

Selective Rhodium-Catalyzed Hydroformylation with the Tri- and Tetrakisphosphine Ligands $(\text{CH}_3)_{1,0}\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_{3,4}$. Formation of $\text{Rh}[\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3](\text{CO})$ via $\text{CH}_3\text{-Si}$ Bond Cleavage and Structure of This Rh(I)-Si Bonded Complex

Dan E. Hendriksen,^{*†} Alexis A. Oswald, Gerald B. Ansell, Susan Leta, and Rodney V. Kastrup

Corporate Research Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801

Received June 7, 1988

The flexible, nonchelating phosphine ligands $(\text{CH}_3)_{1,0}\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_{3,4}$ have been prepared and used in the rhodium-catalyzed hydroformylation of 1-butene to yield unusually high selectivity to the linear aldehyde product at low ligand/rhodium ratios of 3-4. During continuous hydroformylation with the ligand $\text{CH}_3\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$, the inactive complex $\text{Rh}[\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3](\text{CO})$ is formed, via a $\text{CH}_3\text{-Si}$ bond cleavage. This is the first reported Rh(I)-Si bonded complex. It has been characterized by ^{31}P and ^{13}C NMR, IR, and an X-ray crystal structure. The complex crystallizes from toluene in the trigonal space group $P\bar{3}$ with $a = b = 13.574$ (4) Å, $c = 12.838$ (2) Å, and $Z = 2$. The structure was refined to $R = 0.058$ and $R_w = 0.063$ for 1056 observed reflections. Each molecule is trigonal bipyramidal with a threefold axis of symmetry about the Si-Rh-CO core. The Rh-Si bond length is 2.398 (4) Å; the carbonyl is constrained by the chelating phosphines to occupy an axial position and has a somewhat lengthened Rh-C bond of 1.916 (18) Å.

Introduction

The rhodium-catalyzed hydroformylation reaction¹⁻³ is used industrially on a large scale for the production of linear aldehydes from linear α -olefins, e.g. eq 1. These

$$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO} \quad (1)$$

aldehydes are intermediates to alcohols, acids, plasticizers, and other commercial products. Some undesired branched aldehyde is always produced in the hydroformylation reaction. The type and amount of phosphine used as ligand in the catalyst complex strongly influence the degree of this side reaction. A high concentration of triaryl,^{4,5} or alkylarylmonophosphine^{6,7} provides good selectivity even at temperatures as high as 140°C. These are not effective at low ligand/rhodium ratios. The flexible diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 2-10$) have been investigated with rhodium complexes. With $n = 2$ or 3 these are chelating⁸ and yield poor selectivity to n -aldehyde.⁹⁻¹² With $n = 4$, ^{31}P NMR evidence demonstrates that the ligand is monodentate at ligand/rhodium = 5.¹³ A maximum selectivity to linear aldehyde is found at $n = 5$, and with $n = 6-10$ the hydroformylation selectivity is the same as with monophosphines.¹⁴ Investigators at Celanese have used two classes of rigid, chelating, diphosphines at low ligand/rhodium ratios to obtain good hydroformylation selectivity. These diphosphines are based on a ferrocene^{13,15,16} or cyclobutane^{13,16-18} framework.

We report in this paper the results obtained in rhodium-catalyzed hydroformylation with use of the homologous series of phosphines $(\text{CH}_3)_{4-n}\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_n$ ($n = 1-4$) (1-4) and the unusual selectivity obtained with the flexible, nonchelating tri- and tetrakisphosphines 3 and 4. In the course of a continuous reaction with ligand 3, the inactive complex $\text{Rh}[\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3](\text{CO})$ (5) was formed, apparently via cleavage of a $\text{CH}_3\text{-Si}$ bond. We report the structure of this first example of a Rh(I)-Si bonded complex.

Experimental Section

For both batch and continuous reactions, $\text{Rh}(\text{CO})_2(\text{acac})$ was obtained from Engelhard, and polymerization grade 1-butene was obtained from Phillips Chemical Co. For the batch reactions, primary standard mixtures of H_2/CO were from Matheson, and 2-ethylhexyl acetate was from City Chemical. Diphenylphosphine was obtained from Organometallics, trivinylmethylsilane from Petrarch Systems, and tetravinylsilane from PCR Research Chemicals. Phosphine preparations were carried out under nitrogen in a glovebox. NMR spectra were obtained on a JEOL FX 90Q multinuclear NMR spectrometer. ^{31}P chemical shifts are referenced to 1 M H_3PO_4 .

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[†] Present address: Exxon Chemical Company, Basic Chemicals Technology, P.O. Box 4900, Baytown, Texas 77522-4900.

Batch Reactions. An Autoclave Engineers 316 stainless-steel 300-mL autoclave was used for the batch reactions. This was equipped with a gas reservoir which held the appropriate mixture of H_2 and CO at a pressure higher than that in the autoclave. As the hydroformylation proceeded, this H_2 /CO mixture was fed to the autoclave through a precision pressure regulator in order to maintain a constant pressure in the autoclave. The H_2 /CO entered the reactor below the level of the solution through a sintered metal gas disperser, which improved gas/liquid mass transfer. The reaction was followed by the decrease in pressure of the H_2 /CO gas reservoir as measured with a digital Heise pressure transducer.

The batch reactions were performed in the following manner. $Rh(CO)_2(acac)$, phosphine ligand, and 2-ethylhexyl acetate solvent were placed in the autoclave in air. Sufficient solvent was used to bring the catalyst charge to 80 g. The autoclave was sealed, flushed with nitrogen, and brought to temperature. The external autoclave heater was controlled separately from the internal proportional cooling coils. Cooling was used to achieve fine temperature control. With the stirrer off, 20 g of 1-butene was added to the autoclave from a bomb, and the initial H_2 /CO mixture (generally 5/1) was charged to the autoclave through the olefin addition bomb to the desired pressure. The stirrer was started to initiate the reaction and was brought to 1500 rpm. Immediately the valve connecting the H_2 /CO reservoir to the autoclave was opened, and the progress of the reaction was monitored by the pressure drop in this reservoir. The H_2 /CO ratio fed during the reaction was generally 52/48 in order to maintain a constant H_2 /CO ratio in the autoclave during the reaction. Other ratios were used as necessary.

Reactions were run to 50% olefin conversion. The reaction was then stopped by cooling the reaction solution rapidly with the internal cooling coils and by removing the autoclave furnace and placing an ice bath around the autoclave. The reactor vapor phase was sampled, the autoclave was vented and opened, and the liquid contents were removed. Both the vapor phase and the final solution were analyzed by gas chromatography, and the results were used to calculate selectivities to normal and branched aldehydes, 2-butenes, and butane. The rate and selectivities were not influenced by gas-liquid mass transfer if the time to reach 50% conversion of olefin was 6 min or more. If necessary, the amount of rhodium was decreased in a second run to slow down the reaction rate. The rate is first-order in both rhodium and 1-butene concentrations and independent of hydrogen and carbon monoxide partial pressures. The rate constants are reported as $k_{\text{obsd}}/[Rh]$.

Continuous Reaction. The continuous hydroformylation was carried out in a 2-L autoclave from Autoclave Engineers. The hydrogen, carbon monoxide, and vaporized 1-butene were continuously sparged into the catalyst solution, which was about half the volume of the autoclave. The solution was stirred at 1000 rpm, and under these conditions the rate was not dependent on gas-liquid transfer. Both the pressure and the temperature of the reaction were carefully controlled. All products left the reactor in the vapor phase along with the unreacted feeds. This reactor effluent was cooled, and the condensed organic liquids were collected and analyzed by GC. The off-gas volume was measured, and the composition was analyzed on-line by a dedicated Carle GC.

$CH_3Si(CH_2CH_2PPh_2)_3$ (3). Four batches of $MeSi(CH=CH_2)_3$ (40 g, 0.32 mol) with Ph_2PH (190 g, 1.02 mol, 5% excess) were irradiated in a quartz vessel with two Hanau UV lamps with stirring at 115–125 °C for 72 h. Remaining reactants were removed under vacuum (0.1 Torr, 275 °C). The product was crystallized from hot toluene, washed with cold methanol, and dried under vacuum. A second crop was obtained. The product was then recrystallized from hot ethanol/toluene (85/15), washed with ethanol, and dried under vacuum: yield 687 g, 77%; mp 98–101 °C; ^{31}P NMR (C_6D_6 /toluene) δ -11.5; ^{13}C NMR (CH_2Cl_2) δ 21.6 (CH_2-P , J_{C-P} = 15.6 Hz), 8.8 (CH_2-Si , J_{C-P} = 11.7 Hz), -5.7 (CH_3-Si). Anal. Calcd for $C_{43}H_{45}P_3Si$: C, 75.64; H, 6.64; P, 13.61. Found: C, 76.64; H, 6.96; P, 13.00.

$Si(CH_2CH_2PPh_2)_4$ (4). $Si(CH=CH_2)_4$ (27.2 g, 0.20 mol) with Ph_2PH (149.5 g, 0.804 mol, 5% excess) was irradiated in a quartz vessel with two Hanau UV lamps with stirring for 32 h with the temperature raised from 95 to 200 °C to keep the mixture liquid. The product was washed with hot toluene, recrystallized from

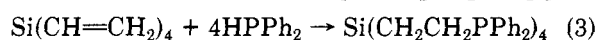
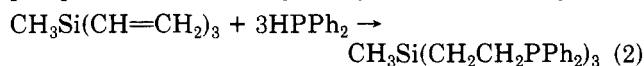
hot xylene, washed with cold xylene, and dried under vacuum: yield 66.9 g, 38%; mp 198–199 °C; ^{31}P NMR (C_6D_6 /toluene, 90 °C) δ -11.0. Anal. Calcd for $C_{56}H_{56}P_4Si$: C, 76.34; H, 6.41; P, 14.06. Found: C, 76.54; H, 6.38; P, 13.61.

$Rh[Si(CH_2CH_2PPh_2)_3](CO)$ (5). This light yellow rhodium complex was filtered from the cooled catalyst solution after the continuous hydroformylation (1.6 g). It was recrystallized from hot toluene: IR (KBr) 1940 (vs) cm^{-1} ; ^{31}P NMR (CD_2Cl_2) δ 60.5 (J_{P-Rh} = 151.4 Hz); ^{13}C NMR (CD_2Cl_2) δ 33.2 (CH_2-P , J_{C-P} = 19 Hz, J_{C-Rh} = 11 Hz), 16.1 (CH_2-Si , J_{C-P} = 13 Hz, J_{C-Rh} = 24 Hz), CO not observed. Anal. Calcd for $C_{43}H_{42}P_3SiRhO$: C, 64.66; H, 5.30; P, 11.63; Rh, 12.88. Found: C, 64.06; H, 5.46; P, 11.1; Rh, 12.9.

X-ray Analysis. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer and were corrected for absorption (μ = 5.83 cm^{-1} , empirical ψ scan technique). All calculations were performed by using the SDP package provided by Enraf-Nonius. A structure based on 31 atoms (Rh, Si, O, P, 15 C, 12 H) was determined by the solution of a three-dimensional Patterson function and then the application of successive Fourier synthesis and least-squares structure factor calculations. The hydrogen positions and thermal parameters were not refined. All non-hydrogen positions were refined with anisotropic thermal parameters. Least-squares refinement converged with residuals of R = 0.058 and R_w = 0.063, using 1056 data with $I > 2\sigma(I)$; the esd of an observation of unit weight was 1.513.

Results and Discussion

Though alkyldiphenyldiphosphines, both chelating and nonchelating, have been explored as ligands in rhodium-catalyzed hydroformylation, there have been no previous investigations of nonchelating alkyldiphenyl tri- or tetraphosphines. Representative of this class are two homologous ligands, $CH_3Si(CH_2CH_2PPh_2)_3$ and $Si(CH_2CH_2PPh_2)_4$, which may be conveniently prepared by the UV-initiated free radical chain addition of diphenylphosphine to either trivinylmethylsilane or tetravinylsilane.



The corresponding mono- and diphosphines $(CH_3)_3SiCH_2CH_2PPh_2$ and $(CH_3)_2Si(CH_2CH_2PPh_2)_2$ have also been prepared by analogous routes for comparison.

It was desired to test these novel phosphine ligands in reactions under industrially relevant conditions of temperature and pressure and under essentially constant partial pressures of hydrogen and carbon monoxide reactants. 1-Butene was chosen as the olefin reactant, since it would yield not only the linear and branched aldehyde products and the butane byproduct from hydrogenation but would provide a measure of isomerization activity to 2-butenes as well. The 2-butenes that are formed do not react further in these reaction systems.

Comparison of Homologous Phosphines. The results of 1-butene hydroformylation with each of the phosphines 1–4 are presented in Table I. These reactions were conducted at a constant phosphorus concentration, with the ligand/rhodium ratio varied to yield a constant phosphorus/rhodium ratio of 12. These low concentrations of ligand allow the observation of marked differences in catalyst performance, and since the ligand/rhodium ratio is always three or above, there is always sufficient ligand to form the $HRh(CO)L_3$ complex with no necessity to form ligand-bridged dimeric complexes.

The trend in the rates of reaction shows an approximate twofold decrease in rate with each additional phosphorus in the ligand molecule, at the constant phosphine concentration. With monophosphines it is known that the rate of hydroformylation decreases as the phosphine concentration is increased.^{1,6} Hence, though these ligands are

Table I. Batch 1-Butene Hydroformylation at P/Rh = 12 with Mono-, Di-, Tri-, and Tetraphosphines^a

expt	ligand	ligand/Rh	rate, M ⁻¹ min ⁻¹	<i>n</i> -pentanal/ total pentanal, %	selectivities to products, %			
					<i>n</i> -pentanal	2-methyl- butanal	2-butenes	butane
1	(CH ₃) ₃ SiCH ₂ CH ₂ PPh ₂	12.0	330	77	67	19	8	6
2	(CH ₃) ₂ Si(CH ₂ CH ₂ PPh ₂) ₂	6.0	123	86	78	12	6	4
3	CH ₃ Si(CH ₂ CH ₂ PPh ₂) ₃	4.0	77	90	82	9	6	3
4	Si(CH ₂ CH ₂ PPh ₂) ₄	3.0	41	90	83	10	6	2
5	PPh ₃	12.0	430	77	59	18	19	5
6	PPh ₃	280 ^b	200	88	76	11	10	4

^a *T* = 110 °C; pressure = 1500 kPa; H₂/CO = 5/1; [Rh] = 1.0 mM; solvent is 2-ethylhexyl acetate; 50% 1-butene conversion. ^b [Rh] = 0.5 mM.

Table II. Batch 1-Butene Hydroformylation with CH₃Si(CH₂CH₂PPh₂)₃ Ligand^a

expt	<i>T</i> , °C	pressure, kPa	ligand/Rh	rate, M ⁻¹ min ⁻¹	<i>n</i> -pentanal/ total pentanal, %	selectivities to products, %			
						<i>n</i> -pentanal	2-methyl- butanal	2-butenes	butane
1	110	1500	1.0	77	80	73	18	6	3
2	110	1500	1.5	89	87	79	12	6	3
3	110	1500	2.0	84	87	80	12	6	3
4	110	1500	3.0	83	90	81	9	6	4
5	110	1500	4.0	77	90	82	9	6	3
6	110	1000	3.0	70	90	81	9	7	2
7	110	2500	3.0	81	84	80	15	4	2
8	110	3000 ^b	3.0	83	92	77	7	7	9
9	120	2500	1.3 ^c	134	78	74	21	4	1
10	120	2500	6.7 ^d	112	84	79	15	4	2
11	120	2500	33.3	20	85	81	15	3	1
12	145	2500	3.0 ^e	270 ^e	76	51	16	31	3
13	145	2500	7.5 ^e	132	83	70	14	12	5
14	145	2500	46.7	111	88	78	11	8	4
15	145	2500	165 ^f	9	91	81	8	7	4
16	145	2500 ^g	66 ^h	47	89	82	10	6	2

^a H₂/CO = 5/1; [Rh] = 1.0 mM; solvent is 2-ethylhexyl acetate; 50% 1-butene conversion. ^b H₂/CO = 11/1 (1500 kPa of 5/1 H₂/CO plus 1500 kPa H₂). ^c [Rh] = 0.25 mM. ^d [Rh] = 0.5 mM. ^e Rate decreases during run. ^f [Rh] = 2.0 mM. ^g H₂/CO = 1.5/1. ^h [Rh] = 5.0 mM.

Table III. Batch 1-Butene Hydroformylation with Si(CH₂CH₂PPh₂)₄ Ligand^a

expt	<i>T</i> , °C	pressure, kPa	ligand/Rh	rate, M ⁻¹ min ⁻¹	<i>n</i> -pentanal/ total pentanal, %	selectivities to products, %			
						<i>n</i> -pentanal	2-methyl- butanal	2-butenes	butane
1	110	1500	1.0	44	88	78	11	8	3
2	110	1500	2.0	42	91	83	8	7	2
3	110	1500	3.0	41	90	83	10	6	2
4	110	1000	3.0	36	94	86	6	7	2
5	110	2500	3.0	41	85	80	14	5	2
6	120	2500	1.1	84	83	76	15	6	4
7	120	2500	2.5	79	88	81	12	5	2
8	145	2500	1.0 ^b	206 ^c	74	46	16	35	3
9	145	2500	3.0 ^b	220 ^c	85	73	13	10	4
10	145	2500	5.0 ^b	148 ^c	86	73	12	11	5
11	145	2500	7.5	95	88	77	11	8	4
12	145	2500	30 ^b	9	88	76	10	11	4

^a H₂/CO = 5/1; [Rh] = 1.0 mM; solvent is 2-ethylhexyl acetate; 50% 1-butene conversion. ^b [Rh] = 0.25 mM. ^c Rate decreases during run.

nonchelating, they behave as though they provide a progressively higher effective concentration of phosphine in the region around each rhodium center. The bridge length of five atoms between phosphorus atoms in these ligands is short enough to keep the unbound phosphines close to the rhodium center but not so short as to promote chelation.

Selectivity to the desired *n*-pentanal product increases significantly through the ligand series 1–3, with selectivity to all of the byproducts decreasing. No additional benefit is gained by continuing to the tetraphosphine, as the selectivities are essentially the same for 3 and 4. With monophosphines, a higher concentration yields a better selectivity to linear aldehyde. Again, 3 and 4 behave as though they provide a higher effective phosphine concentration. The reason for this selectivity effect with monophosphines remains a matter of some controversy,¹⁹

as does the hydroformylation mechanism itself.²⁰ Also shown in Table I are comparison reactions with PPh₃ both at the same ligand/rhodium ratio of 12 and at a much higher ratio of 280. Though the reaction rate with PPh₃ as ligand is much faster, the selectivity to *n*-pentanal of 59% at L/Rh = 12 contrasts with the selectivity of 82% obtained with ligands 3 and 4.

Reaction Variables with Ligands 3 and 4. The rate and selectivity of the hydroformylation reaction depend mostly on the temperature, ligand/rhodium ratio, and the carbon monoxide partial pressure. The data for the two ligands are shown in Tables II and III. The effect of each

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Table IV. Continuous Rhodium-Catalyzed Hydroformylation of 1-Butene with the $\text{CH}_3\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ Ligand (3)

Catalyst Solution	
ligand/Rh	4
[Rh]	4.2 mM
initial volume	0.93 L
solvent	
pentanal trimer	375 g
pentanal	410 g
Reaction Conditions	
temperature	110 °C
P_{total}	800 kPa
P_{CO}	70 kPa
P_{H_2}	640 kPa
feed rates	
1-butene	3 mol/h
hydrogen	570 std L/h
carbon monoxide	75 std L/h
Results	
selectivity	
<i>n</i> -pentanal	88%
2-methylbutanal	4%
normal/branched ratio	22
<i>n</i> -pentanol	1%
2-butenes	1%
butane	7%
initial conversion	15%
initial turnover number ^a	0.032
deactivation time	5 days

^a mol of 1-butene/mol of Rh/s.

variable is the same for both of these ligands.

Temperature. The best balance between reaction rate and selectivity is at the lower temperature of 110 °C, where the reaction is most selective to the desired *n*-pentanal product. At 145 °C the *n*-pentanal selectivity reaches 80% only at the highest ratios of 3/Rh and then at a considerable sacrifice of reaction rate. At the lowest ligand/rhodium ratio tested with 3 and 4 at 145 °C the selectivity to 2-butene exceeds 30%.

Ligand/Rhodium. Increasing the ligand/rhodium ratio in the range 1.0–4.0 at 110 °C has no effect on the reaction rate and affects the selectivity only at the lowest ratios, where an increase from 1.0 to 2.0 slightly increases the selectivity to *n*-pentanal at the expense of branched aldehyde. These same trends are observed at 120 °C. The ligand 4 is not soluble above 3×10^{-3} M at 110 °C in the 2-ethylhexyl acetate solvent chosen for the batch reactions. Since this solvent has similar properties to that used in a commercial continuous reaction, the range over which 4 can be used is sharply limited.

Hydrogen Partial Pressure. The partial pressure of hydrogen was approximately doubled in Table II, experiments 4 and 8. Reaction rate is unaffected, while selectivity to butane doubles to 9%.

Carbon Monoxide Partial Pressure. The total pressure of 5/1 H_2/CO is varied in Table II, experiments 4, 6, and 7. This increase in total pressure increases selectivity to branched aldehyde at the expense of 2-butene with no change in rate. This can be attributed to the change in carbon monoxide partial pressure, as the change in hydrogen partial pressure alone affects only selectivity to butane.

Continuous Reaction with Ligand 3. While the batch hydroformylation reactions identify the range of conditions within which this ligand can form a highly selective catalyst, these results say little about the stability of the catalyst. The definitive method to test a catalyst system for stability is by running the reaction continuously and monitoring activity over time. This was done with ligand

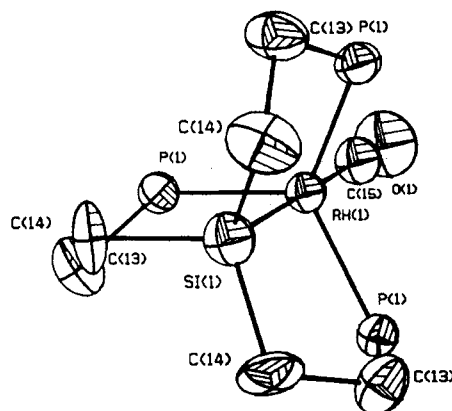


Figure 1. ORTEP drawing of $\text{Rh}[\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3](\text{CO})$ (5) with thermal ellipsoids at the 50% probability level. Phenyl groups are omitted for clarity. Symmetry-related atoms are shown with the same number.

Table V

A. Crystal Data	
formula	$\text{RhC}_{43}\text{H}_{42}\text{OP}_3\text{Si}$
fw	798.7
space group	$P\bar{3}$
lattice constants	
$a = b, \text{Å}$	13.574 (4)
$c, \text{Å}$	12.838 (2)
$V, \text{Å}^3$	2048.5
Z	2
$\rho_{\text{calcd}}, \text{g/cm}^3$	1.295
B. Data Collection	
diffractometer	Enraf-Nonius CAD-4
radiatn	Mo $K\alpha$, 0.7107 Å
monochromator	graphite
temp, °C	22
scan type	Ω -2 θ
scan range, deg	$0 < 2\theta < 45$
scan speed, deg/min	4–20
reflectns examined	2338
reflectns obsd	1056 ($h, k, \pm l$)
criterion	$I > 2\sigma(I)$
abs corr	
μ, cm^{-1}	5.83
scan type	ψ scans

3; the reaction conditions and results are shown in Table IV. The CO partial pressure is about 0.3 that used in the batch experiments, while the H_2 partial pressure is about 0.5 that used previously. The flow of excess H_2/CO is necessary to remove the pentanal product in the vapor phase. The selectivity to *n*-pentanal was very good, approaching 90%, and only minimal (1%) hydrogenation of pentanal to pentanol was observed. However, the initial activity of the catalyst was not as high as expected, and this activity decreased steadily to zero over the course of 5 days. Upon cooling the reaction solution and draining it from the reactor, a light yellow crystalline precipitate was found. This was determined to be a rhodium carbonyl complex by IR. Since the rhodium complex formed at the beginning of the reaction was completely soluble, it was of interest to determine the nature of the final rhodium complex, to see if it was a product of catalyst degradation. The results from IR, NMR, and an elemental analysis were not sufficient to unambiguously identify the product, so a crystal structure determination was undertaken.

X-ray Crystal Structure. The crystal structure unambiguously identifies the complex recovered from the continuous hydroformylation catalyst solution as $\text{Rh}[\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3](\text{CO})$ (5) with a Rh–Si bond. A labeled ORTEP drawing of the inner coordination sphere of the complex is shown in Figure 1. A summary of crystallo-

Table VI. Atomic Positional Parameters for Rh[Si(CH₂CH₂PPh₂)₃](CO) and Their Estimated Standard Deviations^a

atom	x	y	z
Rh(1)	0.3333 (0)	0.6667 (0)	0.7939 (2)
P(1)	0.1843 (3)	0.6999 (3)	0.8224 (3)
Si(1)	0.3333 (0)	0.6667 (0)	0.9807 (5)
O(1)	0.3333 (0)	0.6667 (0)	0.555 (1)
C(1)	0.0592 (10)	0.6351 (10)	0.737 (1)
C(2)	-0.0462 (10)	0.5520 (11)	0.768 (1)
C(3)	-0.1354 (11)	0.5055 (12)	0.700 (2)
C(4)	-0.1230 (12)	0.5376 (15)	0.600 (2)
C(5)	-0.0207 (16)	0.6159 (22)	0.567 (2)
C(6)	0.0716 (13)	0.6691 (19)	0.636 (1)
C(7)	0.2151 (9)	0.8478 (9)	0.818 (1)
C(8)	0.3033 (10)	0.9269 (9)	0.759 (1)
C(9)	0.3233 (12)	1.0360 (12)	0.749 (1)
C(10)	0.2569 (13)	1.0715 (11)	0.801 (1)
C(11)	0.1685 (12)	0.9950 (11)	0.863 (1)
C(12)	0.1476 (11)	0.8846 (12)	0.869 (1)
C(13)	0.1225 (10)	0.6505 (11)	0.953 (1)
C(14)	0.2232 (10)	0.7008 (11)	1.030 (1)
C(15)	0.3333 (0)	0.6667 (0)	0.645 (2)
H1	-0.0591 (0)	0.5285 (0)	0.8427 (0)
H2	-0.2092 (0)	0.4443 (0)	0.7253 (0)
H3	-0.1894 (0)	0.5015 (0)	0.5538 (0)
H4	-0.0137 (0)	0.6426 (0)	0.4934 (0)
H5	0.1469 (0)	0.7310 (0)	0.6095 (0)
H6	0.3522 (0)	0.9038 (0)	0.7241 (0)
H7	0.3858 (0)	1.0905 (0)	0.7039 (0)
H8	0.2734 (0)	1.1498 (0)	0.7912 (0)
H9	0.1212 (0)	1.0186 (0)	0.9012 (0)
H10	0.0832 (0)	0.8296 (0)	0.9111 (0)
H11	0.0669 (0)	0.6747 (0)	0.9687 (0)
H12	0.0798 (0)	0.5680 (0)	0.9562 (0)
H13	0.2553 (0)	0.7825 (0)	1.0361 (0)
H14	0.1990 (0)	0.6704 (0)	1.0999 (0)

^a Hydrogen atoms were not refined.**Table VII. Selected Bond Lengths (Å) and Angles (deg) for Rh[Si(CH₂CH₂PPh₂)₃](CO)**

Bond Lengths			
Rh(1)-Si(1)	2.398 (4)	Si(1)-C(14)	1.883 (9)
Rh(1)-P(1)	2.312 (2)	P(1)-C(1)	1.838 (8)
Rh(1)-C(15)	1.916 (18)	P(1)-C(7)	1.835 (9)
C(15)-O(1)	1.146 (12)	P(1)-C(13)	1.841 (8)
Bond Angles			
P(1)-Rh(1)-P(1)	117.63 (6)	C(1)-P(1)-C(7)	99.0 (4)
P(1)-Rh(1)-C(15)	99.09 (6)	C(1)-P(1)-C(13)	103.1 (4)
C(15)-Rh(1)-Si(1)	180.00	C(1)-P(1)-Rh(1)	120.0 (3)
P(1)-Rh(1)-Si(1)	80.91 (6)	C(13)-P(1)-Rh(1)	110.9 (3)
C(14)-Si(1)-C(14)	108.8 (4)	C(7)-P(1)-Rh(1)	117.8 (3)
C(14)-Si(1)-Rh(1)	109.8 (3)	C(7)-P(1)-C(13)	103.9 (4)
Si(1)-C(14)-C(13)	108.0 (6)		
C(14)-C(13)-P(1)	106.4 (1)		

graphic data and the experimental conditions is given in Table V and the Experimental Section. The atomic coordinates are listed in Table VI, and the important bond lengths and angles are given in Table VII. The complex is trigonal-bipyramidal. The two molecules per unit cell are situated on two positions of threefold symmetry, with the threefold axis along the Si-Rh-CO atoms, so that each arm of the triphosphine is equivalent.

The complex is apparently formed via an unusual rhodium-promoted carbon-silicon bond cleavage which removes the methyl group from the starting ligand CH₃Si(CH₂CH₂PPh₂)₃. This methyl group is presumably converted to methane by reductive elimination from a rhodium methyl hydride intermediate. Alternatively, acetaldehyde could be formed. The lack of a hydride in the product complex accounts for the inactivity of this species for hydroformylation. Carbon-silicon bond cleavage in tetraalkyl silanes has previously been observed in the

presence of trichlorosilane and chloroplatinic acid.²¹ Platinum complexes have also been observed to cleave the Si-C bond in (trimethylsilyl)acetylenes.^{22,23} Recently P-C bond cleavage in triarylphosphines during rhodium-catalyzed hydroformylation has been reported.^{24,25} A related complex, Rh[CH(CH₂CH₂PBu_t)₂]HCl, is formed by C-H bond cleavage, also at the central atom of a five-atom bridge between phosphines.²⁶

To our knowledge this is the first Rh(I)-Si bonded complex to be characterized and reported. In contrast, a number of Rh(III)-Si complexes have been prepared.²⁷ The first Ir(I)-Si complex has only recently been reported.²⁸ The Rh(I)-Si bond length of 2.398 (4) Å compares with a Rh(III)-Si bond length of 2.203 (4) Å in RhHCl(SiCl₃)(PPh₃)₂.²⁹ The Rh-P bond length of 2.312 (2) Å is in the normal range for five-coordinate Rh(I) complexes, e.g., 2.315 (8)-2.336 (8) Å in RhH(CO)(PPh₃)₃³⁰ and 2.303 (2)-2.330 (2) Å in Rh₂Br₂(μ-CO)(μ-dppm)₂.³¹ Complex 5 and the Ir(I)-Si complex [Ir(PPh₂CH₂CH₂SiMe₂)(PPh₃)(CO)₂] are both trigonal-bipyramidal with the Si axial and the chelating phosphine(s) equatorial. However, in this iridium complex the PPh₃ is axial and trans to the Ir-Si bond with the carbonyls equatorial, while in 5 the three chelating phosphines constrain the carbonyl to an axial position trans to the Rh-Si bond. This accounts for the significantly lengthened Rh-C bond distance of 1.916 (18) Å compared with 1.829 (28) Å in RhH(CO)(PPh₃)₃.³⁰ Other crystallographic data are given in the supplementary material.

NMR Data. The NMR spectra of 5 are in agreement with the crystal structure of the compound. Of particular interest is the large coordination shift in the ³¹P NMR (δ = 60.5 ppm), consistent with the known deshielding effect of the five-membered ring.³² This is also illustrated by the known complex HRh(Ph₂PCH₂CH₂PPh₂)₂, with δ = 54.3 ppm.^{33,34} In contrast, 4, when exchanged with PPh₃ in HRh(CO)(PPh₃)₃, shows δ = 37.1 ppm, which is comparable to δ = 34.6 ppm found with the homologous monophosphine in HRh(CO)(Ph₂PCH₂CH₂SiMe₃)₃.⁶

Acknowledgment. We gratefully acknowledge the skilled technical assistance of R. A. Cook, T. G. Jermansen, and E. J. Mozeleski in the syntheses and reactions reported. We also acknowledge helpful discussions with Drs. T. R. Halbert and J. S. Merola.

Supplementary Material Available: Tables listing anisotropic thermal parameters, bond lengths, and bond angles and an ORTEP drawing of the PPh₂ group in 5 (4 pages); a listing of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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