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The Regioselective Hydroformylation of Vinylsilanes. A Remarkable Difference in the Selectivity and Reactivity of Cobalt, Rhodium, and Iridium Catalysts

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The zwitterionic rhodium complex, Rh(COD)BPh_4, produces 2-(trimethylsilyl)propanal selectively in the hydroformylation of trimethylvinylsilane under quite mild conditions [100 °C, 200 psi ($CO:H_2$ = 1:2), 1.5–3 h]. Excess hydrogen is crucial for obtaining the branched aldehyde as the major product (B:L = 70:30). This is the first reported example of an α-selective hydroformylation of vinylsilanes. The potentially useful α-silyl aldehydes are difficult to prepare and isolate by other means, but using this procedure they can be obtained in one step from commercially available vinyltrimethylsilane, albeit in low isolated yields (20–30%). The addition of as little as 2 equiv of PPh_3 causes a complete shift in the selectivity yielding the linear isomer as the major product in the hydroformylation of vinyltriethylsilane (B:L = 7:93). The isolated yield increases from 30% to 91% after only 1.5 h. Iridium catalysts yielded the linear aldehydes (3-(trialkylsilyl)propanal) with excellent regioselectivities (90–100%) without the addition of any phosphine. A competing reaction is hydrogenation of the starting material. This can be suppressed by increasing the amount of CO in the gas mixture ($CO:H_2$ = 7:1). Of those complexes examined, hydrated $IrCl_3$ (after preactivation at 160 °C) gave the best selectivity for the linear isomer (98–100%). The cationic complex, $[Ir(COD)_2]^+BF_4^-$, also gave the linear aldehyde predominantly (95–97%) in 75–80% yields. Although most of the cobalt complexes tested were unreactive, the cationic cobalt cluster $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]BPh_4$ was the most active catalyst for the hydroformylation of vinyltriethylsilane. At 100 °C, this complex completed six turnovers per minute, yielding the linear silyl aldehyde as the major product (B:L = 24:76).

Introduction

Recently, the utility of the zwitterionic rhodium complex, Rh(COD)BPh_4,[1] (designated as Rh^{zw}) has been reported for a variety of carbonylation reactions.[2] This complex was found to be a highly selective catalyst for the hydroformylation of aryl alkenes, vinyl ethers, and 1,1-disubstituted alkenes.[3] We were interested in examining this complex and the yet unexplored Ir(COD)BPh_4[1] and $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]BPh_4$,[4] as catalysts for the hydroformylation of vinylsilanes.

Silyl aldehydes are valuable synthetic intermediates, difficult to prepare by conventional methods.[5] Since the trialkylsilyl group is a latent carbanion, silyl aldehydes may function as bifunctional reagents.[6] The branched silyl aldehyde 1 is a convenient olefin precursor. Treatment with a Grignard reagent should generate a 1,2-silanol, which can be converted to the corresponding (*Z*)- or (*E*)-alkene by base or Lewis acid-promoted elimination[5d] (see Scheme 1). The linear silylaldehyde 2 is equivalent to a 1,3-dipole and is a simpler alternative to Nakamura's cyclopropane ketals.[7]

The hydroesterification of vinylsilanes has been effected in excellent regiocontrol by Takeuchi et al.[8a] Cobalt catalysts gave only the branched esters, and palladium catalysts yielded the linear esters.[8b] Such control was not possible in the related hydroformylation reactions. The branched aldehyde could only be obtained as a 1:1 mixture with the linear isomer.[8c] In order to obtain the linear aldehyde selectively in the rhodium-catalyzed hydroformylations, a very large excess (50–80 equiv) of phosphine ligand was required.[8c]

We now report the regioselective hydroformylation of several vinylsilanes with the noted complexes. Conditions were developed using the zwitterionic rhodium complex

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[•] Abstract published in *Advance ACS Abstracts*, April 1, 1994.

[1] Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339.

[2] (a) Alper, H.; Zhou, J.-Q. *J. Chem. Soc., Chem. Commun.* **1993**, 316; (b) *J. Org. Chem.* **1992**, *57*, 3729. (c) Zhou, J.-Q.; Alper, H. *J. Org. Chem.* **1992**, *57*, 3328. (d) *J. Chem. Soc., Chem. Commun.* **1991**, 233.

[3] Amer, I.; Alper, H. *J. Am. Chem. Soc.* **1990**, *112*, 3674.

[4] (a) Olson, W. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 7657. (b) Chini, P.; Ercoli, R. *Gazz. Chim. Ital.* **1958**, *88*, 1170.

[5] α-(Trimethylsilyl) aldehydes are notoriously difficult to prepare and isolate. Jackson et al. [(a) Doyle, M. M.; Jackson, W. R.; Perlmutter, P. *Aust. J. Chem.* **1989**, *42*, 1907] have reported that the methods described by Enders for the preparation of α-silyl aldehydes and a modification of the Meyers method failed in their hands: (b) Enders, D.; Lohray, B. B. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 351. (c) Comins, D.; Meyers, A. *Synthesis* **1978**, 403. Hudrlik et al. have similarly reported that they have not been able to prepare trimethylsilyl acetaldehyde or simple α-(trimethylsilyl) *n*-alkyl aldehydes by rearrangements of α,β-epoxy silanes or by oxidations of β-hydroxy silanes: (d) Hudrlik, P. F.; Hudrlik, A. M.; Misra, R. N.; Peterson, D.; Withers, G. P. Kulkarni, A. K. *J. Org. Chem.* **1980**, *45*, 4444. The *in situ* preparation of α-(trimethylsilyl) aldehydes has been reported: (e) Sato, T.; Abe, T.; Kuwajima, I. *Tetrahedron Lett.* **1978**, 259. α-(Triisopropylsilyl) aldehydes have been prepared by oxidation of 1,2-silanols with NCS: (f) Birkofer, L.; Quittmann, W. *Chem. Ber.* **1985**, *118*, 2874. α-(Triisopropylsilyl) and α-(triphenylsilyl) aldehydes have been prepared by rearrangements of the corresponding oxiranes: (g) Muchowski, J. M.; Naef, R.; Maddox, M. L. *Tetrahedron Lett.* **1985**, 5375. (h) Eisch, J. J.; Trainor, J. T. *J. Org. Chem.* **1963**, *28*, 2870. Attempts to prepare the trimethylsilyl or even the dimethylphenylsilyl analogs using the same method reportedly failed: (i) Wilt, J.W.; Kolewe, O.; Kraemer, J. F. *J. Am. Chem. Soc.* **1969**, *91*, 2624. 2-(Triethylsilyl)propanal was prepared by the $Ni(CO)_4$-promoted addition of Et_3SiH to acrolein: (j) Chukovskaya, E. T.; Freidlina, R. K. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1963**, 761; *Chem. Abstr.* **1963**, *59*, 7551h. 2- and 3-(trimethylsilyl)propanal were prepared in low yield (ca.16%) as a 1:1 mixture by the cobalt carbonyl catalyzed hydroformylation of vinyltrimethylsilane: (k) Burkhard, C. A.; Hurd, D. T. *J. Org. Chem.* **1952**, *17*, 1107. β-(Trialkylsilyl) aldehydes have been prepared by the Pt-catalyzed hydrosilation of protected acrolein and subsequent acid-catalyzed deprotection: (l) Sadykhazde, S. I.; Mardanov, M. A.; Sultanova, Z. B.; Sultanov, R. A. *Azerb. Khim. Zh.* **1966**, *6*, 29; *Chem. Abstr.* **1967**, *67*, 64470u (see also ref 5f). Oxidation of the 1,3-silanols with Ag_2NO_3/Celite yielded β-(triphenylsilyl) aldehydes (see ref 5f).

[6] Trost, B. M. *Pure Appl. Chem.* **1988**, *60*, 1615.

[7] (a) Nakamura, E; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 7360. (b) Murai, S.; Ryu, I.; Sonoda, N. *J. Organomet. Chem.* **1983**, *250*, 121.

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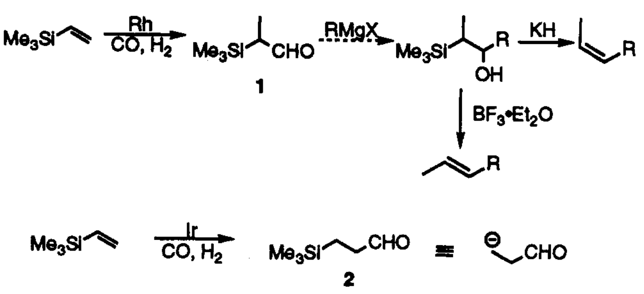
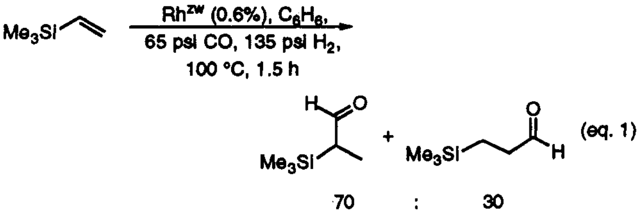
Scheme 1



under which the branched aldehyde is produced in excess over the linear. To the best of our knowledge, this is the first report of a hydroformylation process which produces an α-silyl aldehyde as the major product.



The iridium complexes tested were found to be highly selective for the production of the linear isomer (90–100% of the total aldehyde), *without the addition of any phosphine ligands.*[9]

Results and Discussion

Rhodium Catalysts. In an attempt to optimize the amount of the branched isomer produced in the hydroformylation of vinyltrimethylsilane, we examined the effects of the temperature, reaction time, solvent, and CO, H_2 pressures. It was found that of these factors, the most important was the amount of CO and H_2 in the system. When the reaction was run using a 1:2 CO:H_2 ratio, the branched to linear ratio ranged from 70:30 to 60:40 as judged by capillary GC and ^{1}H NMR analysis. The optimum conditions found for the production of 2-(trimethylsilyl)propanal were 0.6% Rh^{zw}, 70 psi CO, 130 psi H_2, 100 °C, 1.5 h, 1 M in dry benzene (see Table 1).

Along with the branched and linear aldehydes, a small amount of the product of a 1,3-silicon shift (Brook rearrangement)[10] was detected by GC and NMR (its structure was confirmed by analogy to the corresponding triethylsilyl enol ether, see eqs 2 and 3). The amount of this rearrangement product is variable depending on the solvent used. In toluene-d_8 there was no silyl enol ether produced after 1.5 h but in benzene-d_6 12% silyl enol ether was detected after the same time.

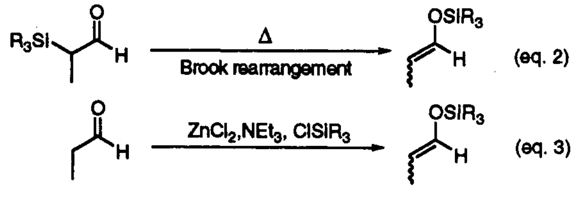
Table 1. Hydroformylation of Vinyltrimethylsilane Catalyzed by Rh^{zw} [a]

entry	time (h)	solvent	% isolated yield[b]	B:L[c]
1	4	benzene	27	56:44
2	3	benzene	34	57:43
3	1.5	benzene	20	70:30
4	1.5	benzene-d_6	31[d]	60:40
5	1.5	toluene-d_8	50[d]	60:40

[a] Reaction conditions: 3.2 mmol substrate 1 M in dry distilled solvent, 0.6% Rh (0.019 mmol), 65 psi CO, 135 psi H_2, 100 °C. [b] Of both linear and branched aldehydes. [c] B:L = branched:linear, not including branched aldehyde lost as enol silyl ether. [d] NMR yield (vs added internal standard).

Rh^{zw} proved to be a good catalyst for the production of the branched aldehyde in the hydroformylation of vinyltrimethylsilane (entry 3, Table 1), but the isolated yields of the aldehyde products were poor (20–40%). We therefore turned our attention to vinyltriethylsilane, since the corresponding silyl aldehydes and enol silyl ethers would be less volatile.[11]

The added bulk of the ethyl groups caused a shift in the branched to linear ratios but also allowed for the isolation of the aldehyde products in as high as 91% yield (*vide infra*). With this substrate we were also able to obtain accurate GC conversions and isolate the silyl enol ether produced by a Brook rearrangement of the α-silyl aldehyde (eq 2, R = Me, Et). To confirm the structure, the silyl enol ether was synthesized by an independant route (eq 3, R = Et).[12]



Under standard conditions (65 psi CO, 135 psi H_2, 1 M C_6H_6, 100 °C, 1.5 h), the triethylsilyl aldehyde was isolated in 34% yield as a 35:65 ratio of branched to linear isomers (Figure 1). Increasing the time to 4 h allowed us to obtain the aldehydes in 66% isolated yield. Further increases in the reaction time improved the conversion but lowered the GC and isolated yields.[13]

Rh^{zw} catalyzes the hydroformylation of vinyltriethylsilane in a variety of solvents, including ethers, chlorohydrocarbons, and aromatics. The effects of solvent on yield and conversion are shown in Table 2.

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(8) (a) Takeuchi, R.; Ishii, N.; Sugiura, M.; Sato, N. *J. Org. Chem.* **1992**, *57*, 4189. (b) Takeuchi, R.; Ishii, N.; Sato, N. *J. Chem. Soc., Chem. Commun.* **1991**, 1247. (c) Takeuchi, R.; Sato, N. *J. Organomet. Chem.* **1990**, *393*, 1. (d) This technique has been used before, and a *tert*-butyldiphenylsilyl substituent was found to be necessary for the more demanding 1,2-disubstituted olefins: Doyle, M. M.; Jackson, W. R.; Perlmutter, P. *Tetrahedron Lett.* **1989**, *30*, 233.

(9) In fact, the addition of phosphine ligands was found to drastically inhibit the Ir^{zw}-catalyzed hydroformylation reaction. This is in stark contrast to the hydroformylations catalyzed by neutral rhodium complexes[8c] where large excesses of phosphines are necessary to obtain the linear isomer in good selectivity. For the hydroformylation of vinyltrimethylsilane, 50 equiv of PPh_3 (based on Rh) are required to obtain >95% linear when $Rh_6(CO)_{16}$ is used, and 80 equiv are required when $HRh(CO)(PPh_3)_3$ is used. Alternatively, platinum or cobalt catalysts can be used, but these require more severe conditions.

(10) For leading references see: (a) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. (b) *Pure Appl. Chem.* **1966**, *13*, 215. (c) Brook, A. G.; Bassindale, A. R. Molecular Rearrangements of Organosilicon Compounds. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; part 2, p 149. For specifically 1,3 rearrangements see: (d) Brook, A.G.; MacRae, D. M.; Limburg, W. W. *J. Am. Chem. Soc.* **1967**, *89*, 5493.

(11) After assembly of the Parr autoclave, it is standard procedure to flush the autoclave three times with carbon monoxide. Since the starting material is low boiling (bp 55 °C), some of it is undoubtably lost during this procedure. In order to minimize this loss, the autoclave was cooled prior to purging. According to Takeuchi (ref 8c), 2- and 3-(trimethylsilyl)-propanal boil at ca. 130 °C. Since they are sensitive to preparative chromatography using either silica gel or alumina, purification from catalyst was affected using reduced pressure distillation. This also might account for the low yields. After 1.5 h, the NMR yield of 2- and 3-(trimethylsilyl)propanal was 50% in toluene-d_8 and 31% in benzene-d_6. This compares nicely with the results of vinyltriethylsilane (34% in benzene and 53% in toluene after 1.5 h). It is therefore likely that the low isolated yields are a physical and not chemical problem.

(12) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807.

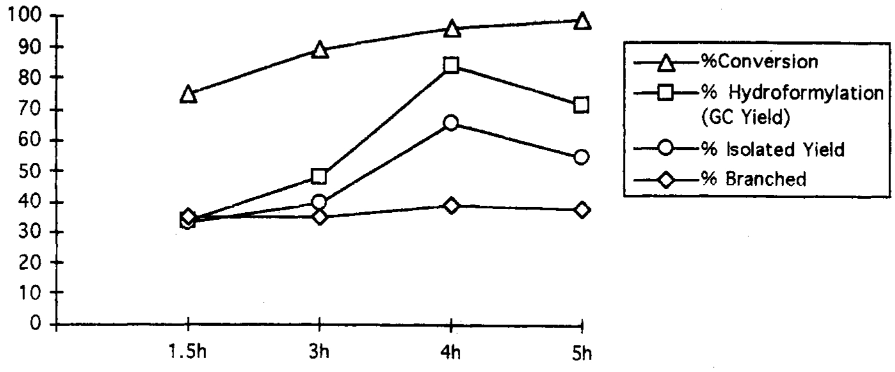

Figure 1. Rhodium zwitterion catalyzed hydroformylation of vinyltriethylsilane in benzene.

Table 2. Rh^{zw}-Catalyzed Hydroformylation of Vinyltriethylsilane in Various Solvents[a]

entry	solvent	% Hf^{n} [b]	% convn	% 1,3-Si shift	B:L[c]
1	C_6H_6	34	74	6	35:65
2	$PhCH_3$	53	95	8	34:66
3	$PhCF_3$	53	95	11	28:72
4	PhOMe	34	*d*	6	28:72
5	Et_2O	27	32	4	30:70
6	THF	28	38	4	39:61
7	CH_2Cl_2	33	74	10	23:77
8	$CHCl_3$	38	95	20	5:95

[a] Reaction conditions: 3.2 mmol substrate (1 M in dry distilled solvent), 0.6% catalyst (0.019 mmol), 65 psi CO, 135 psi H_2, 100 °C, 1.5 h. [b] HF^{n} = hydroformylation. GC yield of both linear and branched aldehydes. [c] B:L = branched:linear, not including branched aldehyde lost as enol silyl ether. [d] Conversion not measured due to interference by PhOMe signal.

Table 3. Rh^+-Catalyzed Hydroformylation of Vinyltriethylsilane in Various Solvents[a]

entry	solvent	time (h)	% Hf^{n} [b]	% convn	% 1,3-Si shift	B:L[c]
1	C_6H_6	3	50	84	3	35:65
2	C_6H_6	1.5	40	82	6	33:67
3	$PhCH_3$	1.5	31	78	6	29:71
4	$PhCF_3$	1.5	17	37		19:81
5	PhOMe	1.5	25	*d*	5	20:80
6	Et_2O	3	NR			
7	$CHCl_3$	3	NR			

[a] Reaction conditions: 3.2 mmol substrate (1 M in dry distilled solvent), 0.6% catalyst (0.019 mmol), 65 psi CO, 135 psi H_2, 100 °C. [b] Hf^{n} = hydroformylation. GC yield of both linear and branched aldehydes. [c] B:L = branched:linear, not including branched aldehyde lost as enol silyl ether. [d] Conversion not measured due to interference by PhOMe signal.

The hydroformylation reaction was stopped after 1.5 h in order to accurately compare the different solvents. (The same procedure is used later during the additive study.) Of the solvents tried, the best are toluene and α,α,α-trifluorotoluene. It can also be seen from Table 2 that there is an increased amount of Brook rearrangement when the reaction is run in halogenated solvents (see entries 3, 7, and 8).

The hydroformylation of vinyltriethylsilane was also examined with the cationic complex $[Rh(COD)_2]^+BF_4^-$, (designated as Rh^+).[14] Unlike Rh^{zw}, the activity of Rh^+ was drastically affected by the solvent. Of those examined, only aromatic solvents were suitable (see Table 3). Stabilization of the low-ligated metal by complexation of the arene solvent may be responsible for this pronounced solvent effect. For Rh^{zw}, stabilization could be provided by the tetraphenylborate counterion in nonaromatic solvents.

A more traditional method for stabilizing transition metal catalysts is the addition of phosphine ligands. If the lack of reactivity of Rh^+ in nonaromatic solvents is related to a lack of stabilizing ligands, the addition of phosphines should provide this stabilization. In fact, although Rh^+ does not catalyze the hydroformylation in diethyl ether, when 1 equiv of triphenylphosphine is added to the reaction mixture, the hydroformylation products can be obtained in 93% yield. A similar effect was observed in the Rh^+/C_6H_6 system where the yield was increased from 40% to 93% upon the addition of PPh_3 (entries 3 and 4 in Table 4). This effect was extended to the Rh^{zw}/C_6H_6 hydroformylation of vinyltriethylsilane where the strongly σ-donating phosphine likely displaces the coordinated tetraphenylborate.

In all the cases examined, the addition of PPh_3 increased the amount of the linear isomer.[15] In fact, by adding as little as 2 equiv of PPh_3, the selectivity changes from 35:65 (B:L) to 7:93 (compare entries 6 and 8 in Table 4). It has been postulated[15d] that in the presence of large excesses of phosphine, the dissociation of phosphine from a rhodium complex is inhibited. It is possible that the phosphine ligands bond more effectively to the cationic rhodium center, decreasing the extent of dissociation.

With the cationic or zwitterionic rhodium complexes, the addition of 2–4 equiv of PPh_3 improves the activity of the catalyst. After only 30 min, a quantitative yield of 3-(triethylsilyl)propanal was obtained (Table 4, entry 9). The reaction even proceeded to 86% yield after only 1.5 h at 65 °C (entry 10). Finally, the addition of pyridine

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(13) It should be noted that in most of the rhodium-catalyzed hydroformylations, the conversions are higher than would be expected on the basis of the yields. This is due to the production of another compound during the reaction. The structure of this compound has not yet been determined but appears to be some type of oligomer. Since this is not produced during the iridium-catalyzed hydroformylations which are run at the same temperature for equal or longer times, it does not result from simple thermal decomposition of the aldehydic products.

(14) $[Rh(COD)_2]^+BF_4$ (hydrated) purchased from Aldrich showed identical catalytic activity and selectivity in the hydroformylation of vinylsilanes as that prepared by the addition of $AgBF_4$ to a solution of $[Rh(COD)Cl]_2$ in THF containing excess COD: (a) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089. However, commercially available $[Rh(COD)_2]^+OTf^-$ gave much lower yields of the silyl aldehydes and exclusively the linear isomer under identical conditions. Crabtree et al. have reported some pronounced counterion effects in catalytic reactions, especially when the substrate is weakly coordinating: (b) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738. (c) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.

(15) It is well known that the addition of triphenylphosphine increases the amount of the linear isomer in Rh-catalyzed hydroformylations. Ratios of >50:1 (PPh_3:Rh) are usually required for optimum L:B ratios. (a) Pittman, C. U.; Honnick, W. D.; Yand, J. J. *J. Org. Chem.* **1980**, *45*, 2132. (b) Pruett, R. L. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 239. (c) Pruett, R. L. and Smith, J. A. Ger. Pat. 2062703, 1971; *Chem. Abstr.* **1971**, *75*, 109844. The excess phosphine produces a rhodium complex containing multiple phosphine ligands creating a more sterically hindered environment: (d) Evans, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3133.

Table 4. Effect of Additives on the Rh$^+$- and Rh^{zw}-Catalyzed Hydroformylations of Vinyltriethylsilane in Various Solvents[a]

entry	catalyst	time (h)	*T* (°C)	solvent	additive	% Hf^n [b]	B:L[c]
1	Rh$^+$	3	100	Et_2O	none	NR[d]	
2	Rh$^+$	1.5	100	Et_2O	PPh_3 (1 equiv)[e]	93	20:80
3	Rh$^+$	1.5	100	C_6H_6	none	40	33:67
4	Rh$^+$	1.5	100	C_6H_6	PPh_3 (1 equiv)	93	22:78
5	Rh$^+$	1.5	100	C_6H_6	py (2 equiv)[f]	22	33:67
6	Rh^{zw}	1.5	100	C_6H_6	none	34	35:65
7	Rh^{zw}	1.5	100	C_6H_6	PPh_3 (1 equiv)	98 (91)	20:80
8	Rh^{zw}	1.5	100	C_6H_6	PPh_3 (2 equiv)	97	7:93
9	Rh^{zw}	0.5	100	C_6H_6	PPh_3 (4 equiv)	100 (90)	7:93
10	Rh^{zw}	1.5	65	C_6H_6	PPh_3 (4 equiv)	86	7:93
11	Rh^{zw}	1.5	100	C_6H_6	py (2 equiv)	33	34:66

[a] Reaction conditions: 3.2 mmol substrate (1 M in dry distilled solvent) 0.6% catalyst (0.019 mmol), 65 psi CO, 135 psi H_2. [b] Hf^n = hydroformylation. GC yields of both linear and branched aldehydes, isolated yields in parentheses. [c] B:L = branched:linear. Not including branched aldehyde lost as enol silyl ether. [d] No reaction. [e] per rhodium atom. [f] py = pyridine.

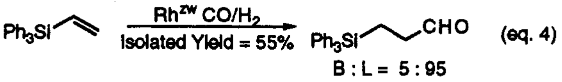
Table 5. $[Ir(COD)_2]^+BF_4^-$-Catalyzed Hydroformylation of Vinyltriethylsilane[a]

entry	$CO:H_2$ (psi)	*T* (°C)	% linear	% Hf^n [b]	% convn	% H_2^n [c]	% isolated yield	ratio (Hf^n:H_2^n)
1	65:135	100	100	12	100	63	9	16:84
2	300:300	100	95	33	100	60	23	35:65
3	600:600	100	100	32	100	55	24	37:63
4	500:100	100	97	79	100	25	65	76:24
5	1000:100	100	100	20	37	4		86:14
6	700:100	100	97	80	83	15	60	84:16
7[d]	350:50	100	99	33	36	6		84:16
8[d]	700:100	140	90	80	99	11	60	87:13
9[e]	700:100	60	97	36	70	4		90:10

[a] Reaction conditions: 3.2 mmol substrate, 1.8% catalyst (0.058 mmol), 1 M in dry distilled benzene, 3 h. [b] Hf^n = hydroformylation. [c] H_2^n = hydrogenation. [d] 5 h. [e] 26 h.

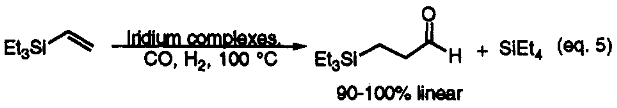
(entry 11) to the reaction mixture had virtually no effect on the hydroformylation of vinyltriethylsilane.[16]

The linear silyl aldehyde could also be obtained by increasing the bulk of the silyl substituent.[8d] Thus, the hydroformylation of vinyltriphenylsilane was performed with Rh^{zw} under the standard conditions, in the absence of phosphine to yield the linear isomer with 95% selectivity (eq 4).



Of the rhodium catalysts examined to date for the hydroformylation of vinyltrimethylsilane, Rh^{zw} is the only one capable of producing the branched aldehyde in excess over the linear (B:L = 70:30). Using vinyltriethylsilane, the corresponding aldehydes could be obtained in up to 91% isolated yield, but with this substrate the branched to linear ratio was at best 35:65.

Iridium Catalysts. Using the standard conditions developed for the rhodium systems, we examined the activity of the analogous iridium complexes, $Ir(COD)BPh_4$ (Ir^{zw}) and $[Ir(COD)_2]^+BF_4^-$ (Ir$^+$). While Ir^{zw} was almost completely unreactive under these conditions, 100% conversion was achieved using Ir$^+$. Although the major product of this reaction was tetraethylsilane,[17] the selectivity for the linear aldehyde was remarkably good (90–100%, eq 5). Increasing the amount of carbon monoxide in the gas mixture (from 1:2 to 7:1 $CO:H_2$) suppressed the hydrogenation. Under these conditions, the linear aldehyde was obtained in 80% GC and 60% isolated yields (B:L = 3:97, entry 6, Table 5).



The effect of temperature was also examined. At 60 °C a slight improvement in the ratio of hydroformylation to hydrogenation was noted, but overall the reaction temperature had little effect on this ratio.

The optimum conditions for the hydroformylation of vinyltriethylsilane with Ir$^+$ were thus found to be 1.8% catalyst, 1 M in dry benzene, 100 °C, 3 h, 700 psi CO and 100 psi H_2. We next examined hydrated iridium trichloride under these conditions and found that it did not catalyze the reaction. However, the addition of 1.5–2 equiv (based on iridium) of either $AgPF_6$ or $AgBF_4$ produced a species which catalyzed the hydroformylation after extended periods of time (see Table 6, entries 3 and 4). It was adventitiously discovered that pretreating this mixture at 160 °C[18] for 45–60 min in the presence of CO and H_2 substantially decreased the time required for the reaction (Table 6, entries 5 and 6).[19] Using this preactivation protocol, $IrCl_3$ catalyzed the hydroformylation of vinyltriethylsilane in 3 h *without the addition of silver salts.*

Since Rh$^+$ was only active in aromatic solvents and the Ir$^+$–catalyzed reactions were run in benzene, the solvent

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(16) The addition of pyridine has been shown to decrease the activity of the hydroformylation catalyst so that higher pressures and temperatures are required. (a) Imyanitov, N. S.; Rudkovskii, D. M. *Zh. Prikl. Khim.* 1966, *39*, 2811; *Chem. Abstr.* 1967, *66*, 75465. (b) Lapidus, A. L.; Yan, Y. B.; Alpatov, N. I.; Ogibin, Y. N. *USSR Pat.* 859350, 1981; *Chem. Abstr.* 1982, *96*, 122206.

(17) Iridium catalysts typically give more hydrogenation than their rhodium counterparts. Thomas, J. A. Br. Pat. 1367623, 1974; *Chem. Abstr.* 1975, *82*, 142591.

(18) It was found that pretreatment at 160 °C or greater (bath temperature) was necessary to activate the iridium complexes. Even 155 °C was insufficient.

(19) When IrX_3H_2O is heated at 150 °C under carbon monoxide, the corresponding halocarbonyls, $IrX_2(CO)_2$ and $IrX(CO)_3$, are produced. Iridium carbonyl is a minor product of this reaction and is produced as a mixture of $Ir_4(CO)_{12}$ and $[Ir(CO)_4]_n$: *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; John Wiley and Sons: New York, 1968; Vol. 1, pp 17 and 227. The haloiridium(I) carbonyls are likely precursors of the corresponding hydrides (see ref 15d).

Table 6. Iridium Trichloride Catalyzed Hydroformylation of Vinyltriethylsilane[a]

entry	time (h)	solvent	% linear	% Hf^{n} [b]	% convn[c]	% H$_2$^{n} [d]	additive	preactivation (°C/h)
1	3	PhH/CH_2Cl_2	NR[e]				none	
2	3	PhH/$CHCl_3$	NR				none	
3	14	PhH/$CHCl_3$	100	54	100	21	$AgPF_6$	
4	O/N[f]	PhH/$CHCl_3$	100	50	66	10	$AgBF_4$	
5	3	PhH/$CHCl_3$	NR				$AgBF_4$	
6	3	PhH/$CHCl_3$	98	59	92	16	$AgBF_4$	160/1.0
7	3.5	$CHCl_3$	100	54	99	32	$AgBF_4$	160/0.75
8	3	$CHCl_3$	100	46	99	18	none	160/0.75
9	3	$CHCl_3$	NR				none	

[a] Reaction conditions: 3.2 mmol substrate, 1.8% catalyst (0.058 mmol), 1 M in dry distilled solvent, 100 °C, 700 psi CO, 100 psi H_2, 1.5–2 equiv of additive. [b] Hf^{n} = hydroformylation. [c] Convn = conversion. [d] H_2^{n} = hydrogenation. [e] NR = no reaction. [f] O/N = overnight.

Table 7. Catalytic Activity of the Iridium Zwitterionic Complex in the Hydroformylation of Vinyltriethylsilane[a]

entry	time (h)	% catalyst	T (°C)	% linear	% Hf^{n} [b]	% convn[c]	% H$_2$^{n} [d]	preactivation (°C/h)
1	3	0.6	100	91	8	19	3	
2	3	0.6	100	91	87[e]	100	16	160/1
3	3	0.6	60	NR[f]				160/1
4	3	0.1	100	90	33	51	6	160/1
5	9	0.1	100	94	(73)[g]	100		160/1
6	1.5	0.6	160	91	70	100	21	
7	4	0.6	100	91	29	43	7	
8	5	0.6	100	93	82	100	26	

[a] Reaction conditions: 3.2 mmol substrate, 0.6% (0.019 mmol) catalyst, 1 M in dry distilled $CHCl_3$, 700 psi CO, 100 psi H_2. [b] Hf^{n} = hydroformylation. [c] Convn = conversion. [d] H_2^{n} = hydrogenation. [e] 75% isolated yield. [f] NR = no reaction. [g] Isolated yields.

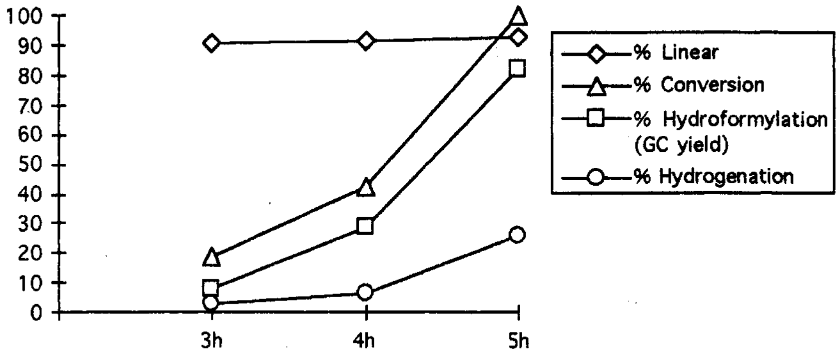

Figure 2. Effect of time on the activity of Ir^{zw} in the hydroformylation of vinyltriethylsilane.

initially chosen for the $IrCl_3$ catalyzed reaction was a 1:1 mixture of benzene and chloroform. However, it was found that unlike Rh$^+$, both Ir$^+$ and $IrCl_3$ were able to catalyze the hydroformylation of vinyltriethylsilane in the absence of an aromatic solvent.

The preactivation protocol described above was also applied to the zwitterionic iridium complex, Ir^{zw}. After being heated at 160 °C for 45–60 min under CO and H_2 prior to the addition of substrate, Ir^{zw} did indeed catalyze the hydroformylation reaction. Although the selectivity for the linear isomer is consistently better for the $IrCl_3$ system, there is less hydrogenation in the Ir^{zw}–catalyzed reactions and the isolated yields are much improved.

The substance obtained by pretreatment of Ir^{zw} as previously described completes two catalytic cycles per minute. Using a substrate to catalyst ratio of 1000 : 1, 3-(triethylsilyl)propanal was isolated in 73% yield as a 6:94 mixture of branched to linear isomers after only 9 h (Table 7, entry 5). When Ir$^+$ and $IrCl_3$ were used for the hydroformylation of vinyltriethylsilane, 50:1 substrate to catalyst ratios were employed and 3–5 h were required for 100% conversion.

In the hydroformylation reactions catalyzed by Ir^{zw} without preactivation, the yield is only 8% after 3 h. If the reaction is left for 5 h, the conversion is 100% and the yield increases to 82% (see Figure 2 and Table 7, entries 1 and 8).

It is clear from Figure 2 that there is an induction period of approximately 3 hours for the conversion of the zwitterionic iridium complex to the catalytically active species. Since after 5 h at 100 °C, the reaction mixture still contained undissolved Ir^{zw}, it is reasonable to assume that even though 100% conversion was observed, only a portion of the iridium complex added at the beginning of the reaction had been converted to the catalytically active species.

Again using the preactivation protocol, the catalytic activity of several other iridium complexes was tested (see Figure 3).

All the Ir(I) complexes tested, with the exception of Vaska's complex, were effective catalysts for the hydroformylation of vinyltriethylsilane with or without preactivation.[20] $Ir_4(CO)_{12}$ was only slightly active after pretreatment. After the preactivated-Ir^{zw}–catalyzed hydroformylation reaction, a small amount of a bright yellow solid is suspended in the pale yellow solution. IR analyses suggest that this material is a mixture of $Ir_4(CO)_{12}$ and $[Ir(CO)_3]_n$.[19] On the basis of the unreactivity of $Ir_4(CO)_{12}$ even after pretreatment, it is likely that these Ir(0) carbonyls are only byproducts of the conversion of

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(20) Vaska's complex has been reported to be much less active in the hydroformylation reaction than its rhodium analog, $[RhCl(CO)(PPh_3)_2]$ (see ref 15d and references cited therein).

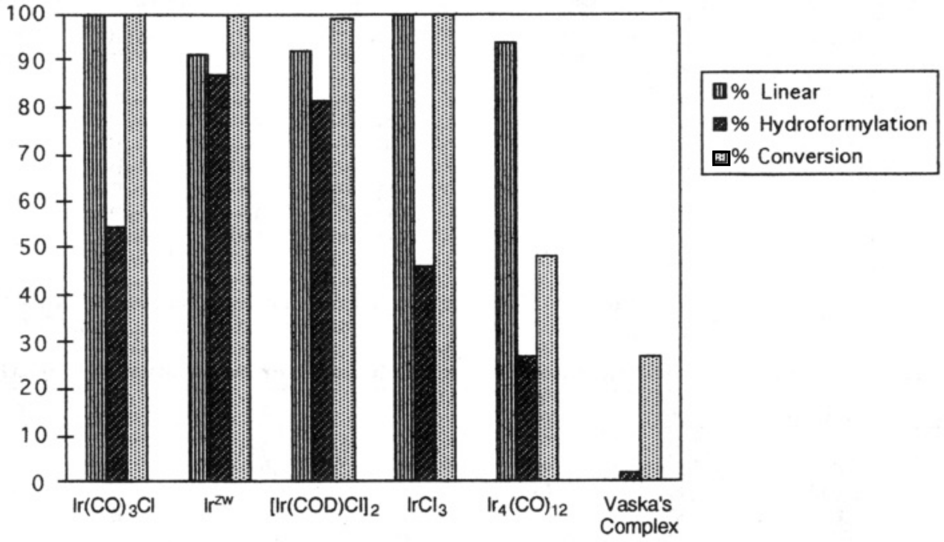

Figure 3. Activity of iridium catalysts after preactivation for 1 h at 160 °C under CO and H_2 in the hydroformylation of vinyltriethylsilane.

Ir^{zw} to the catalytically active species. The iridium(I) complexes $Ir(CO)_3Cl$ and Ir(COD)Cl, like Ir^{zw} and Ir^+, were able to catalyze the hydroformylation of vinyltriethylsilane without preactivation.

In the Rh^{zw}-catalyzed hydroformylation, the addition of triphenylphosphine had a dramatic effect on the reaction (see Table 4). The isolated yields were increased from 0–40% to 91–93%, and the linear aldehyde was the major isomer when triphenylphosphine was added. However, when as little as 1 equiv of triphenylphosphine was added to a solution of preactivated Ir^{zw}, the hydroformylation of vinyltriethylsilane was completely suppressed.

It has been demonstrated that 90–100% of the aldehyde produced during the Ir-catalyzed hydroformylation of vinyltrialkylsilanes is linear. The inclusion of triphenylphosphine in the coordination sphere of iridium must make complexation of the trialkylsilane substituted olefins difficult. This supposition is supported by the failure of Vaska's complex to catalyze the hydroformylation of these sterically demanding substrates.

Cobalt Catalysts. Unlike $IrCl_3$, cobalt chloride (hydrated or anhydrous) did not catalyze the hydroformylation of vinyltriethylsilane after preactivation or upon the addition of silver salts. Although it was not possible to obtain the exact cobalt analogs of the cationic and zwitterionic rhodium and iridium complexes described thus far, the cationic cobalt cluster, $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]BPh_4$,[4] was found to be an effective catalyst for the hydroformylation of vinyltriethylsilane. It is somewhat similar to the zwitterionic complexes since it is cationic and each cobalt atom contains a η^6-coordinated benzene.

Using 0.1% of this cationic cobalt cluster, vinyltriethylsilane was hydroformylated in 3 h (5.5 turnovers per minute) yielding the linear isomer as the major product (B:L = 24:76). Unlike the rhodium-catalyzed hydroformylations, the crude reaction mixture contained some hydrogenated starting material ($Hf^n:H_2^n$ = 77:23).[21]

Conclusions

Rhodium cationic and zwitterionic complexes proved to be superior catalysts for the hydroformylation of vinylsilanes, producing either α- or β-silyl aldehydes depending on the reaction conditions. Under optimized conditions, vinyltrimethylsilane was hydroformylated to yield the branched isomer as the major product (60–70% of the total aldehyde produced). Iridium complexes showed completely opposite selectivities, producing the linear aldehyde as 90–100% of the total aldehyde produced. This is a convenient alternative to the existing methodology which requires the addition of a vast excess of tertiary phosphine. The cationic cobalt cluster tested was more active than any of the other complexes examined, completing 1000 turnovers in 3 h (>5 turnovers per minute). The linear aldehyde was the major product, but the selectivity was better in the iridium-catalyzed hydroformylations.

The iridium and rhodium complexes examined also had completely different responses to the addition of triphenylphosphine. The addition of only 2 equiv of triphenylphosphine had a drastic effect on the regioselectivity of the Rh^{zw}- and Rh^+-catalyzed hydroformylations of vinyltriethylsilane yielding almost exclusively the linear isomer (B:L = 7:93). Furthermore, the isolated yield was consistently greater than 90% after as little time as 0.5 h. On the other hand, the addition of only 1 equiv of triphenylphosphine to a solution of preactivated Ir^{zw} completely inhibited the hydroformylation of vinyltriethylsilane.

It is possible, by employing either the rhodium or iridium zwitterionic catalysts, to obtain selectively the branched or linear silyl aldehydes by the hydroformylation of commercially available vinyltrialkylsilanes. The linear aldehyde can also be obtained selectively by the addition of 2 equiv of triphenylphosphine to the Rh^{zw}- or Rh^+-catalyzed reactions. The hydroformylation reactions described represent a one-step preparation of synthetically useful α- and β-silyl aldehydes.

Experimental Section

All ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 200- or 300-MHz Gemini operating at 200 and 300 MHz for ^1H and 50 and 75 MHz for ^{13}C, respectively. NMR data are reported

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[21] It was previously noted (ref 17) that iridium catalysts afford more hydrogenation than the analogous rhodium complexes. Usually cobalt catalysts give less than 5% hydrogenation (Pruett, R. L. *Adv. Organomet. Chem.*, **1979**, *17*, 12), but significant amounts of alkane result from some substituted olefins.

in chemical shifts relative to tetramethylsilane as the internal standard, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, b = broad and m = multiplet), integration, and assignment. NMR spectra were run in $CDCl_3$ containing 0.03% TMS or in C_6D_6. Proton spectra were referenced to 7.24 ppm for $CDCl_3$ or 7.16 for C_6D_6 and carbon to 77.0 ppm for $CDCl_3$ or 128.0 for C_6H_6. Infrared data were collected on a Bomem MB-100 FT-IR spectrometer. Liquid samples were run neat using sodium chloride disks. Solid samples were obtained using fabricated KBr disks. Gas chromatographic analyses were performed on a Varian 3300 using a DB1 capillary column and a Varian 4270 integrator.

All air- and/or moisture-sensitive reactions were performed in glassware flame dried under nitrogen purified by passing through a Drierite tower. Solvent solutions and liquid reagents were transferred with syringes and double-ended needles (cannulas) using standard inert atmosphere techniques. Air-sensitive solids were handled using standard Schlenk techniques and transferred using a glovebag.

Solvents were dried using the drying agents listed and distilled under a dry atmosphere: benzene, anisole, diethyl ether, and tetrahydrofuran from sodium metal/benzophenone ketyl over nitrogen; chloroform and α,α,α-trifluorotoluene from P_2O_5; dichloromethane, toluene, and triethylamine from calcium hydride under Drierite in air; methanol from $Mg(OMe)_2$ under nitrogen; and propanal from $MgSO_4$ under nitrogen. Vinylsilanes were used as purchased from Aldrich, Lancaster, or Fluka Chemical Companies.[22] $Rh(COD)BPh_4$, $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]BPh_4$, and $[Rh(COD)_2]^+BF_4^-$ were synthesized according to the literature (see ref 1, 4, and 14c, respectively). Commercially available $[Rh(COD)_2]^+BF_4^-$ gave identical results. We thank Dr. Ibrahim Amer and Dr. Yuri Goldberg for the preparation of $Ir(COD)BPh_4$ and $[Ir(COD)Cl]_2$, respectively. Carbon monoxide and UHP hydrogen were supplied by Air Products.

The following chemicals were used as purchased or, after purification (*vide supra*), from the following suppliers: *meta*-dimethoxybenzene and propanal from Eastman Chemical Co.; deuterated acetone from Cambridge Isotope Laboratories; zinc chloride from Fischer Scientific; vinyltriethylsilane and vinyltrimethylsilane from Lancaster Synthesis Inc.; aluminum bromide, bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate monohydrate, chlorotriethylsilane, cobalt(II) chloride (hydrated and anhydrous), deuterated chloroform, benzene-d_6, toluene-d_8, silver hexafluorophosphate, silver tetrafluoroborate, sodium tetraphenylborate, α,α,α-trifluorotoluene, triethylamine, triphenylphosphine, vinyltriethylsilane, and vinyltrimethylsilane from Aldrich Chemical Co.; and bis (1,5-cyclooctadiene)iridium(I) tetrafluoroborate, chlorocarbonylbis(triphenylphosphine)iridium, chlorotricarbonyliridium(I), dicobaltoctacarbonyl, iridiumcarbonyl and iridium(III) chloride (anhydrous and hydrated) from Strem Chemical Co.

Autoclaves were purchased from Parr Instrument Co. (screw cap bomb no. 4712 and gauge block assembly no. 4316).

General Procedure for the Hydroformylation Reactions. An autoclave, its glass liner, and a magnetic stirring bar were dried in an oven and cooled in a drybox. The liner was charged with the catalyst (0.019 mmol, 0.6% unless otherwise noted), vinylsilane (3.2 mmol), and solvent (3 mL). An additional amount of solvent (from 2–9 mL) was placed in the autoclave prior to insertion of the liner. The gauge and gauge block assembly were attached. The CO line was flushed three times with CO, and the system was also pressurized and flushed three times with CO, gradually increasing the pressure to the desired level. The system was then filled with the required amount of CO and the hydrogen line attached. The line was flushed three times, and the system was pressurized to the desired level. The autoclave was placed in the center of an oil bath on a heater stirrer preset to the reaction temperature. After the appropriate time, the autoclave was removed from the oil and cooled in either air or water. The excess gas was discharged and the system disassembled. The contents were analyzed first by GC using added *m*-dimethoxybenzene as the internal standard. GC yields and conversions are accurate to at best ±5%. The products were then isolated by Kugelrohr reduced pressure distillation after removal of the volatiles *in vacuo*. After isolation, NMR analyses were performed and the spectra compared with the literature.[23] The trimethylsilyl aldehydes were found to be extremely sensitive to air, decomposing to give the corresponding acids and/or unidentified products within hours. As previously reported,[5] the stability of the aldehyde increases as the steric bulk of R in SiR_3 increases. Thus, the triethyl silyl aldehydes were considerably more stable than the trimethyl analogs, but oxidation was still observed after several days exposure to air.

The higher boiling 2- and 3-(triphenylsilyl)propanals were purified by flash chromatography on silica gel. Separation of the branched isomer from the linear was possible by careful chromatography. Specifically, the crude reaction mixture was adsorbed onto silica gel by dissolution in ether, addition of silica gel, and removal of the volatiles *in vacuo*. The powder thus obtained was added to a silica gel column prepacked with hexanes. The polarity of the eluant was gradually increased to 10% ether in hexanes and the desired fractions collected and analyzed by ^1H NMR.

Acknowledgment. We are grateful to British Petroleum and to the Natural Sciences and Engineering Research Council of Canada for support of this research. We also thank Johnson Matthey for providing a loan of rhodium chloride. C.C. thanks NSERC for a postgraduate scholarship and Dr. Vladimir Grushin for kindly reading this manuscript.

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[22] No difference was noted when the hydroformylation was performed using vinylsilanes that had been stirred over basic alumina under nitrogen, distilled, dried over $MgSO_4$, and filtered. However, older samples of vinylsilane were purified as described.

[23] For 2- and 3-(trimethylsilyl)propanal, see refs 2k and 8c. For 3-(triphenylsilyl)propanal, see ref 2f. For 2-(triethylsilyl)propanal, see ref 2j (spectra not reported). For 3-(triethylsilyl)propanal, see ref 2l (spectra not reported). 3-(Triethylsilyl)propanal. ^1H NMR: 0.52 (q, $J = 8.0$ Hz, 6H, $SiCH_2CH_3$); 0.73–0.79, (m, 2H, $SiCH_2CH_2CHO$); 0.92 (t, $J = 8.0$ Hz, 9H, $SiCH_2CH_3$); 2.31–2.38 (m, 2H, $SiCH_2CH_2CHO$); 9.72 (t, $J = 2.8$ Hz, 1H, CHO). ^{13}C NMR: 2.8, 2.9, 7.11, 38.1, 202.7. IR: 1696 cm^{-1}. 2-(Triethylsilyl)propanal. ^1H NMR: 0.66 (q, $J = 7.8$ Hz, 6H, $SiCH_2CH_3$); 0.96 (t, $J = 7.8$ Hz, 9H, $SiCH_2CH_3$); 1.19 (d, $J = 6.7$ Hz, 3H, $SiCHCH_3$); 2.5 (qd, $J_1 = 6.7$ Hz, $J_2 = 2.3$ Hz, 1H, $SiCHCHO$); 9.72 (m, 1H, CHO). ^{13}C NMR: 2.4, 7.06, 7.9, 40.5, 202.9. IR: 1724 cm^{-1}.