Molecular Engineering in Homogeneous Catalysis: One-Phase Catalysis Coupled with Biphase Catalyst Separation. The Fluorous-Soluble $HRh(CO)\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_3$ Hydroformylation System

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Abstract: The hydroformylation of decene-1 was studied in the presence of the fluorous-soluble $P[CH_2CH_2(CF_2)_5CF_3]_3$ modified rhodium catalyst at 100 °C and 1.1 MPa of CO/H_2 (1:1) in a 50/50 vol % toluene/$C_6F_{11}CF_3$ solvent mixture, which forms a homogeneous liquid phase at and above 100 °C. $P[CH_2CH_2(CF_2)_5CF_3]_3$ was selected on the basis of a semiempirical calculation of the electronic properties of $P[(CH_2)_x(CF_2)_yCF_3]_3$ ($x = 0$, $y = 2$, 4 and $x = 0-5$, $y = 2$) and prepared by the reaction of PH_3 with $CH_2{=}CH(CF_2)_5CF_3$. The solution structure of $HRh(CO)\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_3$ (**1**) in $C_6F_{11}CF_3$ is similar to that of $HRh(CO)(PPh_3)_3$ (**2**) in toluene and $HRh(CO)\{P(m\text{-}C_6H_4SO_3Na)_3\}_3$ (**3**) in water. High-pressure NMR of **1** under 2.1−8.3 MPa of CO/H_2 (1:1) revealed that **1** is in equilibrium with $HRh(CO)_2\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_2$ (**4**). Kinetic studies show that the reaction is first order in both rhodium and decene-1. While the reaction is inhibited by $P[CH_2CH_2(CF_2)_5CF_3]_3$, the normal/iso (n/i) ratio of the aldehyde increases with increasing phosphine concentration. The catalytic activity of the $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst is similar to that of the nonfluorous analogue $Rh/P[(CH_2)_7CH_3]_3$ catalyst and is an order of magnitude lower than that of the Rh/PPh_3 catalyst. Surprisingly, the n/i product selectivity of $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ is closer to the selectivity of the Rh/PPh_3 catalyst than that of the $Rh/P[(CH_2)_7CH_3]_3$ catalyst. The fluorous biphase catalyst recovery concept was tested in a semicontinuous hydroformylation of decene-1 with the $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst. During 9 consecutive reaction/separation cycles, a total turnover of more than 35 000 was achieved with a loss of 1.18 ppm of Rh/mol of undecanals. The fluorous-soluble $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst was also tested for the continuous hydroformylation of ethylene using the high-boiling fluorous solvent FC-70, which allows continuous removal of propanal at the reaction temperature of 110 °C. The long-term stability of the $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst is better than that of the Rh/PPh_3 catalyst. Thus, the $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst is the first catalyst system which can be used for the hydroformylation of both low and high molecular weight olefins and provides facile catalyst separation for both low and high molecular weight aldehydes.

Introduction

Biological systems frequently combine molecular and engineering principles to achieve total control of a single chemical reaction or a multistep chemical process. On the contrary, many industrial processes have been developed by performing extensive chemical engineering on chemistries which have intrinsic limitations on maximum performance. Furthermore, changing environmental concerns and regulations are placing additional requirements on process performance, which cannot always be achieved by reengineering existing processes. Since many of these limitations have a molecular origin, a new interdisciplinary field, frequently called *molecular engineering*, is emerging with the ultimate goal to solve chemical process problems through detailed structural modification at the molecular level.

Homogeneous organometallic catalysis is particularly well suited for molecular engineering, as the performance of the catalyst can be controlled by the careful selection of metals and ligands.[1] Some of the recent results include fine-tuning catalytic activity[2] and/or selectivity,[3] novel catalyst designs for facile product separation,[4] and control of runaway reactions.[5] Despite recent advances,[1c] the lack of efficient catalyst recycling represents a major obstacle for the industrial applications of

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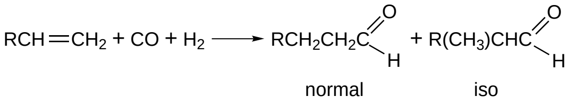
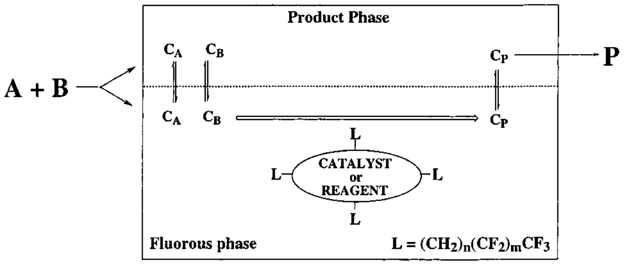
many homogeneous organometallic catalysts. For example, the hydroformylation of olefins is an important industrial process for the production of aldehydes from olefins, CO, and H_2 in the presence of homogeneous transition-metal catalysts.[6] One of the most challenging problems associated with the triphenylphosphine-modified rhodium catalyst system (Rh/PPh_3)[7] has



been the separation of higher aldehydes (C_n > 8) from the catalyst without deactivating the catalyst.[8] The use of an aqueous biphase system, in which the water phase contains the $P(m\text{-}C_6H_4SO_3Na)_3$-modified rhodium catalyst,[9] offers an easy separation of the organic products, and it has been used commercially for the hydroformylation of propylene.[10] However, since the catalytic reaction occurs in the aqueous phase, the potential application of the aqueous biphase system is limited by the solubility of the olefins (C_n > 7) in the catalyst containing the aqueous phase.[11]

We have recently developed a novel concept for performing stoichiometric and catalytic reactions using *fluorous biphase systems* (FBSs).[12] The FBS is based on the limited miscibility of perfluorinated alkanes, perfluorinated dialkyl ethers, and perfluorinated trialkylamines with nonfluorinated compounds.[13] The fluorous biphase systems consist of a fluorous phase containing a dissolved reagent[12,14] or catalyst[12,15] and a product phase with limited solubility in the fluorous phase which could be any common organic or nonorganic solvent (Scheme 1). The fluorous biphase concept was first demonstrated for the hydroformylation of decene-1 using the tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphine-modified rhodium catalyst ($Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$).[12] It was designed to achieve several process requirements with a single catalyst, including (1) the possibility to use the same catalyst for the hydroformylation of lower and higher molecular weight olefins, (2) facile and effective separation of the aldehydes from the catalyst, (3) appropriate coordination power of the ligand to keep the active rhodium species stable and prevent rhodium from leaching out of the fluorous phase, (4) comparable activity and selectivity with the commercially used Rh/PPh_3 catalyst system, and (5) the advantages of single-phase catalysis with biphase product separation by running the reaction at higher temperatures, where the system forms a single phase, and separating the products from the fluorous catalyst at lower temperatures. We now report our detailed study on the fluorous-soluble hydroformylation catalyst, $HRh(CO)\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_3$ (**1**).

Scheme 1



Results and Discussions

Selection of the Fluorous-Soluble Phosphine. Although perfluoroalkylated triphenylphosphines were already known,[16] we were concerned that the aromatic C−H and C−F bonds do offer dipole−dipole interactions,[17] making aryl- and perfluoroaryl-containing ligands soluble in common organic solvents and thus less desirable for fluorous biphase systems. According to the available liquid−liquid miscibility data,[13] it was clear that the best fluorous solubility could be achieved by attaching three perfluorinated alkyl groups (fluorous ponytails) to the phosphorus atom.[12] However, the attachment of the highly electron-withdrawing fluorous ponytails directly to the phosphorus atom could significantly lower the coordinating power

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Table 1. Electronic and Physical Properties of $P[(CH_2)_x(CF_2)_yCF_3]_3$, $P[(CH_2)_3CH_3]$, and PPh_3

species	P lone-pair level, eV	P Mulliken population (q)	protonation energy, eV	P−H, Å	∠HPL, deg
$P[CF_2CF_3]_3$	−11.7	0.83	−6.5	1.189	85.9
$P[(CF_2)_3CF_3]_3$	−11.7	0.83	−6.4	1.192	85.4
$P[CH_2CF_2CF_3]_3$	−10.6	0.62	−7.7	1.205	86.3
$P[(CH_2)_2CF_2CF_3]_3$	−9.9	0.48	−8.3	1.218	92.3
$P[(CH_2)_3CF_2CF_3]_3$	−9.5	0.40	−8.6	1.225	91.8
$P[(CH_2)_4CF_2CF_3]_3$	−9.3	0.38	−8.8	1.226	92.0
$P[(CH_2)_5CF_2CF_3]_3$	−9.2	0.36	−8.9	1.228	91.8
$P[(CH_2)_3CH_3]_3$	−8.7	0.33	−9.3	1.230	91.7
PPh_3	−9.0	0.67	−9.9	1.226	61.6

of the phosphine. We hypothesized that the insertion of "insulating" methylene groups [$-(CH_2)-$] before the fluorous ponytails could circumvent this problem. The selection of the number of $-(CH_2)-$ units between the phosphorus atom and the perfluoroalkyl moiety was based on semiempirical calculations of the electronic properties of $P[(CH_2)_x(CF_2)_yCF_3]_3$ ($x = 0$, $y = 2$ or 4 and $x = 0-5$, $y = 2$), $P[(CH_2)_3CH_3]$, and PPh_3. The calculations were performed using the UniChem version of MNDO93 and employed the PM3 parameter set.[18] Full geometry optimizations were performed. Since the purpose of the calculations was to determine the number of $-(CH_2)-$ spacer units necessary to minimize the effect of the strongly electron-withdrawing perfluoroalkyl moieties, the relative trends in the results and not the absolute numbers are of interest. Although similar calculations using different parameter sets or more advanced techniques might give different absolute numbers, it is felt that the established accuracy of the method used is sufficient to determine the relative trends.[19]

Phosphines (PR_3) are primarily electron-donating ligands with donation occurring through the lone pair of the phosphorus atom. Besides direct electronic interactions, steric factors also play an important role in the coordination chemistry of phosphines.[20] In a molecular orbital picture, the ability of species to donate charge to a given acceptor can be characterized by the energy gap between the donor and the acceptor orbitals and their spatial overlap. Thus, a first approximation to the effect of the perfluoroalkyl units is the position of the P lone-pair orbital. In addition, the amount of charge on the P atom should also correlate with the size of the lone pair and, hence, its ability to donate electrons. The P lone-pair eigenvalues and the P Mulliken charge for $P[(CH_2)_x(CF_2)_yCF_3]_3$ ($x = 0$, $y = 2$ or 4 and $x = 0-5$, $y = 2$), $P[(CH_2)_3CH_3]$, and PPh_3 are listed in Table 1. In addition, the protonation energies (ΔE) of the PR_3 species for the reaction of $H^+ + PR_3 \rightarrow HPR_3^+$ were calculated and are included in Table 1. Zero-point-energy corrections would need to be included to obtain the corresponding ΔH's. Negative values imply that the protonated ligand is more stable. It is unrealistic to compare these results directly with the measured values because solvent effects are not included. For comparison, the value calculated for H_2O is −5.8 eV. In an attempt to characterize the potential for steric interactions, the minimum angles subtended by the proton, phosphorus, and R are also reported in Table 1. The results clearly show that the electronic properties of $P[(CH_2)_x(CF_2)_yCF_3]_3$ ($x = 0$, $y = 2$ or 4 and $x = 0-5$, $y = 2$) can be tuned by varying the number of methylene groups between the phosphorus atom and the perfluoroalkyl moiety. The effect of perfluoroethyl ponytails, which are sufficient models for longer perfluoroalkyl groups, is small for two ($x = 2$) and essentially negligible for three ($x = 3$) methylene units. However, the differences between the electronic properties of $P[(CH_2)_xCF_2CF_3]_3$ with more than three methylene groups ($x > 3$) and $P[(CH_2)_3CH_3]_3$ are small but finite. These results suggest that the insertion of two methylene groups ($x = 2$) is enough to lower the electron-withdrawing effect of the fluorous ponytails. To obtain high fluorous solubility, the attachment of perfluorohexyl groups seems appropriate, as the three perfluorohexyl groups provide a fluorous domain of about 75% of the total volume of $P[CH_2CH_2(CF_2)_5CF_3]_3$.

Synthesis and Characterization of $P[CH_2CH_2(CF_2)_5CF_3]_3$. Since the reported synthesis for $P[CH_2CH_2(CF_2)_5CF_3]_3$ gave rather low yields in our hands,[21] we developed a new procedure based on the well-known reaction of PH_3 with olefins.[22] The reaction of PH_3 (25 mmol) with $CH_2{=}CH(CF_2)_5CF_3$ (100 mmol) was performed in the presence of azobis(isobutyronitrile) (AIBN) at 100 °C for 2 h. ^{31}P NMR of the reaction mixture showed the formation of 20% $P[CH_2CH_2(CF_2)_5CF_3]_3$, 4% $HP[CH_2CH_2(CF_2)_5CF_3]_2$, and 2% $H_2P[CH_2CH_2(CF_2)_5CF_3]$. Further addition of AIBN and heating the solution to 80 °C for 8 h resulted in the disappearance of the mono- and dialkylphosphines. After purification, we obtained 26% $P[CH_2CH_2(CF_2)_5CF_3]_3$. It has recently been shown that the yield could be increased to 53% by performing the addition of PH_3 to $CH_2{=}CH(CF_2)_5CF_3$ at lower temperatures (80−85 °C) for 24 h.[23] NMR and MS data are in agreement with the formula of $P[CH_2CH_2(CF_2)_5CF_3]_3$.

Characterization of $HRh(CO)\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_3$ (1). The fluorous-soluble **1** was prepared by reacting 0.1 mmol of $Rh(CO)_2(acac)$ with 0.3 mmol of $P[CH_2CH_2(CF_2)_5CF_3]_3$ in $C_6F_{11}CF_3$ (perfluoromethylcyclohexane) and treating the fluorous phase with 2.74 MPa of CO/H_2 (1:1) at 80 °C for 2 h. The ^1H NMR in $C_6F_{11}CF_3$ shows a quartet at −11.82 ppm ($J_{H-P} = 14$ Hz), which becomes a doublet of quartets by preparing the sample with 99% enriched ^{13}CO ($J_{H-C} = 35$ Hz). The ^{31}P NMR spectrum shows a doublet of doublets at 19.76 ppm ($J_{P-Rh} = 149.3$, $J_{P-H} = 14$ Hz) for the phosphine ligand. When the same solution is prepared with ^{13}CO, the $^{31}P\{^1H\}$ NMR spectrum shows a doublet of doublets ($J_{P-Rh} = 149.3$, $J_{P-C} = 10$ Hz). Finally, the $^{13}C\{^1H\}$-NMR shows a doublet of quartets at 205.4 ppm ($J_{Rh-C} = 50$, $J_{P-C} = 10$ Hz). The IR spectrum of **1** in $C_6F_{11}CF_3$ shows two bands at 2004 and 1976 cm^{-1}, which are attributed to the rhodium hydride and the terminal carbonyl ligand vibrations, respectively. This was confirmed by preparing a ^{13}CO-labeled **1**, which resulted in a shift of the rhodium terminal carbonyl ligand vibration from 1976 to 1930 cm^{-1}. Thus, the overall structure of **1** is very similar to those of $HRh(CO)(PPh_3)_3$ (**2**)[7a−d] and $HRh(CO)\{P(m\text{-}C_6H_4SO_3Na)_3\}_3$ (**3**).[24]

Mechanistic studies on phosphine-modified hydroformylation catalysts (Rh/PR_3) have clearly established that the coordinatively unsaturated species $\{HRh(CO)(PR_3)_2\}$ and $\{HRh(CO)_2(PR_3)\}$ are key intermediates. Their reaction with olefins leads to competing catalytic cycles involving one or two phosphine ligands on the rhodium (Scheme 2).[7] It is believed that the active rhodium species with two phosphine ligands or one

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[18] UniChem is a computational chemistry software package developed by Cray Research, Inc. Included within the package is the MNDO93 program developed by W. Thiel and co-workers.

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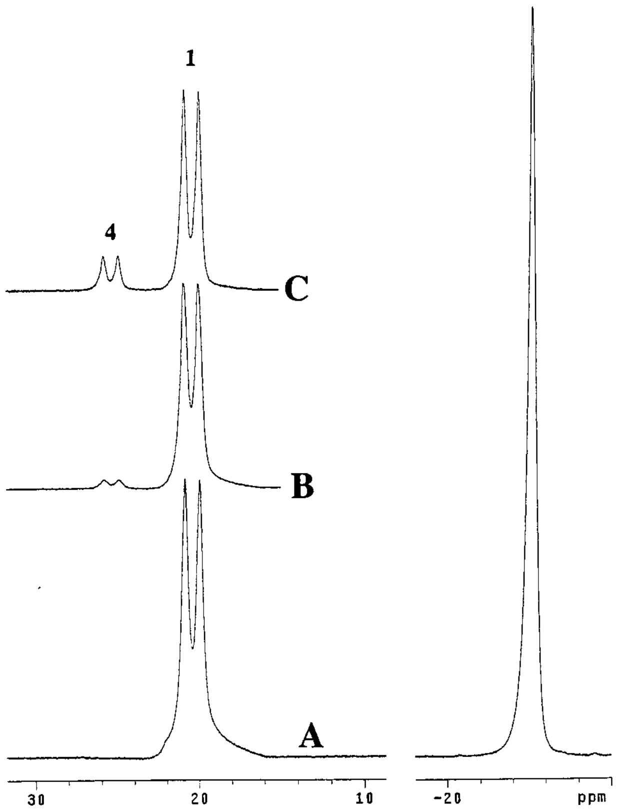
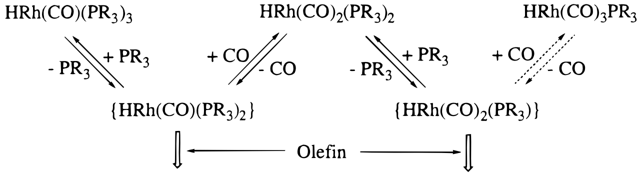


Figure 1. High-pressure $^{31}P\{^{1}H\}$ NMR spectra of $HRh(CO)\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_3$ (**1**) in the presence of 3 equiv of $P[CH_2CH_2(CF_2)_5CF_3]_3$ under (A) N_2, (B) 2.07 MPa of CO/H_2 (1:1), and (C) 8.27 MPa of CO/H_2 (1:1) in $C_6F_{11}CF_3$.

Scheme 2



phosphine ligand gives higher and lower normal/iso (n/i) ratios, respectively. These two species could form via ligand dissociation from $HRh(CO)_x(PR_3)_{4-x}$ (PR_3 dissociation, $x = 1$ or 2; CO dissociation, $x = 2$ or 3). While $HRh(CO)(PR_3)_3$ and $HRh(CO)_2(PR_3)_2$ have been shown to be the dominant species in the equilibrium under CO/H_2 (1:1), $HRh(CO)_3PR_3$ has not been observed.[7]

The reaction of 0.1 mmol of **1** with carbon monoxide in the presence of 0.3 mmol of $P[CH_2CH_2(CF_2)_5CF_3]_3$ under different CO/H_2 (1:1) pressures was studied by high-pressure $^{31}P\{^{1}H\}$ NMR (Figure 1). When a solution of **1** in $C_6F_{11}CF_3$ was treated with 2.07 MPa of CO/H_2 (1:1), a new doublet appeared at 24.8 ppm ($J_{P-Rh} = 148.5$ Hz), the intensity of the resonance at 19.76 ppm for **1** decreased, and the intensity of the resonance at −25.2 ppm for the free ligand increased according to Scheme 2, indicating the formation of $HRh(CO)_2\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_2$ (**4**). By increasing the CO/H_2 (1:1) pressure to 8.27 MPa, the concentration of **1** decreased further and the concentrations of **2** and the free ligand increased proportionally. Finally, when the CO/H_2 (1:1) pressure was decreased to 0.1 MPa and the solution was purged with N_2, **1** re-formed quantitatively. Detailed high-pressure NMR studies on the equilibria shown in Scheme 2 involving $HRh(CO)_x(PR_3)_{4-x}$ ($x = 1-2$; R = $(CH_2)_7CH_3$, $CH_2CH_2(CF_2)_5CF_3$, Ph, and m-$C_6H_4SO_3Na$) are in progress and will be published elsewhere.

Hydroformylation of Decene-1. Our initial study on the hydroformylation of decene-1 with the $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst proved the feasibility of the fluorous biphase concept.[12] We report here a detailed kinetic study in which the catalytic performance of the $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst is compared with that of the commercially used Rh/PPh_3 and the nonfluorous analogue $Rh/P[(CH_2)_7CH_3]_3$ catalysts. The possible kinetic and selectivity effects of the fluorous solvent $C_6F_{11}CF_3$ have also been tested by using the Rh/PPh_3 catalyst, which is soluble in a 50/50 vol % toluene/$C_6F_{11}CF_3$ solvent mixture at and above 100 °C.

The hydroformylation of decene-1 with all three catalysts was carried out in batch autoclaves at 100 °C and 1.1 MPa of CO/H_2 (1:1) in a 50/50 vol % toluene/$C_6F_{11}CF_3$ solvent mixture or in toluene. The concentration of Rh ranged from 0.02 to 2.2 mmol/L, and in all experiments, an excess of phosphine was used ($P/Rh > 3$). It is important to note that at the reaction conditions, the 50/50 vol % toluene/$C_6F_{11}CF_3$ solvent mixture formed a *single homogeneous phase* in the presence of all three catalysts at the ligand concentrations studied.

The reaction is first order in the concentration of rhodium for all three catalysts. The turnover frequency (TOF: mole of aldehyde/mole of Rh/second) vs conversion plot for the $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst (Figure 2) is linear, indicating first-order reaction in decene-1. The nonzero intercept reflects a less than 100% hydroformylation selectivity which will be addressed later. As expected, for a first-order reaction, the ln(1 − conversion/100) vs time plots are linear to more than two half-lives (Figure 3). The slopes of these plots yield reaction rates (integral method) which are essentially identical with the TOF/[decene-1] values obtained from the differential method described in the Experimental Section. The reaction is also first order in the concentration of the substrate with the nonfluorous analogue $Rh/P[(CH_2)_7CH_3]_3$ at all conditions studied. However, the kinetic response of the Rh/PPh_3 catalyst is more complicated. While at high concentrations of PPh_3 (ca. 0.2 mol/L) only first-order kinetics can be observed, at low phosphine concentrations (ca. 0.02 mol/L), a saturation in decene-1 occurs (see the Appendix for data and detailed discussion).

The kinetic response of the $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst to changes in decene-1 concentration is more similar to that of the $Rh/P[(CH_2)_7CH_3]_3$ catalyst than that of the Rh/PPh_3 catalyst. These results are in good agreement with our modeling prediction on the electronic nature of the fluorous-soluble $P[CH_2CH_2(CF_2)_5CF_3]_3$. The two CH_2 groups can indeed shield the electron-withdrawing effect of the fluorous ponytails, and thus, $P[CH_2CH_2(CF_2)_5CF_3]_3$ is more basic than PPh_3. In fact, recent solution calorimetric investigation of CO substitution in $[Rh(CO)_2Cl]_2$ with $P[CH_2CH_2(CF_2)_5CF_3]_3$ indicates that its electronic parameters are similar to those of PMe_2Ph.[25]

While the hydroformylation of decene-1 is inhibited by $P[CH_2CH_2(CF_2)_5CF_3]_3$, the n/i ratio of the aldehyde increases with increasing phosphine concentrations (Figure 4 and Table 2). GC analysis of the aldehyde products shows the formation of undecanal and 1-methyldecanal only up to 98% conversion of decene-1. The highest measured n/i ratio is 7.84 at 0.3 mol/L $P[CH_2CH_2(CF_2)_5CF_3]_3$ concentration. The olefin isomerization selectivity is about 10%, and it does not seem to be affected by the concentration of the ligand. Since the hydroformylation rate of internal olefins is much slower than that of a terminal double bond,[7] the formed internal olefins remain largely unconverted in the reactor. The dominating isomer olefin product is decene-2. The overall isomer distribution of the product decene mixture

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(25) Li, C.; Nolan, S. P.; Horváth, I. T. *Organometallics* Submitted.

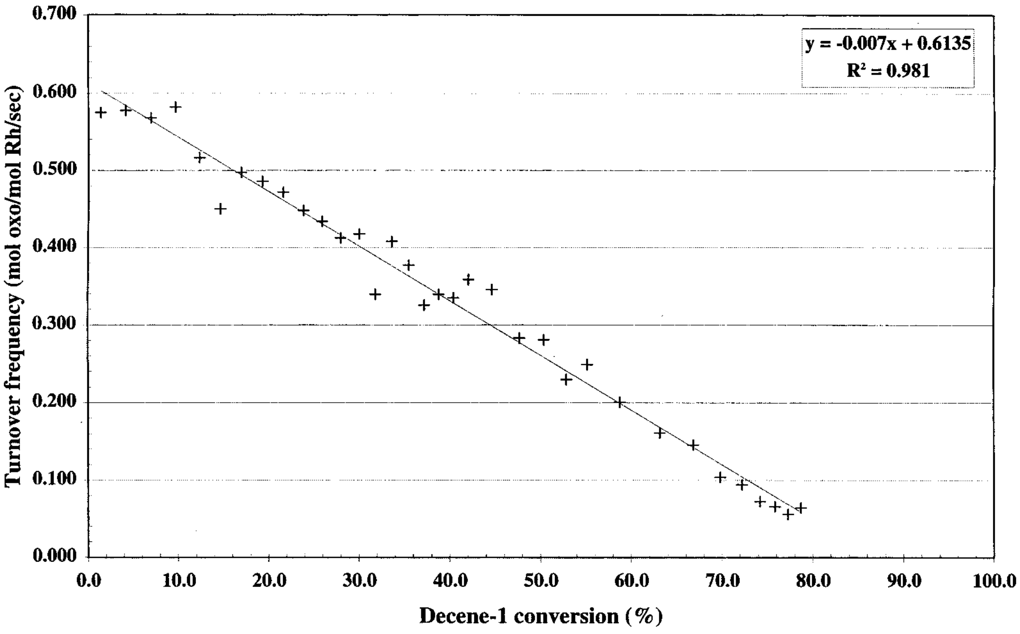

Figure 2. Rate of hydroformylation of decene-1 with Rh/P[$CH_2CH_2(CF_2)_5CF_3$]$_3$ catalyst in a 50/50 vol % toluene/$C_6F_{11}CF_3$ solvent mixture at 100 °C and 1.1 MPa of CO/H_2 (1:1) as a function of conversion. [Rh] = 0.814 mmol/L, [P[$CH_2CH_2(CF_2)_5CF_3$]$_3$] = 22.1 mmol/L, and [decene-1]$_{t=0}$ = 1.012 mol/L.

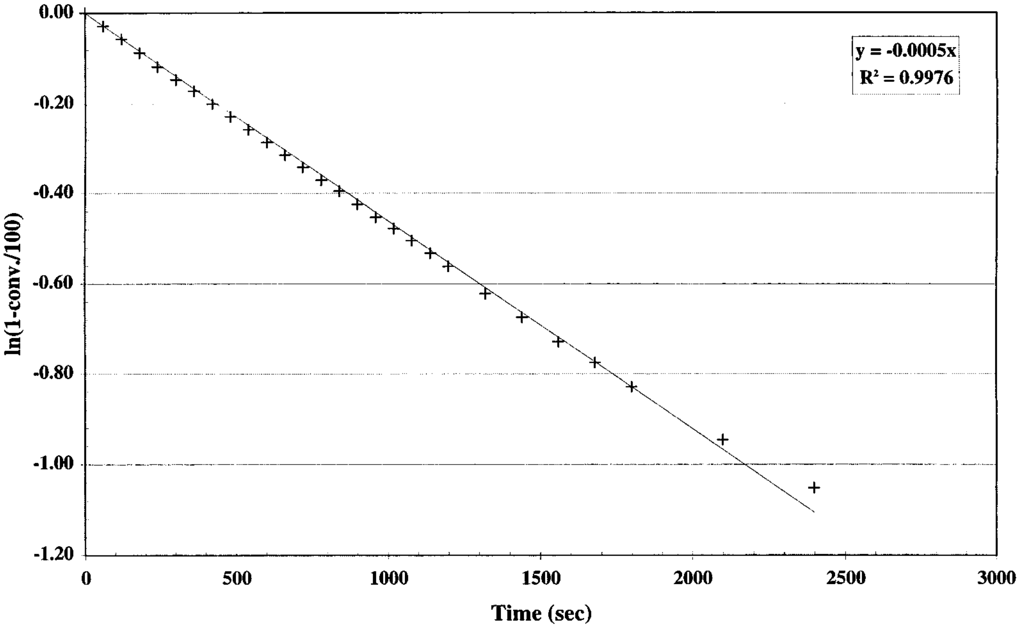

Figure 3. ln(1 − conversion/100) vs time plot rate for the hydroformylation of decene-1 with Rh/P[$CH_2CH_2(CF_2)_5CF_3$]$_3$ catalyst in a 50/50 vol % toluene/$C_6F_{11}CF_3$ solvent mixture at 100 °C and 1.1 MPa of CO/H_2 (1:1). [Rh] = 0.814 mmol/L, [P[$CH_2CH_2(CF_2)_5CF_3$]$_3$] = 22.1 mmol/L, and [decene-1]$_{t=0}$ = 1.012 mol/L.

conforms with a stepwise double-bond migration through repeated olefin addition and β-elimination cycles. Finally, less than 1% of decene-1 is hydrogenated to decane.

Based on the most coherent mechanism of the reaction,[26] it should be clear that the distribution of Rh intermediates with different CO/phosphine ligand ratios depends on the relative concentrations of CO and phosphine. At constant partial pressure of CO (as in this study), the determining factor thus becomes the concentration of the phosphine ligand. Our data are in full agreement with this prediction (Table 2). Although it is customary in the literature to report kinetic and selectivity data as a function of P/Rh ratio,[1b,6,27] we did not find any correlation between those values when excess phosphine (P/Rh > 3) is present. Rather, we found that the TOF/[decene-1] and product selectivities are independent of the P/Rh ratio and solely depend on the concentration of the phosphine, as long as the CO/H_2 ratio, total pressure, solvent, and temperature are

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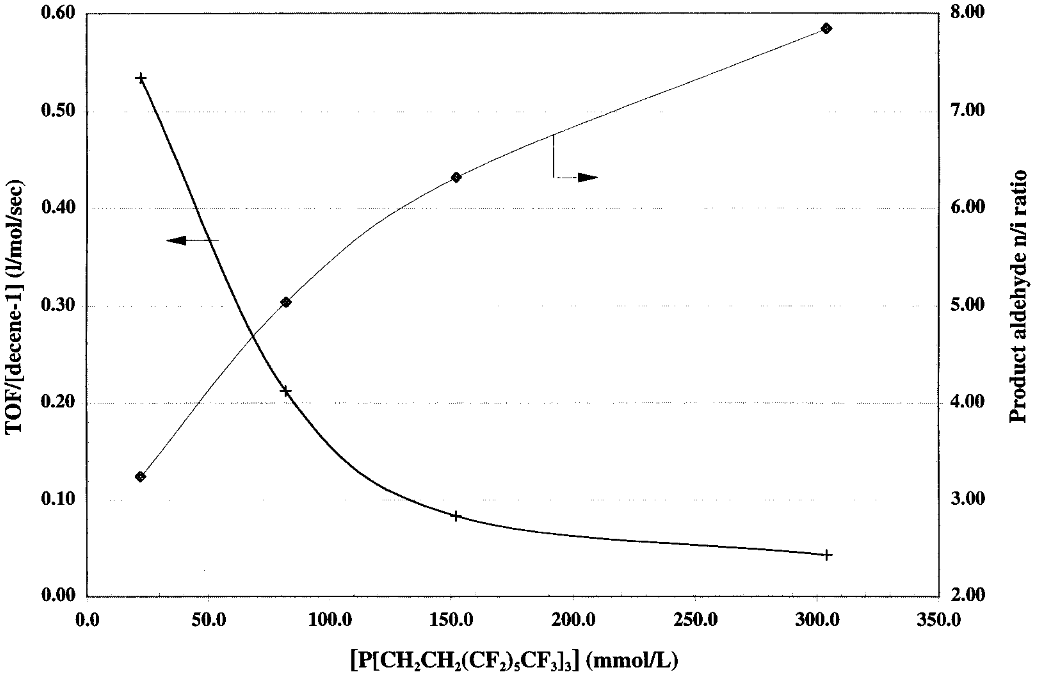

Figure 4. Effect of $P[CH_2CH_2(CF_2)_5CF_3]_3$ concentration on the rate and n/i ratio in the hydroformylation of decene-1 with $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst in a 50/50 vol % toluene/$C_6F_{11}CF_3$ solvent mixture at 100 °C and 1.1 MPa of CO/H_2 (1:1).

Table 2. Effect of the Phosphine Concentration on the Activity and n/i Selectivity of the $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ Catalyst in the Hydroformylation of Decene-1 in 50/50 vol % Toluene/$C_6F_{11}CF_3$ Solvent Mixture at 100 °C and 1.1 MPa of CO/H_2 (1:1)

$[P[CH_2CH_2(CF_2)_5CF_3]_3]$, mmol/L	P/Rh	TOF/[decene-1], (L/mol)/s	n/i
22.1	27	0.60	3.25
22.5	39	0.49	3.25
22.3	28	0.51	3.20
41.3	76	0.40	4.35
82.1	79	0.21	5.04
152.2	103	0.08	6.32
304.0	102	0.04	7.84

Table 3. Effect of the Ligands on the Activity and Selectivity of the Phosphine-Modified Rh Catalyst in the Hydroformylation of Decene-1 in 50/50 vol % Toluene/$C_6F_{11}CF_3$ Solvent Mixture at 100 °C and 1.1 MPa of CO/H_2 (1:1)

ligand[a]	TOF/[decene-1] (L/mol)/s	n/i	selectivity, % aldehyde	isomrzn	decane
$P[CH_2CH_2(CF_2)_5CF_3]_3$	0.53 ± 0.05	3.2	91.1	8.9	0.4
PPh_3	6.27 ± 0.30	3.2	91.8	8.2	0.0
$P[(CH_2)_7CH_3]_3$	0.22 ± 0.03	2.3	96.4	3.6	0.0

[a] [L] = 23.0 ± 1.5 mmol/L.

Table 4. Effect of Solvent on the Rate and Selectivity of the Rh/PPh_3 Catalyst in the Hydroformylation of Decene-1 at 100 °C and 1.1 MPa of CO/H_2 (1:1)[a]

solvent	TOF/[decene-1], (L/mol)/s	n/i	selectivity, % aldehyde	isomrzn	decane
toluene	6.3 ± 0.3	3.2	91.8	8.2	0.0
toluene/$C_6F_{11}CF_3$ = 1	4.1 ± 0.8	3.6	91.2	8.8	0.0

[a] $[PPh_3]$ = 23.2 ± 0.3 mmol/L.

the same. Similar results were obtained for the Rh/PPh_3 catalyst as well (see Appendix).

The catalytic activity of the $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst is similar to that of the nonfluorous analogue $Rh/P[(CH_2)_7CH_3]_3$ and is an order of magnitude lower than that of the Rh/PPh_3 catalyst (Table 3). Unlike the activity, the n/i product selectivity of $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ is closer to the selectivity of the Rh/PPh_3 catalyst than that of the $Rh/P[(CH_2)_7CH_3]_3$ catalyst (Table 3). The hydrogenation of decene-1 is negligible, with all three catalysts in agreement with earlier low-temperature and low-pressure data.[7d]

The introduction of a fluorous solvent results in minor changes in the activity and selectivity of the Rh/PPh_3 catalyst in the hydroformylation of decene-1 at 100 °C and 1.1 MPa of CO/H_2 (1:1) (Table 4). While the activity of the catalyst is approximately 30% lower in the toluene/$C_6F_{11}CF_3$ solvent mixture than in toluene, the n/i selectivity is somewhat lower in toluene than in toluene/$C_6F_{11}CF_3$. These effects might be due to the differences in gas solubilities. The aldehyde and olefin isomerization selectivities are virtually the same in both solvents. The results for the toluene/$C_6F_{11}CF_3$ solvent systems are consistent with that of a single-phase homogeneous hydroformylation reaction.

The fluorous biphase catalyst-recovery concept was tested in a semicontinuous decene-1 hydroformylation experiment. After each batch reaction, the product was cooled and the formed product and fluorous phases were allowed to separate. The supernatant product phase was siphoned off, and the fluorous catalyst solution left in the autoclave was used in the next run. In 9 consecutive runs, a total *t*urn*o*ver *n*umber (TON: mole of aldehyde/mole of Rh) of more than 35 000 was measured with a 4.2% Rh loss (Table 5). This loss represents 1.18 ppm of Rh loss/mol of aldehyde. The measured Rh loss is quite constant from run to run (Figure 5) and is due to the low but finite solubility of the $Rh/P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst in the product phase. Although no mass balance was established for the fluorous phosphine ligand, the activity and selectivity changes during the experiment indicate some ligand leaching as well. Thus, the rate of reaction and the olefin isomerization selectivity increase while the product aldehyde n/i ratio decreases in consecutive runs as the concentration of the ligand in the catalyst solution is decreased. The olefin hydrogenation selectivity is low and essentially constant through the nine

Table 5. Rhodium Content, Activity, and Selectivity Data for the Semicontinuous Hydroformylation of Decene-1 with the Rh/$P[CH_2CH_2(CF_2)_5CF_3]_3$ Catalyst in 50/50 vol % Toluene/$C_6F_{11}CF_3$ Solvent Mixture at 100 °C and 1.1 MPa of CO/H_2 (1:1)[a]

cycle	Rh in the reactor, μmol	TOF/[decene-1], (L/mol)/s	n/i	selectivity, % aldehyde	isomrzn	decane
1	15.626	0.279	4.47	91.5	7.83	0.7
2	15.544	0.315	4.09	89.4	9.86	0.7
3	15.455	0.379	3.94	89.3	10.1	0.6
4	15.375	0.356	3.76	89.5	9.93	0.6
5	15.304	0.384	3.64	89.1	10.30	0.6
6	15.226	0.419	3.59	89.0	10.33	0.6
7	15.139	0.496	3.51	88.9	10.57	0.5
8	15.060	0.484	3.57	88.3	11.01	0.6
9	14.976	0.488	3.51	88.3	11.03	0.6

[a] [$P[CH_2CH_2(CF_2)_5CF_3]_3$] in cycle 1: 42.7 mmol/L.

cycles. These trends can be recognized in the previously discussed (vide supra) batch kinetic experiments when the ligand concentration is the independent variable. Although the fluorous components are slowly removed with the organic product, it has to be emphasized that this semicontinuous experiment serves only as a demonstration of the FBS concept, and neither the process nor the catalytic system is optimized. The use of heavier fluorous solvents and longer fluorous ponytails on the phosphine should further decrease the rhodium loss, and with simple engineering solutions (e.g., distillation of the product and catalyst recycle), virtually all Rh and ligand losses can be eliminated.

Continuous Hydroformylation of Ethylene. The performance of the Rh/$P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst was also tested in the hydroformylation of ethylene (Table 6) using FC-70 (isomers of perfluorotripentylamine) as a solvent. Just like in the hydroformylation of decene-1, the reaction was found to be first-order for both ethylene and Rh. Since the solubility of ethylene has not been measured in the reaction mixture, the rate of reaction is referenced to the partial pressure of ethylene in the gas phase. The results show that while the rate of reaction is the same within experimental error at CO partial pressures of 460 and 210 kPa, the selectivity of ethane is doubled at the lower CO partial pressure. These observations are in agreement with some earlier reports. Thus, zero kinetic order in CO has been reported[7h] for the hydroformylation of propylene. Also, the strong suppression of olefin hydrogenation by CO has been reported by Wilkinson et al.[7c] The negative first order for CO in the hydrogenation of the substrate, on the other hand, is predicted by the mechanism[26] since the 16-electron alkyl intermediate ($RRh(CO)_{3-x}L_x$, $x = 1$ or 2) can be trapped by CO and follow the hydroformylation route rather than olefin hydrogenation.

The activation energy of the reaction was measured at two CO/H_2 ratios, and the average value of 20.0 kcal/mol (83.7 kJ/mol) is essentially the same as reported for the hydroformylation of propylene.[7h] Oswald and co-workers reported 22 kcal/mol for butene-1.[7j] Chaudhari et al. have reported in a series of papers the activation energies for the hydroformylation of hexene-1,[28a] decene-1,[28c] and dodecene-1[28e] to be 28, 11.8, and 13.7 kcal/mol, respectively. These latter values, however, were obtained from an engineering fit of experimental data; thus, the activation energies can be model dependent, which may explain their wide variance and some of those unusually low values.

The stability of the catalyst was tested in a *c*ontinuous *s*tirred *t*ank *r*eactor (CSTR) with ethylene at 110 °C for 2 months. As it is depicted by Figure 6, no measurable deactivation occurred during that period despite the low ethylene concentration and relatively high temperature, both of which are known to destabilize the industrial Rh/PPh_3 catalyst.[8b,d,f] In fact, the activity maintenance of the Rh/$P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst was better than the one reported for Rh/PPh_3,[8c] which later lost 0.2% activity per day at the same temperature but a higher ethylene partial pressure (46 kPa). These results again manifest the similarity of $P[CH_2CH_2(CF_2)_5CF_3]_3$ as a modifying ligand to trialkylphosphines rather than to triarylphosphines. Replacement of the aryl groups of the phosphine ligand with alkyl groups has been reported[8e] to increase the stability of the phosphine-modified rhodium catalysts.

Conclusions

We have established that the Rh/$P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst system can be used for the hydroformylation of ethylene and decene-1 and the product propanal and undecanals can be separated from the catalyst by distillation or phase separation, respectively. The solution structure of $HRh(CO)\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_3$ (**1**) is similar to that of $HRh(CO)(PPh_3)_3$ (**2**) and $HRh(CO)\{P(m\text{-}C_6H_4SO_3Na)_3\}_3$ (**3**). High-pressure NMR revealed that **1** is in equilibrium with $HRh(CO)_2\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_2$ (**4**) under CO/H_2 (1:1). The long-term stability of the Rh/$P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst during the continuous hydroformylation of ethylene is better than that of the Rh/PPh_3 catalyst. Kinetic studies on the hydroformylation of ethylene and decene-1 show that the reaction is first order in both rhodium and olefin. While the hydroformylation of decene-1 is inhibited by $P[CH_2CH_2(CF_2)_5CF_3]_3$, the n/i ratio of the undecanals increases with increasing phosphine concentration. The catalytic activity of the Rh/$P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst is similar to that of the nonfluorous analogue Rh/$P[(CH_2)_7CH_3]_3$ catalyst and is an order of magnitude lower than that of the Rh/PPh_3 catalyst. In contrast, the n/i product selectivity of Rh/$P[CH_2CH_2(CF_2)_5CF_3]_3$ is closer to the selectivity of the Rh/PPh_3 catalyst than that of the Rh/$P[(CH_2)_7CH_3]_3$ catalyst. The fluorous biphase catalyst recovery concept was tested in a semicontinuous hydroformylation of decene-1 with the Rh/$P[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst. During 9 consecutive reaction/separation cycles, a total turnover of more than 35 000 was achieved with a loss of 1.18 ppm of Rh/mol of undecanals.

Rh/$P[CH_2CH_2(CF_2)_5CF_3]_3$ is the first catalyst system which can be used for the hydroformylation of both low and high molecular weight olefins and provides facile catalyst separation for both low and high molecular weight aldehydes. Finally, the most intriguing aspect of this catalyst system is that it combines the advantages of one-phase catalysis with biphase product separation by running the reaction at higher temperatures and separating the products at lower temperatures.

Experimental Section

Solvents (toluene, anhydrous, Aldrich; perfluoromethylcyclohexane or $C_6F_{11}CF_3$, Fluorochem; FC-70, isomers of perfluorotripentylamine, 3M; and Freon-225, isomers of dichloropentafluoropropane, Asahi Glass Co. Ltd.; and decene-1, 99.0%, Chemsampco) were thoroughly deaerated but otherwise were used as received. All gases (ethylene, UHP grade, and CO/H_2 (1:1), UHP grade, both from MG Industries), PPh_3 (M&T), $P[(CH_2)_7CH_3]_3$, hexadecane (anhydrous, 99+%, Aldrich), and $Rh(acac)(CO)_2$ (99%, Strem) were used as received. Tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphine, $P[CH_2CH_2(CF_2)_5$-

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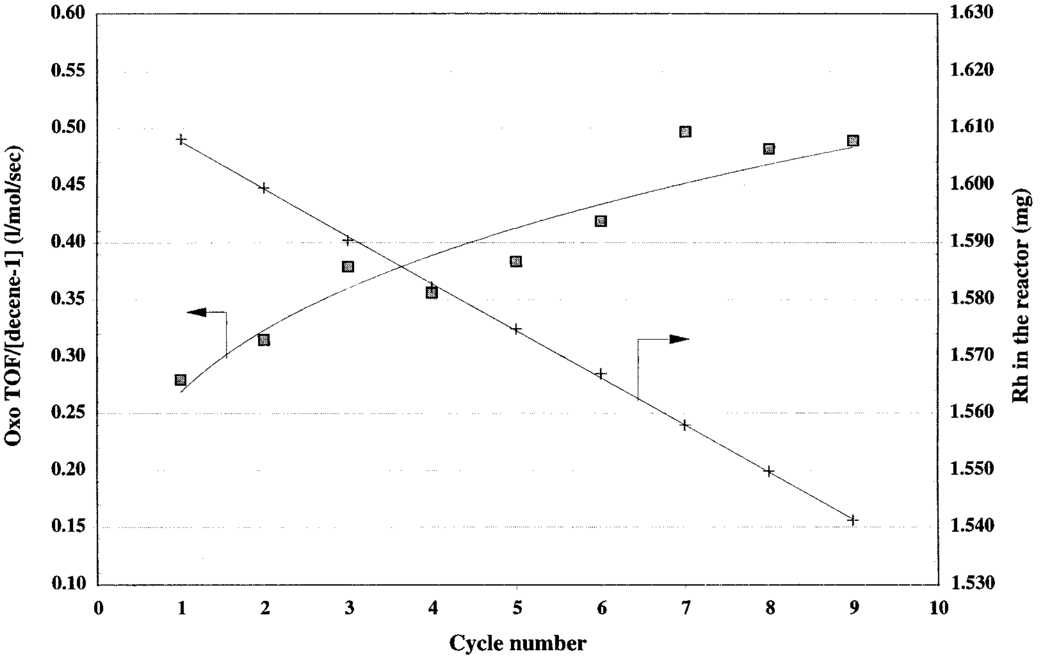

Figure 5. Rate of hydroformylation of decene-1 and rhodium content of the reactor as a function of reaction cycle in the semicontinuous hydroformylation of decene-1 with Rh/P[$CH_2CH_2(CF_2)_5CF_3$]$_3$ catalyst in a 50/50 vol % toluene/$C_6F_{11}CF_3$ solvent mixture at 100 °C and 1.1 MPa of CO/H_2 (1:1). [Rh] = 0.814 mmol/L, [P[$CH_2CH_2(CF_2)_5CF_3$]$_3$] = 42.7 mmol/L, and [decene-1]$_{t=0}$ = 1.012 mol/L.

Table 6. Continuous Hydroformylation of Ethylene with the Rh/P[$CH_2CH_2(CF_2)_5CF_3$]$_3$ Catalyst in FC-70

[Rh], mmol/L	[L],[a] mmol/L	p_{CO}, kPa	p_{H_2}, kPa	*T*, °C	TOF/$p_{C_2H_4}$, mmol oxo/mol Rh/kPa C_2H_4/s	selectivity, %	
						propanal	ethane
2.171	43.4	458	417	79.9	0.612	99.3	0.7
2.171	43.4	457	416	90.0	1.583	99.3	0.7
2.171	43.4	462	415	100.0	3.292	99.3	0.7
2.171	43.4	216	437	101.8	3.260	98.5	1.5
3.205	44.1	210	431	80.0	0.645	98.8	1.2
3.205	44.1	206	430	89.9	1.600	98.7	1.3
3.205	44.1	210	432	100.0	3.060	98.5	1.5
3.205	44.1	210	435	110.0	4.651	98.2	1.8

[a] L = P[$CH_2CH_2(CF_2)_5CF_3$]$_3$.

CF_3]$_3$, was prepared, purified, and analyzed as described later. All organic compounds were checked for purity by GC (Perkin-Elmer Autosystem, Hewlett-Packard Pona column). NMR spectra were recorded on a Varian 400-MHz spectrometer. High-pressure NMR experiments were performed using single-crystal sapphire NMR tubes; their design has been described elsewhere.[29] IR spectra were recorded on a Mattson Galaxy 5020 spectrometer. Rhodium analyses were performed on an inductively coupled plasma−atomic emission spectrometer (ICP/AES), Jarrell-Ash Model 1100, with argon gas flow and torch alignment. The ICP/AES instrument was calibrated with 10 ppm rhodium solution.

Synthesis of Tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphine A 100-mL glass-lined autoclave was charged under N_2 with 35 g (100 mmol) of 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octene, 0.6 g of azobis(isobutyronitrile) (AIBN), and 0.85 g (25 mmol) of PH_3 at room temperature. The mixture was stirred and heated to 100 °C and kept at that temperature for 2 h. After the reactor was cooled to room temperature, the unreacted PH_3 was vented to a scrubber containing an aqueous solution of 37% formaline and 0.05% $RhCl_3$. GC and ^{31}P NMR (in CF_2ClCCl_2F) showed the formation of $H_2PCH_2CH_2(CF_2)_5CF_3$ (2%, −139.3 ppm, t, J_{P-H} = 189 Hz), HP[$CH_2CH_2(CF_2)_5CF_3$]$_2$ (4%, −67.1 ppm, d, J_{P-H} = 194 Hz), and P[$CH_2CH_2(CF_2)_5CF_3$]$_3$ (20%, −24.9 ppm). Addition of more AIBN (0.25 g) and heating the solution at 80 °C for 8 h resulted in the disappearance of the mono- and dialkylphosphines. The reaction mixture was diluted with $C_6F_{11}CF_3$ (25 mL) and washed with toluene (4 × 15 mL). Distillation under vacuum (155 °C at 0.3 mmHg) yielded 26% tris-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphine. $^{31}P\{^1H\}$ NMR ($C_6F_{11}CF_3$): −25.2 ppm. ^1H NMR (neat): 1.87 (br, 6H, $C_6F_{13}CH_2$) and 1.39 (br, 6H, CH_2P) ppm. ^{19}F NMR (neat): −80.8 (t, *J* = 10.2 Hz, CF_3), −114.3 (CH_2CF_2), −120.9 (CF_2), −121.9 (CF_2), −122.4 (CF_2), and −125.5 (CF_2) ppm. MS: M^+ = 1072 (calcd: 1072).

In Situ Preparation of HRh(CO){P[$CH_2CH_2(CF_2)_5CF_3$]$_3$}$_3$ (1). A 10-mL vial was charged with 0.026 g (0.1 mmol) of solid Rh(acac)(CO)$_2$ and 0.322 g (0.3 mmol) of P[$CH_2CH_2(CF_2)_5CF_3$]$_3$ in 3 mL of $C_6F_{11}CF_3$ under N_2 in a glovebox. After the mixture was stirred for 30 min, the light-yellow solution was placed in a sapphire NMR tube. The tube was placed in a safety shield and charged with 2.74 MPa of CO/H_2 (1:1). The tube was transferred to a heater and kept at 80 °C for 2 h. The tube was placed into the safety shield and transferred to a hood, and the pressure was slowly released. The solution was transferred into a 10-mm glass NMR tube and purged with N_2. Multinuclear NMR and IR measurements showed the quantitative formation of **1**.

High-Pressure NMR of 1 under CO/H_2 (1:1). A sapphire NMR tube was charged with a solution of 0.335 g (0.1 mmol) of **1** and 0.335 g (0.3 mmol) of P[$CH_2CH_2(CF_2)_5CF_3$]$_3$ in 3 mL of $C_6F_{11}CF_3$ under N_2 in a glovebox. The tube was placed in a safety shield and pressurized with CO/H_2 (1:1) to the required pressure. After the tube was transferred in the safety shield to the top of the magnet, the tube was lowered into the probe of the magnet. After the measurement was complete, the tube was lifted into the safety shield and transferred to a hood, and the pressure was slowly released. The solution was transferred to a 10-mm glass NMR tube and purged with N_2. $^{31}P\{^1H\}$ NMR measurement showed that only **1** was present.

Hydroformylation of Decene-1. For kinetic measurements, Rh stock solutions were prepared by using toluene for PPh_3 or

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(29) Horváth, I. T.; Ponce, E. C. *Rev. Sci. Instrum.* **1991**, *62*, 1104.

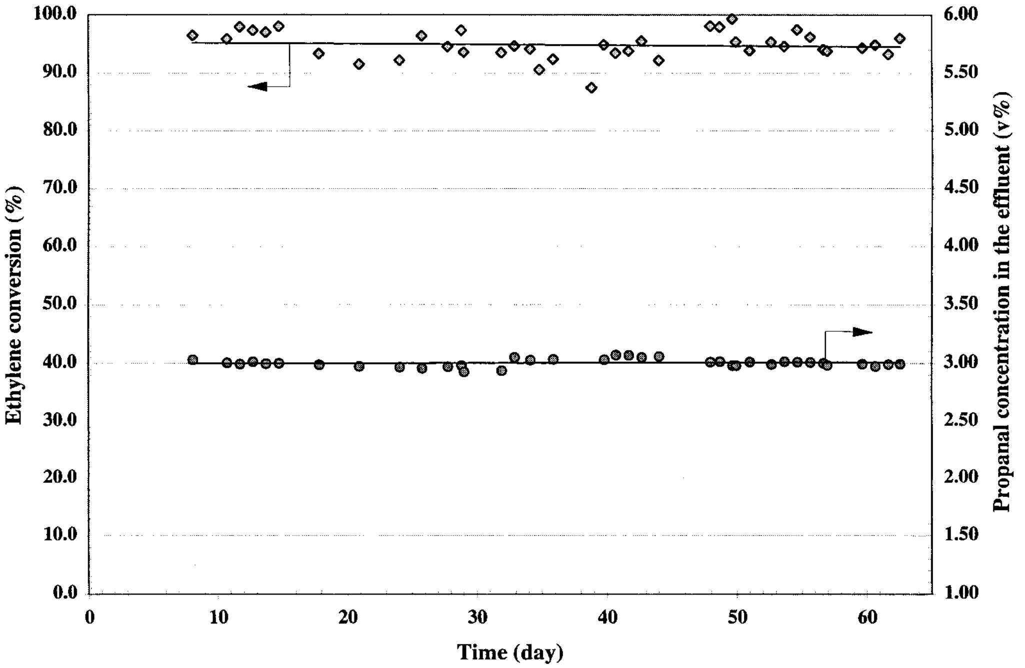

Figure 6. Continuous hydroformylation of ethylene with Rh/P$[CH_2CH_2(CF_2)_5CF_3]_3$ catalyst in FC-70 at 110 °C and 1.04 MPa of total pressure using 745.7 cm^3/min feed rate. [Rh] = 3.2 mmol/L and $[P[CH_2CH_2(CF_2)_5CF_3]_3]$ = 44.1 mmol/L. The steady-state composition in the reactor is CO (206 kPa, 19.6 vol %), H_2 (426 kPa, 40.6 vol %), $CH_2{=}CH_2$ (4 kPa, 0.4 vol %), CH_3CH_3 (<1 kPa, <0.1 vol %), CH_3CH_2CHO (32 kPa, 3.0 vol %), and CH_4 (376 kPa, 35.8 vol %).

$P[(CH_2)_7CH_3]_3$ and $C_6F_{11}CF_3$ or FC-70 for $P[CH_2CH_2(CF_2)_5CF_3]_3$. Stock solutions were made by weighing (±0.1 mg) the solvent, $Rh(acac)(CO)_2$, and the phosphine (P/Rh ratio of ca. 10) into a sealed bottle. The final catalyst solutions with the required composition were prepared by weighing the Rh stock solution, additional phosphine, and solvent(s).

Kinetic experiments were performed in a 150- or a 300-mL Autoclave Engineers' autoclave. The configurations of both units were identical. The reactors were connected to their volume-calibrated gas feed vessels (*PVT* tank) through a high-precision pressure-regulator valve. The reactors and feed vessels were equipped with certified Omega digital thermocouples and pressure gauges. The temperatures of the reactors were maintained within ±0.5 °C.

The Rh charge at each condition was adjusted to ensure that the initial gas-consumption rate was below the mass-transfer limit, established by variable stirrer-speed experiments. The rate and selectivity values obtained in the two autoclaves at the same conditions were statistically indistinguishable. The reproducibility was checked by carrying out at least two runs at each condition.

In a typical experiment, carried out in the 300-mL autoclave, 80 mL of catalyst solution was prepared in a Vacuum Atmospheres glovebox from the rhodium stock solution, the corresponding phosphine, and the solvent(s). The solution was charged into the reactor under N_2. The reactor was then flushed and pressurized with CO/H_2 (1:1) to ca. 500 kPa. Twenty milliliters of olefin was charged in the glovebox into a 75-mL injection bomb, which was then mounted into the CO/H_2 (1:1) feed line of the reactor. The catalyst was performed under CO/H_2 (1:1) at the reaction temperature. High-pressure $^{31}P\{^1H\}$ NMR experiments were carried out under identical conditions to verify the formation of the equilibrium mixture of the rhodium hydrides with a general formula of $HRh(CO)_x(PR_3)_{4-x}$ ($x = 1$ and 2).

The reaction was initiated by injecting the olefin into the reactor and bringing the pressure up to 1.1 MPa with CO/H_2 (1:1). The pressure in the reactor was maintained constant by making up the consumed CO/H_2 (1:1) from the *PVT* tank. The conversion was followed by recording the pressure drop in the *PVT* tank. The reaction was stopped by rapid cooling of the reactor after 80−95% conversion.

After the reaction mixture was cooled to room temperature, the product was removed under N_2. In the case of 50/50 vol % toluene/$C_6F_{11}CF_3$ biphase mixtures, Freon-225 was added to the stirred reactor before removing the products. The addition of Freon-225 increased the mutual solubilities and created a single liquid phase. Aliquot samples of the product were prepared under nitrogen for GC analysis by adding a known amount of *n*-hexadecane as an internal standard. Mass balances were established for all organic components and were typically 100 ± 5%, except for the phosphines, for which the mass balances were typically 100 ± 20%.

The turnover frequency (TOF) used in the kinetic analysis is defined as the rate of olefin conversion by 1 mol of rhodium and is expressed as the moles of olefin converted to aldehydes per mole of rhodium per second:

$$\mathrm{TOF} = \{(\mathrm{d}n_{\mathrm{olefin}}/\mathrm{d}t)_t\}/n_{\mathrm{Rh}}$$

The rate of olefin conversion is calculated from the *PVT* pressure vs time data by approximating $(\mathrm{d}n_{\mathrm{olefin}}/\mathrm{d}t)_t$ with the finite difference of $(\Delta n_{\mathrm{olefin}}/\Delta t)_t$ and utilizing the fact that $\Delta n_{\mathrm{olefin}} = (\mathrm{constant})\Delta p_{PVT}$:

$$(\mathrm{d}n_{\mathrm{olefin}}/\mathrm{d}t)_{t_i} \cong (\Delta n_{\mathrm{olefin}}/\Delta t)_{t_i} = (\mathrm{constant})(\Delta p_{PVT}/\Delta t)_{t_i}$$

where

constant = (total moles of oxo product)/
(total *PVT* pressure drop)

For the semicontinuous hydroformylation of decene-1, the autoclave was fitted with a dip leg that reached ca. 5 mm above

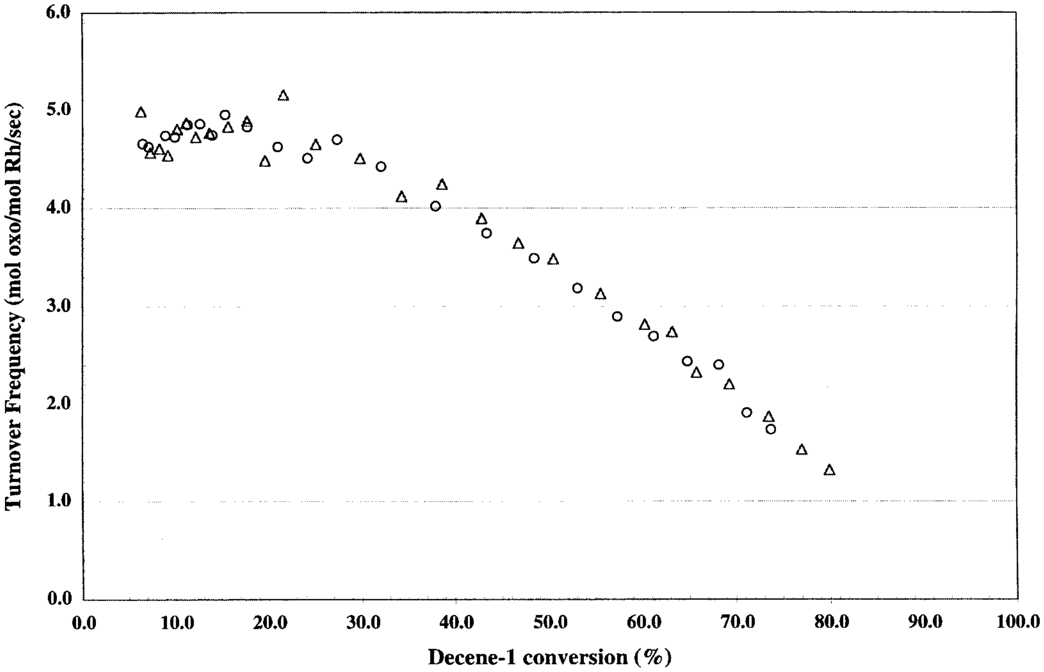

Figure 7. Rate of hydroformylation of decene-1 with Rh/PPh$_3$ catalyst at low PPh$_3$ concentrations in toluene at 100 °C and 1.1 MPa of CO/H$_2$ (1:1) as a function of conversion. △: [Rh] = 0.036 mmol/L, [PPh$_3$] = 23.0 mmol/L, and [decene-1]$_{t=0}$ = 1.04 mol/L. ○: [Rh] = 0.025 mmol/L, [PPh$_3$] = 23.1 mmol/L, and [decene-1]$_{t=0}$ =1.08 mol/L.

the heavier fluorous phase. Individual runs were carried out as described earlier for the kinetic experiments. At the end of each run, the reactor was cooled to 15 °C; then the stirrer was stopped, and the supernatant product phase was removed from the reactor. The weight and the GC analysis of the product provided a mass balance for all organic components. For Rh balance, the concentration of Rh in each product and in the final catalyst solution was determined by ICP-AES. For each consecutive run, the catalyst solution was rapidly heated to the reaction temperature and a fresh charge of decene-1 was injected to initiate the reaction.

Hydroformylation of Ethylene. The continuous-flow hydroformylation of ethylene was carried out in a 500-mL Autoclave Engineers' zipperclave. The catalyst solution was prepared by reacting 0.202 g (0.78 mmol) of Rh(acac)(CO)$_2$ with 11.57 g (10.80 mmol) of P[CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$]$_3$ in 465 g of FC-70 under N$_2$ in a glovebox and was charged into the reactor as described for the hydroformylation of decene-1. The gaseous feed components, H$_2$, CO, C$_2$H$_4$, and CH$_4$ internal standard, were individually fed via Brooks mass-flow controllers.

Mass balances for each component were obtained independently of each other and typically were 100 ± 10% for CO and H$_2$ and 100 ± 5% for ethylene. At the end of the experiment, the formation of 4% O=P[CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$]$_3$ was observed by ^{31}P{^{1}H} NMR.

Rhodium Analysis. Aliquots of the product or the catalyst phase were removed. The residue was ashed with 1 mL of concentrated H$_2$SO$_4$ and muffled at 530 °C for at least 8 h. The remaining residue was fused with 0.5 g of K$_2$S$_2$O$_7$. The fusate was solubilized in a 10% H$_2$SO$_4$ solution. The rhodium analysis was perfomed using ICP-AES instrumentation with matrix-matched standards (3.3% RSD).

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Table 7. Effect of PPh$_3$ Concentration on the Activity and n/i Selectivity of the Rh/PPh$_3$ Catalyst in the Hydroformylation of Decene-1 in Toluene at 100 °C and 1.1 MPa of CO/H$_2$ (1:1)

[PPh$_3$], mmol/L	P/Rh	TOF/[decene-1], (L/mol)/s	n/i
228.6	602	0.78	4.8
228.8	993	0.73	4.7
23.7	223	6.25	3.2
23.1	639	6.58	3.2
23.0	917	5.98	3.2

Appendix

Hydroformylation of Decene-1 with the Rh/PPh$_3$ Catalyst. The kinetic response of the Rh/PPh$_3$ catalyst with respect to the concentration of the decene-1 is not uniform. While at high concentrations of PPh$_3$ (ca. 0.2 mol/L) only first-order kinetics can be observed, at low phosphine concentrations (ca. 0.02 mol/L), a saturation kinetics occurs (Figure 7). Mass-transfer limitation can be excluded since the measured maximum rate of gas consumption is well below the experimentally determined mass-transfer limit and the maximum TOF is independent of the concentration of Rh (Figure 7).

Saturation kinetics for decene-1[28c] and dodecene-1[28e] using the Rh/PPh$_3$ catalyst has been previously observed. Similar kinetic response has been reported[7d] for the hydroformylation of hexene-1 in benzene at 25 °C with HRh(CO)(PPh$_3$)$_3$ (**2**), with no excess PPh$_3$ present. In their study, the maximum TOF does depend on the concentration of **2**. However, at their conditions (no excess ligand and low [Rh]), the kinetic order for Rh is less than one, while with excess ligand it is one for a variety of substrates and ligands.[7i,h,28] Data obtained in the present study are also consistent with a first kinetic order for Rh.

The existence of decene-1 saturation suggests a rate-limiting step at the saturation limit before which there is a quasi-equilibrium involving the olefin. In the most coherent mechanism published to date,[26] the earliest such possible equilibrium step is the formation of HRh(C$_7$H$_{15}$CH=CH$_2$)(CO)$_x$(PPh$_3$)$_{3-x}$ (x = 1 or 2) but can also involve the alkyl [C$_9$H$_{19}$Rh(CO)$_x$(L)$_{4-x}$ and C$_7$H$_{15}$CH(CH$_3$)Rh(CO)$_x$(L)$_{4-x}$] or the acyl [C$_9$H$_{19}$CORh(CO)$_x$(L)$_{4-x}$ and C$_7$H$_{15}$CH(CH$_3$)CORh(CO)$_x$(L)$_{4-x}$] (x = 1, 2, or 3) intermediates as well. The corresponding rate-limiting steps are olefin and CO insertion or H$_2$ activation, respectively. Tolman and Faller have proposed[26] that at the saturation limit, the rate-limiting step is H_2 activation, while at low olefin concentrations the limiting rate is olefin addition to $HRh(CO)_x(PPh_3)_{3-x}$ ($x = 1$ or 2). The buildup of a non-acyl intermediate has been reported from in situ CIR−FTIR studies of reacting phosphine-modified Rh catalyst systems.[7o] The authors have assigned the observed IR spectrum to an 18-electron alkyl complex. They also proposed[26] that the shift from first to zero order is due to a shift in the rate-limiting step from CO insertion in the alkyl intermediate to CO dissociation from $HRh(CO)_2(L)_2$, which later is the dominating species under typical hydroformylation conditions with Rh/PPh_3. NMR kinetic data,[7l,n] however, make this later scenario less likely, since it has been found that the dissociation of CO and phosphine is rapid on the time scale of catalytic hydroformylation.

For comparison, the effect of PPh_3 concentration on the activity and selectivity of the Rh/PPh_3 catalyst in the hydroformylation of decene-1 in toluene was also established under similar conditions (Table 7). We found that the TOF/[decene-1] and product selectivities are independent of the P/Rh ratio and solely depend on the concentration of the phosphine, as long as the CO/H_2 ratio, total pressure, solvent, and temperature are the same.

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