Synthesis of New Hemilabile Amphiphilic Phosphines. Complexing Properties toward Ruthenium(II) and Catalytic Activity for Hydrogenation of Prenal

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Received July 27, 1999

New functionalized phosphines R−$(C_6H_4)(OCH_2CH_2)_nPPh_2$ {**1** (R = *tert*-octyl, $n = 1$), **2** (R = *tert*-octyl, $\bar{n} = 5$), **3** (R = *tert*-octyl, $\bar{n} = 13$), **4** (R = *n*-nonyl, $\bar{n} = 1.4$), **5** (R = *n*-nonyl, $\bar{n} = 5$), **6** (R = *n*-nonyl, $\bar{n} = 11$)}, $CH_3(OCH_2CH_2)_3PPh_2$ (**7**), $CH_3(OCH_2CH_2)_3PPhR$ (**8**, R = isopentyl), and $HOCH_2CH_2(OCH_2CH_2)_2PPhR$ (**9**, R = *n*-octyl) have been synthesized. These ligands contain polyether and hydrophobic groups in the same molecule and, therefore, can lead to compounds that combine hemilabile (polyether groups) and amphiphilic (hydrophobic and hydrophilic groups) properties. Complexation studies with Ru(II) have been performed, and the unusual tridentate (*O, O, P*) coordination mode has been characterized. The hemilabile character has been shown by evolution from the tridentate (*O, O, P*) coordination mode to the bidentate (*O, P*) and monodentate (*P*) after a reaction between CO and [$RuCl_2$(**8**)-(PPh_3)]. Dinuclear [$Ru_2Cl_4L_5$] complexes have been obtained from ligands with a short polyether chain (**1**, **4**). The catalytic selective hydrogenation of an α,β-unsaturated aldehyde (prenal) with ruthenium complexes prepared in situ from $RuCl_3$ and ligands **1**−**6** has been carried out in a 2-propanol/water mixture. Conversions to prenol to the order of 90% or higher are observed with selectivity of 90−96% after 20 min at $P = 30$ bar and $T = 50$ °C. The most active systems have been observed with ligands containing long polyether chains.

Introduction

The design and synthesis of new functionalized ligands, capable of improving certain properties in transition metal complexes, has become a central topic in the development of inorganic and organometallic chemistry. Phosphines are one of the most versatile ligands, since they can lead to stable metal−phosphorus bonds and, at the same time, very different functionalizations may be introduced by means of the groups bound to the phosphorus atom. Consequently, functionalized phosphine ligands have become a field of interest, which has led to important industrial applications such as water-soluble[1] and asymmetric phosphines.[2]

In recent years, some authors have shown interest in searching for amphiphilic ligands, which contain hydrophilic and hydrophobic groups, since they may lead to metal complexes with special and interesting properties.[3] These ligands can anchor a transition metal atom in a molecule with the properties of a surface-active agent, yielding metal complexes with similar properties. Therefore, amphiphilic metal complexes can accumulate at the interfaces and, at the same time, can aggregate to form supramolecular systems.[4] This microheterogeneous arrangement of metal centers in the reaction medium can be advantageous for some catalytic processes.[5] Some examples of ligands with amphiphilic properties have been reported, most of them amphiphilic phosphines.[3,6]

Another class of functionalized ligands that are strongly related with homogeneous catalysis are hemilabile phosphorus−oxygen ligands.[7] These can lead to metal complexes with weak metal−oxygen bonds, which may create reversible empty coordination sites favorable for catalytic activity.

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(2) (a) Kagan, H. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: Orlando, 1985; Vol. 5, Chapter 1. (b) Brunner, H.; Zettlmeier, W. *Handbook of Enantioselective Catalysis with Transition Metal Compounds*; VCH: Weinheim, 1993; Vols. I and II.

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10.1021/om9905916 CCC: $18.00
Publication on Web 11/25/1999

In this context, we decided to explore the synthesis of new functionalized phosphines that feature the combination of both properties described above: amphiphilic (bound to hydrophilic and hydrophobic groups) and hemilabile (bound to ether groups). The synthesis of these new ligands was designed using poly(ethylene glycol) monoalkyl ethers as starting materials for the following reasons. (1) These compounds are common since they are used extensively as nonionic surfactants and interesting ligands may be prepared by straightforward methods. (2) The hydrophilic/hydrophobic character and the structure of the hydrophobic group may be easily modified by using poly(ethylene glycol) monoalkyl ethers with different alkyl and polyether chains as starting material with minor changes in the method of synthesis. This last point is important in order to modulate the characteristics of ligands with the aim of optimizing a catalytic process. To our knowledge, only a very few examples of ligands with related characteristics have been reported: water-soluble catalysts based on functionalized poly(ethylene glycol)[8] and ethoxylated tris(*p*-hydroxyphenyl)phosphines which exhibit thermoregulated phase-transfer function.[9]

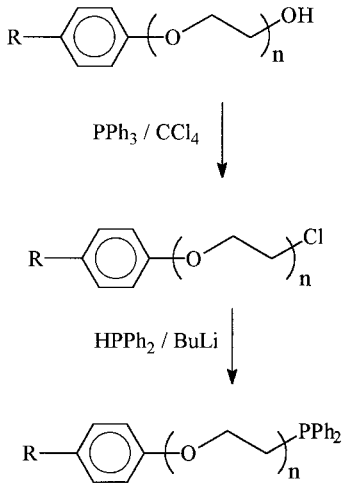
In this paper we report (1) the synthesis and characterization of nine new amphiphilic phosphines, (2) the study of complexing properties of synthesized ligands toward ruthenium(II), (3) an unprecedented mode of bonding of an ether−phosphine ligand, and (4) the use of some reported ligands, associated with Ru(II), in the catalytic selective hydrogenation of α,*β*-unsaturated aldehydes. Part of this work has been communicated previously.[10]

Results and Discussion

Synthesis of ligands. Ligands **1**−**6** were synthesized in two steps starting from the corresponding commercial nonionic surfactants IGEPAL[11] as shown in Scheme 1.

In the first step, alkyl chlorides were obtained from alcohols in high yields by the reaction of the poly(ethylene glycol) monoalkyl ethers with an excess of triphenylphosphine in carbon tetrachloride. The remaining triphenylphosphine and the triphenylphosphine oxide were easily isolated as insoluble solids in the reaction medium. Phosphines **1**−**6** were prepared by reacting the appropriate alkyl chloride with lithium diphenylphosphide at 0 °C in diethyl ether. Ligand **1** crystallizes as a white solid in ethanol, while ligands **2**−**6** were obtained as pale yellow oils. Ligands **1**−**6**

Scheme 1



1 (R = C_8H_{17}; n = 1), **2** (R = C_8H_{17}; $\bar{n}$ = 5), **3** (R = C_8H_{17}; $\bar{n}$ = 13)

4 (R = C_9H_{19}; $\bar{n}$ = 1.4), **5** (R = C_9H_{19}; $\bar{n}$ = 5), **6** (R = C_9H_{19}; $\bar{n}$ = 11)

were characterized by NMR spectroscopy. The more relevant data are the ^{31}P spectra (a signal at $\delta \approx -21$ ppm) and the shifts and coupling with the phosphorus nucleus observed in ^1H and ^{13}C spectra for methylene groups placed in the α and *β* positions with respect to the phosphorus atom. It should be pointed out that ligand **1** was isolated as a single compound (although the starting material was the nonionic surfactant IGEPAL CA210, which is a mixture of polyethethylene glycol monoalkyl ethers ($\bar{n}$ = 1.5), only the pure compound $(CH_3)_3CCH_2C(CH_3)_2C_6H_4O(CH_2)_2P(C_6H_5)_2$ was obtained after crystallization). Ligands **2**−**6**, however, were obtained as mixtures of compounds with the same structure but with different ethoxylation grades in accordance with the nature of the initial nonionic surfactants. The average *n* value for each ligand was established by ^1H NMR spectroscopy and is shown in Scheme 1.

Ligands **7**−**9** (Scheme 2) were prepared in order to have ligands available that were related to **1**−**6** with some modifications in their molecular structure. Ligand **7** is interesting for purposes of comparison since it is similar to **1**−**6** but without the hydrophobic chain. Ligands **8** and **9** have the phosphorus atom placed between the polyether and the hydrophobic chains. Ligand **7** was synthesized from triethylene glycol monomethyl ether by a method similar to ligands **1**−**6**. Ligands **8** and **9** were prepared in two steps as shown in Scheme 2. In the first step, the isopentyl and *n*-octyl diphenylphosphines were prepared by reacting lithium diphenylphosphide with isopentyl bromide and octyl chloride, respectively. Second, reductive cleavage of one phosphorus−aryl bond with lithium led to the corresponding alkylarylphosphide, which reacted with triethylene glycol monomethyl ether chloride and triethylene glycol monochlorohydrin to yield **8** and **9**, respectively. It should be emphasized that ligand **9** was achieved in good yield from triethylene glycol monochlorohydrin by direct reaction with butyllithium without

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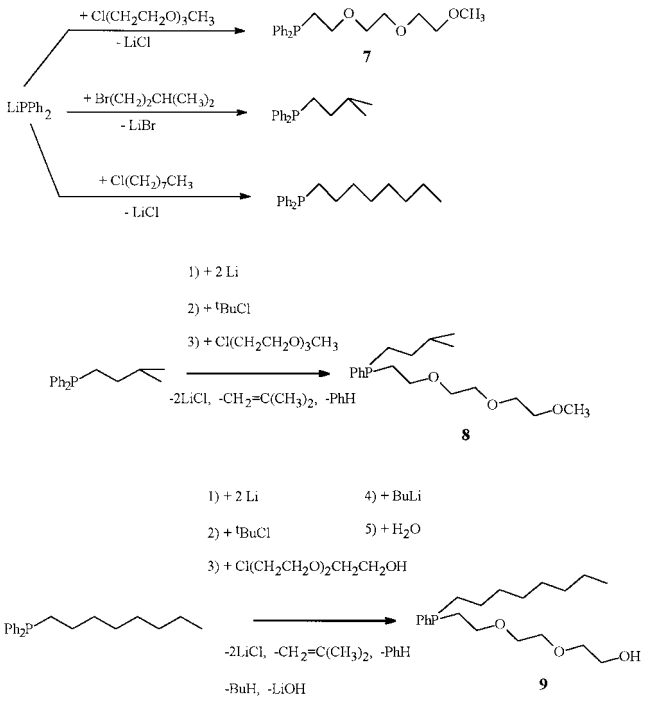
(11) These products are ethoxylated alkylphenols with different ethoxylation grades. Since they are not pure compounds, the length of the polyether chains displayed in Scheme 1 are actually the mean value of a mixture of compounds with the same structure but with different ethoxylation grades.

Scheme 2



the use of alcohol protective groups.[12] Ligands **7**−**9** were obtained as colorless oils and were characterized by NMR spectroscopy.

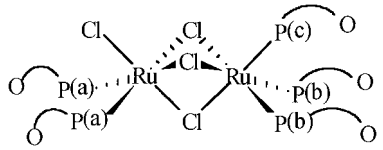
Ruthenium(II) Complexes. Previous studies of ether phosphine complexing properties toward Ru(II)[7] have shown their ability to act as mono (*P*) or bidentate (*O, P*) ligands consistent with their hemilabile character. In contrast to previously studied ligands, **2**−**9** contain at least two oxygen atoms which can be simultaneously coordinated to the metal atom so a tridentate (*O, O, P*) or higher coordination mode is possible.

Since ligands **2**−**6** are mixtures of compounds with the same structure but with different ethoxylation grades, the study of their coordination properties has been limited to NMR spectroscopy in solution. In contrast, ligands **1**, **7**, **8**, and **9** are not mixtures, so their study is less restricted than that of **2**−**6**. Moreover, their study can supply information that can be useful to understand the behavior of ligands **2**−**6**.

Reactions with $RuCl_3 \cdot 3H_2O$. The reaction of $RuCl_3 \cdot 3H_2O$ with a 3-fold excess of **1**−**9** in 2-propanol/H_2O (95:5) did not lead to the isolation of solids with the exception of **1**. The ^{31}P NMR spectra of the solutions obtained from the reaction with **2**−**9** show multiple resonances at 20−60 ppm, some of them being broad. This observation suggests the formation of mixtures after reaction with $RuCl_3 \cdot 3H_2O$ and is consistent with the complicated stereochemistry described in the literature for the hemilable P−O ligands with the $RuCl_2$ fragment.[7]

The chemical behavior of ligand **1** is quite different from ligands **2**−**9** in accordance with their physical and chemical properties. For ligand **1** the bidentate (*P, O)* coordination is hindered by an aryl group. In addition, it can barely manifest amphiphilic properties since only one oxygen atom is present in the polyether chain, and finally, it is the sole ligand prepared that crystallizes as a white solid. Thus, the reaction between ligand **1** and $RuCl_3 \cdot 3H_2O$, in the same conditions as previously described for ligands **2**−**9**, affords a brown microcrystalline solid. Its ^{31}P NMR spectrum at room temperature shows a singlet at 42.2 ppm and a broad AB_2 pattern at 23.7 and 29.5 ppm. Different recrystallizations of this complex afforded solids, which showed identical spectra with the same integration ratio between the three resonances (2:1:2). These results are in accordance with the assignment of these signals to different phosphorus atoms of a unique compound and suggest a polynuclear nature for this complex. The elemental analysis is also in agreement with this hypothesis and suggests a stoichiometry $[Ru_2Cl_4(\mathbf{1})_5]$. Polynuclear ruthenium(II) complexes have been extensively described in the literature,[14] as well as the high stability of six-coordinated Ru(II) complexes containing a triply bridge chloride, which is particularly favorable with tertiary phosphine ligands without bulky groups.[15] Hence, we propose for this complex a structure similar to those previously reported for other dinuclear Ru(II) complexes (Scheme 3) such as $[Ru_2Cl_4L_5]$ ($L = PPh_2Et$, $PPhEt_2$),[15] $[(PPh_3)_2(PF_3)Ru(\mu\text{-}Cl)_3RuCl(PPh_3)_2]$,[16] and $[(L)(\widehat{P}P)Ru(\mu\text{-}Cl)_3RuCl(\widehat{P}P)]$ ($\widehat{P}P$ = diphosphine).[17]

Scheme 3



The broad AB_2 pattern observed at room temperature induced us to do low-temperature NMR experiments (Figure 1). At 193 K we observed the splitting of the singlet at 42.2 ppm to an AB system and the AB_2 pattern evolves to an ABC spin system. This is consistent with the proposed structure in Scheme 3 if we admit that the ligand conformation suppresses the equivalence of the two $P^{(a)}$ and the two $P^{(b)}$ nuclei. This inequivalence could be favored by hydrophobic interactions between *tert*-octyl groups as well as by steric hindrance.

Reactions with $RuCl_2(PPh_3)_3$. The complexity detected in the reactivity of our ligands with $RuCl_3 \cdot 3H_2O$ induced us to search for another approach in order to simplify the coordination study. With this aim, we undertook the phosphine substitution in the ruthenium(II) complex $RuCl_2(PPh_3)_3$ with ligands **1**−**9**. Previous studies of this reaction with ether phosphines revealed the formation of *trans*-dichloro-*cis*-bis(ether phosphine)-ruthenium(II) complexes as shown in Scheme 4.[18]

(12) Some examples of hydroxy phosphine preparation from hydroxy compounds without the use of OH-protective groups have been previously described.[13] The experimental method used for the synthesis of **9** from (*n*-octyl)PPh_2 enables the phosphine to be obtained in one step with good yield and purity.

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(14) *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1987; Vol. 4, Chapter 45.5.5.1, and references therein.
(15) Armit, P. W.; Boyd, A. S. F.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1663.
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(18) Lindner, E.; Möckel, A.; Mayer, H. A.; Kühbauch, H.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1993**, *32*, 1266.

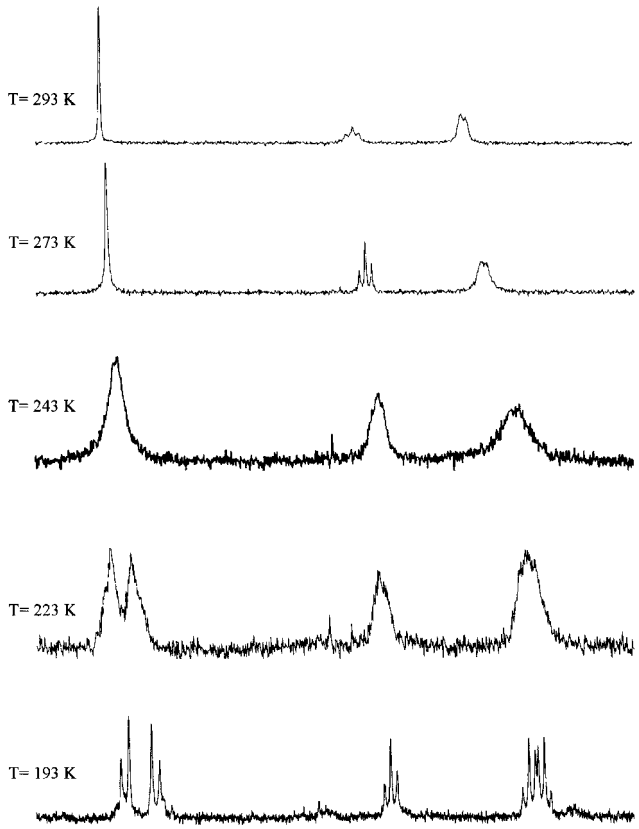
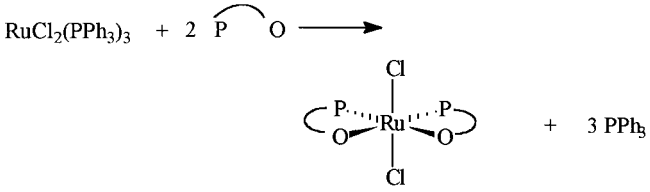


Figure 1. $^{31}P\{^1H\}$ NMR spectra of $[Ru_2Cl_4(\mathbf{1})_5]$ at different temperatures.

Scheme 4



As mentioned in the previous section, the study of this reaction with **2**−**6** was limited to NMR spectroscopy on account of the nature of these ligands. The reaction in dichloromethane between **1**−**6** and $RuCl_2(PPh_3)_3$ in a molar ratio 2:1 leads to the formation of dark red solutions. The ^{31}P NMR spectra of these solutions show a signal at −5 ppm assigned to free triphenylphosphine, and there is no trace of free ligands **1**−**6**. These results are in agreement with the phosphine substitution reaction described above. Nevertheless, previously reported ^{31}P NMR spectra of *trans*-dichloro-*cis*-bis(ether phosphine)ruthenium(II) complexes[19] show a single resonance at $\delta \approx 64$ ppm, while with ligands **2**, **3**, **5,** and **6** a quite broad resonance at $\delta \approx 58$ ppm with the characteristic shape of an AB system is observed ($J \approx 40$ Hz). Unfortunately, these compounds are waxy, and it was not possible to determine an X-ray structure; so based on the NMR results, the following possibilities are tentatively proposed (Scheme 5). The η^3 (*POO*) coordination is attractive since it has been well established for ligand **8**,[10] but other possibilities with two nonequivalent phosphorus atoms should also be considered.

In accordance with their chemical nature,[19] ligands **1** and **4** show a substantially different behavior from ligands **2**, **3**, **5**, and **6**. The ^{31}P NMR spectrum of the solution obtained after reaction of $RuCl_2(PPh_3)_3$ with **1** denotes the presence of (a) free triphenylphosphine, (b) characteristic signals of the previously observed $[Ru_2Cl_4(\mathbf{1})_5]$ complex in the direct reaction between $RuCl_3 \cdot 3H_2O$ and **1**, and (c) traces of an unidentified complex characterized by two doublets at $\delta = 50.7$ and 38.3 ppm ($J_{PP} = 39$ Hz).

Ligand **4** leads to a complicated ^{31}P NMR spectrum that suggests the presence of a mixture of ruthenium complexes. Some remarkable signals are a broad band at 58 ppm (δ similar to those observed for ligands with a long polyether chain **2**, **3**, **5**, **6**), broad resonances between 25 and 45 ppm (δ similar to that observed with ligand **1**, which has no polyether chain), and a resonance at 64 ppm (δ similar to *trans*-dichloro-*cis*-bis(ether phosphine)ruthenium(II) complexes (Scheme 4). This singular behavior may be related to the composition of **4**,[19] which contains molecules with short polyether chains (in comparison with **2**, **3**, **5**, and **6**) coexisting with the molecule with the phenolic oxygen as the only oxygen atom (similar to **1**).

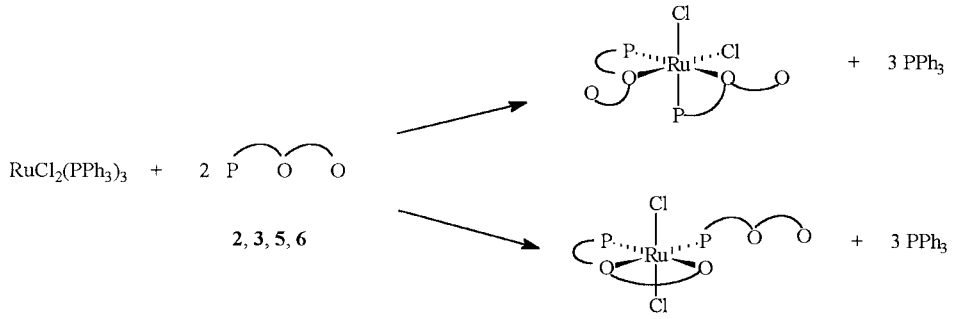
In contrast to the fact that solid compounds could not be isolated from the reaction between **1**−**6** and $RuCl_2(PPh_3)_3$, ligands **7**−**9** lead to the formation of dark red solutions, from which solid compounds were isolated. Single crystals were only obtained from ligand **8**, and the X-ray structure was determined and has been communicated previously.[10] The structure of this complex, $[RuCl_2(\mathbf{8})(PPh_3)]$, is outlined in Scheme 6, showing the coordination around the ruthenium atom with the two chlorine atoms in trans position, the ligand **8** η^3 bonded through the phosphorus and two oxygen atoms in meridional position, and the triphenylphosphine in the remaining coordination site.

The most remarkable features of this molecular structure are the unprecedented η^3 (*O*, *O*, *P*) coordination mode of the hemilabile ligand **8** and the long Ru−O distance (2.436(7) Å) between the metal and the oxygen atom in trans position to the phosphorus atom of ligand **8**. The significant difference between the two Ru−O distances[20] in the complex $[RuCl_2(\mathbf{8})(PPh_3)]$ suggests that this structural difference could be reflected in a different labile character of the two oxygen atoms. To check this hypothesis, the reactivity of $[RuCl_2(\mathbf{8})(PPh_3)]$ with PBu_3 and CO was studied by ^{31}P NMR spectroscopy (Scheme 7). After adding 1 mol of PBu_3 to $[RuCl_2(\mathbf{8})(PPh_3)]$, the dichloromethane red solution immediately turned green. However, the ^{31}P NMR spectrum at room temperature showed the resonances of $[RuCl_2(\mathbf{8})(PPh_3)]$ and free triphenylphosphine, suggesting that the newly formed complexes were fluxional. By lowering the temperature to 233 K, two groups of new sharp resonances were observed: for one, two doublets of the same intensity at δ 69.5 and 42.4 ppm ($J_{PP} = 42$ Hz), for another, a triplet at δ 70.6 ppm and a doublet at δ 16.3 ppm ($J_{PP} = 29$ Hz) with a 1:2 intensity ratio, consistent with the formation of $[RuCl_2(\mathbf{8})(PBu_3)]$ and $[RuCl_2(\mathbf{8})$-

(19) Ligand **1** is a pure compound with a sole oxygen atom in the phenoxy group. Although ligand **4** is a mixture of molecules, it also contains a molecule with a sole oxygen atom in the phenoxy group. In addition, the other molecules with more oxygen atoms display polyether chains shorter than **2**, **3**, **5**, and **6**.

(20) Ru−O (trans to PPh_3) = 2.191(6), Ru−O (trans to **8**) = 2.436(7).

Scheme 5

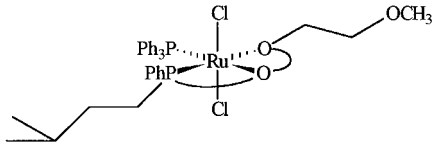


$(PBu_3)_2$], respectively, as shown in Scheme 7. The unanticipated replacement of PPh_3 by PBu_3 should be pointed out, since this result is contrary to the expected addition of PBu_3 to [$RuCl_2$(**8**)(PPh_3)] by displacement of the most labile oxygen atom. Nevertheless, we cannot rule out that the first step of the reaction mechanism could be the opening of the Ru−O bond, consistent with the hemilabile character of the oxygen atom, followed by PBu_3 addition.

In contrast to the unexpected substitution of PPh_3 by PBu_3, the reaction of [$RuCl_2$(**8**)(PPh_3)] with CO is consistent with the predicted hemilabile character for ligand **8**. Indeed, carbon monoxide was bubbled in a dichloromethane solution of [$RuCl_2$(**8**)(PPh_3)] at room temperature, and after a few minutes the red solution turned yellow. The ^{31}P NMR spectrum showed two sharp doublets at δ 11.7 and 26.4 ppm (J_{PP} = 251 Hz), indicating the existence of two different phosphorus atoms in trans position. The IR spectrum shows a single band in the ν(CO) region (2005 cm^{-1}) consistent with two trans CO ligands. All these facts support the hypothesis that the two Ru−O bonds are open after the addition of two CO ligands to [$RuCl_2$(**8**)(PPh_3)] to form the all-*trans*-[$RuCl_2(CO)_2$(**8**)(PPh_3)] complex (Scheme 7). A dichloromethane solution of this complex was heated to reflux, and the new ^{31}P NMR spectrum also showed two phosphorus atoms in trans position (J_{PP} = 292 Hz), now at 45.8 and 48.0 ppm. The IR spectrum of this solution showed a band at 1970 cm^{-1} in the ν(CO) region, in agreement with a CO in trans position to chloride.[18] These data are consistent with the formation of [$RuCl_2$(CO)(**8**)(PPh_3)], in which the two phosphines are trans and the CO ligand is in trans position to chloride (Scheme 7). The changes observed in the coordination mode of ligand **8** after the reaction between [$RuCl_2$(**8**)(PPh_3)] and CO should be emphasized. It moves successively from η^3 (*POO*) in the initial complex to η^1 (*P*) in [$RuCl_2(CO)_2$(**8**)(PPh_3)] and to η^2 (*PO*) in [$RuCl_2$(CO)(**8**)(PPh_3)], revealing the coordination versatility of ligand **8**. The reactivity of [$RuCl_2$(**8**)(PPh_3)] displayed in Scheme 7 can be associated with the steric and electronic features of CO and PBu_3.

The last salient feature of complex [$RuCl_2$(**8**)(PPh_3)] is shown by the molecular arrangement in the crystal structure. As can be seen in Figure 2, $RuCl_2$(**8**)(PPh_3) molecules are disposed in such a way that hydrophobic isopentyl groups are close together. The shortest intermolecular C−C distances (4.04 Å) are similar to those previously reported for compounds that exhibit representative hydrophobic interactions such as surfactants.[21] It has been postulated that hydrophobic interactions perform a significant role when the hydrophobic chain is constituted by five carbon atoms or more,[22] so this result may be perceived as a sign of the contribution of hydrophobic interactions in the chemical behavior of amphiphilic metal complexes.

Scheme 6



$RuCl_2$(**8**)PPh_3

With regard to the reaction between $RuCl_2(PPh_3)_3$ and **9**, a solid compound was obtained which shows a ^{31}P NMR spectrum in solution that is closely related with the spectrum of the above complex [$RuCl_2$(**8**)(PPh_3)]: two sharp doublets at δ = 63.3 and 58.8 ppm (J = 43 Hz). This similar chemical behavior can be understood considering their similar chemical structure, since both are dialkylaryl phosphines bonded to a hydrophobic chain and to a short polyether chain. Finally, a solution of the solid compound obtained after the reaction between **7** and $RuCl_2(PPh_3)_3$ displays a ^{31}P NMR spectrum with a singlet resonance at δ = 62.3 ppm, concordant with the results obtained with other ether phosphines (Scheme 4) and in contrast to the behavior described above for all the other ligands reported in this work. This result should be emphasized because **7** is the ligand that is most similar to previously reported ether phosphines. It contains only two more ethylene glycol groups with respect to $Ph_2PCH_2CH_2OCH_3$.[18] Consequently, there could be a possible influence of the hydrophobic group on the coordination properties of amphiphilic ligands, in contrast with the role of the polyether chain length. Thus, after reacting with $RuCl_2(PPh_3)_3$, ligands with a hydrophobic group and different polyether chains (**2**, **3**, **5**, and **6**) tend to exhibit similar ^{31}P NMR spectra, which are different from spectra obtained with ligands without a hydrophobic group (**7** and $Ph_2PCH_2CH_2OCH_3$).

Catalysis. Selective hydrogenation of α,β-unsaturated aldehydes is an attractive homogeneous catalytic process because the corresponding unsaturated alcohols

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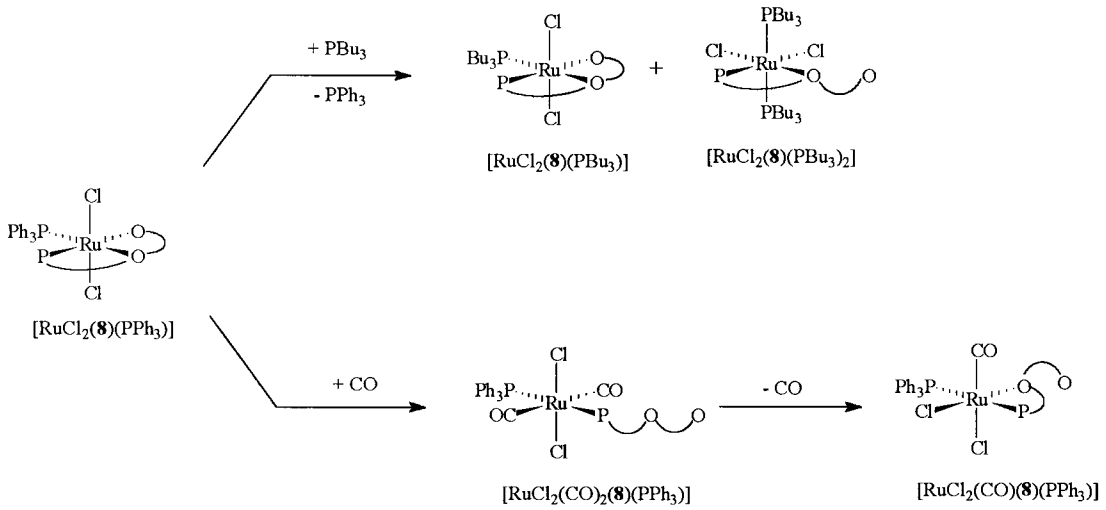
Scheme 7



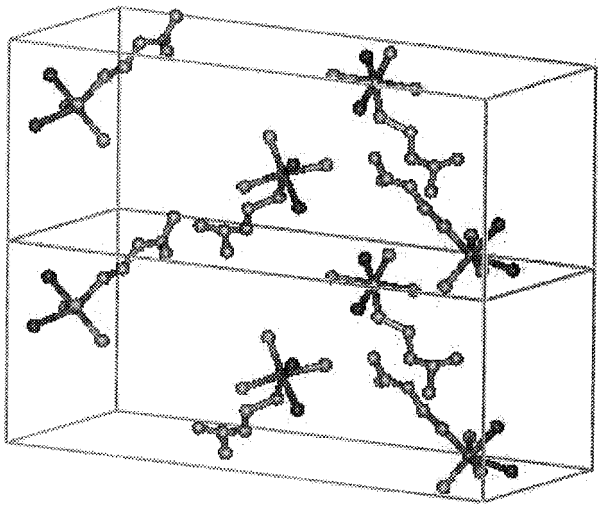
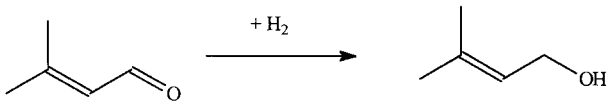


Figure 2. Schematic representation of molecular packing in the [$RuCl_2$(**8**)(PPh_3)] complex. For the sake of clarity only Ru, Cl, O (bonded to Ru), and P atoms and isopenytl groups are presented.

Scheme 8



are valuable products in the field of fragrance and flavor chemistry.[23] A limited number of catalytic systems based on ruthenium complexes that allow C=O hydrogenation over C=C have been reported.[24] For the purpose of appraising the performance of the amphiphilic ligands **1**−**6** in catalysis, we examined the catalytic hydrogenation of 3-methyl-2-butenal (prenal) to 3-methyl-2-butenol (prenol) in 2-propanol/water mixtures (Scheme 8).

The catalysts were generated in situ from $RuCl_3$ with a ligand excess.[25] This is the simplest approach to the preparation of catalysts from ligands **1**−**6**, in view of the practical problems in isolating their corresponding pure ruthenium complexes since **2**−**6** are mixtures of molecules with the same structure but with a different ethoxylation grade.

The substrate 3-methyl-2-butenal was catalytically hydrogenated to 3-methyl-2-butenol in 2-propanol/water under mild conditions (30 bar H_2, 50 °C) by a catalyst preparation from $RuCl_3$ and 3 equiv of ligands **1**−**6**. Reactions were performed for 20−160 min. The data from Table 1 demonstrate that high conversions of the starting compound were achieved after 20 min, in particular by ligands with long polyether chains. The gas chromatography analysis of reaction products shows that with the exception of prenal and prenol there are only traces of minor compounds, 3-methyl-1-butanol being the most abundant (≤1%). All reactions performed show reasonably high regioselectivity, allylic alcohol percentages of the hydrogenated products being on the order of 90% or higher. A possible hydrogen transfer from 2-propanol was ruled out since no prenol was obtained in a test reaction without hydrogen.

The reported catalytic system shows higher efficiency and selectivity than ruthenium catalysts based on triphenylphoshine, and the results are similar to those observed with TPPTS in biphasic medium (Table 2). As mentioned in the Introduction, one of the most attractive aspects of amphiphilic ligands **1**−**6** is the plausible modulation of their properties by changing the polyether chain length and the hydrophobic group structure. Hence, in this case the comparison between the results obtained with the different ligands is particularly relevant. For instance, ligands **1** and **4** show a notably different behavior, which can be related to the limited solubility of the corresponding ruthenium complexes in the reaction medium. Thus, in both processes the formation of solid compounds was observed, and the solid obtained from ligand **1** could be identified as [Ru_2Cl_4(**1**)$_5$] by ^{31}P NMR. In the same way, ligand **4** afforded the most distinct conversions with respect to the $^{i}PrOH/H_2O$ ratio (t = 20 min), which is also associated with the low solubility of its complexes in the most polar medium. On the other hand, ligands **2**, **3**, **5**, and **6** lead to soluble complexes, which result in more efficient catalysts, and manifest a similar behavior. Indeed, all

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Table 1. Catalytic Hydrogenation of Prenal to Prenol with $RuCl_3$ and Ligands 1−6

	conversion (%)[a]								
	reaction time = 20 min		reaction time = 35 min		reaction time = 50 min		reaction time = 65 min		reaction time = 160 min
ligand	^{i}PrOH/H_2O (95:5)	^{i}PrOH/H_2O (80:20)	^{i}PrOH/H_2O (95:5)	^{i}PrOH/H_2O (80:20)	^{i}PrOH/H_2O (95:5)	^{i}PrOH/H_2O (80:20)	^{i}PrOH/H_2O (95:5)	^{i}PrOH/H_2O (80:20)	^{i}PrOH/H_2O (95:5)
1							38(85)	36(84)	92(90)
2	75(95)	75(95)	100(93)	100(91)					
3	74(94)	91(92)	95(93)	100(90)					
4	64(95)	35(94)	92(96)	74(92)	100(94)	99(89)			
5	93(96)	100(93)	100(95)						
6	78(96)	100(95)	100(94)						

[a] In parentheses, selectivity in % prenol.

Table 2. Catalytic Hydrogenation of Prenal to Prenol with Several Ruthenium Complexes[25]

catalyst	$P(H_2)$ (bar)	T (°C)	time (h)	conversion, %	selectivity (prenol), %
$H_2Ru(PPh_3)_4$[a]	30	50	2.5	100	91
$RuCl_2(PPh_3)_3$[a]	30	50	3	81	80
$HRuCl(CO)(PPh_3)_3$[a]	30	50	3	33	38
$HRu(OAc)(PPh_3)_3$[a]	30	50	7	60	73
$RuCl_3$/4PPh_3[a]	20	35	9	69	93
$RuCl_3$/5TPPTS[b]	20	35	1	100	97

[a] Solvent = ^{i}PrOH/water (95:5). [b] Biphasic medium = toulene/water.

these ligands display high conversions at 20−35 min with selectivity to the order of 90−96%, and a slight improvement is observed by increasing the medium polarity. Although this preliminary catalytic study does not lead to notable differences between ligands **2**, **3**, **5**, and **6**, Table 1 suggests a slight improvement in ligands with linear nonyl hydrophobic chains with respect to ligands with bulky *tert*-octyl groups. If this trend could be corroborated in future works, it will correlate with better packing of linear hydrophobic groups in supramolecular structures.

Experimental Section

All reactions were performed under nitrogen by standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin-Elmer 1710 FT spectrometer. The NMR spectra were recorded on a Bruker AC400 (Servei de Ressonància Magnètica Nuclear de la Universitat Autònoma de Barcelona) and AM250 (Laboratoire de Chimie de Coordination) instruments. All chemical shift values are given in ppm and are referenced with respect to residual protons in the solvent for proton spectra to solvent signals for ^{13}C spectra and to phosphoric acid for phosphorus spectra.

The nonionic surfactants IGEPAL were purchased from Aldrich Chemical Co., and $RuCl_3$ was obtained from Johnson Matthey. The complex $RuCl_2(PPh_3)_3$ was prepared by published procedures.[26] Microanalyses were performed in the Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona.

Synthesis of 1. (a) Synthesis of $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_nCl$ ($\bar{n} \approx 1.5$). Triphenylphosphine (34.1 g, 0.13 mol) was added to a solution of the nonionic surfactant IGEPAL CA210 (29.4 g, ≈ 0.11 mol) in carbon tetrachloride (100 mL), and the mixture was heated to reflux for 1 h. In this period, the precipitation of $P(O)Ph_3$ as a white solid was observed. The mixture was allowed to cool to room temperature, and hexane (100 mL) was added in order to complete the precipitation of $P(O)Ph_3$ and the PPh_3 in excess. Solids were separated by filtration and washed with hexane (50 mL). The resulting solution was evaporated under vacuum, and the alkyl chloride was obtained as a colorless oil. Yield: 29.0 g (≈99%).

(b) Synthesis of $(CH_3)_3CCH_2C(CH_3)_2C_6H_4OCH_2CH_2PPh_2$ (1). A hexane solution of *n*-butyllithium (1.6 M, 0.13 mol, 80 mL) was added dropwise over 30 min with stirring to a solution of Ph_2PH (0.10 mol) in diethyl ether (100 mL) and cooled at 0 °C, and the resulting red solution was stirred at this temperature for a further 30 min. Next, to this cooled solution was added dropwise via cannula, with stirring, a cooled solution (0 °C) of alkyl chloride $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_n$-Cl ($\bar{n} \approx 1.5$, ≈ 0.10 mol, 29.0 g) in diethyl ether (100 mL) and stirred for a further 20 min at 0 °C. The cold bath was removed, and the mixture was allowed to warm to room temperature, stirred for 20 min, and brought to reflux for 3 h. The resulting reaction mixture was cooled to room temperature, EtOH (2 mL) and deoxygenated water (2 mL) were added to hydrolyze the remaining excess BuLi reagent, and the solvent was removed by vacuum evaporation. Deoxygenated water (70 mL) was added to the mixture and was extracted with portions (3 × 60 mL) of hexane, the organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure to give a colorless oil. After addition of EtOH (100 mL) a white precipitate was formed, which was filtered and washed with cold EtOH. Yield: 19.8 g (≈95%, based on the 50% abundance of $(CH_3)_3CCH_2C(CH_3)_2C_6H_4OCH_2CH_2Cl$ in the alkyl chloride mixture).

Significant NMR Data. $^{31}P\{^1H\}$ NMR (acetone-d_6): −20.7. ^1H NMR ($CDCl_3$; except phenyl resonances): 0.65 (s, $(CH_3)_3$), 1.27 (s, $(CH_3)_2$), 1.63 (s, CH_2, *tert*-octyl), 2.52 (t, $^3J_{HH}$ = 7.5 Hz, CH_2−P), 4.03 (q(apparent), $^3J_{PH} \approx {}^3J_{HH}$ = 7.5 Hz, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 28.3 (d, $^1J_{PC}$ = 13.2 Hz, CH_2P), 31.5 (s, $(CH_3)_2$), 31.6 (s, $(CH_3)_3$), 32.2 (s, CMe_3), 37.8 (s, CMe_2), 56.4 (s, CH_2, *tert*-octyl), 65.1 (d, $^2J_{PC}$ = 25.8 Hz, CH_2O).

Synthesis of 2−6. All these ligands were prepared by procedures analogous to that described above for ligand **1**, and the specific data of these preparations are as follows.

Ligand 2. (a) $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_nCl$ ($\bar{n} \approx 5$): IGEPAL CA520 (42.7 g, ≈ 0.1 mols), PPh_3 (34.1 g, 0.13 mol), CCl_4 (90 mL). Yield: 44.5 g (≈99%).

(b) $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_nPPh_2$ ($\bar{n} \approx 5$) (2): $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_5Cl$ (44.5 g, ≈ 0.10 mol), Ph_2PH (19.1 g, 0.10 mol), BuLi 1.6 M (69 mL, 0.11 mol). Yield: 55.8 g (≈94%).

Significant NMR Data. $^{31}P\{^1H\}$ NMR (acetone-d_6): −20.4. ^1H NMR ($CDCl_3$; except phenyl resonances): 0.65 (s, $(CH_3)_3$), 1.27 (s, $(CH_3)_2$), 1.63 (s, CH_2, *tert*-octyl), 2.34 (t, $^3J_{HH}$ = 7.5 Hz, CH_2−P), 3.4−4.1 (m, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 28.6 (d, $^1J_{PC}$ = 12.6 Hz, CH_2P), 31.5 (s, $(CH_3)_2$), 31.6 (s, $(CH_3)_3$), 32.2 (s, CMe_3), 56.8 (s, CH_2, *tert*-octyl), 67.1 (s, 18H, CH_2O), 68.4 (d, $^2J_{PC}$ = 25.8 Hz, PCH_2CH_2O), 69.6−70.7 (m, CH_2O).

Ligand 3. (a) $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_nCl$ ($\bar{n} \approx 12$): IGEPAL CA720 (29.4 g, ≈ 0.04 mols), PPh_3 (20.5 g,

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0.078 mols), CCl_4 (90 mL). To remove the residual $P(O)Ph_3$, the oil obtained after evaporation under reduced pressure was dissolved in MeOH/H_2O (1:1). Water was slowly added until a white cloudiness was observed, two phases were formed, and the upper phase, which was rich in $P(O)Ph_3$, was removed. This purification method was repeated until ^{31}P NMR spectroscopy showed insignificant levels of phosphine oxide in the final product. Yield: 19.6 g (≈65%).

(b) $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_nPPh_2$ ($\bar{n} \approx 12$) (3): $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_{12}Cl$ (31.1 g, ≈ 0.04 mol), Ph_2PH (7.7 g, 0.04 mol), BuLi 1,6 M (32 mL, 0.05 mol). Yield: 34.0 g (≈92%).

Significant NMR Data. $^{31}P\{^1H\}$ NMR (acetone-d_6): −20.4. ^1H NMR ($CDCl_3$; except phenyl resonances): 0.65 (s, $(CH_3)_3$), 1.28 (s, $(CH_3)_2$), 1.64 (s, CH_2, *tert*-octyl), 2.34 (t, $^3J_{HH}$ = 8.0 Hz, CH_2−P), 3.4−4.1 (m, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 28.6 (d, $^1J_{PC}$ = 12.6 Hz, CH_2P), 31.5 (s, $(CH_3)_2$), 31.6 (s, $(CH_3)_3$), 32.2 (s, CMe_3), 56.8 (s, CH_2, *tert*-octyl), 60.7 (s, CH_2O), 67.1 (s, CH_2O), 68.4 (d, $^2J_{PC}$ = 25.8 Hz, PCH_2CH_2O), 69.3−70.7 (m, CH_2O).

Ligand 4. (a) $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_nCl$ ($\bar{n} \approx 1.4$): IGEPAL CO210 (31.7 g, ≈ 0.11 mol), PPh_3 (34.1 g, 0.13 mol), CCl_4 (90 mL). Yield: 33.5 g (≈ 99%).

(b) $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_nPPh_2$ ($\bar{n} \approx 1.4$) (4): $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_{1.4}Cl$ (30.0 g ≈ 0.10 mol), Ph_2PH (19.1 g, 0.10 mol), BuLi 1.6 M (75 mL, 0.12 mol). Yield: 44.9 g (≈90%).

Significant NMR Data. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −21.3. ^1H NMR ($CDCl_3$; except phenyl resonances): 0.3−1.7 (m, *n*-nonyl), 2.36 (t, $^3J_{HH}$ = 7.6 Hz, $C_{(aryl)}$−$OCH_2CH_2OCH_2CH_2$−P), 2.50 (t, $^3J_{HH}$ = 7.7 Hz, $C_{(aryl)}$−OCH_2CH_2−P), 3.5−4.2 (m, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 8−55 (m, nonyl), (28.2 (d, $^1J_{PC}$ = 13.9 Hz, $C_{(aryl)}$−OCH_2CH_2P), 28.7 (d, $^1J_{PC}$ = 15.6 Hz, $C_{(aryl)}$−$OCH_2CH_2OCH_2CH_2$−P), 64.5 (d, $^2J_{PC}$ = 27.9 Hz, $C_{(aryl)}$−OCH_2CH_2P), 67.0 (s, $C_{(aryl)}$−OCH_2CH_2O), 68.5 (d, $^2J_{PC}$ = 24.4 Hz, $C_{(aryl)}$−$OCH_2CH_2OCH_2CH_2$−P), 69.1 (s, $C_{(aryl)}$−OCH_2CH_2O).

Ligand 5. (a) $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_nCl$ ($\bar{n} \approx 5$): IGEPAL CO520 (20.0 g, ≈ 0.05 mol), PPh_3 (16,0 g, 0.06 mol), CCl_4 (90 mL). Yield: 18.7 g (≈90%).

(b) $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_nPPh_2$ ($\bar{n} \approx 5$) (5): $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_5Cl$ (18.7 g, ≈ 0.04 mol), Ph_2PH (7.5 g, 0.04 mol in 80 mL of Et_2O), BuLi 1.6 M (28 mL, 0.05 mol). Yield: 22.4 g (≈ 90%).

Significant NMR Data. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −21.7. ^1H NMR (acetone-d_6; except phenyl resonances): 0.3−1.7 (m, *n*-nonyl), 2.32 (t, $^3J_{HH}$ = 7.6 Hz, CH_2−P), 3.5−4.2 (m, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 8−55 (m, nonyl), 68.2 (d, $^2J_{PC}$ = 26.2 Hz, OCH_2CH_2−P), 60−72 (m, OCH_2).

Ligand 6. (a) $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_nCl$ ($\bar{n} \approx 11$): IGEPAL CO720 (26.0 g, ≈ 0.04 mol), PPh_3 (22.6 g, 0.086 mol), CCl_4 (90 mL). The same procedure previously described in the synthesis of the alkyl chloride of ligand **3** should be performed with the oil obtained after evaporation under vacuum. Yield: 16.5 g (≈62%).

(b) $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_nPPh_2$ ($\bar{n} \approx 11$) (6): $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_{11}Cl$ (23.2 g, ≈ 0.03 mol), Ph_2PH (5.6 g, 0.03 mol), BuLi 1.6 M (21 mL, 0.03 mol). Yield: 24.3 g (≈87%).

Significant NMR Data. $^{31}P\{^1H\}$ NMR (acetone-d_6): −20.4. ^1H NMR (acetone-d_6; except phenyl resonances): 0.4−1.8 (m, *n*-nonyl), 2.34 (t, $^3J_{HH}$ = 7.6 Hz, CH_2−P), 3.4−4.2 (m, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 8−55 (m, nonyl), 68.2 (d, $^2J_{PC}$ = 24.4 Hz, OCH_2CH_2−P), 60−72 (m, OCH_2).

Synthesis of 7. (a) $CH_3(OCH_2CH_2)_3Cl$. This alkyl chloride was prepared by a procedure analogous to that described above for ($(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_2Cl$), but the final product was purified by distillation (T = 65 °C, $P \approx 0.1$ mmHg). The specific data of this preparation are as follows: $CH_3(OCH_2CH_2)_3OH$ (48.2 g, 0.29 mol), PPh_3 (100 g, 0.38 mol), CCl_4 (150 mL). Yield: 33.6 g (63%).

(b) $CH_3(CH_2CH_2O)_3PPh_2$ (7). This phosphine was prepared by a procedure analogous to that described above for ligand **1**, and the specific data of this preparation are as follows: $CH_3(OCH_2CH_2)_3Cl$ (18.3 g, 0.10 mol), Ph_2PH (19.1 g 0.10 mol), BuLi 1.6 M (69 mL, 0.11 mol). Yield: 30.2 g (91%). This phosphine was also prepared starting with PPh_3 instead of Ph_2PH by the procedure described in the synthesis of ligand **8** (yield = 81%).

Significant NMR Data. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −22.3. ^1H NMR ($CDCl_3$; except phenyl resonances): 2.36 (t, $^3J_{HH}$ = 7.5 Hz, CH_2−P), 3.31 (s, CH_3), 3.4−3.7 (m, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 28.5 (d, $^1J_{PC}$ = 12.6 Hz, CH_2P), 58.6 (s, CH_3), 68.2 (d, $^2J_{PC}$ = 23.9 Hz, CH_2CH_2P), 69.8−71.6 (m, CH_2O).

Synthesis of 8. (a) $(CH_3)_2CH(CH_2)_2PPh_2$. To a stirred solution of triphenylphosphine (26.2 g, 0.10 mol) in THF (150 mL) was added finely cut lithium (2.0 g, 0.29 mol), and the mixture was stirred for 3 h at room temperature. The obtained dark red-brown solution was separated via cannula from the excess lithium, and *tert*-butyl chloride (9.3 g, 0.10 mol) was added dropwise with continuous stirring. The resulting red solution was stirred at room temperature for a further 20 min. This solution was cooled at −78 °C, and a solution of $Br(CH_2)_2CH(CH_3)_2$ (15.1 g, 0.10 mols) in THF (50 mL) was dropwise added with vigorous stirring, yielding a colorless solution with a white precipitate. Next, a drop of BuLi (1.6 M in hexane) was added to the mixture, and the solution turned a slightly red color, which faded after some seconds. This process was repeated until a permanent slightly red color was obtained. Then, a few milliliters of water was cautiously added to hydrolyze any excess BuLi, and the solvent was removed in vacuo. The residual oil was extracted in hexane (2 × 100 mL)/water(100 mL). The organic phase was dried with Na_2SO_4, and the resulting solution was evaporated to dryness. The product was obtained as a colorless oil. Yield: (21.5 g) (84%). $^{31}P\{^1H\}$ NMR (acetone-d_6): −15.3.

(b) PPh[$(CH_2)_2CH(CH_3)_2$][$(CH_2CH_2O)_3CH_3$] (8). This ligand was prepared by a procedure analogous to that described above for isopentyldiphenylphosphine but using isopentyldiphenylphosphine as starting material instead of triphenylphosphine and $CH_3(OCH_2CH_2)_3Cl$ as the alkyl halide. The specific data of this preparation are as follows: $(CH_3)_2CH(CH_2)_2PPh_2$ (9.8 g, 0.038 mol), Li (0.8 g, 0.11 mol), $(CH_3)_3CCl$ (4.2 mL, 0.039 mol), $CH_3(OCH_2CH_2)_3Cl$ (7.0 g, 0.038 mol). Yield: 10.2 g (82%) of colorless oil.

Significant NMR Data. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −30.0. ^1H NMR ($CDCl_3$; except phenyl resonances): 0.6−1.8 (m, isopentyl), 1.98 (t, $^3J_{HH}$ = 7.6 Hz, CH_2−P), 3.2−3.8 (m, CH_2O, CH_3O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 21.9−34.7 (m, isopentyl), 58.7 (s, CH_3O), 68.5 (d, $^2J_{PC}$ = 22.0 Hz, OCH_2CH_2P), 69.7−71.8 (m, CH_2O).

Synthesis of 9. (a) $CH_3(CH_2)_7PPh_2$. This compound was prepared by a procedure analogous to that described above for isopentyldiphenylphosphine but using octyl chloride instead of isopentyl bromide. The specific data are as follows: PPh_3 (50.0 g, 0.19 mol in 200 mL THF), Li (3.5 g, 0.50 mol), $(CH_3)_3CCl$ (17.7 g, 0.19 mol), $CH_3(CH_2)_7Cl$ (28.3 g, 0.19 mol). Yield: 48.2 g (85%) of a pale yellow oil. $^{31}P\{^1H\}$ NMR (acetone-d_6): −15.0.

(b) PPh[$(CH_2)_7CH_3$][$(CH_2CH_2O)_2CH_2CH_2OH$] (9). To a stirred solution of $Ph_2P(CH_2)_7CH_3$ (30.3 g, 0.10 mol) in THF (150 mL) was added finely cut lithium (2.0 g, 0.29 mmol), and the mixture was stirred for 3 h at room temperature. The obtained dark brown solution was separated via cannula from the excess lithium, and *tert*-butyl chloride (9.5 g, 0.10 mol) was dropwise added with continuous stirring. The resulting orange solution was stirred at room temperature for a further 20 min. This solution was cooled at −78 °C, and a solution of $Cl(CH_2CH_2O)_2CH_2CH_2OH$ (17.2 g, 0.10 mol) in THF (50 mL) and a

solution of BuLi (1.6 M in hexane, 64 mL, 0.1 mol) were simultaneously and dropwise added with vigorous stirring. When both additions were finished, a colorless solution with a white precipitate was obtained. Next, a drop of BuLi (1.6 M in hexane) was added to the mixture, and the solution turned a slightly red color, which faded after some seconds. This process was repeated until a permanent slightly red color was obtained. A few milliliters of water was cautiously added to hydrolyze any excess BuLi, and the solvent was removed in vacuo. The residual oil was extracted in hexane (3 × 100 mL)/water (100 mL). The organic phase was dried over Na_2SO_4 and the resulting solution was evaporated to dryness. The product was obtained as a pale yellow oil. Yield: 29.4 g (83%).

Significant NMR Data. $^{31}P\{^1H\}$ NMR (acetone-d_6): −30.0. ^1H NMR ($CDCl_3$; except phenyl resonances): 0.8−1.8 (m, octyl), 2.02 (t, $^3J_{HH}$ = 8.0 Hz, CH_2−P), 3.4−3.8 (m, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 13.9 (s, CH_3), 22.4 (s, CH_2−CH_3), 25.7 (d, $^2J_{PC}$ = 13.2 Hz, PCH_2CH_2−hexyl), 28.1 (d, $^1J_{PC}$ = 10.7 Hz, CH_2P), 28.6 (d, $^1J_{PC}$ = 12.6 Hz, CH_2P), 29.0−31.6 (m, octyl), 61.4 (CH_2O), 68.7 (d, $^2J_{PC}$ = 22.0 Hz, PCH_2CH_2O), 69.9−72.3 (m, CH_2O).

Synthesis of $[Ru_2Cl_4(1)_5]$. A deoxygenated solution of $RuCl_3 \cdot 3H_2O$ (0.5 g, 1.9 mmol) in methanol (95:5, 30 mL) was heated to reflux for 5 min. To the resulting cold solution was added **1** (11.5 mmol, 4.8 g), and the resulting solution was heated to reflux for 3 h. The methanol solution was cooled, and a dark brown solid crystallized, which was recrystallized in hot 2-propanol. Yield: 0.95 g (41%).

Anal. Calcd for $C_{140}H_{175}Cl_4O_5P_5Ru_2$•: C, 69.01; H, 7.24. Found: C, 68.51; H, 7.52. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, T = 293 K): 42.2 (s), 29.5 (t, b), 23.7 (d, b). ^1H NMR ($CDCl_3$; except phenyl resonances): 0.66 (s, $(CH_3)_3$), 0.67 (s, $(CH_3)_3$), 1.26 (s, $(CH_3)_2$), 1.62 (s, CH_2, *tert*-octyl), 2.5−3.7 (b, CH_2−P and CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$; except phenyl resonances): 26.5 (b, CH_2P), 31.5 (s, CH_3), 31.7 (s, CH_3), 32.2 (s, CH_3), 37.8 (s, CMe_2), 56.8 (s, CH_2, *tert*-octyl), 64.5 (b, CH_2O).

Reactivity of 2−9 with $RuCl_3 \cdot 3H_2O$. In a representative procedure, a deoxygenated solution of $RuCl_3 \cdot 3H_2O$ (0.05 g, 0.19 mmol) in 2-propanol/water (95:5, 30 mL) was heated to reflux for 5 min. To the resulting cold solution was added 0.57 mmol of ligand, and the mixture was heated to 50 °C for 3 h. Solvents were evaporated in vacuo, and the resulting dark oil was extracted with hexane (10 mL). The resulting oil was evaporated to dryness in vacuo. The ^{31}P NMR was measured with a portion of this final oil.

Synthesis of $[RuCl_2(8)(PPh_3)]$. A solution of $RuCl_2(PPh_3)_3$ (1.24 g, 1.4 mmol) and **8** (0.90 g, 2.8 mmol) in dichlorometane (20 mL) was stirred for 1 h. The resulting dark solution was evaporated in vacuo, yielding to a dark oil, which was extracted with pentane in order to eliminate free phosphines. The extraction was repeated until the dark oil was transformed into a dark solid. The resulting dark solid was dried in vacuo and crystallized in MeOH. Yield: 0.20 g (38%).

Anal. Calcd for $C_{36}H_{46}Cl_2O_3P_2Ru$•: C, 56.84; H, 6.10. Found: C, 56.53; H, 5.96. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, T = 293 K): 58.8 (d), 63.3 (d), (J_{PP} = 43.3 Hz). ^1H NMR (CD_2Cl_2; except phenyl resonances): 0.6−1.6 (m, isobutyl), 2.3−2.5 (m, CH_2P), 2.6−2.8 (m, CH_2P), 3.17 (s, CH_3O), 3.2−4.4 (m, CH_2O).

Reactivity of $[RuCl_2(8)(PPh_3)]$ with PBu_3 and CO. PBu_3. A solution of crystalline $[RuCl_2(\mathbf{8})(PPh_3)]$ (20 mg, 0.026 mmol) in CD_2Cl_2 (1 mL) was prepared, and 0.5 mL of this solution were placed in a NMR tube and frozen by liquid nitrogen. A solution of PBu_3 (6.5 μL, 0.026 mmol) in CD_2Cl_2 (1 mL) was prepared, and 0.5 mL was added to the NMR tube and frozen again in liquid nitrogen. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR (T = 233 K): 16.3 (d, $^2J_{PP}$ = 29.5 Hz, $[RuCl_2(\boldsymbol{8})(PBu_3)_2]$), 42.4 (d, $^2J_{PP}$ = 42 Hz, $[RuCl_2(\mathbf{8})(PBu_3)]$), 69.5 (d, $^2J_{PP}$ = 42 Hz, $[RuCl_2(\mathbf{8})(PBu_3)]$), 70.6 (t, $^2J_{PP}$ = 29.5 Hz, $[RuCl_2(\boldsymbol{8})(PBu_3)_2]$).

CO. Carbon monoxide was bubbled through a solution of $[RuCl_2(\mathbf{8})(PPh_3)]$ (200 mg, 0.26 mmol) in CH_2Cl_2 (10 mL). Almost immediately a color change was observed from red to yellow, and the NMR and IR spectra from this solution were obtained. $^{31}P\{^1H\}$ NMR (insert acetone-d_6): 11.7 (d, $^2J_{PP}$ = 251 Hz, $[RuCl_2(CO)_2(\mathbf{8})(PPh_3)]$), 26.4 (d, $^2J_{PP}$ = 251 Hz, $[RuCl_2(CO)_2(\boldsymbol{8})(PPh_3)]$). IR ($CH_2Cl_2$, ν_{CO}, cm^{-1}): 2005.

The above dichloromethane solution was allowed to reflux for 45 min, and the ^{31}P NMR and IR spectra were newly obtained. $^{31}P\{^1H\}$ NMR (acetone-d_6): 45.8 (d, $^2J_{PP}$ = 292 Hz, $[RuCl_2(CO)(\mathbf{8})(PPh_3)]$, 48.0 (d, $^2J_{PP}$ = 292 Hz, $[RuCl_2(CO)(\boldsymbol{8})(PPh_3)]$). IR ($CH_2Cl_2$, ν_{CO}, cm^{-1}): 1970.

Reactivity of 1−7 and 9 with $RuCl_2(PPh_3)_3$. In a representative procedure, a solution of $RuCl_2(PPh_3)_3$ (0.05 mmol) and the corresponding ligand (0.10 mmol) in dichlorometane (20 mL) was stirred for 1 h. The resulting solution was evaporated in vacuo, yielding a dark oil, which was used to measure the ^{31}P NMR spectrum. The same procedure was used for ligand **7**, but the final oil was dissolved in ^{i}PrOH and, after cooling, a dark solid was isolated. The oil obtained from the preparation with ligand **9** was vigorously stirred with pentane (the complex is not soluble in this solvent) for several minutes. The pentane solution was rejected, fresh pentane added, and the process repeated until the dark oil was transformed into a dark solid. $^{31}P\{^1H\}$ NMR (acetone-d_6).

1: {22.9 (b), 28.4 (t, $^2J_{PP}$ = 30 Hz), 41.0 (s), 38.3 (d, $^2J_{PP}$ = 39 Hz), 50.7 (d, $^2J_{PP}$ = 39 Hz)}.

2: {58.4 (d, $^2J_{PP}$ = 40 Hz), 58.7 (d, $^2J_{PP}$ = 40 Hz)}.

3: {58.6 (b)}.

4: {28.0 (b), 31.0 (b), 38.6 (b), 41.0 (b), 53.9 (b), 58.8 (b), 64.2 (s)}.

5: {58.4 (d, $^2J_{PP}$ = 40 Hz), 58.7 (d, $^2J_{PP}$ = 40 Hz)}.

6: {58.4 (d, $^2J_{PP}$ = 43 Hz), 58.8 (d, $^2J_{PP}$ = 43 Hz)}.

7: {62.2 (s)}.

9: {58.8 (d, $^2J_{PP}$ = 43 Hz), 63.3 (d, $^2J_{PP}$ = 43 Hz)}.

Catalysis. The products of the catalytic reactions were identified by GC and mass analysis. Gas chromatography was run on a KONIK KNK-3000-HRGC equipped with a Chromosorb W-HP packed column. The peaks were identified by GC/MS techniques. The GC detector sensitivity was calibrated by comparison with authentic samples.

Hydrogenation Procedure. A typical experiment was performed in a glass-lined stainless steel autoclave with magnetic stirring (1000 rpm). Hydrated ruthenium chloride (146 mg, 0.5 mmol) and 1.5 mmol of ligand were placed in the autoclave vessel, which was closed. Air was evacuated under vacuum and replaced with nitrogen. A purged solution of 2 mL (20 mmol) of 3-methyl-2-butenal in 15 mL of 2-propanol/water was transferred to the autoclave by means of a cannula. The reactor was placed in a thermostated oil bath for 20 min with vigorous stirring to allow formation of the catalyst precursor and to reach the desired temperature in the reaction vessel. Next, H_2 (30 bar) was introduced in the reactor. Samples were extracted using a syringe with purge each time.

Acknowledgment. This research was supported by the Direccion General de Investigación Científica y Técnica.

OM9905916