

Synthesis of polydiphenylphosphite derivatives of [60]fullerene and their reactions with metal complexes

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Abstract

Fullerenol $C_{60}(OH)_{12}$ reacts with chlorodiphenylphosphine to yield a polydiphenylphosphite derivative, $C_{60}(OPPh_2)_{12}$ (**1**), which easily oxidizes and hydrolyzes giving different products, two of them, of composition $C_{60}(OPPh_2)_x(OH)_6 \cdot 6DPA \cdot x(H_2O)$ ($x = 6, 12$) (**3a'**) and $C_{60}[OP(O)Ph_2]_5(OH)_7 \cdot 7DPA$ (**3b**) were fully characterized (DPA = diphenylphosphinic acid). A FAB study of **3b** was performed. Compounds $C_{60}(OPPh_2)_{12-x}(OH)_x$ ($x = 0, 1; x = 6, 3a$) act as polydiphenylphosphite ligands and can be protected from oxidation by complexation. Rh, Mo and Ru complexes containing ligands **1** and or **3a** have been isolated and characterized by analytical and spectroscopic methods. © 1997 Elsevier Science S.A.

Keywords: Fullerenol; Fullerenepolydiphenylphosphite; Rh complexes; Mo complex; Ru complexes

1. Introduction

Fullerenols $C_{60}(OH)_x$ are easily accessible by diverse preparative methods [1–8], but their reactivity has been scarcely studied and only partially esterified fullerenols with organic acids [1,2], and urethane-connected polyether dendritic polymers [9] have been described. We have recently reported on the reactions of fullerenols with functionalized propyltrialkoxysilanes $X(CH_2)_3Si(OR)_3$ ($X = Cl, R = Me; X = NH_2, R = Et$) [10].

The fullerenol used here is a material of composition $C_{60}(OH)_{12}$, prepared as described by Chiang et al. [5] by hydrolysis of polycyclosulfated precursors, which is probably not a single compound. Two from 15 possible isomers have been predicted as the most likely structures for $C_{60}(OH)_{12}$ in a recent theoretical study based on considerations of thermodynamical stabilities and the cyclosulfation and hydrolysis mechanisms [11]. Although the 6,6-addition is the most favoured in the formation of polycyclosulfates, the most favourable sites for the attack of two water molecules are those located on adjacent carbons to the 6,6-junctions occupied by SO_4 groups.

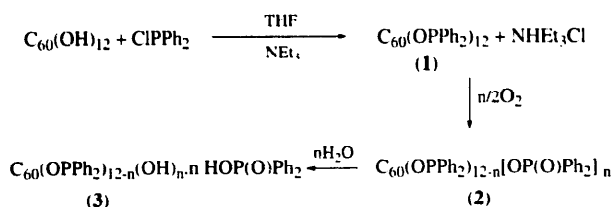
In this paper, we describe our results on the reaction of this fullerenol $C_{60}(OH)_{12}$ with chlorodiphenylphosphine, which leads to the formation of polydiphenylphosphite-[60]fullerene ligands, as well as the characterization of some of their oxidation and hydrolysis products. The reactivity of these new polydiphenylphosphite-[60]fullerene ligands towards a number of metal complexes is also described. Tertiary phosphines and P-chiral phosphinites bearing a fullerene substituent have been previously described and used as ligands for the preparation of Pt(II) and Pd(II) complexes [12,13].

2. Results and discussion

2.1. Preparation and characterization of polydiphenylphosphite-[60]fullerene ligands and their oxidation and hydrolysis products

Fullerenol $C_{60}(OH)_{12}$ [5,10] reacts with chlorodiphenylphosphine in dry and deaerated THF, in the presence of triethylamine, according to Scheme 1, to yield initially a product of composition $C_{60}(OPPh_2)_{12}$ (**1**). This product is sensible to air and oxidizes slowly to give orange-brown solids $C_{60}(OPPh_2)_{12-n}[OP(O)Ph_2]_n$ (**2**). The $C_{60}-OP(O)Ph_2$ bonds are ex-

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Scheme 1.

tremely sensitive to hydrolysis and mixtures of composition $\text{C}_{60}(\text{OPPh}_2)_{12-n}(\text{OH})_n \cdot n\text{DPA} \cdot x\text{H}_2\text{O}$ (**3**) (DPA = diphenylphosphinic acid, $\text{HOP}(\text{O})\text{Ph}_2$) were formed by hydrolysis of the partially oxidized products **2** (Scheme 1), from which colourless crystals of DPA could be isolated. Totally oxidized and only partially hydrolyzed products were also isolated.

Because of its high sensitivity to air, **1** could not be fully characterized and only IR spectra of freshly prepared samples were obtained. The most characteristic IR bands of **1** are those of the 1200–950 and 750–300 cm^{-1} regions, specially the strong bands at 1194, 506 and 487 cm^{-1} and the absence of strong bands at 960, 548 and 524 cm^{-1} is indicative of a low oxidation grade. This product is probably a mixture of isomers derived from the starting mixture of the two or three most favoured isomers of $\text{C}_{60}(\text{OH})_{12}$, with S_6 or D_3 symmetry [11], none of which contain OH groups on adjacent carbons.

Partially oxidized and totally hydrolyzed products $\mathbf{3a} \cdot 6\text{DPA} \cdot x\text{H}_2\text{O}$ [$\mathbf{3a} = \text{C}_{60}(\text{OPPh}_2)_6(\text{OH})_6$] could be isolated and characterized. IR bands in the 1200–950 and 750–300 cm^{-1} regions appear modified with respect to those of **1**, and the characteristic band of free diphenylphosphinic acid at 955 cm^{-1} is of medium intensity. Only phenyl signals are observed in the ^1H NMR(CDCl_3) and solid-state ^{13}C NMR spectra. The absence of observable signals for the carbons of the fullerene cage can be explained considering the great difference in relative abundance of both class of carbons. So, whereas the 60 carbons of the fullerene cage should be distributed in two sp^2 and sp^3 groups of signals corresponding to non-equivalent carbons, the signals of all 144 phenyl carbons should appear in the narrow range 128–133 ppm. Analytical data correspond to hydrated species ($x = 6, 12$) mixed with variable amounts of the ammonium salt NHEt_3Cl . As derived from **1**, ligand **3a** must be also a mixture of isomers.

A totally oxidized and partially hydrolyzed product $\text{C}_{60}[\text{OP}(\text{O})\text{Ph}_2]_{12} \cdot n\text{H}_2\text{O}$ ($= \text{C}_{60}[\text{OP}(\text{O})\text{Ph}_2]_{12-n}(\text{OH})_n \cdot n\text{HOP}(\text{O})\text{Ph}_2$) was isolated and fully characterized when freshly prepared and dried **1** was stored in a Schlenk tube under non-dried air for two weeks. The IR spectrum differs also from those of **1** and **3a** in the regions mentioned above and also shows characteristic bands of diphenylphosphinic acid. Solid-state ^{31}P NMR

spectrum shows only a broad signal centered at 28.56 ppm, whereas the corresponding signal of DPA at 28.64 ppm is a sharp singlet. Analytical data and IR spectrum correspond to a partially hydrolyzed product with seven water molecules, $\text{C}_{60}[\text{OP}(\text{O})\text{Ph}_2]_5 \cdot (\text{OH})_7 \cdot 7\text{DPA}$ (**3b**).

A mass spectroscopic study of **3b** was performed using the fast cesium ion bombardment (LSIMS) technique. The most abundant ions are those related with diphenylphosphinic acid, which appear centered at m/z 219 (100, DPA + H) and 203 (50, $\text{HOPPh}_2 + \text{H}$). The remaining ion clusters correspond to fragments of the starting fullerene derivative of different sizes, the lightest of them being those related with the coranulene carbon core (C_{20}). The existence of numerous ion clusters clearly separated by multiples of 16 ± 2 (O, OH, OH_2) and 217 ($\text{OP}(\text{O})\text{Ph}_2$) can be noted, providing evidence of oxygens and $\text{OP}(\text{O})\text{Ph}_2$ groups attached to the fullerene cage in the starting derivative and its fragmentation ions. Three series of consecutive weight loss or separation of 217 mass units from ions at m/z 1905 (A^+), 1415 (B^+), and 1168 (C^+) are clearly observed. The $\text{OP}(\text{O})\text{Ph}_2$ groups seem to be attached also in fragmentation ions as light as that appears at m/z 497, separated by 217 mass units from the relatively intense peak at m/z 279 ($\text{C}_{19}(\text{OH})_3$). There are numerous other sequences of peaks separated by 16 ± 2 mass units. The remarkable low intensity of the ion peak at 720 (6/33, 0.18), corresponding to C_{60} and the very low intensity of the peaks above m/z 1200 mass units can also be noted. This fact indicates the fast cleavage of the C– $\text{OP}(\text{O})\text{Ph}_2$ bonds of the starting fullerene derivative and the easy elimination of free diphenylphosphinic acid resulting from partial hydrolysis of this product. However, it is observable that a peak corresponding to the fragment with the highest mass at m/z 1905 (A^+) and a relative intensity of 0.09 (100/33²), to which the formula $\text{C}_{60}(\text{OH})_4\text{O}_2[\text{OP}(\text{O})\text{Ph}_2]_5$ can be assigned, is in a good accordance with the analytical data of this partially hydrolyzed starting compound $\text{C}_{60}(\text{OH})_7[\text{OP}(\text{O})\text{Ph}_2]_5 \cdot 7\text{DPA}$ (**3b**). There is also an ion peak at m/z 1269, to which can be assigned the formula $\text{C}_{60}(\text{OH})_2\text{O}_5[\text{OP}(\text{O})\text{Ph}_2]_2$, with seven oxygens bonded to the fullerene cage. Fig. 1 shows the principal relations between ion peaks with m/z higher than 720 (C_{60}).

In spite of the high sensitivity of the C– $\text{OP}(\text{O})\text{Ph}_2$ bonds to hydrolysis, these bonds seem to be stronger than those of C–OOCR bonds resulting from partial esterification of a similar fullereneol [2] against Cs^+ bombardment. In general, **3b** differs considerably from fullereneols in the bombardment with Cs^+ , giving rise to multiple fragments of variable size containing O, OH or $\text{OP}(\text{O})\text{Ph}_2$ attached groups, most of them have a number of carbons lower than 60. Some of these, with relatively high m/z values, could have been formally considered as carbon deficient [60]fullerene cages with

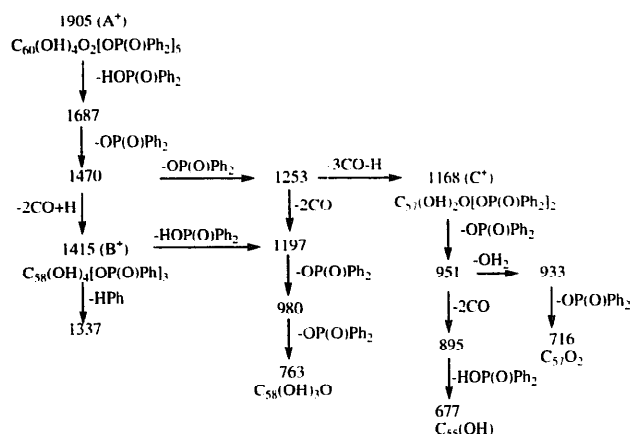


Fig. 1. Principal correlations between peaks with m/z higher than 600 amu (C_{50}) in the positive ion FAB (LSIMS) mass spectrum of $C_{60}(OH)_7[OP(O)Ph_2]_5 \cdot 7HOP(O)Ph_2$.

a number of O (and/or OH) and $OP(O)Ph_2$ attached groups, which could be derived by abstraction of several CO groups from the $C_{60}-O$ bonds of the starting compound. Peaks at m/z 1415 (B^+), to which can be assigned the formula $C_{58}(OH)_4[OP(O)Ph_2]_3$, and at 1168 (C^+ , $C_{57}(OH)_2O$) [$OP(O)Ph_2]_2$] and the remaining peaks of the series derived from them, mentioned above, are good examples (Fig. 1).

From all our data of this totally oxidized and partially hydrolyzed product **3b**, we can conclude that the samples used for the different studies could be hydrolyzed in a different grade during manipulation. So IR spectrum and analytical data seem to correspond to samples with a considerable degree of hydrolysis, whereas the presence of free diphenylphosphinic acid is not clearly observed in the solid-state ^{31}P NMR spectrum. However, the DTA curve shows an endothermic peak of low intensity at $170^\circ C$ without weight loss in the corresponding TG curve, which could be due to melting of diphenylphosphinic acid (mp $193-195^\circ C$). On the other hand, the MS study leads to the conclusion that at least five $OP(O)Ph_2$ groups remain attached in the sample used for this experiment.

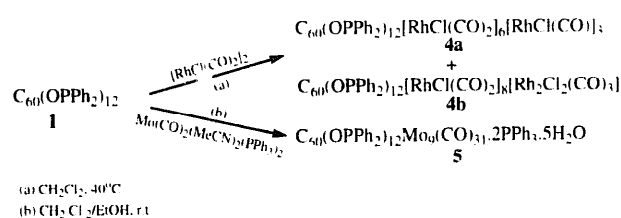
Since the fullerene-polydiphenylphosphite ligands **1** and **3** ($n < 12$) are easily oxidizable and **1** could be not fully characterized, a series of metal complexes of both fullerene ligands have been prepared, in which an effective protection of the $OPPh_2$ groups from oxidation was achieved. Diphenylphosphinic acid is difficult to be separated from ligand **3**, and the complexes obtained from the mixtures formed in the hydrolysis of **2** (Scheme 1) are impurified frequently with free diphenylphosphinic acid.

2.2. Reactions of ligand **1** with metal complexes

Freshly prepared ligand **1** reacts with $[RhCl(CO)_2]_2$ under mild conditions to yield a brown product of

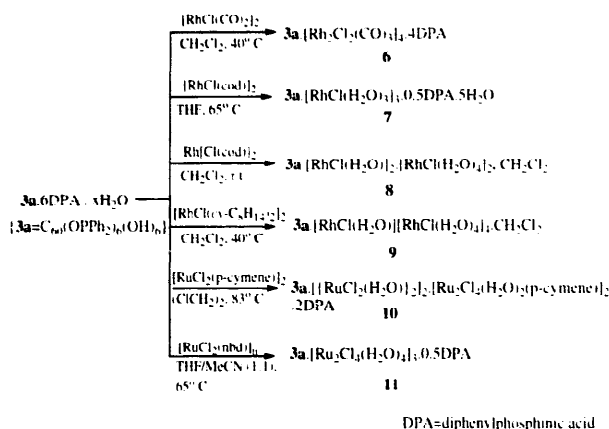
composition $C_{60}(OPPh_2)_{12}[RhCl(CO)_2]_6[RhCl(CO)]_3$ (**4a**), with an intense $\nu(CO)$ IR band at 2060 cm^{-1} , as the principal fraction, in which all $OPPh_2$ groups attached to fullerene would be coordinated to rhodium (Scheme 2). A second carbonyl band at 1990 cm^{-1} of lower intensity is also present in the IR spectrum of this fraction. The band at 2060 cm^{-1} can be due to the *trans*- $[PRhCl(CO)_2]$ majority coordinated species and the second band at 1990 cm^{-1} , to monocarbonyl species $[P_2RhCl(CO)]$, since complexes *trans*- $[RhCl(CO)(PR_3)_2]$ with $\nu(CO)$ towards 1980 cm^{-1} are preferentially formed in the reaction of $[RhCl(CO)_2]_2$ with tertiary phosphines for a molar ratio $P/Rh_2 > 1:1$ [14]. A composition $C_{60}(OPPh_2)_{12}[RhCl(CO)_2]_9$ is also analytically possible for the principal fraction isolated in this reaction. Another lower intensity carbonyl band at 2009 cm^{-1} appears in the IR spectrum of the second fraction isolated (**4b**), and the principal band at 1260 cm^{-1} is broader at both sides of this band. In this case, the majority-coordinated species *trans*- $[PRhCl(CO)_2]$ could be accompanied by the binuclear tricarbonyl species $[PRh(CO)(\mu-Cl)_2Rh(CO)_2]$ [14]. All IR bands of the ligand **1** in the $1200-400\text{ cm}^{-1}$ region appear modified, but the characteristic bands of free diphenylphosphinic acid in this region are absent. Only phenyl signals are observed in the 1H NMR spectrum.

Ligand **1** reacts also with $Mo(CO)_2(MeCN)_2(PPh_3)_2$ under mild conditions to give an orange-brown product of composition $C_{60}(OPPh_2)_{12}Mo_9(CO)_{31} \cdot 2PPh_3 \cdot 5H_2O$ (**5**) as the principal fraction. A very intense and two weak carbonyl IR bands at 1885 , 1938 and 2010 cm^{-1} , respectively, are observed, which could be due to *trans*-tricarbonyl or *trans*-tetracarbonyl octahedral species. Bands at 1993 vw , 1919 w and 1890 vs cm^{-1} and at 1952 vw and 1903 s cm^{-1} were reported for *trans*- $Mo(CO)_3[OPPh_3]_3$ and *trans*- $Mo(CO)_4(PPh_3)_2$, respectively [15]. Modified infrared bands of ligand **1** are also present. Only phenyl and water signals are observed in the 1H NMR spectrum of this product, which confirms the absence of MeCN ligands. IR absorptions at 3420 vs and at 1630 m cm^{-1} also indicate the presence of water. On this basis, a possible formula for product **5** is $C_{60}(OPPh_2)_{12}[Mo(CO)_4]_4[Mo(CO)_4(PPh_3)_2]_2 \cdot 3Mo \cdot 7CO \cdot 5H_2O$, with only $[Mo(CO)_4]$ species coordinated to two *trans*-P of $OPPh_2$ or PPh_3 , in which three



(a) CH_2Cl_2 , $40^\circ C$
(b) $CH_2Cl_2/EtOH$, r.t.

Scheme 2.



Scheme 3.

additional Mo atoms would be coordinated to residual OPPh_2 and CO ligands and to η^2 -fullerene double bonds. Water molecules would be not coordinated to Mo.

The low yield referred to the ligand (37–38%) of these reactions can be noted.

2.3. Reactions of ligand **3a** ($n = 6$) with metal complexes

Ligand **3a**, $\text{C}_{60}(\text{OPPh}_2)_6(\text{OH})_6$, mixed with free DPA, as a hydrolysis product of the partially oxidized ligand $\text{C}_{60}(\text{OPPh}_2)_6[\text{OP}(\text{O})\text{Ph}_2]_6$, reacts with different dimeric or polymeric complexes of rhodium and ruthenium to yield the products represented in Scheme 3, in which the bridging $\mu\text{-Cl}$ bonds can be broken, and diene or arene ligands are displaced. So ligand **3a** reacts with $[\text{RhCl}(\text{CO})_2]_2$ under mild conditions to yield a product of composition $\text{C}_{60}(\text{OPPh}_2)_6(\text{OH})_6[\text{Rh}_2\text{Cl}_2(\text{CO})_3]_4$ (**6**), with two strong IR carbonyl bands at 2080 and (2030 sh) 2008 cm^{-1} , in which $[\text{PRh}(\text{CO})(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$ seems to be the coordinated rhodium species. This species is preferentially formed when the reaction is performed in a molar ratio $\text{P}/\text{Rh}_2 < 1/1$, and shows carbonyl IR bands at 2080, 2030 and 2009 cm^{-1} in the complex with PPh_3 [14]. The lower content in coordinating groups OPPh_2 in ligand **3a** can explain the different composition of the reaction products **4** and **6** of $[\text{RhCl}(\text{CO})_2]_2$ with ligands **1** and **3**. A longer reaction time can also favour the formation of the dicarbonylic *trans*- $[\text{PRhCl}(\text{CO})_2]$ species in product **4**.

Reactions of ligand **3a** with dimeric rhodium complexes $[\text{RhCl}(\text{cod})]_2$ and $[\text{RhCl}(\text{C}_8\text{H}_{14})]_2$ lead to formation of products **7**, **8** and **9**, respectively, in which cod and cyclooctene ligands are totally displaced, but **7** and **8** seem to be contaminated with some starting rhodium complex. Additional bonding to water molecules complete the coordination of rhodium(I), which can reach

the six-coordination. It is highly probable the coordination of all OPPh_2 groups to Rh. In this case, the six OPPh_2 groups should be coordinated to six bridging $\mu\text{-}[\text{RhCl}(\text{H}_2\text{O})_n]$ units in complex **7**, four bridging $\mu\text{-}[\text{RhCl}(\text{H}_2\text{O})_n]$ and two terminal $[\text{RhCl}(\text{H}_2\text{O})_4]$ units in complex **8** and to two bridging $\mu\text{-}[\text{RhCl}(\text{H}_2\text{O})_n]$ and four terminal $[\text{RhCl}(\text{H}_2\text{O})_4]$ units in complex **9**. The different solvents used in both preparations from $[\text{RhCl}(\text{cod})]_2$ seem to determine the different Rh content in the product obtained, which in the reaction in CH_2Cl_2 , could be isolated free of diphenylphosphinic acid. Compound **9**, obtained in CH_2Cl_2 from $[\text{RhCl}(\text{C}_8\text{H}_{14})]_2$, shows a higher Rh content than **7** and **8** and was isolated also free of DPA. The reaction with the dimeric ruthenium complex $[\text{RuCl}_2(p\text{-cymene})]_2$ in refluxing 1,2-dichloroethane is similar to those earlier described: *p*-cymene ligand is partially displaced by water molecules and bridging ($\mu\text{-Cl}$) ligands complete a five or six-coordination of ruthenium in product (**10**), in which two binuclear bridging $[\text{Cl}(\text{H}_2\text{O})\text{Ru}(\mu\text{-Cl})_2\text{Ru}(\text{H}_2\text{O})\text{Cl}]$ and two binuclear terminal $[\text{Cl}(\text{H}_2\text{O})_2\text{Ru}(\mu\text{-Cl})_2\text{RuCl}(p\text{-cymene})]$ groups seem to be coordinated to the six OPPh_2 groups.

The reaction of ligand **3a** with the polymeric complex $[\text{RuCl}_2(\text{nbnd})]_n$ requires the presence of MeCN to break partially the bridging $\mu\text{-Cl}$ bonds and a product **11** is obtained, in which norbornadiene is displaced, water molecules and bridging $\mu\text{-Cl}$ ligands being necessary to complete the six-coordination of ruthenium. So three binuclear bridging $[\text{Cl}(\text{H}_2\text{O})_2\text{Ru}(\mu\text{-Cl})_2\text{Ru}(\text{H}_2\text{O})_2\text{Cl}]$ groups could be attached to the six OPPh_2 groups. A minority possible complex $[\text{Ru}(\text{MeCN})_4(\text{nbnd})\text{Cl}]_2$ seems to be mixed with this product, on the basis of the spectroscopic and analytical data.

The yields referred to ligand **3a** are generally high (> 71%) in all these reactions. The presence of 12 OPPh_2 substituents in ligand **1**, distributed on the fullerene cage accordingly with the symmetry (S_6 or D_3) of the most favoured isomers of the starting fullerene [11], renders, probably more difficult with respect to **3a**, the reactions with the more hindered coordinating groups of this ligand.

It can be noted that the presence of DPA in some of these products and sometimes crystals of this acid were isolated from washing solvents or residual solutions after precipitation can be noted. Water ligands of the different complexes and diphenylphosphinic acid come from the partially oxidized and totally hydrolyzed ligand **3a**, which shows a high tendency to hydration. The use of THF instead of CH_2Cl_2 or $(\text{ClCH}_2)_2$ seems to lead to formation of more hydrated species. All these products were characterized by IR and ^1H NMR spectroscopies and elemental analysis.

From this study, we can conclude that the reactions of ligands **1** and **3a** with metal complexes lead to

formation of new products containing metallic species coordinated to the diphenylphosphite groups attached to fullerene. Although these products are mixtures of isomers, their composition is reproducible for reactions performed in the same conditions. Studies on catalytic properties of some of these products are in progress.

3. Experimental

C_{60} was separated from refined mixed fullerene (MER, about 80% C_{60}) by flash chromatography as previously described [16]. All reactions were carried out under an atmosphere of dry N_2 free of oxygen. Solvents were purified and dried by standard methods. Fullerenol $C_{60}(OH)_{12}$ was prepared as earlier described [5,10], by hydrolysis of a polycyclosulfated fullerene obtained by reaction of C_{60} with fuming sulfuric acid (33% SO_3). Metal complexes $[RhCl(CO_2)]_2$ [17], $[RhCl(cod)]_2$ [18], $[RhCl(C_8H_{14})]_2$ [19], $[RuCl_2(p\text{-cymene})]_2$ [20] and $[RuCl_2(nbd)]_n$ [21] were prepared by literature methods. Elemental analyses were performed at the ICMM (CSIC), using plasma (Ru, Mo) or atomic absorption (Rh) techniques for analyses of metals. IR spectra were recorded with a Pye Unicam SP-3-300 spectrophotometer or a Nicolet 20 SXC FT-IR spectrophotometers, using KBr disks. NMR spectra in solution were recorded on a Varian Gemini 200. High-resolution ^{13}C MAS or CP/MAS NMR spectra of powdered samples, in some cases also with a Toss sequence, in order to eliminate the spinning side bands, were recorded at 100.63 MHz, 6 μs 90° pulse width, 2 ms contact time and 5–10 recycle delay, using a Bruker MSL 400 spectrometer equipped with an FT unit. The spinning frequency at the magic angle (54°44') was 4 kHz. Solid-state ^{31}P NMR spectra of some samples were recorded on the same spectrometer at 161.97 MHz with spinning frequencies at the magic angle of 3 and 4 kHz. Differential thermal analysis (DTA) and thermogravimetric (TG) curves were obtained using a Stanton STA 781 simultaneous thermal analyzer. Samples were heated in an O_2 flow (50 ml min^{-1}) at 10°C min^{-1} heating rate, in the temperature range 25–1000°C. Mass spectra were performed at the UAM (SIdI), using the fast cesium ion bombardment (liquid secondary ion mass spectrometry, LSIMS) technique.

Except in the case of ligands washed with water, all samples contain a variable amount of NH_4Cl .

3.1. Preparation of fullerene-polydiphenylphosphite ligand (1) and characterization of their oxidation and hydrolysis derivatives (3a and 3b)

To a suspension of $C_{60}(OH)_{12}$ (50 mg, 0.054 mmol) in dried THF, freshly distilled over sodium, containing 65.5 mg (0.645 mmol) of triethylamine, chlorodiphe-

nilphosphine (142.86 mg, 0.645 mmol) was added dropwise, in an ice bath, under stirring, and after this addition, the reaction mixture was stirred overnight at room temperature. The ammonium salt formed was filtered off and the orange-brown solution was evaporated under vacuum to yield an orange-brown solid **1** (127 mg, 75%), of composition $C_{60}(OPPh_2)_{12}$, which oxidizes slowly in air to give orange-brown solids of composition $C_{60}(OPPh_2)_{12-n}[OP(O)Ph_2]_n$ (**2**). The $C_{60}-OP(O)Ph_2$ bonds of **2** are easily hydrolyzed and mixtures of composition $C_{60}(OPPh_2)_{12-n}(OH)_n \cdot nHOP(O)Ph_2 \cdot xH_2O$ (**3**) are formed by hydrolysis of the partially oxidized product, from which colourless crystals of diphenylphosphinic acid were isolated and identified. Although impurified with diphenylphosphinic acid, the mixtures **3** ($n < 12$) can be used as fullerenic ligands containing 12- n $OPPh_2$ active groups for formation of complexes. The characterization of ligand **1** could be not completely performed, and that of pure $C_{60}(OPPh_2)_6(OH)_6$ (**3a**) was impossible. However, two samples containing this ligand, $3a \cdot 6DPA \cdot xH_2O$ ($x = 6, 12$), were isolated and characterized. A totally oxidized and partially hydrolyzed product $C_{60}[OP(O)Ph_2]_5(OH)_7 \cdot 7HOP(O)Ph_2$ (**3b**) was also fully characterized. It can be noted that the ammonium salt NH_4Cl is soluble enough in THF and CH_2Cl_2 , not to be totally eliminated by filtration, and samples free of nitrogen were obtained only by washing with water of solutions of the products in CH_2Cl_2 .

3.1.1. $C_{60}[OPPh_2]_{12}$, freshly obtained (**1**)

IR: 3059 w, 1592 w, 1483 s, 1436 s, 1194 vs, 1150 sh, 1129 m, 1114 s, 1095 sh, 1068 m, 1041 w, 1030 w, 996 w, 950 w br, 747 m, 735 m, 720 s, 694 vs, 552 mw, 529 sh, 506 s, 487 s, 455 w, 392 w, 365 w, 299 vw.

3.1.2. $C_{60}(OPPh_2)_6(OH)_6 \cdot 6DPA \cdot 6H_2O$ (**3a'**) = $3a \cdot 6DPA \cdot 6H_2O$

IR: 3426 s, br, 3059 m, 15922 m, 1483 m, 1436 s, 1194 vs, 1129 s, 114 s, 1095 m, 1068 m, 1041 w, 1030 w, 996 m, 950 m, 747 m, 720 s, 649 vs, 552 s, 529 m, 506 s, 487 s, 414 w, 399 w, 365 vw, 299 w. 1H NMR ($CDCl_3$, 200 MHz): d 7.90–7.60 (m, 48H, Ph), 7.55–7.20 (m, 72H, Ph), 6.16 (s br, 18 H: OH + H_2O), 3.02 (q, $J = 7.2$ Hz, 18H, CH_2 of NH_4Cl), 1.22 (t, $J = 7.2$ Hz, 27H, Me of NH_4Cl). ^{13}C NMR solid-state (CP/MAS-TOSS): d 135.50–126.92 (m, nPh), 47.95 (s, CH_2 of NH_4Cl), 9.96 (s, Me of NH_4Cl). Anal. Found: C, 69.33; H, 4.92; N, 1.08. Calc. for $3a' \cdot 3NH_4Cl$: $C_{222}H_{192}Cl_3N_3O_{30}P_{12}$: C, 69.08 H, 5.01 N, 1.09.

A more hydrated ligand, $3a \cdot 6DPA \cdot 12H_2O \cdot 2NH_4Cl$, with similar IR, was also isolated and characterized. Anal. Found: C, 67.46; H, 4.80; N, 0.68. Calc for $C_{216}H_{188}Cl_2N_2O_{36}P_{12}$: C, 67.73; H, 4.95; N 0.73.

3.1.3. $C_{60}[OP(O)Ph_2]_5(OH)_7 \cdot 7DPA$ (**3b**)

This product was formed from **1**, dissolved in CH_2Cl_2 , washed with water to eliminate NH_4Cl , dried, precipitated with Et_2O , and stored in a Schlenk tube under non-dried air. Anal.: Found C, 70.55; H, 4.02; P, 10.89. Calc. for $C_{204}H_{134}O_{31}P_{12}$: C, 70.96; H, 3.91; P, 10.76%. IR: 3420 s, br, 3059 w, 1582 w, 1480 w, 1436 s, 1186 sh, 1172 s, 1152 w, 1126 s, 1105 sh, 1090 w, 1066 w, 995 w, 960 ms, 742 m, 720 s, 690 vs, 548 s, 522 s, 495 sh, 430 m, 330 w. ^{31}P NMR solid-state (MAS) spectrum shows an asymmetrical system of broad rotational bands. The CP/MAS spectrum also shows an asymmetrical system of more sharp rotational bands, which changes with the rotational speed of rotor, the gravity center of the system appearing at 28.56 ppm. MS (LSIMS, positive ion, m-nba + tfa matrix, mass of the highest ion peak in the fragmentation groups) m/z (relative high of peak in brackets): 77 (25), 141 (8), 203 (50), 219 (100), 241 (10), 261 (11), 263 (5), 279 (42), 307 (12), 403 (5), 412 (13), 437 (9), 497 (5), 523 (6). m/z (relative high of peak $\times 33$ in brackets): 538 (6), 543 (13), 545 (65), 551 (11), 572 (17), 583 (32), 621 (17), 637 (41), 655 (36), 677 (14), 693 (12), 697 (15), 709 (11), 715 (54), 721 (10), 763 (100), 895 (6), 933 (8), 951 (32), 980 (58), 1168 (14). m/z (relative high of peak $\times 33^2$ in brackets): 1213 (11), 1253 (11), 1269 (7), 1324 (2), 1337 (20), 1370 (3), 1415 (23), 1447 (2), 1470 (56), 1687 (28), 1806 (3), 1826 (5), 1905 (100). MS (LSIMS, positive ion, m-nba matrix, mass of the highest ion peak in the fragmentation groups) m/z (relative high of peak in brackets): 77 (14), 141 (11), 201 (49), 219 (100), 261 (16), 279 (37), 386 (6), 403 (15), 419 (17), 437 (8), 479 (8), 523 (5). m/z (relative high $\times 33$ in brackets): 538 (12), 545 (24), 551 (4), 571 (33), 583 (100), 587 (22), 605 (49), 621 (15), 637 (34), 655 (47), 665 (14), 679 (10), 681 (7), 679 (28), 708 (6), 715 (90), 72 (12), 933 (19).

3.1.4. Thermal analysis

The DTA curve shows peaks at 170°C (endothermic, without weight loss), 365°C (exothermic, with a large weight loss due principally to combustion of all phenyl groups), 440°C (exothermic, with a small weight loss, resulting from oxidation of P, accompanied with a gradual sublimation of P_2O_5 and C_{60}) and 595°C (exothermic, with a small weight loss due to combustion of residual C_{60}). TG curve shows between 250 and 404°C a weight loss of 67.3%; between 404 and 555°C, 16.8% and between 555 and 1000°C, 7.7%. A weight loss clearly due to elimination of water molecules is not observed. A solid residue (8.2%) was identified as P_2O_5 (phenyl groups in **3b** are 53.6%, C_{60} is 20.9% and P, 10.8%; 8.2% of P_2O_5 implies only 33% of the total P in the residue). The endothermic peak at 170°C in the DTA curve can be due to melting of DPA (mp 193–195°C) contained in **3b**.

3.2. Reactions of $C_{60}(OPPh_2)_2$ (**1**) with metal complexes

3.2.1. Reaction with $[RhCl(CO)_2]_2$

30 mg (0.0096 mmol) of freshly prepared **1** and 19 mg (0.05 mmol) of $[RhCl(CO)_2]_2$ were stirred at 40°C in CH_2Cl_2 (25 ml). After 24 h, the brown solid formed (**4a**) was filtered off and washed several times with Et_2O (7.8 mg). A second brown solid (**4b**) was isolated from the brownish-yellow filtrate by precipitation with Et_2O (10.3 mg). Total yield 18.1 mg (32% with respect to Rh; 37% with respect to ligand).

3.2.2. $C_{60}(OPPh_2)_{12}[RhCl(CO)_2]_6[RhCl(CO)]_3$ (**4a**) or $C_{60}(OPPh_2)_{12}[RhCl(CO)_2]_9$ (**4a'**)

Anal. Found: C, 54.62; H, 3.31; N, 0.53; Rh, 17.22. Calc. for **4a**. $2NH_4Cl$, $C_{231}H_{152}Cl_{11}N_2O_{27}Rh_9P_{12}$: C, 54.66; H, 3.02; N, 0.55; Rh, 18.24. Calc. for **4a'**. $2NH_4Cl$, $C_{234}H_{152}Cl_{11}N_2O_{30}Rh_9P_{12}$: C, 54.47; H, 2.97; N, 0.54; Rh, 17.95. IR (cm^{-1}): 3065 w, 2060 vvs $\nu(CO)$, 1990 m $\nu(CO)$, 1585 w, 1480 w, 1440 s, 1180 ms, 1150 ms, 1121 s, 1099 vs, 1062 ms, 1028 ms, 996 mw, 950 sh, 748 m, 724 m, 710 m, 692 vvs, 615 w, 580 sh $\delta(RhCO)$, 560 vvs $\delta(RhCO)$, 535 sh, 530 sh, 515 sh. 1H NMR ($CDCl_3$, 200 MHz): δ 7.85–7.65 (m br, 2 nH, Ph), 7.55–7.35 (m br, 1 nH, Ph), 7.30 (m, 2 nH, Ph) (n = number of phenyl groups).

3.2.3. $C_{60}(OPPh_2)_{12}[RhCl(CO)_2]_8[Rh_2Cl_2(CO)_3]$ (**4b**)

Anal. Found: C, 53.35; H, 2.85; N, 0.32; Rh, 18.72. Calc. for **4b**. NH_4Cl , $C_{223}H_{120}Cl_{11}NO_{31}P_{12}Rh_{10}$: C, 53.01; H, 2.64; N, 0.27; Rh, 19.83. IR (cm^{-1}): 3065 w, 2060 vvs $\nu(CO)$, 2009 m $\nu(CO)$, 1990 sh $\nu(CO)$, 1630 (m br, 1585 w, 1440 s, 1180 m, 1160 m, 1121 ms, 1099 vvs, 1062 m, 1028 s, 996 s, 950 sh, 745 m, 705 ms, 692 vvs, 612 w, 585 m $\delta(RhCO)$, 560 vvs $\delta(RhCO)$, 527 ms, 510 ms.

3.3. Reaction with $[Mo(CO)_2(MeCN)_2(PPh_3)_2]$

3.3.1. $C_{60}(OPPh_2)_{12}Mo_9(CO)_{31} \cdot 2PPh_3 \cdot 5H_2O$ (**5**)

To a solution of 44 mg (0.058 mmol) of $[Mo(CO)_2(MeCN)_2(PPh_3)_2]$ in a mixture of CH_2Cl_2 (30 ml) and $EtOH$ (5 ml) 30 mg (0.0096 mmol) of **1** were added. After 24 h under stirring at room temperature, and concentration of the reddish-brown reaction mixture, diethyl ether was added to give an orange-brown precipitate, which was filtered off and washed three times with Et_2O (21.5 mg, 57% with respect to Mo, 38% with respect to ligand). Anal. Found: C, 58.70; H, 3.51; Mo, 13.53; N, 0.60. Calc. for **5**. $2 \cdot 5NH_4Cl$, $C_{286}H_{200}Cl_{2.5}Mo_9N_{2.5}O_{48}P_{14}$: C, 58.97 H, 3.46; Mo, 14.82 N, 0.60. IR (cm^{-1}): 3420 s br, 3060 w, 2010 vw $\nu(CO)$, 1935 w $\nu(CO)$, 1885 vvs $\nu(CO)$, 1630 m br, 1585 w, 1470 m, 1435 s, 1185 ms, 1155 ms, 1125 sh, 1110 s, 1090 s, 1070 ms, 995 m, 965 sh, 755 ms,

740 ms, 725 s, 690 vs, 625 w $\delta(\text{MoCO})$, 616 w $\delta(\text{MoCO})$ 570 s, 545 vs, 520 vs, 400 m $\nu(\text{MoC})$. $^1\text{H NMR}$ (CDCl_3 , 200 MHz): δ 7.61–7.49 (m, 3 *n*H, Ph), 7.45–7.31 (m, 2 *n*H, Ph), 1.74 (s br, H_2O) (signals of methylene and methyl groups of NHEt_3Cl at 3.02 and 1.26 ppm were also observed).

3.4. Reactions of $\text{C}_{60}(\text{OPPh}_2)_6(\text{OH})_6$ (**3a**) with metal complexes

For all these reactions with metal complexes the products $\mathbf{3a} \cdot 6\text{DPA} \cdot x\text{H}_2\text{O}$ (**3a'**, $x = 6$ or 12) were used [$\mathbf{3a} = \text{C}_{60}(\text{OPPh}_2)_6(\text{OH})_6$].

3.5. Reaction with $[\text{RhCl}(\text{CO})_2]_2$

3.5.1. $\text{C}_{60}(\text{OPPh}_2)_6(\text{OH})_6$ [$\text{Rh}_2\text{Cl}_2(\text{CO})_4$]₄ (**6**)

30 mg of **3a'** ($x = 6$) $\cdot 3\text{NHET}_3\text{Cl}$ (0.0078 mmol) and $[\text{RhCl}(\text{CO})_2]_2$ (19.1 mg, 0.049 mmol, 0.098 meq.) were refluxed in deaerated CH_2Cl_2 (20 ml) under N_2 for 6 h. A brown minority product was filtered off and the solution was evaporated. The brownish residue was washed several times with Et_2O to yield a brown solid (33 mg, 58% with respect to Rh; 91% with respect to ligand). By evaporation of the yellow ethereal solution resulting from washing, some colourless crystals, identified as DPA, were isolated. Anal. Found: C, 53.05; H, 3.60; N, 0.55; Rh, 17.23. Calc. for **6**. $4\text{DPA} \cdot 2\text{NHET}_3\text{Cl} \cdot 2\text{H}_2\text{O}$, $\text{C}_{204}\text{H}_{146}\text{Cl}_{10}\text{N}_2\text{O}_{34}\text{P}_{10}\text{Rh}_8$: C, 52.62; H, 3.16; N, 0.60 Rh, 18.03. IR (cm^{-1}): 3400 w br, 3060 w, 2080 vs $\nu(\text{CO})$, 2008 vs $\nu(\text{CO})$, 1592 w, 1485 w, 1439 s, 1397 vw, 1313 w, 1191 s, 1183 s, 1156 m, 1133 s, 1118 sh, 1072 m, 1053 m, 1030 sh, 990 sh, 965 vs, 755 m, 728 vs, 694 vs, 617 w, 552 vs [includes $d(\text{RhCO})$], 521 s, 490 sh, 437 m, 330 w, 295 w. $^1\text{H NMR}$ (CDCl_3 , 200 MHz) δ 7.71–7.62, m, 2 *n*H, Ph), 7.42–7.33 (m, *n*H, Ph), 7.32–7.21 (m, 2 *n*H, Ph).

3.6. Reactions with $[\text{RhCl}(\text{cod})]_2$

3.6.1. $\text{C}_{60}(\text{OPPh}_2)_6(\text{OH})_6$ [$\mu\text{-RhCl}(\text{H}_2\text{O})_3$]₃ (**7**)

31 mg of **3a'** ($x = 12$) $\cdot 2\text{NHET}_3\text{Cl}$ (0.008 mmol) and $[\text{RhCl}(\text{cod})]_2$ (15 mg, 0.03 mmol, 0.06 meq. Rh), were refluxed in dry and deaerated THF (20 ml) for 24 h under N_2 . After evaporation of solvent, the reddish-brown residue was washed with Et_2O several times and dried under vacuum (22 mg, 42% referred to Rh, 86% referred to ligand). By evaporation of the yellow ethereal washing solution, a yellow residue (25 mg) was obtained, which was identified as a mixture of the starting complex and DPA (IR and $^1\text{H NMR}$). Anal. Found: C, 57.62; H, 4.24; N, 0.48; Rh, 10.38. Calc. for **7**. $0.25[\text{RhCl}(\text{cod})]_2 \cdot 0.5 \text{DPA} \cdot \text{NHET}_3\text{Cl} \cdot 5\text{H}_2\text{O}$, $\text{C}_{148}\text{H}_{116.5}\text{Cl}_{4.5}\text{N}_{0.27}\text{P}_{6.5}\text{Rh}_{3.5}$: 57.96, H, 3.99; N, 0.46; Rh, 11.74. IR (cm^{-1}): 3400 m br, 3060 w, 2944 vw, 2875 vw, 1620 m, 1592 w, 1485 w, 1439 s, 1179 ms,

1156 m, 1130 vs, 1100 sh, 1068 m, 1037 m, 1018 w, 996 m, 961 s, 755 m, 728 s, 690 vs, 552 s, 533 m, 521 m, 437 w, 322 w. $^1\text{H NMR}$ (CDCl_3 , 200 MHz) δ 7.72–7.69 (m, 2 *n*H, Ph), 7.43–7.39 (m, *n*H, Ph), 7.34–7.39 (m, 2 *n*H, Ph). Signals of cod in the starting complex at 4.22, 2.49 and 1.76 ppm and those of Et groups in NHET_3Cl at 2.96 and 1.10 ppm are also observed. A broad signal between 8.2 and 6.8 ppm and a signal at 6.52 ppm could be due to protons of coordinated water molecules and OH groups.

3.6.2. $\text{C}_{60}(\text{OPPh}_2)_6(\text{OH})_6$ [$\mu\text{-RhCl}(\text{H}_2\text{O})$]₂ \times [$\text{RhCl}(\text{H}_2\text{O})_4$]₂ (**8**)

Reaction of 30 mg of **3a'** ($x = 12$) $\cdot 2\text{NHET}_3\text{Cl}$ (0.0078 mmol) and $[\text{RhCl}(\text{cod})]_2$ (15 mg, 0.03 mmol, 0.06 meq. Rh) in CH_2Cl_2 (20 ml) at room-temperature leads after 20 h under stirring, partial evaporation of solvent and addition of Et_2O , to a light brown precipitate of a product with a slightly higher Rh content as **7** and free of DPA (20 mg, 43% referred to Rh, 81% referred to ligand). By evaporation of the yellow ethereal washing solution, a yellow residue (10 mg) was obtained, which was identified as a mixture of the starting complex and DPA (IR and $^1\text{H NMR}$). Anal. Found: C, 55.54; H, 4.17; N, 0.83; Rh, 12.04. Calc. for **8**. $0.5[\text{RhCl}(\text{cod})]_2 \cdot \text{CH}_2\text{Cl}_2 \cdot 2\text{NHET}_3\text{Cl}$, $\text{C}_{145}\text{H}_{120}\text{Cl}_8\text{N}_2\text{O}_{22}\text{P}_6\text{Rh}_4$: C, 55.75 H, 3.87; N, 0.89; Rh, 13.18. IR (cm^{-1}): 3400 ms br, 3051 mw, 2952 w, 2875 w, 1623 m br, 1585 w, 1478 mw, 1432 s, 1394 vw, 1179 w, 1156 w, 1122 s, 1099 s, 1065 m, 1034 s, 1019 ms, 992 ms, 839 mw, 747 m, 720 ms, 690 vs, 548 s, 537 s, 510 sh, 437 vvw, 335 mw, 320 ms br. $^1\text{H NMR}$ (CDCl_3 , 200 MHz) δ 7.76–7.67 (m, 2 *n*H, Ph), 7.55–7.20 (m, 3 *n*H, Ph). Signals of cod in the starting complex at 4.22, 2.49 and 1.76 ppm and those of Et groups in NHET_3Cl at 2.96 and 1.10 ppm are also observed. A broad signal between 8.2 and 6.2 ppm could be due to protons of coordinated water molecules and OH groups.

3.7. Reaction with $[\text{RhCl}(\text{cy-C}_8\text{H}_{14})]_2$ ($\text{cy-C}_8\text{H}_{14}$) = cyclooctene)

3.7.1. $\text{C}_{60}(\text{OPPh}_2)_6(\text{OH})_6 \cdot [\mu\text{-RhCl}(\text{H}_2\text{O})][\text{RhCl}(\text{H}_2\text{O})_4]_4$ (**9**)

The reaction was carried out in deaerated CH_2Cl_2 (20 ml) between 40 mg of **3a'** ($x = 12$) $\cdot 2\text{NHET}_3\text{Cl}$ (0.0104 mmol) and 20.5 mg (0.04 mmol, 0.08 meq. Rh) of the Rh complex. The reddish-brown solution was heated at 40°C overnight, under stirring. After filtration, the solution was concentrated to 5 ml and, by addition of Et_2O , a reddish-brown solid appears, which was washed several times with Et_2O and dried under vacuum (25 mg, 46% referred to Rh, 71% referred to ligand). Anal. Found: C, 51.20; H, 3.93; N, 0.76; Rh, 14.72. Calc. for **9**. $2\text{NHET}_3\text{Cl} \cdot \text{CH}_2\text{Cl}_2$, $\text{C}_{145}\text{H}_{134}\text{Cl}_9$

$N_2O_{29}P_6 Rh_5$; C, 51.40; H, 3.99; N, 0.83; Rh, 15.19. IR (KBr, cm^{-1}) 3420 s br, 3051 w, 2929 vw, 2860 vw, 1627 m br, 1589 w, 1482 w, 1435 s, 1179 sh, 1160 sh, 1122 vs, 1100 sh, 1065 m, 1034 m, 1011 s, 992 s, 747 m, 720 ms, 690 s, 555 sh, 537 ms, 437 vw. 1H NMR ($CDCl_3$, 200 MHz) δ 7.80–7.70 (m, 2 nH, Ph), 7.56–7.20 (m, 3 nH, Ph). Signals of Et groups in NH_2Et_3Cl at 2.96 and 1.10 ppm are also observed. A broad signal between 8.2 and 6.2 ppm could be due to protons of OH and coordinated water molecules.

3.8. Reaction with $[RuCl_2(p\text{-cymene})]_2$

3.8.1. $C_{60}(OPPh_2)_6(OH)_6[[RuCl_2(H_2O)]_2]_2[Ru_2Cl_4(H_2O)_2(p\text{-cymene})]_2$ (**10**)

33 mg of **3a'** ($x = 12$) · $2NH_2Et_3Cl$ (0.0086 mmol) and 31 mg of $[RuCl_2(p\text{-cymene})]_2$ (0.0506 mmol, 0.1012 meq Ru) were refluxed in 1,2-dichloroethane (10 ml) for 48 h under stirring in a N_2 atmosphere. After filtration of an unidentified reddish-black precipitate, the deep-green solution was evaporated to dryness, and the residue was redissolved in CH_2Cl_2 and precipitated with toluene/ Et_2O 1:1. The black-green precipitate was centrifuged and washed two times with toluene and three times with Et_2O (27 mg, 50% referred to Ru, 71% referred to ligand). Anal. Found: C, 49.61; H, 3.59; N, 0.11; Ru, 18.53. Calc. for **10**, $2DPA \cdot 0.33 NH_2Et_3Cl$, $C_{178}H_{137.33}Cl_{16.33}N_{0.33}O_{24}P_8Ru_8$; C, 49.71, H, 3.22, N, 0.11; Ru, 18.80. IR (cm^{-1}) 3428 ms br, 3051 w, 2958 w, 2905 vw, 1630 m br, 1585 w, 1480 w, 1435 s, 1190 sh, 1180 ms, 1155 w, 1135 vs, 1100 sh, 1060 m, 1030 m, 1005 w, 990 m, 960 s, 755 m, 730 s, 696 vs, 550 s, 528 s, 445 m, 338 m, 330 m, 305 w. 1H NMR ($CDCl_3$, 200 MHz) δ 7.78–7.59 (m 2 nH, Ph), 7.58–7.16 (m, 3 nH, Ph), 5.47 (d, 7 Hz, 0.25 nH, *p*-cymene), 5.35 (d, 7 Hz, 0.25 nH, *p*-cymene), 5.00–3.16 (s br, 2 nH, H_2O), 2.92 (hept., 8 Hz, 0.12 nH, *p*-cymene), 2.16 (s, 0.37 nH, Me *p*-cymene), 1.30, (s, 0.37 nH, Me *p*-cymene), 1.26 (s, 0.37 nH, Me, *p*-cymene).

3.9. Reaction with $[RuCl_2(nbd)]_n$

3.9.1. $C_{60}(OPPh_2)_6(OH)_6 \cdot [Ru_2Cl_4(H_2O)_4]_3$ (**11**)

31 mg of **3a'** ($x = 12$) · $2NH_2Et_3Cl$ (0.008 mmol) and 31 mg of $[RuCl_2(nbd)]_n$ (0.12 mmol of Ru) were refluxed in THF/ $MeCN$ 1:1 (8 ml) under stirring for 24 h in a N_2 atmosphere. After filtration of unreacted Ru complex, the orange-red solution was evaporated, and the reddish-brown solid was washed three times with Et_2O and dried in vacuum (32 mg, 46% referred to Ru, 98% referred to ligand). Anal. Found: C, 48.04; H, 2.97; N, 2.01; Ru, 16.58. Calc. for **11**, $[RuCl(MeCN)_4(nbd)]Cl_2 \cdot 0.5 DPA \cdot NH_2Et_3Cl$, $C_{159}H_{131.5}Cl_{15}N_5O_{25}P_{6.5}Ru_7$; C, 48.31 H, 3.35; N, 1.77 Ru 17.89 IR (cm^{-1}) 3428 ms br, 3068 w, 3051 w, 2958 w, 2910 w, 2266 vw, 1650 m br, 1589 w, 1482 w, 1435

s, 1176 s, 1126 s, 1100 sh, 1065 m, 1034 m, 1011 sh, 992 sh, 956 ms, 752 m, 724 s, 692 s, 550 s, 522 s, 432 mw, 326 mw br, 314 sh, 260 m. 1H NMR (DMSO, 200 MHz) δ 7.77–7.65 (m, 2 nH, Ph), 7.55–7.42 (m, 3 nH, Ph), 5.08 (m, 0.31 nH, nbd), 3.86–3.37 (m of nbd, obscured by an intense signal of water in DMSO at 3.55 ppm), 2.66–2.59 (m of nbd, obscured by an intense signal of Me in DMSO at 2.51 ppm), 2.08 (s, 0.35 nH, free $MeCN$), 1.77 (s, 0.12 nH, $MeCN$), 1.53 (s, 0.46H, $MeCN$) (n = number of phenyl groups; signals of NH_2Et_3Cl at 3.10 and at 1.18 ppm are also observed).

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