I) COMPLEXES

Compound [b]	Description	Melting point (°C)	$\nu(C\equiv O)$ (cm^{-1}) [a]	NMR proton chemical shifts (τ, ppm) [c]		
				Phenyl [d]	$CH_2(Si)$	$CH_3(Si)$
$RhCl(CO)(PPh_2CH_2SiMe_3)_2$	Yellow crystals	165	1960	1.98–2.77	7.56	10.14
$RhCl(CO)(PPh_2CH_2–D_4)_2$	yellow oil		1962	2.14–2.81	7.89	9.89, 10.02
$RhI(CO)(PPh_2CH_2SiMe_3)_2$	red-orange crystals	160 (dec.)	1960	1.98–2.73	7.56	10.14
$RhI(CO)[PPh_2(CH_2)_3SiMe_3]_2$	dark-red oil		1960	1.98–2.73	7.14	10.02
$RhI(CO)(PPh_2CH_2–D_4)_2$	red-orange oil		1960	2.14–2.81	7.89	9.89, 10.02

[a] Spectra of crystalline materials determined in KBr pellets; those of oils determined with salt plates. [b] $PPh_2CH_2D_4$ is the abbreviation used to denote the ligand $PPh_2CH_2(Me)\overline{Si(OSiMe_2)_3O}$. [c] Spectra obtained at ambient temperature on dilute solutions in deuterochloroform with a cyclohexane reference. [d] Signals were a complex multiplet in the range indicated.

The nature of the halogen was not of great concern to us in the preparative aspects of our project and we were content to isolate and study the iodo derivatives. However, $RhCl(CO)(PPh_2CH_2SiMe_3)_2$ was prepared for comparative purposes by this procedure using carefully distilled $Me_3SiCH_2PPh_2$. The complexes prepared by this route usually could be isolated in a reasonably pure form in about 80% yields by crystallization or solvent extraction methods. However, final purification of the compounds was always made by silica gel chromatography.

The halogen exchange caused by small amounts of LiI is somewhat surprising since previous work has shown that $RhCl(CO)(PPh_3)_2$ can be boiled with LiI in acetone without any conversion to the analogous rhodium(I) iodide derivative [15]. Furthermore, one can use phosphinated organosilanes prepared "in situ" via the iodide route in the previously described phosphine exchange reaction without any halogen exchange being observed. This leads us to suspect that in the dimer splitting reactions, the facile halogen exchange involves the proposed *cis*-chloro intermediate [16] $RhCl(CO)_2L$ rather than the final $RhCl(CO)L_2$ product. Sodium iodide, a reactant used in the initial conversion of the chloromethylsilane to the iodomethylsilane is known to lead to a halogen exchange with $RhCl(CO)L_2$ derivatives in acetone [15,17]. However, this compound was not present in our systems since in each case, the iodomethyl compound always was distilled prior to use.

The phosphinated organosilicon transition-metal complexes prepared were either yellow or reddish-orange oils or crystals that were soluble in common organic solvents. All the derivatives exhibited strong infrared carbonyl absorptions at approximately 1960 cm^{-1}, typical of rhodium(I) complexes of this type. The characteristic C—H stretches of the alkylsilicon grouping were in the 2850—3000 cm^{-1} region and the bands characteristic of methyl on silicon were at about 1250, 850 and 750 cm^{-1} [18]. The Si—O stretch of the cyclosiloxane derivative was at 1105 cm^{-1}.

The properties (Table 1) of the phosphinated organosilicon—metal complexes were not radically different from those of other *trans*-halocarbonylbis(phosphine)rhodium(I) derivatives and by analogy our derivatives are assumed to be of *trans*-configuration. The melting points of the crystalline derivatives are normal, being intermediate between the triarylphosphine derivatives [$RhXCO(PPh_3)_2$: X = Cl, m.p. 196—197°C; X = I, m.p. 177—180°C] [14,19] and the silphos derivatives [$RhXCO(silphos)_2$: = Cl, m.p. 138—142°C; X = I, m.p. 126—135°C] [1]. The melting point of $RhCl(CO)(PPh_2CH_2SiMe_3)_2$ is about the same as the ethyl derivative $RhCl(CO)(PPh_2CH_2CH_3)_2$ (153—160°C) [17].

All of the complexes were relatively stable thermally and could easily be handled in air during routine experimental operations. Of the two crystalline derivatives obtained, only $RhI(CO)(PPh_2CH_2SiMe_3)_2$ showed signs of decomposition at its melting point. After storing the compounds for six months in a nitrogen atmosphere at room temperature, the intensities of their carbonyl absorptions at 1960 cm^{-1} diminished somewhat, indicating that some decomposition had occurred during this period.

Several of the complexes described above were examined as catalysts in the hydroformylations of hex-1-ene.

$$\text{hex-1-ene} + CO + H_2 \xrightarrow{\text{catalyst}} \text{n-heptanal} + \text{iso-heptanal} \qquad (4)$$

TABLE 2

PRODUCT DISTRIBUTION OBTAINED FOR THE HYDROFORMYLATION OF HEX-1-ENE CATALYZED BY $RhCl(CO)(PPh_3)_2$ AND SOME *trans*-HALOCARBONYLBIS(PHOSPHINOALKYLORGANOSILANE)RHODIUM(I) COMPLEXES [a]

Catalyst	Yield (%) [b]				
	hex-1-ene	$n\text{-}C_7H_{14}O$	$i\text{-}C_7H_{14}O$	Other [c]	n/i
$RhCl(CO)(PPh_3)_2$	0.6	61.2	35.0	3.2	1.8
$RhCl(CO)(PPh_2CH_2SiMe_3)_2$	1.7	64.2	32.6	1.2	2.0
$RhI(CO)(PPh_2CH_2SiMe_3)_2$	4.1	34.7	54.8	6.4	0.6
$RhI(CO)[PPh_2(CH_2)_3SiMe_3]_2$	74.6	18.9	4.1	2.4	4.6
$RhI(CO)(PPh_2CH_2\text{—}D_4)_2$	52.7	28.8	12.2	6.3	2.4

[a] Reactions were carried out at 100°C and 1000 psi pressure of CO/H_2 (1/1) in an autoclave for 3 h. The molar ratio of olefin to rhodium was approximately 1000/1. [b] Yield determined by gas chromatographic analysis. [c] A small amount of *cis/trans* hex-2-ene was identified with the products.

The results are summarized in Table 2. The product distribution obtained for $RhCl(CO)(PPh_3)_2$ and $RhCl(CO)(PPh_2CH_2SiMe_3)_2$ were rather similar. Both systems produced a better than 98% conversion of hex-1-ene to products and the ratio of normal/iso (n/i) aldehyde product approached 2. These results are consistent with the presence of a phosphine coordinated rhodium(I) carbonyl chloride catalytic precursor and are only slightly different from the results previously reported for the hydroformylation of hex-1-ene and pent-1-ene by *trans*-halocarbonylbis(tertiary phosphine)rhodium(I) complexes at 70°C/100 atm [20]. Under these latter conditions, the observed n/i aldehyde ratios were approximately 2.7. Lower n/i ratios of aldehyde products generally result at higher temperatures [20].

It can be noted from the data given in Table 2 that the iodo derivatives used in our experiments produced lower overall conversions than the chloro complexes tested. This is not unexpected since in hydroformylation experiments involving pent-1-ene, $RhI(CO)(PPh_3)_2$ is known to give lower overall conversions than the analogous chloro derivative [20]. What is surprising is that there is a striking variation of overall conversions and n/i aldehyde product ratios within the series. For example, $RhI(CO)(PPh_2CH_2SiMe_3)_2$ causes a good overall conversion but has a very poor n/i aldehyde product ratio while $RhI(CO)[PPh_2(CH_2)_3SiMe_3]_2$ causes a low overall conversion, but has a high n/i aldehyde product ratio. The result for $RhI(CO)(PPh_2CH_2\text{—}D_4)_2$ is intermediate between the two extremes. This seems to imply that the catalysts for these systems exist in an equilibrium which, depending on the ligand(s) present, can be shifted under the reaction conditions from one related active species to another [21]. In such an equilibrium, the removal or loss of the phosphine ligand from the complex and its subsequent replacement by CO would have the effect of producing a catalytic species that would favor lower n/i aldehyde product ratios concomitant with an increased rate of reaction. Catalytic species with higher phosphine ratios would result in slower reactions that would have relatively high n/i ratios of aldehyde product. Thus, the extent of reaction and product distribution would depend on which catalytic species is favored in a particular experiment.

This, of course, would be determined by the ability of the phosphine to remain coordinated and compete with CO as a ligand.

$$trans\text{-}[RhXCOL_2] \xrightarrow{H_2/CO} \underset{(A)}{[HRh(CO)_2L_2]} + HX \quad (5)$$

$$[HRh(CO)_2L_2] + CO \rightleftharpoons \underset{(B)}{[HRh(CO)_3L]} + L \quad (6)$$

$$[HRh(CO)_3L] + CO \rightleftharpoons \underset{(C)}{[HRh(CO)_4]} + L \quad (7)$$

(Reactivity: $C > B > A$, selectivity: $A > B > C$)

Thus, the results suggest that of the three iodides investigated in this work, $RhI(CO)(PPh_2CH_2SiMe_3)_2$ undergoes a very facile decomposition under hydroformylation conditions and that in this case the actual catalyst is most likely a rhodium species which does not contain coordinated phosphine groupings.

Even though the reasons for the catalytic behavior of the individual rhodium(I) complexes investigated in this research are likely to be more involved than we naively have assumed, the experiments did point out that the nature of the phosphinoalkylorganosilicon ligand may have a significant effect in determining the degree of conversion and general product distribution of a typical hydroformylation reaction. We plan to examine more properties of transition-metal complexes containing phosphinated organosilicon derivatives in future work.

Experimental

Apparatus and techniques

All work with air-sensitive materials was carried out in a dry nitrogen atmosphere in a glove-box. Infrared and proton NMR spectra were obtained on Perkin—Elmer Model 457 and Hitachi—Perkin—Elmer instruments, respectively. Microanalyses were performed by Geller Laboratories.

In most cases, final purification of the products was achieved by using silica gel chromatography. The compounds were dissolved in benzene and added to a glass column packed with Baker chromatography grade silica gel. The column is then eluted with n-heptane which removes the unreacted phosphine. The product then can be isolated by eluting the column with a 50/50 mixture of benzene and n-heptane or with pure benzene. Some decomposition of the products may occur on the column and rapid elution is essential. In all cases, the product purity is checked by infrared and proton NMR spectral measurements and by thin-layer chromatography.

Materials

Solvents were dried by standard procedures and distilled under a nitrogen atmosphere. The commercially available chloroalkylorganosilicon compounds could be converted to the analogous iodoalkyl derivatives by refluxing them with NaI in acetone for 18—24 h. The reaction mixture is concentrated to about 30—40 ml and shaken with water (100 ml). The non-aqueous phase containing the iodomethyl derivative is extracted, dried over $MgSO_4$, and distilled (b.p.: ICH_2SiMe_3 134—140°C, lit. value 139.5° [22]; $ICH_2(CH_2)_2SiMe_3$, 145—150°C; ICH_2-D_4, 85°/1 mHg). *trans*-RhCl(CO)$(PPh_3)_2$ (m.p. 195—197°, lit. value 195—197°) was prepared by the reaction of $Rh_2(CO)_4Cl_2$ with triphenylphosphine [14]. The phosphinated organosilicon compounds were obtained by the reaction of $LiPPh_2$ (prepared by the reaction of $ClPPh_2$ with lithium in tetrahydrofuran) with either the chloro- or iodo-alkylorganosilicon derivatives in tetrahydrofuran. Sufficient $LiPPh_2$ (0.2 *M* in THF) is added until a red color persists. A single drop of methanol is added to destroy the excess $LiPPh_2$ and the solution is then evaporated to near dryness. The residual phosphinated organosilicon compound is then extracted into benzene for further reaction. The undissolved LiI is removed by filtration. In one case $Me_3SiCH_2PPh_2$ was distilled (b.p. 170°/1 mmHg, lit. [23] 139—143°C/0.6 mmHg after the reaction. However, over half the material was lost during this final purification and such distillations were not attempted on the other derivatives.

The 1/1 H_2/CO mixture (99+ %) used in the hydroformylation reaction was obtained commercially.

Preparations (Refer to Table 1 for properties)

(a) RhCl(CO)(PPh$_2$CH$_2$SiMe$_3$)$_2$

(i) By the reaction of RhCl(CO)(PPh$_3$)$_2$ with Me$_3$SiCH$_2$PPh$_2$. A benzene solution of $Me_3SiCH_2PPh_2$ (100 ml) prepared from $LiPPh_2$ and Me_3SiCH_2I (7.5 mmol) was allowed to react with RhCl(CO)$(PPh_3)_2$ (1.5 mmol) for 15 h at room temperature. Approximately 75 ml of the benzene solvent was evaporated and the RhCl(CO)$(PPh_2CH_2SiMe_3)_2$ (0.3 mmol, 20% yield) was recovered by silica gel chromatography. Anal. Found: C, 55.8; H, 6.0. $C_{33}H_{42}ClOP_2Si_2Rh$ calcd.: C, 55.7; H, 6.0%.

(ii) By the reaction of Rh$_2$(CO)$_4$Cl$_2$ with Me$_3$SiCH$_2$PPh$_2$. $Rh_2(CO)_4Cl_2$ (4.8 mmol) was added to a benzene solution of distilled $Me_3SiCH_2PPh_2$ (9.6 mmol, prepared by the reaction of $LiPPh_2$ with Me_3SiCH_2I). Evolution of CO began immediately and the mixture acquired an orange color. After the evolution of CO ceased, the reaction mixture was evaporated to about 40 ml volume and filtered. The filtrate was added to 200 ml of n-heptane and again filtered. The RhCl(CO)$(PPh_2CH_2SiMe_3)_2$ could not be crystallized from n-heptane and was recovered (3.8 mmol, 79% yield) by using silica gel chromatography.

(b) RhCl(CO)(PPh$_2$CH$_2$—D$_4$)$_2$

A benzene solution of PPh_2CH_2—D_4 (1.5 mmol) prepared from $LiPPh_2$ and $ClCH_2$—D_4 was allowed to react with RhCl(CO)$(PPh_3)_2$ (1.5 mmol) for 15 h. Evaporating part of the solvent and purifying the remaining soluble material as described in (a) produced RhCl(CO)$(PPh_2CH_2$—$D_4)_2$ (0.15 mmol, 10% yield). No evidence for the presence of the monosubstituted product was obtained.

The interaction of a large excess of PPh_2CH_2—D_4 (15 mmol) with RhCl(CO)-$(PPh_3)_2$ (1.5 mmol) for 9 h produced, after purification as described above, the disubstituted product RhCl(CO)$(PPh_2CH_2$—$D_4)_2$ (0.75 mmol) in a 50% yield.

(c) RhI(CO)(PPh$_2$CH$_2$SiMe$_3$)$_2$

A benzene solution of $Rh_2(CO)_4Cl_2$ (5 mmol) was added to a benzene solution of undistilled $Me_3SiCH_2PPh_2$ prepared from the reaction of Me_3SiCH_2I (10 mmol) with $LiPPh_2$. Evolution of CO began immediately and the reaction acquired a red color. When the CO evolution ceased the reaction mixture was reduced to a volume of about 40 ml, added to 200 ml of n-heptane, and filtered. The $RhI(CO)(PPh_2CH_2SiMe_3)_2$ is obtained as a precipitate after cooling the filtrate overnight in a refrigerator. A second crop of crystals could be obtained by evaporating the filtrate to dryness, dissolving the residue in 25 ml of benzene, adding the benzene solution to 200 ml of n-heptane, followed by cooling the mixture as described above. The total yield of $RhI(CO)(PPh_2CH_2SiMe_3)_2$ was 4.3 mmol, 85% yield. Anal. Found: C, 49.4; H, 5.2; Rh, 12.5. $C_{33}H_{42}IOP_2Si_2Rh$ calcd.: C, 49.4; H, 5.3; Rh, 12.8%.

(d) $RhI(CO)[PPh_2(CH_2)_3SiMe_3]_2$ *and (e)* $RhI(CO)(PPh_2CH_2—D_4)_2$

These two complexes were prepared by the same general procedures given in (c) however, they could not be crystallized from n-hexane. The $Me_3Si(CH_2)_3PPh_2$ and $D_4—CH_2PPh_2$ derivatives were recovered in approximately 65% yields by evaporating the n-hexane filtrate. If purity checks indicated that further purification was needed, the complexes were dissolved in benzene and purified on the silica gel column. Anal. [for (d)] Found: C, 51.6; H, 6.0. $C_{37}H_{50}IOP_2Si_2Rh$ calcd.: C, 51.8; H, 5.9%.

Hydroformylation experiments

A 200-ml stainless steel Aminco rocking autoclave was charged with solvent (benzene, 50 g), alkene (hex-1-ene, 0.5 mol) and catalyst (usually 0.5 mmol). The vessel was sealed, placed in a rocking heater purged three times with 1/1 synthesis gas (CO/H_2) then filled to the desired pressure (typically 1000 psi) with 1/1 synthesis gas. If necessary, a diaphram compressor is used to raise the available cylinder pressure to the predetermined level. The rocking mechanism and heaters are activated and the progress of the reaction is followed on a temperature recorder and pressure gauge. The pressure drop, indicative of reaction began as the temperature approached 90°C and continued throughout the run, which was normally held at an operating temperature of 100°C. At the run's completion, the rocker and heater were turned off and the autoclave allowed to cool overnight to room temperature. Gas samples were taken and analyzed by mass spectroscopy and gas liquid chromatography. The remaining gas was then vented to the atmosphere through a purge line. The pressure vessel was opened and the contents transferred to a rotating vacuum evaporator to remove the solvent. The products were analyzed on a Hewlett—Packard Model 5830 Gas Chromatograph equipped with a flame ionization detector.

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