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Hydrosoluble transition-metal coordination compounds of triphenylphosphine *m*-trisulfonate

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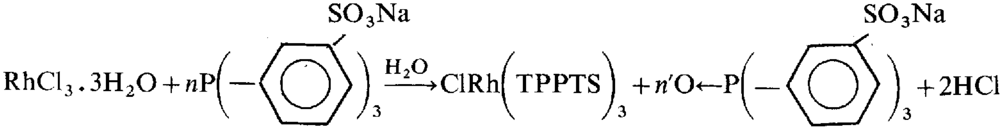
By using ^{31}P NMR and IR techniques it is established that the basicities of triphenylphosphine *m*-trisulfonate (TPPTS) and triphenylphosphine (PPh_3) are in the same order of magnitude. This highly hydrosoluble phosphine is a convenient ligand for the synthesis of hydrosoluble coordination compounds of molybdenum(0), palladium(II), platinum(II) and rhodium(I). The exchange of TPPTS with ligands other than PPh_3 (nitriles, carbon monoxide, olefins, chloride) can be used to obtain the desired complexes. However, because redox reactions between metal salts, water and TPPTS are possible, the synthesis of low-valent precursors must be carried out and the experimental conditions have to be carefully controlled to avoid side-reactions and the participation of the sulfonate anions in competitive reactions.

Keywords: Triphenylphosphine *m*-trisulfonate, basicity, coordination compounds, with molybdenum(0), palladium(II), platinum(II), rhodium(I), hydrosoluble organometallic and coordination compounds

INTRODUCTION

Major restrictions to wider industrial utilization of homogeneous catalysis turn around the important problem of separating the products from the catalysts, and their recycling. Among the possible solutions, we are interested in the design of water-soluble transition-metal compounds able to catalyze reactions of water-immiscible substrates. This can be realized by the association of transition metals with hydrophilic phosphines such as diphenylphosphinobenzene-*m*-sulfonate (dpm),[1] [2-(diphenylphosphino)ethyl]trimethylammonium salts (amphos)[2] and, as described in this paper, by using the highly hydrosoluble triphenylphosphine *m*-trisulfonate (TPPTS).[3] Water-soluble analogues of transition-metal complexes of triphenylphosphine (PPh_3) are obtainable through different pathways. For instance, they can be prepared by adapting literature procedures already described for the reaction of triphenylphosphine with high-valent transition-metal salts under reducing conditions. Otherwise, anion (X) or ligand (L) exchange by TPPTS on mononuclear or polynuclear complexes is also possible.

The first way was explored by using rhodium(III) chloride ($RhCl_3.3H_2O$) and ruthenium(III) chloride ($RuCl_3.3H_2O$) in order to prepare coordination compounds of TPPTS with rhodium(I) and ruthenium(II). However, the hydrophillicity of TPPTS is so high that water cannot be excluded and we have found that a redox reaction occurs between water, the metal salt and the phosphine.[4] As shown in Eqn [1], the phosphine is partially oxidized and the low-valent metal species produced are trapped to afford, *inter alia*, coordination compounds of TPPTS, the structure and stability of which could be studied by ^{31}P NMR.[4]



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Convenient methods to separate such hydrosoluble species do not exist; that is why we turned to ligand exchange. This technique requires knowledge of the basicity of TPPTS versus other ligands. This evaluation is reported in the present paper together with the synthesis and characterization of new water-soluble coordination compounds of molybdenum(0), platinum(II), palladium(II) and rhodium(I).

EXPERIMENTAL

TPPTS, **1**, (Rhône–Poulenc), $RhCl_3.3H_2O$, K_2PtCl_4, $Mo(CO)_6$ and $Cr(CO)_6$ were of commercial origin (Janssen) and used without further purification. Solvents were distilled before use by conventional methods. $KPtCl_3(C_2H_4)$ (Zeise's salt) and $[RhCl\ (COD)]_2$ [COD = *cis*-1,5-cyclo-octadiene] have been prepared using previously described procedures.[5,6] HPLC analyses were performed on an RP-18 column using $(tBu)_4N^+$ as counter-cation and a gradient mixture of H_2O–MeOH as eluant. $^{31}P\{^1H\}$ NMR spectra (32.38 MHz) were recorded on a Brucker WP 80 MHz (external reference 85% H_3PO_4). ^1H NMR spectra (60 MHz) were recorded on a Varian EM 360 (external reference TMS). Preparations and NMR studies of the complexes were carried out under anaerobic conditions. All solvents, especially water, were scrupulously degassed before use.

Basicity of TPPTS

$O \leftarrow P(PhSO_3Na)_3$ or (O-TPPTS, **2**) was obtained by oxidation of **1** with H_2O_2 (10% in aqueous solution) or by sulfonation of PPh_3 with H_2SO_4–SO_3 (65%, 24 h; room temperature).

Synthesis of $O \leftarrow P(PhSO_2Cl)_3$, 3

A mixture of thionyl chloride ($10\ cm^3$, 50 mmol) and DMF ($0.2\ cm^3$) was rapidly added to 4.4 g (7 mmol) of **2**. The mixture was heated at 80°C for 3.5 h and, after cooling, poured on $500\ cm^3$ of ice. The white solid was filtered and washed with water until the washings became neutral. After drying *in vacuo* the product was recrystallized in dichloromethane (CH_2Cl_2). Yield, 76%; m.p. = 212°C; MS, $m/z = 571.8$ (found), 572 (calculated); IR (KBr), $\nu SO\ (cm^{-1}) = 1365$ (s), 1170 (s); ^{31}P NMR (CH_2Cl_2) $\delta = 25.9$ ppm (singlet).

Synthesis of $O \leftarrow P(PhSO_2NMe_2)_3$, 4

Dimethylamine (0.34 g, 3 mmol) in aqueous solution (40%), 0.65 g (6 mmol) of sodium carbonate and $2\ cm^3$ of water were heated to 70°C; 0.57 g (1 mmol) of **3** was then slowly added. The mixture was heated at 70°C for 20 h until it became clear. After cooling, the product was extracted with dichloromethane ($2 \times 20\ cm^3$) and ether ($2 \times 20\ cm^3$). The resulting organic phase was washed with water (2×20 cm) and then dried on magnesium sulfate. The solvents were removed under vacuum and the white product was recrystallized (ether–hexane). Yield, 65%; m.p. = 201°C; IR (KBr) $\nu SO\ (cm^{-1}) = 1340$ (s), 1190 (s); ^1H NMR ($CDCl_3$) $\delta = 8.2$–7.5 ppm (multiplet, Ar–H); 2.7 ppm (singlet, CH_3); ^{31}P NMR (CH_2Cl_2) $\delta = 24.5$ ppm (singlet).

Synthesis of $O \leftarrow P\ (PhSO_3AsPh_4)_3$ 5

A solution of $AsPh_4Cl$ (1.4 g, 3 mmol) in the minimum of water was added to a solution of **2** (0.6 g, 1 mmol) in $2\ cm^3$ of water. The white precipitate was extracted with dichloromethane ($3 \times 100\ cm^3$). The organic phase was dried on magnesium sulphate and the solvent removed under vacuum. The hygroscopic product formed was stored in *vacuo*. IR (KBr) $\nu SO\ (cm^{-1}) = 1200$ (s, broad), 1060(s); ^{31}P NMR (CH_2Cl_2) $\delta = 24.9$ ppm (singlet).

Synthesis of $Mo(CO)_5(TPPTS)$ 6 and chromium analogues

A solution of **1** (1.2 g; 2 mmol) in 25 cm of water was added to a solution of $Mo(CO)_6$ (5.3 g; 20 mmol) in $100\ cm^3$ of THF. The resulting solution was refluxed for 15 h. After cooling at room temperature the mixture was filtered and THF was removed under vacuum. The resulting aqueous solution was filtered again and washed with dichloromethane ($2 \times 20\ cm^3$). After evaporation of water the yellow product was dried *in vacuo*. The conversion of TPPTS was quantitative. IR (Nujol) $\nu SO\ (cm^{-1}) = 1050$ (s), 1200 (s, broad); $\nu CO\ (cm^{-1}) = 1940$ (s), 1980 (m), 2075 (m); ^{31}P NMR (H_2O) $\delta = 41.4$ ppm (singlet); HPLC analysis retention time = 11.5 min (100%). The same procedure was used with $Cr(CO)_6$; a mixture of products $Cr(CO)_4(TPPTS)_2$, $Cr(CO)_5(TPPTS)$ and unreacted TPPTS was obtained. ^{31}P NMR (H_2O) δ (respectively) = 57.7 ppm (7%); 76.8 ppm (57%); -5.5 ppm (36%);

HPLC analysis retention times (min) = 12.5, 11.0, 10.4. $Mo(CO)_5(PPh_3)$, **7** has been prepared and characterized by the method previously described.[7] IR (Nujol) νCO (cm^{-1}) = 1945 (s), 1990 (w), 2075 (m).

Synthesis of TPPTS coordination compounds by ligand exchange

Synthesis of *cis*-$PtCl_2(TPPTS)_2$, 8, from K_2PtCl_4

A mixture of K_2PtCl_4 (98 mg; 0.3 mmol) and TPPTS (360 mg; 0.6 mmol) was dissolved in water. The ^{31}P NMR spectrum of the solution registered immediately showed the expected satellites at $\delta = 13.9$ ppm, $J^{195}Pt—P = 3735$ Hz. Compound **8** could be isolated after removal of water under vacuum (quantitative conversion).

Synthesis of *cis*-$PtCl_2(TPPTS)_2$ 8, from Zeise's salt and isomerization of *trans*-$PtCl_2(TPPTS)_2$, 9

A mixture of Zeise's salt (110 mg, 0.3 mmol) and TPPTS (360 mg, 0.6 mmol) was dissolved in water. The ^{31}P NMR spectrum of the solution registered after 10 min showed the expected satellites for **8** (65%): $\delta = 13.9$ ppm, $J^{195}Pt—P = 3735$ Hz; and **9** (35%): $\delta = 21.9$ ppm; $J\,^{195}Pt—P = 2602$ Hz. After 1 h the percentages of **8** and **9** in the solution were respectively 82% and 18% and after 3 h compound **9** had disappeared.

Synthesis of $PdCl_2(TPPTS)_2$ (*cis* and *trans*), 10

A mixture of $PdCl_2(PhCN)_2$ (380 mg, 1 mmol) and TPPTS (1.2 g, 2 mmol) in ethanol (40 cm^3) and water (15 cm^3) was heated at 60°C for 5 min until the mixture became a limpid red solution. Ethanol is removed under vacuum and the resulting aqueous solution washed with ether and dichloromethane. After removal of water under vacuum the red product was dried *in vacuo* (quantitative conversion). IR (KBr) νSO (cm^{-1}) = 1050 (s), 1200 (s, broad); ^{31}P NMR (H_2O) $\delta = 34.3$ ppm (singlet, 70%), 25.3 ppm (singlet, 30%).

Synthesis of $[Rh(COD)(TPPTS)_2]^+CF_3SO_3^-$, 11

$[RhCl(COD)]_2$ (59 mg, 0.1 mmol) and 63 mg (0.2 mmol) of silver trilfate ($Ag^+CF_3SO_3^-$) were dissolved in 2 cm^{-3} of methanol. After stirring for 15 min the precipitate of silver chloride was filtered and the methanolic solution was added to a solution of TPPTS (304 mg, 0.5 mmol) in 2 cm^3 of water. The yellow solution obtained was stirred for 15 min at room temperature and the methanol evaporated under vacuum (quantitative conversion). ^{31}P NMR (H_2O): $\delta = 30.1$ ppm, ^1J Rh—P = 154 Hz (broad doublet, 100%). ^1H NMR (D_2O) $\delta = 8.2$–7.1 ppm (multiplet, Ar—H), 1.7–2.7 (multiplet, CH_2). ^{13}C NMR (H_2O) δ for coordinated cyclooctadiene = 105.1 ppm (=C—H), 32.9 (CH_2).

Synthesis of (COD)RhCl(TPPTS), 12

A solution of $[RhCl(COD)]_2$ (61 mg, 0.1 mmol) in THF (2 cm^3) was added to 150 mg (0.2 mmol) of TPPTS (**1**) in an aqueous solution of sodium chloride (1 mol dm^{-3}) [or perchloric acid (1 mol dm^{-3}) or hydrochloric acid (1 mol dm^{-3})]. After stirring for 15 min THF was evaporated under vacuum (quantitative conversion). ^{31}P NMR (H_2O, NaCl) $\delta = 31.9$ ppm, ^1J Rh—P = 151 Hz (sharp doublet, 100%); ^1H NMR (D_2O, NaCl) $\delta = 8.1$–7.2 (multiplet, ArH), 1.6–2.8 ppm (multiplet, CH_2).

Synthesis of $RhCl(TPPTS)_3$, 13

TPPTS (**1**) (300 mg, 0.4 mmol) was added to an aqueous solution of **12** obtained as described above. The orange mixture was stirred for 3 h at room temperature until it turned red (quantitative conversion). ^{31}P NMR (H_2O): $\delta P_1 = 34.4$ ppm, ^1J Rh—P_1 = 144 Hz, ^2J P_1—P_2 = 39 Hz (double doublet); $\delta P_2 = 50.8$ ppm, ^1J Rh—P_2 = 193 Hz, ^2J P_1—P_2 = 39 Hz (double triplet).

Synthesis of $[Rh(COD)(TPPTS)]_2$, 14

A solution of $[RhCl(COD)]_2$ (61 mg) in THF (2 cm^3) was added to 150 mg (0.2 mmol) of TPPTS, **1**, dissolved in D_2O (2 cm^3). After removal of THF under vacuum the 31P NMR spectrum showed quantitative conversion: $\delta = 29.7$ ppm, ^1J Rh—P = 144 Hz (broad doublet); a few minutes later 10% of phosphine oxide **2** was formed.

RESULTS AND DISCUSSION

The basicities of TPPTS and PPh_3 are compared by using infrared and ^{31}P NMR techniques. The absorption frequencies of terminal carbonyls in zero-valent mononuclear Group VI coordination compounds of general formula $ML(CO)_5$ depend on the basicity of L.[7] This allows an easy and direct comparison between TPPTS and PPh_3 by measuring the νCO carbonyl stretching frequencies in **7** , $Mo(CO)_5(PPh_3)$, and **6**,

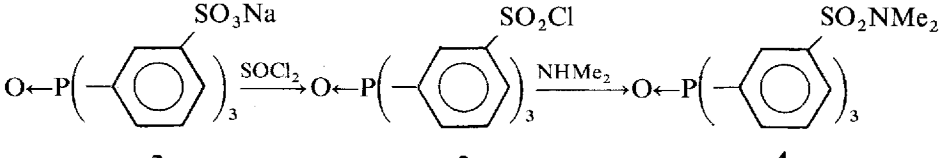
$Mo(CO)_5(TPPTS)$. The values found are very close in agreement owing to similar electronic properties for the two ligands. This conclusion appeared to be in contradiction to the phosphorus chemical shifts,[8] 35 ppm for TPPTS oxide versus 25 ppm for $O \leftarrow PPh_3$. However, in order to remove the solvent influence on the chemical shift, we have transformed the exclusively water-soluble TPPTS into the new products above, soluble in dichloromethane. For instance, the crude hydrated TPPTS oxide was treated successively with $SOCl_2$ and $NHMe_2$ to afford sulfochloride **3** and sulfonamide **4** (Eqn [2]). On the other hand, metathesis of the sodium cation with As^+Ph_4 allows the extraction of compound **5** from the aqueous phase (Eqn [3]).

The chemical shifts for the phosphine oxides **3**, **4** and **5** dissolved in dichloromethane are in the region 23–24 ppm; from these values[6] the pK_a of TPPTS can be estimated to be 3.2 ± 0.2. The pK_a of PPh_3 being 2.85, it can then be assumed that these two phosphines have very close basicities and should behave similarly towards transition metals. This also explains the low selectivities found when exchange of PPh_3 by its sulfonated analogue was attempted and many unsuccessful attempts were made to prepare hydrosoluble complexes by exchanging PPh_3 or CO by TPPTS by using two-phase systems. For instance with $RhCl(PPh_3)_3$ a mixture of mono-, di- and tri-substituted complexes was always obtained and in addition partial oxidation of TPPTS could not be avoided. With $Cr(CO)_6$ a mixture of $Cr(CO)_5(TPPTS)$ and $Cr(CO)_4(TPPTS)_2$ ($\delta\,^{31}P = 76.8$ and 57.7 ppm respectively) is formed even by using a large excess of metal hexacarbonyl. Finally complex **7**, $Mo(CO)_5(TPPTS)$, could be prepared and purified. All these synthetic manipulations are difficult to control and the lack of convenient separation methods renders them useless. However, we now describe a method of replacement of anions or ligands or breaking of dimers which offers good routes for the synthesis of well-defined water-soluble complexes.

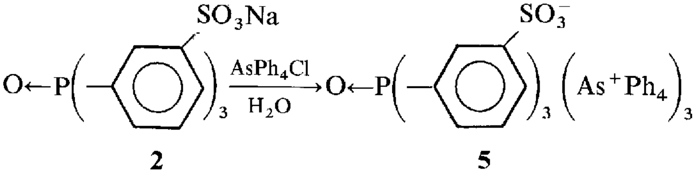
Complex **8**, $PtCl_2(TPPTS)_2$, was readily obtained by adding two equivalents of phosphine to a solution of K_2PtCl_4. The *cis* configuration for **8** was assigned by using ^{31}P NMR spectroscopy ($\delta\,^{31}P = 13.9$ ppm; $J\,^{31}P{-}^{195}Pt = 3735$ Hz). A mixture of **8** and of its *trans* isomer **9** was isolated after reaction of TPPTS on an aqueous solution of Zeise's salt ($\delta\,^{31}P = 21.9$ ppm and $J\,^{31}P{-}^{195}Pt = 2062$ Hz for **9**).

The isomerization of the *trans* to give the thermodynamically stable *cis* complex is complete after 3 h at room temperature. Similar observations were made with $PdCl_2(PhCN)_2$, which affords a mixture of *cis* and *trans*-$PdCl_2(TPPTS)_2$; **10** ($\delta\,^{31}P = 25.3$ and 34.3 ppm). In contrast to the platinum case the palladium compounds do not isomerize in a reasonable period of time.

The coordination chemistry of rhodium(I) has been extensively studied in view of the potential of such water-soluble compounds for two-phase catalysis. The cationic complex **11** is obtained by reaction of silver triflate ($Ag^+CF_3SO_3^-$) on the dimer $[Rh(COD)Cl]_2$ followed by addition of two equivalents of TPPTS (see Scheme 1). The ^1H and ^{13}C NMR spectra are in agreement with the formula and the two equivalent phosphorus atoms show the expected doublet at $\delta = 30.0$ ppm (^1J Rh—P = 154 Hz, to be compared with $\delta = 27.6$ ppm and ^1J Rh—P = 156 Hz for a methanolic solution of $[(NBD)Rh(PPh_3)_2{}^+]$).[9] When the chlorine bridges of the dimer dissolved in THF

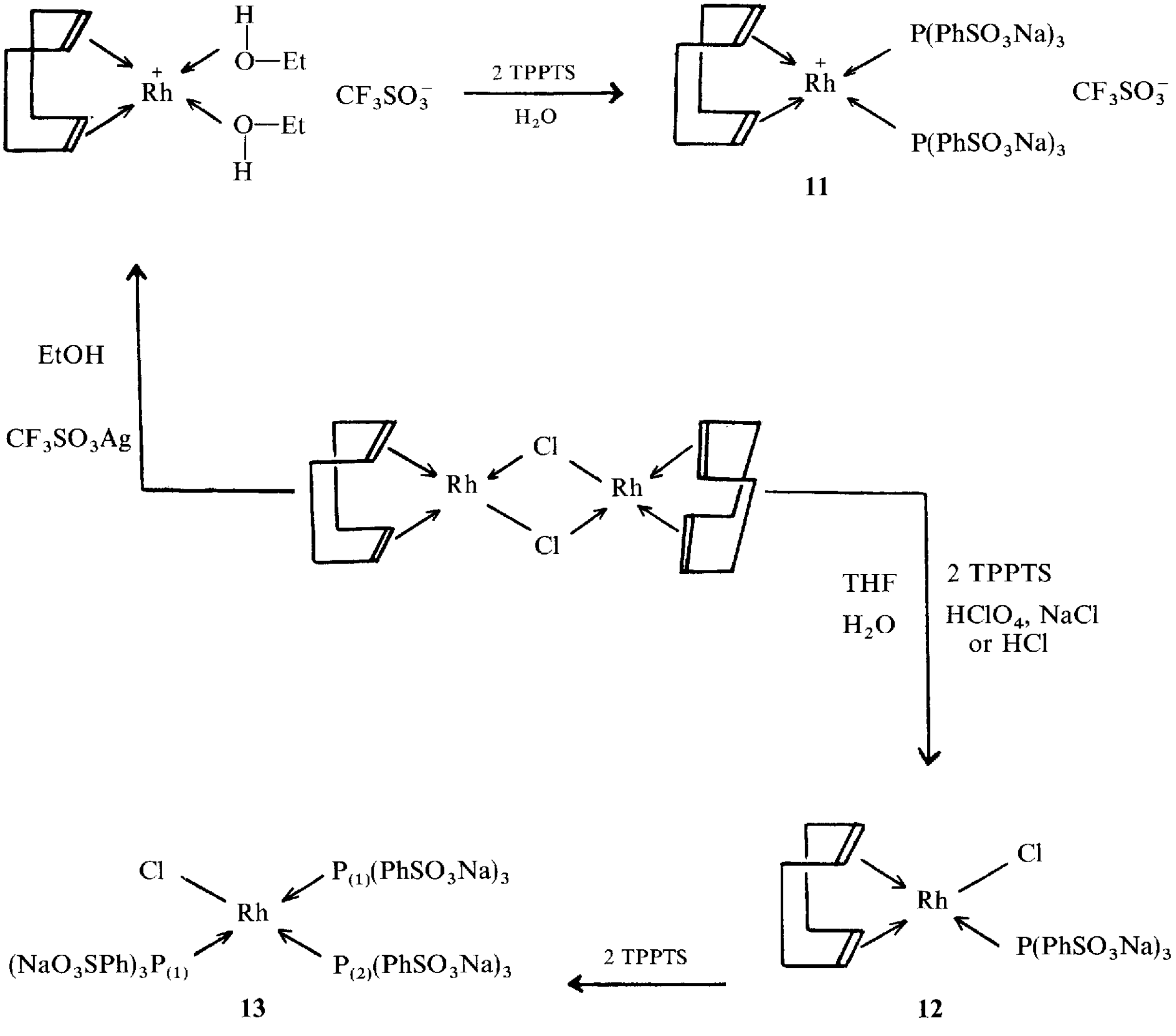


2 **3** **4** [2]



2 **5** [3]

were split by two equivalents of **1** (1 mol dm^{-3} water solution of $HClO_4$ or HCl or NaCl), complex **12** was obtained and characterized by ^1H and ^{31}P NMR. The sharp doublet observed at $\delta = 31.9$ ppm with ^1J Rh—P = 151 Hz correspond to the data reported for (COD) $RhCl(PPh_3)$;[10] $\delta = 31.5$ ppm, ^1J Rh—P = 152 Hz in THF. Finally the dienic ligand in **12** is easily displaced by adding two equivalents of TPPTS. Complex **13** thus obtained shows the expected ^{31}P spectrum, i.e. a pair of doublets for the two equivalent phosphorus atoms ($\delta = 34.4$ ppm, ^1J Rh—P_1 = 144 Hz, ^2J P_1—P_2 = 39 Hz) and a pair of triplets for the atom P_2 *trans* to chlorine ($\delta = 50.8$ ppm, ^1J Rh—P_2 = 193 Hz, ^2J P_1—P_2 = 39 Hz).[11] We must emphasize that the synthesis of compounds **12** and **13** could not be achieved in the absence of NaCl, HCl or $HClO_4$. The ^{31}P NMR spectrum of the new compound **14** formed by addition of two equivalents of TPPTS, dissolved in deaerated water, to a THF solution of $[RhCl(COD)]_2$ shows a doublet at $\delta = 29.7$ ppm with ^1J Rh—P = 144 Hz and W1/2 = 105 Hz. These data are close to the values reported[1] for the dimer $[(COD)Rh(Ph_2PPhSO_3)]_2$; $\delta = 28.4$ ppm, ^1J Rh—P = 146 Hz, for which it was proposed that the monosulfonated phosphine is normally linked to one rhodium atom by the phosphorus lone pair while the sulfonate anion plays the role of bridging ligand by displacement of chloride



SCHEME

anion. This is no longer possible when the ionic strength of the solution is sufficient to prevent the dissociation of the rhodium chlorine bond; moreover at low pH values the sulfonate anions are protonated and cannot coordinate. When a neutral solution containing **14** is observed by ^{31}P NMR we notice that a sharp peak corresponding to TPPTS oxide appears after a few minutes and increases progressively. This shows that the slow decomposition of **14** is accompanied by the oxidation of the metal which in turn oxidizes TPPTS.[4]

Several of the hydrosoluble coordination compounds described have been used to hydrogenate liquid olefins in two-phase systems[12] or water-soluble ethylenic compounds.[13] The platinum derivatives **8** and **9** show a very weak catalytic activity and can be recovered unchanged at the end. However, the palladium and rhodium compounds **10**, **11**, **12** and **13** are efficient and recyclable catalysts for the hydrogenation of various unsaturated carbon–carbon bonds under very mild conditions (room temperature and atmospheric pressure of hydrogen). Spectroscopic studies performed during the catalysis show that rhodium hydrides are formed but also that oxidation of the hydrosoluble phosphine occurs; complementary studies are needed in order to investigate more precisely the mechanisms of these reactions.

CONCLUSIONS

Our results demonstrate that new TPPTS coordination compounds, which are exclusively water-soluble, can be prepared by using low-valent transition-metal precursors. These synthetic manipulations need a careful control of the experimental conditions to avoid for instance the participation of water in a redox process and the competition of sulfonate anions and water with other weak bases. This new family of hydrosoluble transition-metal compounds is of interest both for industrial and fundamental applications. For instance, water-soluble rhodium hydrides can be obtained and further work in this field will be reported later.

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