Study of the complexing properties toward Ru^{II} of new polydentate amphiphilic phosphines containing polyether chains. Unprecedented η^3 mode of bonding of the new ligand PPh[$(CH_2)_3CHMe_2$][$(CH_2CH_2O)_3Me$] and study of its hemilabile character

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New polydentate amphiphilic phosphines containing polyether chains are prepared; unprecedented coordination and reactivity of the hemilabile ligand PPh[$(CH_2)_3CHMe_2$][$(CH_2CH_2O)_3Me$] are found; the η^3 mode of bonding of this ligand is demonstrated by X-ray crystallographic studies.

Recently, several studies have reported interesting performance improvements in catalytic homogeneous or heterogeneous systems after addition of surfactants to the reaction medium.[1] These facts have been related to the formation of micellar solutions, which represent a micro-heterogeneous medium where the reactions can take place at the interface. Furthermore, special advantages in using catalysts containing new ligands with hydrophilic and hydrophobic chains have been claimed.[2]

These observations induced us to prepare transition-metal complexes with amphiphilic ligands,[3] so they may act as catalysts with the properties of a surface-active agent. To our knowledge, only a very few examples of ligands with amphiphilic properties have been reported.[4]

For these reasons, we have developed the synthesis of two new families of functionalized phosphines. These ligands also represent an unprecedented facet in the chemistry of phosphine ligands because these compounds feature the combination of amphiphilic properties and the character of hemilabile ligands[5] which are conferred by the polyether chain.

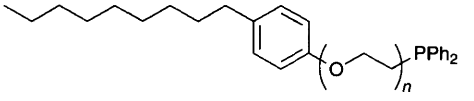
Ligands **1–6** were synthesized in two steps starting from the corresponding commercial nonionic surfactants IGEPAL.[6] Ligands **7** and **8** were synthesized in two steps as shown in Scheme 1.‡

The study of complexing properties of ether phosphines toward ruthenium has been well developed by Bader and Lindner who have shown that these ligands can act as mono- or bi-dentate ligands.[5]

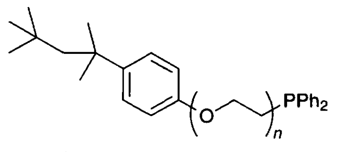
In contrast to these previously studied ligands, **1–8** contain at least two oxygen atoms able to coordinate simultaneously to a metal centre. For this reason we have evaluated their coordination properties toward ruthenium, under similar conditions to those used by these authors.

The direct reaction of $RuCl_3 \cdot 3H_2O$ with a threefold excess of **1–8** leads to a complex mixture as evidenced by broad resonances observed by ^{31}P NMR and no products have been isolated. So we turned to another approach: ligand substitution in [$RuCl_2(PPh_3)_3$]. The action of 2 equiv. of **1–6** in dichloromethane solution leads to the formation of dark red solutions. $^{31}P\{^1H\}$ NMR show the presence of a signal at δ −5 assigned to free triphenylphosphine and quite broad resonances around δ 58 with the characteristic shape of two coupled phosphorus atoms. This result was not consistent with the observations of Lindner *et al.* who observed the formation of *trans*-dichloro-*cis*-bis(ether phosphine-*O,P*) ruthenium(II) complexes in all cases.[5,7] Unfortunately, the compounds were waxy and it was not possible to determine an X-ray structure. Nevertheless, as only one compound and free PPh_3 were detected in the reaction medium, we can propose for these complexes one structure in which the ligands are η^2 bonded and in which one phosphorus atom is *trans* to chlorine and the other *trans* to oxygen.

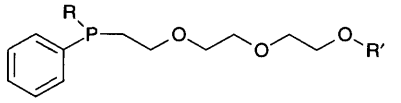
The reaction in dichloromethane solution between 2 equiv. of **7**, **8** and [$RuCl_2(PPh_3)_3$] leads to the formation of a dark red solution from which compounds **9**, **10** were isolated. Their $^{31}P\{^1H\}$ NMR spectra are similar and show the presence of two sharp doublets, in contrast to the complexes with ligands **1–6**.



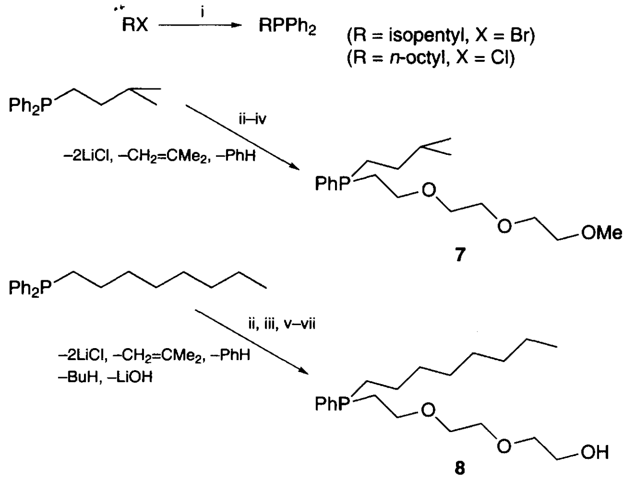
1 (n = 2), **2** (n = 5), **3** (n = 12)



4 (n = 2), **5** (n = 5), **6** (n = 12)



7 (R = isopentyl, R′ = Me), **8** (R = *n*-octyl, R′ = H)



Scheme 1 *Reagents*: i, + $LiPPh_2$, − LiX; ii, 2Li; iii, Bu^{t}Cl; iv, $Cl(CH_2CH_2O)_3Me$; v, $Cl(CH_2CH_2O)_2CH_2CH_2OH$; vi, BuLi; vii, H_2O

Crystals of **9** were obtained and their X-ray structure was determined.‡ An ORTEP view of the molecule is shown in Fig. 1. Although the synthesis was carried out with a racemic mixture of **7**, in the selected crystal only one enantiomer [the (*S*) form] was present. The molecule consists of a ruthenium atom at the centre of a distorted octahedron, coordinated to two chlorine atoms in the *trans* position, to one triphenylphosphine and to **7** η^3 bonded by the phosphorus and two oxygen atoms in a meridional position. This structure resembles previously reported structures of ruthenium(II) complexes containing two hemilabile monoether–phosphine ligands[8] and an isoelectronic cationic complex of rhodium(III) of the 1,8-bis(diphenylphosphino)-3,6-dioxaoctane ligand[9] but this is to our knowledge the first structural characterization of a hemilabile ligand bonded by one phosphorus and two oxygen atoms.

The most characteristic feature of this structure results from the ruthenium–oxygen bond distances: Ru–O(1) is, within experimental error, in the range found for ether–phosphines bound to ruthenium(II) but the Ru–O(2) distance is considerably longer [2.436(7) Å] and to our knowledge is the longest found in such a type of complex.

To check if this lengthening has some consequences for the reactivity of **9**, its reaction with 1 equiv. of PBu_3 was studied. During the addition, the red solution immediately turned green and monitoring the reaction by ^{31}P NMR at room temperature shows that only the resonances of **9** and free PPh_3 are observed. The presence of free PPh_3 indicated that a reaction had occurred but the absence of clearly observable resonances suggests that the newly formed complexes are fluxional. Indeed, by lowering the temperature to 233 K, new sharp resonances appear and two new compounds are observed: one characterized by two doublets of the same intensity centred at δ 69.5 and 42.4 (J_{PP} 42 Hz) and the other by a triplet at δ 70.6 and a doublet at δ 16.3 (J_{PP} 29.5 Hz) in the 1:2 intensity ratio consistent with the formation of $[RuCl_2(\mathbf{7})(PBu_3)]$ **11** and $[RuCl_2(\mathbf{7})(PBu_3)_2]$ **12**. The main feature of these observations is that only the PPh_3 ligand is liberated, contrary to the expected displacement of the O(2) ether arm by PBu_3.[10]

From the NMR data we propose for **11** a structure similar to **9** in which PPh_3 has been replaced by PBu_3 and for **12** a structure where the two PBu_3 ligands are *trans*, the two chlorines *cis* and **7** η^2 bonded.

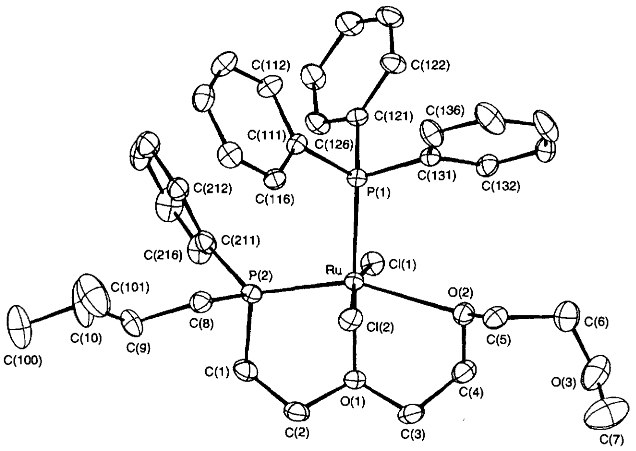


Fig. 1 ORTEP diagram of **9** showing 50% probability ellipsoids. Salient bond distances (Å) and bond angles (°): Ru–Cl(1) 2.387(2), Ru–Cl(2) 2.395(2), Ru–P(1) 2.252(2), Ru–P(2) 2.212(3), Ru–O(1) 2.191(6), Ru–O(2) 2.436(7), Cl(1)–Ru–Cl(2) 166.89(9), P(1)–Ru–O(1) 176.7(2), P(2)–Ru–O(1) 82.7(2), O(1)–Ru–O(2) 73.9(2).

In the absence of kinetic studies it is difficult to draw conclusions about the mechanism of formation of **11**, but our observations clearly show that the product of the reaction of **9** with PBu_3 results from the replacement of PPh_3 by PBu_3. Nevertheless, this does not rule out that the first step of the reaction is the opening of the Ru–O(2) bond consistent with the hemilabile character of **7**.

The reactivity of **9** toward carbon monoxide confirms the hemilabile character of **7**. Indeed, at room temperature by bubbling carbon monoxide the immediate formation of all-*trans*-$[RuCl_2(CO)_2(\mathbf{7})(PPh_3)]$ **13** is observed.

Heating **13** in refluxing dichloromethane leads to the slow formation of $[RuCl_2(CO)(\mathbf{7})(PPh_3)]$ **14** in which the two phosphines are *trans*. The position of the CO band in the IR spectrum is consistent with the CO *trans* to chloride.[7] So in these reactions the ligand **7** moves successively from the η^3 to η^1 and η^2 modes of coordination.

To conclude, this study shows that in contrast to the ligands containing phosphorus and only one ether function, the presence of a polyether chain in phosphines induced original bonding properties as illustrated by the change in geometry of $[RuCl_2L_2]$ complexes for the ligands **1–6** and the unexpected reactivity of complex **9** toward PBu_3.

Footnotes

† *Selected spectroscopic data*: IR(CH_2Cl_2) ν(CO)/cm^{-1}, **13** 2005s, **14** 1970s. ^{31}P NMR [in $CDCl_3$ except compounds **11**, **12** (CD_2Cl_2)] δ: **7** −29.7, **8** −30.3, **9** 58.9(d) 62.9(d) (J_{PP} 43.8 Hz), **10**, 58.8(d) 63.3(d) (J_{PP} = 43.3 Hz), **13** 11.7(d) 26.4(d) (J_{PP} 251 Hz), **14** 45.8(d) 48.0(d) (J_{PP} 292 Hz).

‡ *Crystal data* for compound **9**: $C_{36}H_{46}Cl_2O_3P_2Ru$, M = 760.68; orthorhombic, space group $P2_12_12_1$, a = 10.948(9), b = 11.157(2), c = 29.532(7) Å, U = 3607(3) Å^3, D_c = 1.401 Mg m^{-3}, observed reflections 3610 [$I > 3\sigma(I)$] (Enraf-Nonius CAD4) 400 parameters refined, R = 0.0355, (R_w = 0.0511).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Informations for Authors, Issue No 1.

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