Effect of Ligand Modification on Rhodium-Catalyzed Homogeneous Hydroformylation in Supercritical Carbon Dioxide

Daniel R. Palo and Can Erkey*

Environmental Engineering Program, Department of Chemical Engineering, University of Connecticut, 191 Auditorium Road, Storrs, Connecticut 06269

Received July 19, 1999

Several fluoroalkyl- and fluoroalkoxy-substituted tertiary arylphosphines were synthesized and investigated in the homogeneous catalytic hydroformylation of 1-octene using $HRh(CO)L_3$ (L = tertiary arylphosphine). The activity of the rhodium complex (formed in situ from $Rh(CO)_2(acac)$ and L) increased with decreasing basicity of the phosphine according to the series $[3,5\text{-}(CF_3)_2C_6H_3]_3P > [4\text{-}CF_3C_6H_4]_3P \approx [3\text{-}CF_3C_6H_4]_3P > [4\text{-}CF_3OC_6H_4]_3P > [4\text{-}F(CF_2)_4(CH_2)_3C_6H_4]_3P$. The very weakly basic phosphine $(C_6F_5)_3P$ did not complex with $Rh(CO)_2(acac)$, most likely due to a combination of electronic and steric factors. Steric effects did not play a role in either the activity or selectivity of the rhodium catalysts that were formed under hydroformylation conditions.

Introduction

Tertiary phosphines are by far the most extensively used ligands in homogeneous catalysis.[1,2] Phosphine-modified systems offer several benefits over unmodified systems, including increased catalyst stability, improved reaction rates and selectivities, and enhanced partitioning in two-phase systems. Consequently, hundreds of reports have been published investigating phosphine synthesis, stability, and characterization.

Early research published by Tolman on the steric (θ-value) and electronic (χ-value) properties of phosphine ligands[3−6] inspired numerous subsequent studies aimed at defining and understanding these effects in transition metal systems. Some investigators have published additional θ-measurements, while others have sought to modify the cone angle concept, introducing the ideas of ligand intermeshing, variable cone angle, cone angle radial profiles, and the accessible molecular surface (AMS) model.[7−16]

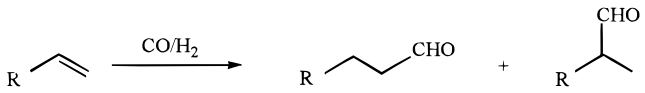
The continued quantification of electronic effects by such measurements as basicity,[17,18] FTIR,[19,20] NMR,[16,18,21] ionization potential,[22] rate of complexation,[23] enthalpy of protonation,[24] electrochemistry,[25] enthalpy of reaction,[26−31] and QALE[32−38] has supplemented Tolman's original χ-value concept. Steric and electronic effects are

* Corresponding author. E-mail: cerkey@engr.uconn.edu. Tel: (860) 486-4601. Fax: (860) 486-2959.

(1) Cornils, B.; Herrmann, W. A. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: Weinheim, Germany, 1996; Vol. 1.
(2) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992.
(3) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.
(4) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.
(5) Tolman, C. A.; Reutter, D. W.; Seidel, W. C. *J. Organomet. Chem.* **1976**, *117*, C30.
(6) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(7) Angermund, K.; Baumann, W.; Dinjus, E.; Fornika, R.; Gorls, H.; Kessler, M.; Kruger, C.; Leitner, W.; Lutz, F. *Chem.—Eur. J.* **1997**, *3*, 755−764.
(8) Trogler, W. C.; Marzilli, L. G. *J. Am. Chem. Soc.* **1974**, *96*, 7589.
(9) Clark, H. C. *Isr. J. Chem.* **1977**, *15*, 210.
(10) DeSanto, J. T.; Mosbo, J. A.; Storhoff, B. N.; Bock, P. L.; Bloss, R. E. *Inorg. Chem.* **1980**, *19*, 3086.
(11) Luo, L.; Nolan, S. P. *Organometallics* **1994**, *13*, 4781.
(12) Smith, J. M.; Taverner, B. C.; Coville, N. J. *J. Organomet. Chem.* **1997**, *530*, 131.
(13) Joerg, S.; Drago, R. S.; Sales, J. *Organometallics* **1998**, *17*, 589.
(14) Pruchnik, F. P.; Smolenski, P.; Wajda-Hermanowicz, K. *J. Organomet. Chem.* **1998**, *570*, 63.
(15) Moore, S. J.; Marzilli, L. G. *Inorg. Chem.* **1998**, *37*, 5329.
(16) Leitner, W.; Buhl, M.; Fornika, R.; Six, C.; Baumann, W.; Dinjus, E.; Kessler, M.; Kruger, C.; Rufinska, A. *Organometallics* **1999**, *18*, 1196.
(17) Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716.
(18) Grim, S. O.; Yankowsky, A. W. *J. Org. Chem.* **1977**, *42*, 1236.
(19) Li, C.; Nolan, S. P.; Horvath, I. T. *Organometallics* **1998**, *17*, 452.
(20) Howell, J. A. S.; Lovatt, J. D.; McArdle, P.; Cunningham, D.; Maimone, E.; Gottlieb, H. E.; Goldschmidt, Z. *Inorg. Chem. Commun.* **1998**, *1*, 118.
(21) Allen, D. W.; Taylor, B. F. *J. Chem. Soc., Dalton Trans.* **1982**, 51.
(22) Weiner, M. A.; Lattman, M.; Grim, S. O. *J. Org. Chem.* **1975**, *40*, 1292.
(23) Amatore, C.; Carre, E.; Jutand, A.; M'Barki, M. A. *Organometallics* **1995**, *14*, 1818.
(24) Sowa, J. R.; Agelici, R. J. *Inorg. Chem.* **1991**, *30*, 3534.
(25) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771.
(26) Serron, S. A.; Luo, L.; Li, C.; Cucullu, M. E.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1995**, *14*, 5290.
(27) Serron, S. A.; Nolan, S. P. *Organometallics* **1995**, *14*, 4611.
(28) Serron, S.; Nolan, S. P.; Moloy, K. G. *Organometallics* **1996**, *15*, 4301.
(29) Serron, S.; Huang, J.; Nolan, S. P. *Organometallics* **1998**, *17*, 534.
(30) Huang, J.; Serron, S.; Nolan, S. P. *Organometallics* **1998**, *17*, 4004.
(31) Haar, C. M.; Nolan, S. P.; Marshall, W. J.; Moloy, K. G.; Prock, A.; Giering, W. P. *Organometallics* **1999**, *18*, 474.
(32) QALE stands for quantitative analysis of ligand effects.
(33) Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650.
(34) Rahman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1.
(35) Woska, D. C.; Wilson, M.; Bartholomew, J.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1992**, *11*, 3343.
(36) Woska, D. C.; Bartholomew, J.; Greene, J. E.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 304.
(37) Wilson, M. R.; Liu, H.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 2044.
(38) Wilson, M. R.; Woska, D. C.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 1742.

10.1021/om990560a CCC: $19.00
Publication on Web 12/10/1999

Scheme 1. Hydroformylation of Olefins

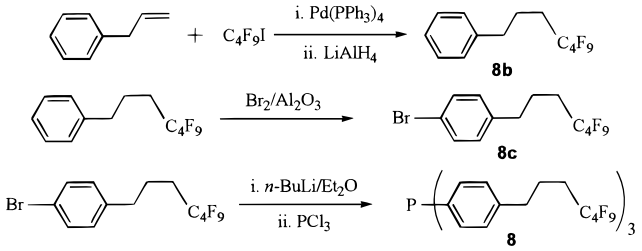


not easily separated, though some successful attempts have been made to quantify each with respect to phosphine behavior.[13,15,16,20,25,30,33,39] In addition, several studies have been published in which the electronic effect is further separated into its σ- and π-components.[13,20,33,34,39,40]

These studies have resulted in a plethora of tabulated information (pK_a, χ, θ, ν(CO), δ(^{1}H), δ(^{31}P), J(M−P)) that can now be utilized in catalyst design. Such fundamental information is quite useful in the modification of phosphine ligands for use in nontraditional applications such as aqueous, fluorous,[41−49] or supercritical fluid systems.[50,51] Quite a few of the studies in such nontraditional applications have focused on hydroformylation, which is the oldest and most widely used homogeneous catalytic reaction involving olefins. This reaction involves the formation of branched or linear aldehydes by the addition of H_2 and CO to a double bond according to Scheme 1.

The linear aldehydes are the preferred products, and the selectivity in such reactions is usually expressed in terms of n:iso ratio, which is the ratio of the linear aldehyde to the branched aldehyde. Rhone-Poulenc/Ruhrchemie successfully demonstrated and commercialized an aqueous-phase process for lower olefin hydroformylation,[1,52] where *meta*-SO_3Na substitution of the aryl rings on the phosphine resulted in excellent catalyst solubility in water. More recently, Horváth and Rábai reported the successful modification of transition-metal/phosphine systems for hydroformylation in fluorous biphase systems (FBS)[41,42] using tri(perfluoroalkyl)-phosphines. Using a technique similar to that in the FBS application, Leitner and co-workers performed ligand modification leading to the demonstration of the first transition-metal/phosphine complex that is highly soluble in supercritical carbon dioxide ($scCO_2$).[53,54]

Scheme 2. Synthesis of Fluoroalkyl-Substituted Arylphosphine 8 with Methylene "Spacers"



We recently reported on the catalysts $RhCl(CO)(PR_3)_2$ (**1**) and $HRh(CO)(PR_3)_3$ (**2**), where R = *p*-$CF_3C_6H_4$.[55−57] Both catalysts were found to be moderately soluble in $scCO_2$ and active in the hydroformylation of various unsaturated substrates at temperatures between 35 and 70 °C. Species **1** showed a significant induction period due to the formation of HCl when **1** is converted to the active catalyst species $HRh(CO)(PR_3)_2$ or $HRh(CO)_2(PR_3)$ under reaction conditions. In our recent report on the hydroformylation of 1-octene in $scCO_2$,[58] the kinetic behavior of **2** in $scCO_2$ was found to be significantly different from the behavior of $HRh(CO)(PPh_3)_3$ in organic solvents. Primary differences included ~0.5 order dependence of the rate on hydrogen concentration and lack of substrate inhibition. Several different factors may be contributing to this behavior, including $scCO_2$ solvent effects, high reactant gas concentrations, and the nature of the modified phosphine. Therefore, comparison of the behavior of various substituted arylphosphines in $scCO_2$ is one step toward determining the reasons for the altered kinetics.

This paper describes the synthesis and characterization of several fluoroalkyl- or fluoroalkoxy-substituted arylphosphines and demonstrates their use in the rhodium-catalyzed homogeneous hydroformylation of 1-octene in $scCO_2$. Complexes analogous to **2** were formed in situ under hydroformylation conditions, and the effects of fluoroalkyl- and fluoroalkoxy-substitution on activity and selectivity were investigated and quantified.

Results and Discussion

All the phosphines were synthesized from the corresponding perfluoroalkyl- or perfluoroalkoxy-substituted aryl bromides, which were all commercially available except 4-bromo-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyl)-benzene (**8c**). Here, we describe an alternative method for preparation of $[4\text{-}F(CF_2)_4(CH_2)_3C_6H_4]_3P$ (**8**) (Scheme 2.)

Comparison was made between the reaction rate for **2** to the rate for the species formed in situ from the phosphine ligand and $Rh(CO)_2(acac)$. As can be seen from Figure 1, no significant difference exists between the two systems in either reaction rate or selectivity. The result of this comparison was taken as confirmation

(39) Drago, R. S.; Joerg, S. *J. Am. Chem. Soc.* **1996**, *118*, 2654.
(40) Golovin, M. N.; Rahman, M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981.
(41) Horvath, I. T.; Kiss, G.; Cook, R. A.; Bond, J. E.; Stevens, P. A.; Rabai, J.; Mozeleski, E. J. *J. Am. Chem. Soc.* **1998**, *120*, 3133.
(42) Horvath, I. T.; Rabai, J. *Science* **1994**, *266*, 72.
(43) Guillevic, M. A.; Arif, A. M.; Horvath, I. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1612.
(44) Juliette, J. J. J.; Horvath, I. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1610.
(45) Bhatacharyya, P.; Gudmunsen, D.; Hope, E. G.; Kemmitt, R. D.; Paige, D. R.; Stuart, A. M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3609.
(46) Fawcett, J.; Hope, E. G.; Kemmitt, R. D. W.; Paige, D. R.; Russell, D. R.; Stuart, A. M.; Cole-Hamilton, D. J.; Payne, M. J. *Chem. Commun.* **1997**, 1127.
(47) Fawcett, J.; Hope, E. G.; Kemmitt, R. D. W.; Paige, D. R.; Russell, D. R.; Stuart, A. M. *J. Chem. Soc., Dalton Trans.* **1998**, 3751.
(48) Sinou, D.; Pozzi, G.; Hope, E. G.; Stuart, A. M. *Tetrahedron Lett.* **1999**, *40*, 849.
(49) Kling, R.; Sinou, D.; Pozzi, G.; Choplin, A.; Quignard, F.; Busch, S.; Kainz, S.; Koch, D.; Leitner, W. *Tetrahedron Lett.* **1998**, *39*, 9439.
(50) Rathke, J. W.; Klinger, R. J. Cobalt Carbonyl Catalyzed Olefin Hydroformylation in Supercritical Carbon Dioxide, U.S. Patent, 1993.
(51) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475.
(52) Cornils, B.; Kuntz, E. *J. Organomet. Chem.* **1995**, *502*, 177.
(53) Kainz, S.; Koch, D.; Baumann, W.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1628.
(54) Koch, D.; Leitner, W. *J. Am. Chem. Soc.* **1998**, *120*, 13398−13404.
(55) Palo, D. R.; Erkey, C. *Ind. Eng. Chem. Res.* **1998**, *37*, 4203.
(56) Palo, D. R.; Erkey, C. *Ind. Eng. Chem. Res.* **1999**, *38*, 2163.
(57) Palo, D. R.; Erkey, C. Rhodium Catalyzed Homogeneous Hydroformylation of Unsaturated Compounds in Supercritical Carbon Dioxide with $[HRh(CO)(P(p\text{-}CF_3C_6H_4)_3)_3]$. In *Reaction Engineering for Pollution Prevention*; Hesketh, R., Abraham, M., Eds.; Elsevier Science (accepted for publication).
(58) Palo, D. R.; Erkey, C. *Ind. Eng. Chem. Res.* **1999**, *38*, 3786.

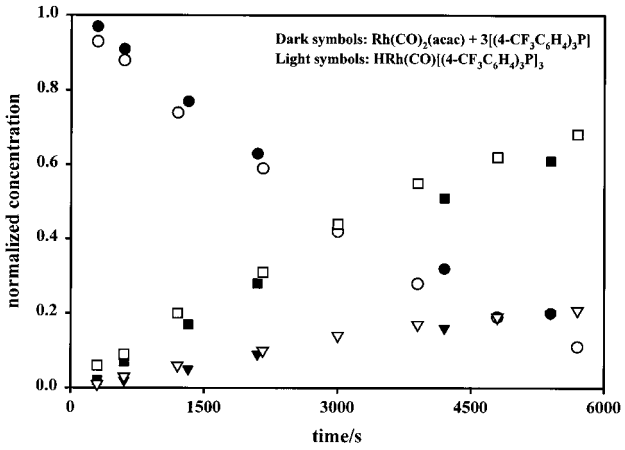


Figure 1. Comparison of catalytic behavior of HRh(CO)-[P(*p*-$(CF_3C_6H_4)_3$]$_3$ with the species formed in situ from Rh-$(CO)_2$(acac) and P(*p*-$(CF_3C_6H_4)_3$: $P = 273$ atm, $T = 50$ °C, $[1\text{-octene}]_0 = 0.95$ M, $[H_2]_0 = [CO]_0 = 1.1$ M, [Rh] = 1.27 mM.

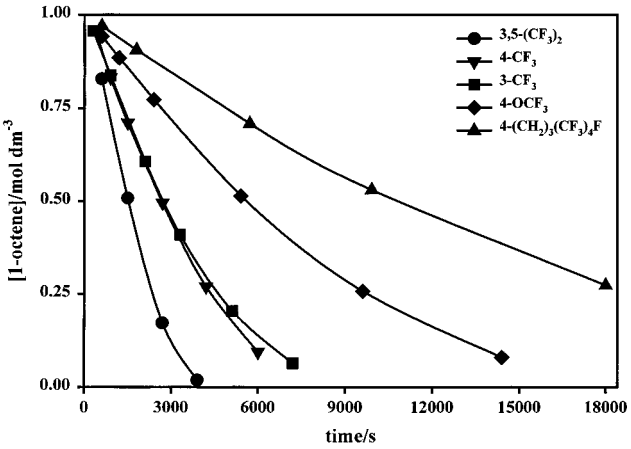


Figure 2. Hydroformylation of 1-octene using HRh(CO)-L_3: $P = 273$ atm, $T = 50$ °C, $[1\text{-octene}]_0 = 0.95$ M, $[H_2]_0 = [CO]_0 = 1.1$ M, [Rh] = 1.27 mM, [P]/[Rh] = 3.0.

that the active catalytic species is the same for the in situ preparations as for the preformed catalysts, HRh-$(CO)L_3$. Thus, in situ preparations of the active catalyst species allow direct comparison of the various catalysts without the need to separately synthesize and purify each complex.

Figure 2 shows the concentration versus time data for the hydroformylation of 1-octene using $Rh(CO)_2$-(acac)/phosphine. All reactions were conducted at identical conditions, as described in the figure caption. Each reaction proceeded smoothly, producing both normal and branched C_9 aldehydes. When $[3,5\text{-}(CF_3)_2C_6H_3]_3P$ (**5**) was the phosphine, approximately 1% conversion to C_8 species resulted, but experiments employing the remaining phosphines of Figure 2 showed no detectable isomerization or hydrogenation.

Table 1 lists the initial rates and selectivities observed for the various ligands under standard reaction conditions. Initial rates were calculated from the linear portion of each rate curve by estimating the slope in mol dm^{-3} s^{-1}. The selectivities listed are those measured at the end of each experiment (between 90% and 98% conversion). Among the various catalyst systems, the initial rates of reaction differ more than 5-fold between the slowest and the fastest. This fact alone speaks of the significant effects phosphine ligands have on the nature of the catalytic species. It is well-known that fluorine has a very strong electron-withdrawing effect on the phosphine, causing the phosphorus lone pair to become less basic, and leading to a significant decrease in the electron density at the metal center.[17,20,24,34] The trend of activity observed among the five phosphines of Figure 2 indicates that less basic phosphines lead to more active hydroformylation catalysts.

The catalytic behavior of the unmodified $Rh(CO)_2$-(acac) catalyst differs fundamentally from that observed for the phosphine-modified catalysts, as seen by comparing Figure 2 and Figure 3. Not only does $Rh(CO)_2$-(acac) show a significant induction period (see Table 1), but the rate of reaction does not decrease with increased conversion as seen for the phosphine-modified systems. This seems to indicate a zero-order dependence of the rate on substrate concentration. Behavior of the system modified with $(C_6F_5)_3P$ (**7**) is identical to that of $Rh(CO)_2$-(acac) alone (see Figure 3, Table 1), indicating that **7** does not significantly displace either CO or acac to form a rhodium−phosphine complex. The lack of interaction between **7** and $Rh(CO)_2$(acac) is probably due primarily to the extremely low basicity of **7**, but no doubt partially due to its steric bulk ($\theta_7 = 184°$).[3] Not surprisingly, an attempt to produce $HRh(CO)[(C_6F_5)_3P]_3$ from **7**, Rh-$(CO)_2$(acac), H_2, and CO in $scCO_2$ also failed.

Syntheses of the various catalysts in $scCO_2$ were performed for the purpose of measuring the NMR and FTIR values listed in Table 2. These NMR measurements on the catalysts shed further light on the fundamental difference between the substituted phosphines and triphenylphosphine (PPh_3). The most recognizable feature of the ^1H NMR spectrum of the complex $HRh(CO)L_3$ is a quartet at $\delta \approx -9.8$, corresponding to the rhodium hydride. The quartet arises from coupling of the hydride with the three equivalent phosphorus nuclei of the complex. For PPh_3, this quartet is only observed at low temperatures, where the phosphine exchange rate is reduced enough to allow resolution of the quartet.[59] For phosphines $(4\text{-}CF_3C_6H_4)_3P$ (**3**), $(3\text{-}CF_3C_6H_4)_3P$ (**4**), **5**, and $(4\text{-}CF_3OC_6H_4)_3P$ (**6**), the quartet is well resolved at 30 °C, indicating a much slower exchange rate for the fluoroalkyl-substituted phosphines than for the more basic PPh_3. However, the quartet is not resolved for the complex formed from $[4\text{-}F(CF_2)_4(CH_2)_3C_6H_4]_3P$ (**8**), indicating a similarity to PPh_3.

It can be seen from Figure 4 that the rate of hydroformylation correlates very well with the value of ν(CO) for the various catalysts, showing a linear dependence. The IR stretching frequency of metal carbonyls is a sensitive indicator of electron density at the metal center, yielding a relative measure of the amount of π-back-bonding from an occupied metal d-orbital to the empty π^*-orbital of the carbonyl.[3,19,20,29,40] The trend in ν(CO) corresponds well with the amount and proximity of the electron-withdrawing fluoroalkyl or fluoroalkoxy groups of the phosphines, with **5** having the greatest effect and **8** having the least effect relative to the value for PPh_3. The phosphines **3** and **4** show identical electronic behavior and almost identical activity/selec-

(59) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1990**, *28*, 81.

Table 1. Hydroformylation of 1-Octene in $scCO_2$ Using $Rh(CO)_2(acac)$ and Various Fluorinated Phosphine Ligands

ligand	$10^6 \times$ initial rate,[a] mol dm^{-3} s^{-1}	induction period, min	selectivity (n:iso ratio)	ν(CO),[b] cm^{-1}	θ, deg
$[3,5\text{-}(CF_3)_2C_6H_3]_3P$ **5**	263	0	3.02	1963	160[c]
$(4\text{-}CF_3C_6H_4)_3P$ **3**	188	0	3.29	1950	145[d]
$(3\text{-}CF_3C_6H_4)_3P$ **4**	185	0	3.13	1950	153[e]
no ligand	166	10	1.54	2068, 2000	
$(C_6F_5)_3P$ **7**	161	10	1.55		184[f]
$(4\text{-}CF_3OC_6H_4)_3P$ **6**	94.8	0	2.99	1934	145[d]
$[4\text{-}F(CF_2)_4(CH_2)_3C_6H_4]_3P$ **8**	51.2	0	3.09	1921	145[d]

[a] Standard conditions: $T = 50$ °C, $P = 273$ atm, $V = 54$ mL, $[\text{substrate}]_0 = 1.0$ M, $[Rh] = 1.2$ mM, $[P]/[Rh] = 3.0$, $[CO]_0 = [H_2]_0 = 1.1$ M. [b] For $HRh(CO)L_3$. [c] From ref 20. [d] Assumed to be the same as PPh_3. [e] Estimated as the average between phosphines **3** and **5**. [f] From ref 3.

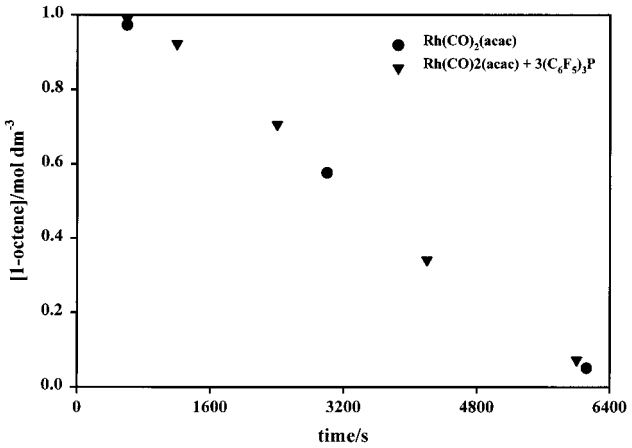


Figure 3. Hydroformylation of 1-octene using $Rh(CO)_2$(acac) alone or modified by $P(C_6F_5)_3$ (3 equiv): $P = 273$ atm, $T = 50$ °C, $[\text{1-octene}]_0 = 0.95$ M, $[H_2]_0 = [CO]_0 = 1.1$ M, $[Rh] = 1.27$ mM.

tivity behavior, while **5**, with a much higher ν(CO) value, also has a significantly higher activity. These results are in agreement with an earlier report that the electronic effect of trifluoromethyl substitution is independent of *ortho*, *meta*, or *para* placement and that the effects of multiple trifluoromethyl substitutions are cumulative.[20] The ability of oxygen and methylene groups to insulate against the electron-withdrawing effects of the fluoroalkyl moieties can be seen for phosphines **6** and **8**, where significant decreases in ν(CO) are accompanied by 50% and 70% decreases in activity, respectively. These results confirm the observation by Leitner that methylene spacers effectively insulate the phosphorus lone pair from the electron-withdrawing effect of the fluoroalkyl chain[53] and also show that oxygen spacers exhibit a similar though less profound effect. While these spacers are effective insulators, they actually decrease the catalytic activity relative to "noninsulated" phosphines. These results on activity are also in agreement with a study conducted in organic solvents using modified phosphine ligands of the form $(4\text{-}XC_6H_4)_3P$, where the rate of hydroformylation of 1-hexene was found to increase with decreasing basicity of the phosphine according to the series $[4\text{-}CF_3C_6H_4]_3P > [4\text{-}ClC_6H_4]_3P > [4\text{-}FC_6H_4]_3P > [4\text{-}HC_6H_4]_3P > [4\text{-}OCH_3\text{-}C_6H_4]_3P > [4\text{-}N(CH_3)_2C_6H_4]_3P$.[60] In the same study, it was also observed that the n:iso ratio increased with decreasing basicity of the phosphines. Surprisingly, such an effect is not observed in this study, where the selectivities for the sterically identical but electronically different phosphines **3**, **6**, and **8** are around 3. Hydroformylation studies conducted in organic solvents usually show that the n:iso ratio decreases with increasing steric bulkiness of the phosphines.[1] This is usually attributed to the formation of the $HRh(CO)_2(R_3P)$ species, which favors the formation of branched products. Surprisingly, such an effect is also not observed in this study, where steric differences among the phosphines have very little if any effect on the n:iso ratio. Phosphines **3** and **4**, which are electronically identical but sterically different ($\theta_3 = 145°$, $\theta_4 = 153°$ [61]), exhibit quite similar activities and selectivities. Furthermore, phosphine **5** ($\theta_5 = 160°$) shows no decrease in selectivity, despite a significant increase in cone angle over phosphine **3**.

Another result of this study was the observation that $Rh(CO)_2$(acac) and $Rh(CO)_2$(hfacac) exhibit significantly different behavior in $scCO_2$. The induction period for $Rh(CO)_2$(acac), as shown in Table 1, is only 10 min, while the induction period for $Rh(CO)_2$(hfacac) inferred from Leitner's data is somewhere between 30 and 60 min.[54] The trifluoromethyl groups of the hfacac moiety seem to inhibit the formation of the active rhodium species under hydroformylation conditions.

Conclusion

We have shown that differences in the extent and location of fluoroalkyl or fluoroalkoxy substitution on tertiary phosphines have a significant effect on the activities of rhodium-based hydroformylation catalysts made therewith. It was shown that the electron-withdrawing effect of fluoroalkyl moieties actually increases the activity of rhodium hydroformylation catalysts of the form $HRh(CO)L_3$, where L is the substituted arylphosphine ligand. Good correlation was observed between activity and carbonyl stretching frequency for the rhodium complexes formed from substituted arylphosphines.

Experimental Section

General Methods. All phosphine and catalyst syntheses were carried out under a nitrogen atmosphere. Phosphines **3** and **7** were purchased from Strem Chemicals and used as received. Fluoroalkyl- or fluoroalkoxy-substituted bromobenzenes, allylbenzene, perfluorobutyl iodide, butyllithium, bro-

(60) Moser, W. R.; Papile, C. J.; Brannon, D. A.; Duwell, R. A.; S.Weininger *J. Mol. Catal.* **1987**, *41*, 271.

(61) Estimated as the average between phosphines **3** and **5**.

Table 2. Properties of Various Fluorinated Phosphine Ligands and Their Complexes with Rhodium as $HRh(CO)L_3$

ligand	free $\delta(^{31}P)$, ppm	complexed as $HRh(CO)L_3$ $\delta(^{31}P)$, ppm	J(Rh−P), Hz	$\delta(^1H)$, ppm	^3J(H−P), Hz	ν(Rh−H), cm^{-1}	ν(CO), cm^{-1}
$(C_6H_5)_3P$	−6.0[a]	39.8[b]	155[b]	−9.7[c]	14[d]	2040[d]	1923[d]
$(4\text{-}CF_3C_6H_4)_3P$ **3**	−6.3	40.2	156	−9.9	14	2038	1950
$(3\text{-}CF_3C_6H_4)_3P$ **4**	−5.4	42.9	156	−9.7	14	2025	1950
$[3,5\text{-}(CF_3)_2C_6H_3]_3P$ **5**	−4.4	44.0	157	−10.0	15	2033	1963
$(4\text{-}CF_3OC_6H_4)_3P$ **6**	−8.9	37.2	155	−9.9	14	2016	1934
$(C_6F_5)_3P$ **7**[e]	−75						
$[4\text{-}F(CF_2)_4(CH_2)_3C_6H_4]_3P$ **8**	−8.1	37.4	153	−9.7	*f*	1969	1921

[a] From ref 6. [b] From ref 64. [c] From ref 59. [d] From ref 65. [e] $HRh(CO)L_3$ did not form. [f] Unresolved at 30 °C.

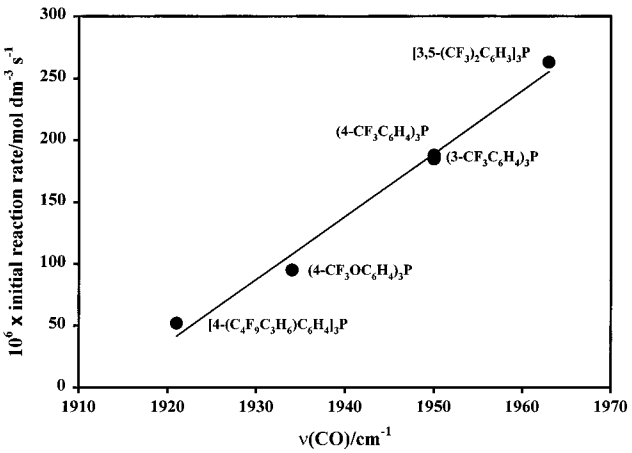


Figure 4. Correlation between rate of 1-octene hydroformylation in $scCO_2$ and ν(CO) for $HRh(CO)L_3$.

mine, and Brockmann alumina were purchased from Aldrich and used as received. Magnesium turnings were obtained from Acros Chemicals and used as received.

Hydroformylation Experiments. Hydroformylation reactions were conducted batchwise in a 54 cm^3 custom-built, high-pressure stainless steel reactor fitted with sapphire windows. The experimental setup is described in detail elsewhere.[57] 1-Octene was freshly distilled from sodium under nitrogen before each experiment. For each hydroformylation experiment, $Rh(CO)_2(acac)$ (6.5×10^{-5} mol, vacuum sealed in a glass ampule), phosphine (2.0×10^{-5} mol), and 1-octene (0.054 mol) were charged to the reactor under nitrogen. The reactor was then sealed, heated to reaction temperature (50 °C), and charged with H_2/CO (0.055 mol each). Finally, CO_2 was charged to the reactor, bringing the total pressure to 273 atm. The presence of a single fluid phase was confirmed visually, with the catalyst being completely dissolved in the reaction mixture. Periodic samples taken during each reaction were analyzed by gas chromatography.

When working with high-pressure equipment, appropriate safety devices should be used, including but not limited to pressure relief mechanisms and explosion barriers.

Phosphine Synthesis. Standard Grignard procedures followed by phosphination were utilized to produce phosphines **4** and **6** from the corresponding commercially available fluoroalkyl- or fluoroalkoxy-substituted bromobenzene. Lithiation was employed in the synthesis of phosphine **5** from the commercially available starting material.

Synthesis of 4. Phosphine **4** was synthesized from 3-bromobenzotrifluoride and PCl_3 according to the procedure given by Miller et al. for producing the *para*-substituted phosphine.[62] Fractional distillation at reduced pressure yielded **4** as a colorless, viscous liquid. Yield: 47%. ^1H NMR ($CDCl_3$): δ 7.65 (1H, d, J = 8 Hz), 7.59 (1H, d, J = 8 Hz), 7.50 (1H, t, J = 8 Hz), 7.42 (1H, t, J = 7 Hz) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.4 (s) ppm. Anal. Calcd for $C_{21}H_{12}F_9P$: C, 54.09; H, 2.59. Found: C, 53.66; H, 2.43.

Synthesis of 6. Phosphine **6** was produced according to the same procedure used for **4**, starting with 4-bromotrifluoromethoxybenzene. Addition of a small amount of iodine was necessary to initiate the Grignard reaction. Fractional distillation at reduced pressure yielded a clear, slightly yellow, viscous liquid. Yield: 12%. ^1H NMR ($CDCl_3$): δ 7.31−7.27 (2H, m), 7.20 (2H, d, J = 8 Hz) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −8.9 (s) ppm.

Synthesis of 8. Using a modification of the procedure by Ishihara et al.,[63] tetrakis(triphenylphosphine)palladium (2.35 g, 2.03 mmol) was added to a solution of allylbenzene (6.76 g, 57.2 mmol) and *n*-perfluorobutyl iodide (19.7 g, 56.9 mmol) in dry hexanes (40 mL) at 0 °C. The solution was slowly heated to 25 °C and maintained at this temperature for 72 h, after which the mixture was filtered and concentrated, yielding a light-sensitive orange/brown oil. Distillation yielded 17.9 g (68%) of 2-iodo-1*H*,1*H*,2*H*,3*H*,3*H*-perfluroheptylbenzene (**8a**). ^1H NMR (400 MHz, $CDCl_3$): δ 4.5 (1H, m, $C_4F_9CH_2CHI$-$CH_2C_6H_5$) ppm.

Compound **8a** (17.9 g, 38.5 mmol) was dissolved in diethyl ether in an addition funnel and added dropwise through a condenser into a round-bottomed flask containing $LiAlH_4$ (2.85 g, 75.2 mmol) dissolved in diethyl ether (20 mL), at 0 °C. The solution was slowly heated to 25 °C and stirred for 2 h, after which distilled water (3 mL), 1 M NaOH (3 mL), and distilled water (6 mL) were added. The two-phase solution was filtered, and the ether phase was removed and dried over $MgSO_4$. Reduction under vacuum gave a crude orange oil, which was vacuum distilled to yield 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluroheptylbenzene (**8b**) (5.6 g, 30%) as a clear oil. ^1H NMR ($CDCl_3$): δ 7.4−7.1 (5H, m), 2.7 (2H, t, J = 8 Hz), 2.1−1.8 (4H, m) ppm. Anal. Calcd for $C_{13}H_{11}F_9$: C, 46.17; H, 3.28. Found: C, 46.06; H, 3.39.

Compound **8b** (3.17 g, 9.4 mmol) dispersed on Brockmann alumina (10.2 g) and bromine (1.9 g, 11.9 mmol) dispersed on Brockmann alumina (10.5 g) were combined and shaken for 1 h. The product was extracted with diethyl ether and fractionally distilled at reduced pressure to yield 4-bromo-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyl)benzene (**8c**) (3.41 g, 87%). ^1H NMR ($CDCl_3$): δ 7.4 (2H, d, J = 6 Hz), 7.0 (2H, d, J = 8 Hz), 2.67 (2H, t, J = 8 Hz), 2.1−1.8 (4H, m) ppm. Anal. Calcd for $C_{13}H_{10}F_9Br$: C, 37.43; H, 2.42. Found: C, 38.33; H, 2.69.

The phosphine, **8**, was produced from **8c** (3.0 g, 7.2 mmol) and PCl_3 (1.1 g, 8.0 mmol) using standard lithiation techniques. Yield: 350 mg, 14%. ^{31}P NMR (400 MHz, $CDCl_3$): δ −8.1 (s) ppm. Calcd for $C_{39}H_{30}F_{27}P$: C, 44.93; H, 2.90. Found: C, 44.76; H, 3.08.

(62) Miller, G. R.; Yankowsky, A. W.; Grim, S. O. *J. Chem. Phys.* **1969**, *51*, 3185.
(63) Ishihara, T.; Kuroboshi, M.; Okada, Y. *Chem. Lett.* **1986**, 1895.
(64) Wu, G.; Washliyen, R. E.; Curtis, R. D. *Can. J. Chem.* **1992**, *70*, 863.
(65) Evans, D.; Yagusky, G.; Wilkinson, G. J. *J. Chem. Soc., A* **1968**, 2660.

Synthesis of $HRh(CO)L_3$. To determine FTIR and NMR values for the various catalysts in this study, each catalyst was synthesized in small quantities in pure $scCO_2$ in the high-pressure reactor described above for the hydroformylation experiments. For each synthesis, $Rh(CO)_2(acac)$ (∼20 mg) along with the respective phosphine (3 equiv) and a magnetic stir bar were charged to the reactor, which was then sealed and purged with a stream of 1:1 H_2/CO for several minutes to remove oxygen. The reactor was then heated to 35−40 °C, charged with H_2/CO (2 equiv), pressurized with CO_2 (205 atm), and stirred for ∼15 min. It was confirmed visually that the phosphine and $Rh(CO)_2(acac)$ were completely dissolved (no solid in reactor, and yellow $scCO_2$ solution). Cooling and venting yielded a crude solid product containing the respective catalyst species, $HRh(CO)L_3$, which were analyzed by ^1H NMR, ^{31}P NMR, and FTIR spectroscopy (see Table 2).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research (ACS-PRF 32299-AC1). We would like to acknowledge the contribution of Jennifer A. Hay in helping develop the synthetic route for phosphine **8** and T. Davis in helping to synthesize **5** and the corresponding rhodium complex. We are also indebted to Gary Lavigne for his assistance with FTIR measurements and to Dr. Thomas Leipert for his assistance with NMR spectroscopy.

OM990560A