Monobranched and hyperbranched dendrimers based on cyclophosphazene containing nitrile and phosphine donors and their Fe and Ru organometallic derivatives

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Abstract

The series of complexes $[N_3P_3(OC_6H_5)_5X \cdot ML_n]PF_6$, $X = OC_6H_4CH_2CN$, $N(CH_3)(CH_2)_2CN$ or $OC_6H_4PPh_2$, and $[N_3P_3(X)_6 \cdot (ML_n)_6](PF_6)_6$, $X = OC_6H_4CH_2CN$ or $N(CH_3)(CH_2)_2CN$ with $ML_n = CpFe(dppe)$ and $CpRu(PPh_3)_2$ have been synthesized by reaction of the corresponding cyclophosphazene ligands: $N_3P_3(OC_6H_5)_5OC_6H_4CH_2CNL_1$, $N_3P_3(OC_6H_5)_5N(CH_3)(CH_2)_2CNL_2$, $N_3P_3(OC_6H_5)_5OC_6H_4PPh_2L_3$, $N_3P_3(OC_6H_4 CH_2CN)_6L_4$ and $N_3P_3(N(CH_3)(CH_2)_2CN)_6L_5$ with the respective organometallic $CpFe(dppe)I$ and $CpRu(PPh_3)_2Cl$ in CH_3OH as solvent and in presence or of NH_4PF_6. The new compounds were characterized by elemental analysis and IR, UV–Visible and multinuclear NMR spectroscopy. Cyclic voltammetry studies indicate that the cyclophosphazene dendrimers act as insulators between the organometallic centers.

Keywords: Dendrimers; Cyclophosphazene; Metal–nitrile complexes; Iron complexes

1. Introduction

Dendrimers chemistry is a rapid developing field of research [1]. Dendrimers offer the prospect of novel material with advantageous properties allowing them to serve, as soluble catalysts [2], dendritic boxes [3], and other supramolecular dendritic arrangements. Since the initial report on this class of molecules by Vögtle in 1978 [4] many different structural classes of dendritic macromolecules have been reported. Two main classes of dendrimers can be distinguished: the classical organic dendrimers [1] and the emergent inorganic dendrimers [5].

The incorporation of transition-metal complexes in both organic and inorganic dendrimers lead to new and interesting materials with specific properties such as the capability to absorb visible light, to give luminescence and to undergo reversible multielectron redox processes [6]. Such species, in fact could find applications as components in molecular electronic and as a photochemical molecular devices for solar energy conversion, information storage and in catalysis [6]. In general metal-containing dendrimers can be classified in two ways: according to the nature of the dendrimer and acording to the nature of the metal. With regarding to the nature of the dendrimer three categories can be distinguished: (see Scheme 1):

(a) Dendrimers with coordination centers at the core.
(b) Dendrimers with coordination centers through all layers and
(c) Dendrimers with coordination centers on the periphery.

On the other hand, with regard to the nature of the metal, dendrimers can be clasified in (i) those that the metal fragments are coordination units and (ii) those that the metal fragments are organometallic units.

Although dendrimers with coordination centers on the periphery have been reported [1,2,6], for those with the dendrimer – core being organic, few examples of inorganic dendrimers with metal coordination or organometallic derivatives on the surface have been reported
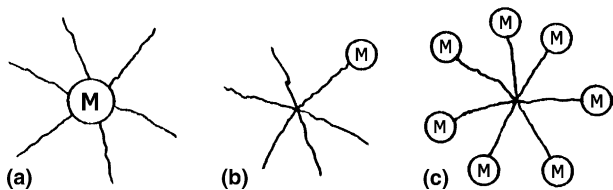
Scheme 1. Schematic representation of three class of metallodendrimers.

[5–8]. In spite of that dendrimers based on cyclophosphazenes have been reported [5], relatively few metal [9] and organometallic [5,8,10] derivatives have been reported. We have recently reported some organometallic derivatives of partially branched cyclophosphazene derivatives [10] and some single transition metal chlorides derivatives [9].

In continuation of our studies, we aimed to investigate the electronic communication between the metallic centers in dendrimers containing six organometallics groups in the peripheral (ligands L_4 and L_5, see Scheme 2) as well as the influence of the X spacer and the nature of the metal, on the electronic transfer between the phosphorus (ring) atom and the metallic center (ligands L_1–L_3).

This communication reports the synthesis and characterization of new inorganic dendrimers based on cyclophosphazene having nitrile and phosphine donor groups and containing their Fe and Ru organometallic derivatives on the surface.

X

(L_1): $OC_6H_4CH_2CN$
(L_2): $N(CH_3)(CH_2)_2CN$
(L_3): $OC_6H_4PPh_2$
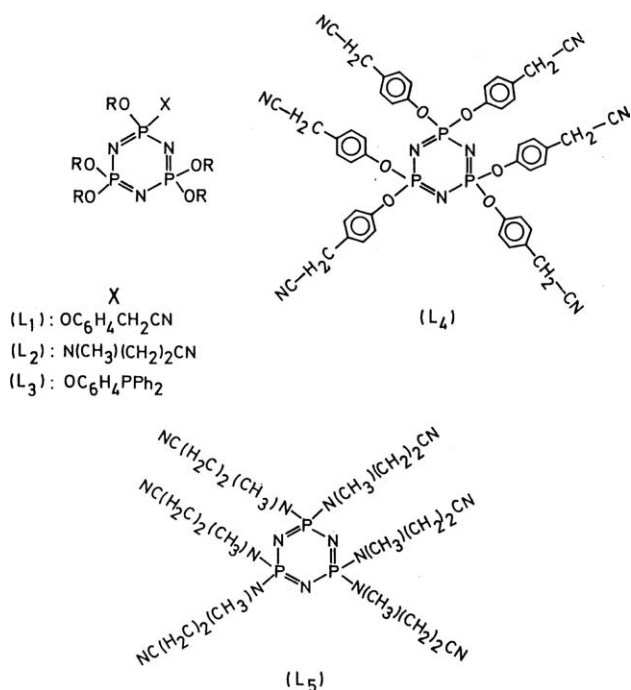
Scheme 2. Formulas for the ligands.

2. Results and discussion

2.1. Synthesis of the ligands

The synthesized ligands are shown in Scheme 2. As expected the synthesis of the dendrimers L_1, L_3 and L_4 was made by the divergent strategy [1], by reaction of $N_3P_3Cl_6$ or $N_3P_3(OC_6H_5)_5Cl$ with $HO-_6H_4CH_2CN$ in acetone and in presence of the K_2CO_3 [9,10]. The ligands L_2 and L_5 were prepared by a similar strategy by reaction of the amine $HN(CH_3)CH_2CH_2CN$ with $N_3P_3Cl_6$ or $N_3P_3(OC_6H_5)_5Cl$ using triethylamine as HCl abstractor. As commonly observed for $N_3P_3(OC_6H_5)_{6-n}(C_6H_5)_n$ or $N_3P_3(OC_6H_5)_{6-}(NHR)_n$ derivatives, the products L_1, L_3, L_4 and L_5 were obtained as yellow or white oil, while L_2 was obtained as a white solid. All the new compounds were fully characterized by elemental analisis (or mass spectra for L_1 and L_4) as well as IR, UV–Visible and ^1H ^{31}P and ^{13}C NMR spectroscopy. The compounds exhibits the typical IR bands of the $N_3P_3(OC_6H_5)_{6-n}(C_6H_5)_n$ ring [11]: v(C-OP) arounds 1200 cm^{-1}, v(PN) around 1100 cm^{-1} and v(P-OC) around 1000 cm^{-1}. Additionally the expected, v(CN) bands for L_1 , L_2, L_4 and L_5 were observed in the range 2245–2228 cm^{-1}, see Table 1.

The ^{31}P NMR spectra of the ligands L_1, L_4 and L_5 exhibit the typical singlet signal expected for these systems while that the ^{31}P NMR spectra for L_2 and L_3 show one triplet and one doublet corresponding to a AB_2 systems. These values are shown in Table 2.

For the ligands L_1, L_3 and L_4, their ^{13}C spectra exhibit all the expected signals for the groups (OC_6H_5), (OC_6H_4X) and $P(C_6H_5)_2$ (accordingly correspond see Section 3). Thus the signal of the CN and CH_2 groups were observed around 117 and 24 ppm, respectively. Full data are shown in Section 3.

2.2. Synthesis of the organometallic derivatives

2.2.1. Iron and ruthenium derivatives of ligands L_1, L_4

Using a previously reported methodology [10], the iron and ruthenim organometallic derivatives of the nitrile ligand L_1 and L_4 were prepared by reaction of the respective dendrimer ligands with the organometallic CpFe(dppe)I and CpRu(PPh$_3$)$_2$Cl respectively, in methanol as solvent and using NH$_4$PF$_6$ as halide abstractor:

(1) [CpFe(dppe)(L_1)][PF$_6$]
(2) [CpRu(PPh$_3$)$_2$(L_1)][PF$_6$]
(3) [[CpFe(dppe)]$_6$ (L_4)][PF$_6$]$_6$
(4) [[CpRu(PPh$_3$)$_2$]$_6$(L_4)][PF$_6$]$_6$

Compounds were characterized by elemental analyses, IR, ^1H ^{31}P, and ^{13}C NMR as well as UV–Visible and cyclic voltammetric methods. The IR spectra of the complexes exhibit the expected bands due to v(N≡P) and v(CN) modes of the free ligand as well as the v(PF$_6$)

Table 1
Selected Ir bands for of the ligands L_1–L_5 and of their Fe and Ru complexes 1–11

	$v(PO–C_6H_5)$	$v(PN)$	$v(P–OC_6H_5)$	$v(CN)$	C_5H_5	C_6H_5
Ligands						
L_1	1259	1177	1117	2245		
L_2		1177		2247		
L_3	1271	1212,1170	1154			
L_4	1265	1171	1100	2247		
L_5	1273	1192	1125	2252		
Complexes						
(1)	1268	1177,1161	1096	2280		711
(2)	1258	1177		2129	1091	696
(3)	1273	1192,1145	1145	2252	1099	690
(4)	1187	1187	1176	2270	1089	696
(5)	1266	1195,1177	1161		1090	705
(6)	1267	1197,1176	1163		1093	680
(7)	1285				1120	696
(8)	1253	1177	1161	2280	1096	696
(9)	1268	1178	1160	2280	1089	692
(10)	1273	1192	1145	2252		696
(11)	1241	1164	1094	2270	1097	698

Table 2
Formulas and ^{31}P NMR data for the ligands L_1–L_5 and of their Fe and Ru complexes 1–11

	$^{31}P(JP-P,Hz)$	(dppe)	PPh_3	PPh_2
Ligands				
L_1 $N_3P_3(OC_6H_5)_5OC_6H_4CH_2CN$	11.66s			
L_2 $N_3P_3(OC_6H_5)_5 N(CH_3)CH_2)_2CN$	18.11t; 2.79d (82.9)			
L_3 $N_3P_3(OC_6H_5)_5OC_6H_4PPh_2$	18.1t; 2.78d(81.4)			−10.47 (s)
L_4 $N_3P_3(OC_6H_4CH_2CN)_6$	11.89 (s)			
L_5 $N_3P_3(N(CH_3)(CH_2)_2CN)_6$	18.5 (s)			
Complexes				
(1) $[CpFe(dppe)(L_1)][PF_6]$	11.42	100.25		
(2) $[CpRu(PPh_3)_2(L_1)][PF_6]$	10.89		44.0	
(3) $[CpFe(dppe)]_6(L_4)][PF_6])_6$	11.30	100.20		
(4) $[CpRu(PPh_3)_2]_6(L_4)][PF_6]$	11.50		42.26	
(5) $[CpFe(dppe)(L_3)][PF_6]$	17.6t; 2.76d(79.3)	92.4		24.0
(6) $[CpRu(PPh_3)_2(L_3)][PF_6]$	18.1t; 2.48d(78.6)		34.6	24.8
(7) $[CpFe(dppe)PPh_2C_6H_4OH][PF_6]$		93		4.6
(8) $[CpFe(dppe)(L_2)][PF_6]$	18.1t; 2.78d (82.98)	86		
(9) $[CpRu(PPh_3)_2(L_2)][PF_6]$	18.09t; 2.77d (82.5)		37.8	
(10) $[CpFe(dppe)]_6(L_5)][PF_6]_6$	18.54	93.6		
(11) $[CpRu(PPh_3)_2]_6(L_5)][PF_6]_6$	18.0		34.93	

An heptuplet signal at −148 ppm corresponding to PF_6 anion was also observed.

band. Values are displayed in Table 1. Characteristic splitting of the $v(N=P)$ bands due to coordination of metal halide to CN groups for dendrimer L_1 and L_4 have been observed recently [9a]. A similar but lesser effect was observed for complexes (1)–(4). Thus, this splitting pattern appears to be typical of metal coordination [9,10]. The complexes (1)–(4) exhibit the expected ^{31}P signal for the N_3P_3 ring namely a singlet sligtly shifted to lower values by coordination effects. This small decrese in the ^{31}P chemical shift is typical of coordination of organometallic fragments [10]. On the other hand the ^{31}P signal of the dppe ligand ligated to CpFe fragment for the complexes (1) and (3) was observed as normal at 100 ppm while the signal of PPh_3 coordinated to the fragment CpRu was normally observed at 44 and 42 ppm. The PF_6 anion was normally observed as a septuplet around −148 ppm. From the ^{13}C NMR spectrum of complexes, it can be clearly corroborated the presence of the groups (OC_6H_5), (OC_6H_4X) $X = CH_2CN$, PPh_2, of the ligands as well as the typical signals of the fragments $P(C_6H_5)_3$ and C_5H_5 (see Section 3).

Thus, these data compare well with those of the nitrile mononuclear model complexes {CpFe(dppe)-NCR][PF$_6$]} [12], as well as other cyclophosphazene organometallic derivatives [10].

2.2.2. The iron and ruthenium derivatives of the ligand L_3

Following a previously reported procedure [13], the complexes:

(5) [CpFe(dppe)(L$_3$)][PF$_6$]

(6) [CpRu(PPh$_3$)$_2$(L$_3$)][PF$_6$]
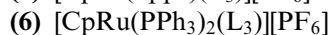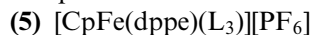
were synthesized from the reaction of the respective organometallic with L$_3$ in methanol as solvent and using NH$_4$PF$_6$ as halide abstractor. As model, we have also prepared the new complex:

(7) [CpFe(dppe)PPh$_2$C$_6$H$_4$OH][PF$_6$]

by reaction of the known PPh$_2$C$_6$H$_4$OH [8d] with the iron organometallic.

The new complexes (5)–(6) were characterized by elemental analyses, IR, ^{1}H and ^{31}P NMR, UV–Visible and cyclic voltammetric methods. IR and NMR data for the complexes are not unusual and they are displayed in Tables 1–3 and in Section 3. It is interesting to mention the v(OH) of (7) at 3420 cm^{-1} and the ^{31}P signal of the PPh$_2$ group at 4.6 ppm significantly shifted from the free value −10 ppm. Similar shifting for the complexes (5) and (6) were observed. As observed for another cyclophosphazenes and polyphosphazenes containing phosphines [8d] a small fraction of phosphine phosphorus as O=PPh$_2$ was detected by the signals at 28.63 and 26.61 ppm for 5 and 6, respectively.

2.2.3. Iron and ruthenium derivatives of the ligands L_2 and L_5

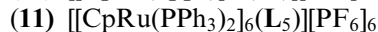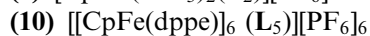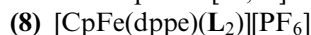These compounds were synthesized using the usual methodology for preparing iron–nitrile and ruthenium–nitrile complexes [10,12]:

(8) [CpFe(dppe)(L$_2$)][PF$_6$]

(9) [CpRu(PPh$_3$)$_2$(L$_2$)][PF$_6$]

(10) [[CpFe(dppe)]$_6$ (L$_5$)][PF$_6$]$_6$

(11) [[CpRu(PPh$_3$)$_2$]$_6$(L$_5$)][PF$_6$]$_6$

Table 3
Electrochemical data for complexes 1–11

	$E1/2$ (V)	ΔE (V)
1	0.81	0.11
2	0.53	0.06
3	0.81	0.14
4	0.50	0.06
5	0.88	0.10
6	0.570	0.088
7	0.884	0.092
8	0.775	0.080
9	0.613	0.073
10	0.767	0.263
11	0.590	0.091

Potential referenced against Ag/AgCl, at 100 mV s^{-1} scan rate, in a 0.1 mol dm^{-1} n-Bu$_4$N[PF$_6$].

The compounds were characterized by elemental analyses, IR, ^{1}H, ^{31}P, as well as UV–Visible and cyclic voltammetric methods. The IR spectra of complexes exhibit the expected bands due to v(N=P) and v(CN) modes of the free ligand as well as the v(PF$_6$) band. Values are displayed in Table 1, The characteristic splitting of v(N=P) upon coordination was also observed. A decrease of the v(CN) band upon coordination suggest the link of the ligand through the CN group instead of the N(CH$_3$) group of the ligand. The complexes (8)–(11) exhibit the expected ^{31}P signal for the N$_3$P$_3$ ring, namely, a singlet (for (10) and (11)) or a triplet and doublet signals (for (8) and (9)) at sligthly shifted lower values by coordination effects. As previously mentioned this small decrease of the ^{31}P chemical shift is typical of organometallic fragments coordination [10]. On the other hand, the ^{31}P signal of the dppe ligand ligated to CpFe fragment for the complexes (8) and (10) was normally observed at 92.4 and 93.6 ppm, respectively. The signal of PPh$_3$ coordinated to the fragment CpRu was observed at 34.6 and 34.9 ppm for (9) and (11), respectively. The PF$_6$ anion was normally observed as a septuplet around −142 ppm. Relatively fast decomposition of the samples in solution precludes the measurements of good ^{13}C NMR spectrum for the complexes.

As previously reported [10c] the ^{31}P chemical shift parameter $\Delta = |\delta\ ^{31}$P(free ligand) $- \delta\ ^{31}$P(complex)| in the systems similar to the organometallic derivatives (1), (2), (5), (6), (8) and (9) is a measure of the electron transfer between the phosphorus atom and the metal atom. From ^{31}P NMR data shown in Table 2 it can be viewed that the Δ parameter is greater for the ruthenium derivatives than for the iron complexes. Thus this parameter does not correlates with the distance of the X spacer as found in another similar systems [10c].

2.2.4. UV–Visible spectra of the complexes

The UV–Visible spectrum of the complexes is dominated by both, the organometallic chromophore and by the nature of the CN or PPh$_2$ groups linked to the metal. Iron complexes having the CpFe(dppe) moiety exhibits well defined absorption maxima arounds 450 nm depending of the N or P donor interaction [10,12,13]. Less intense shoulders arounds 526 and 600 nm have been assigned to the metal–ligand charge transfer transitions (MLCT) [12]. Fig. 1 exhibits the UV–Visible spectrum of (8). Data are shown in Section 3. On the contrary the ruthenium containing dendrimers (9) and (11) exhibits a tail beginning around 500 nm, of a more intense absorption band centered at 350 nm. Thus these absorption patterns are typical of [CpFe(dppe)NCR][PF$_6$], [10,12] of [CpFe(dppe)PPh$_2$-R][PF$_6$] [13], [CpRu(PPh$_3$)$_2$ NCR][PF$_6$] [10,12] and [CpRu(PPh$_3$)$_2$PPh$_2$-R][PF$_6$] [13] complexes.
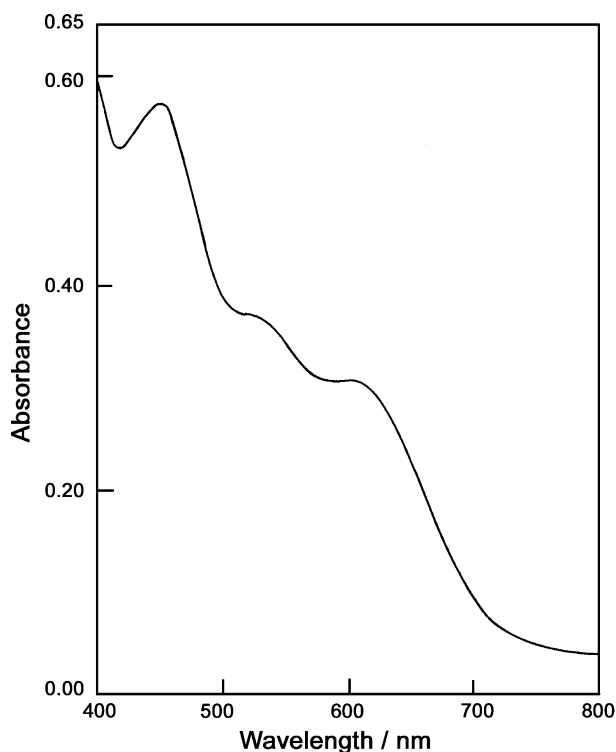
Fig. 1. UV–Visible spectrum for (**8**) in CH_2Cl_2 solution at room temperature.

Fig. 2. Cyclic voltammogram of complexes (**1**) and (**3**) on a graphite electrode ($v = 100$ mV s^{-1}) of a $CH_2Cl_2(n$-Bu$_4$N$^+$PF$_6^-$ solution) containing: complex (**1**), $(2.11 \times 10^{-3}$M$)$ curve upper, and complex (**3**), $(3.4 \times 10^{-4}$M$)$ curve lower.

2.2.5. Cyclic voltammetry studies

There are few reports of electrochemical studies on cyclophosphazene metal complexes [8–10], Cyclic voltammetry for these type of systems provides some insight into the communication degree between the metal centers along the cyclophosphazene [4]. For all the studied complexes one single oxidation wave was observed. In Fig. 2, the cyclic voltammogram of complex (**1**) having one fragment CpFe(dppe) (symbolized [Fe] in the figure) is compared with that containing six iron group the complex (**3**). As shown in Fig. 2, similar CV (similar intensities and shapes) are obtained, being the concentration of the dendrimer (**1**) six times more larger than the complex (**3**), which indicated that their oxidation wave involves the transfer of six electrons at the same potential. Then, the six CpFe(dppe) groups behave as six electroactive non-interacting redox centers around the periphery of the cyclosphosphazene ring.

As is usually observed for this type of organometallic compounds [8–10], only quasi-reversible waves were observed in all the cases. From Table 3 it can be observed that the potential values clearly depend on the π-acceptor capacity of the group linked to the organometallic fragment. For the fragment CpFe(dppe) the most π-acceptor phosphorus induce the highest electron witdrawing effect provoking the most highest potential value, ≈0.88 V. Consistent with this, the weakest π-acceptor ligand nitrile, decrease their potential values in an
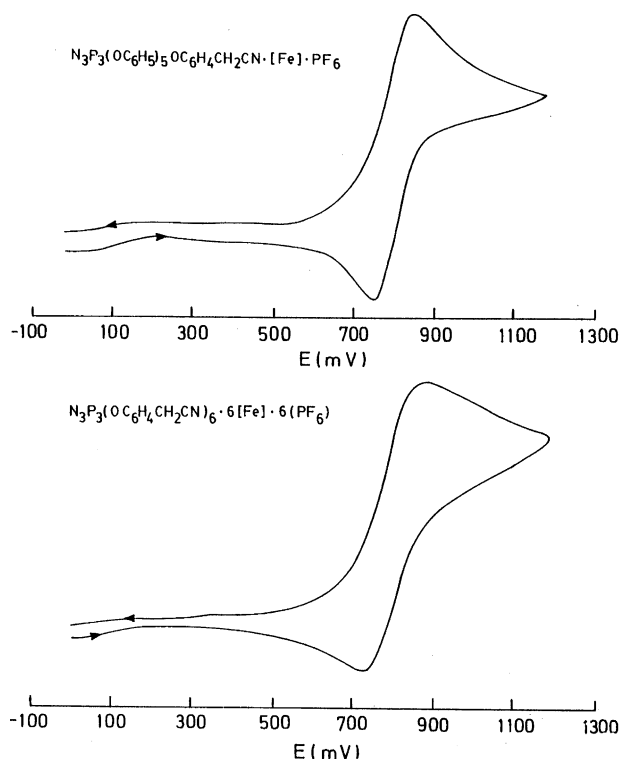
amount which depend on the nature of the spacer (X in the Scheme 2). In the CpRu(PPh$_3$)$_2$ series the opposite tendency was observed. In this case, inductive effects of the group spacer increasing in the order $-C_6H_4O >$ N(CH$_2$)$_2$ could explain the observed order of the potential.

3. Experimental

3.1. General considerations

Infrared spectra were recorded on a FT-Bruker-66V spectrophotometer in Nujol. NMR spectra were recorded on a Bruker AMX 300 spectrometer in chloroform-d$_1$ with TMS (H) $\delta = 0.0$ ppm as internal standard or 85% H$_3$PO$_4$ and downfield positive to the reference as external standard for the ^{31}P measurements.

UV–Visible absorption spectra were recorded using a Varian DMS-90 spectrophotometer with 1 cm optical path cuvettes in CH_2Cl_2 solutions. Elemental analyses were performed on Fisons-Carlo Erba EA 1108, apparatus by CEPEDEQ, Universidad de Chile.

Mass spectra were recorded with a ICP-MS Fisons VG Plasma Quad mass spectrometers.

Electrochemical measurements were made on a Parc model 370 electrochemistry system, using a three electrode device, employing a carbon glassy working electrode, platinum wire counter electrode and saturated calomel reference electrode. Solutions were 10^{-3} M in the complex and 0.1 M in $[NBu_4]PF_6$ as supporting electrolyte. Under the same experimental conditions, $E1/2$ for the ferrocene–ferrocenium complex was 0.64 V with peak separations of about 0.060 V (internal standard). Reactions were carried out under nitrogen using standard Schlenk-tube techniques. Diethylether and n-hexane were dried over sodium and distilled.

$N_3P_3Cl_6$, $HO–C_6H_4–CH_2CN$, $HNCH_3CH_2CH_2CN$, NH_4PF_6 and $CpRu(PPh_3)_2Cl$ were purchased from Aldrich. $CpFe(dppe)I$ was prepared by a previously reported method [9,10]. $N_3P_3(O–C_6H_5)_5Cl$ was prepared using a previously reported method [10b].

3.2. Preparation of ligand and complexes

3.2.1. Ligands

3.2.1.1. Synthesis of $N_3P_3(O–C_6H_5)_5(O–C_6H_4–CH_2–CN)$ (L_1). A mixture of $N_3P_3(O–C_6H_5)_5Cl$ 2.3 g, (3.62 mmol); $HO–C_6H_4–CH_2–CN$ 0.5 g; (3.75 mmol), K_2CO_3 0.97 g; (7.02 mmol) and $[Bu_4N]Br$ 1.7 g; (5.27 mmol) was refluxed in acetone (40 ml) for 20.17 h. The solution was filtered through celite and the solvent evaporated in vacuo. The red oil residue was extracted with toluene to give a red solution. n-Hexane was added to obtain a ligth red oil, which was washed with n-hexane and dried under reduce pressure. Mass spectrum (m/e) 732 M^+. Calc. (732); 691 (M^+-CH_3CN)-^{1}H NMR ($CDCl_3$): 7.1–6.9 (m, OC_6H_5), 6.83–6.73 (m OC_6H_4), 3.71, 3.53 (s, CH_2). ^{13}C NMR ($CDCl_3$, ppm): 150.91, 129.9, 125.46, 121.24, 117.87 (OC_6H_4X), 150.91, 129.21, 121.24, 117.87 ($P(OC_6H_5)$), 116.95 (CN), 24.19 (CH_2). UV/Vis(CH_2Cl_2): $\lambda = 232$ nm.

3.2.1.2. Synthesis of $N_3P_3(O–C_6H_4–CH_2–CN)_6$ (L_4). A mixture of $N_3P_3Cl_6$ 0.26 g, (0.75 mmol); $HO–C_6H_4–CH_2–CN$ 0.8 g; (6 mmol), K_2CO_3 1.54 g; (11.14 mmol) and $[Bu_4N]Br$ 1.5 g; (4.65 mmol) was refluxed in acetone (30 ml) for 51 h. The red solution was filtered through celite and the solvent evaporated in vacuo. The red oil residue was dried in vacuum and extracted with dichloromethane and filtered through celite and dried to obtain a ligth red oil, which was dried under reduce pressure. Mass spectrum (m/e) 927 M^+ Calc. (927), 886 (M^+-CH_3CN). ^{1}H NMR (CD_2Cl_2): 7.21–6.93 (m, OC_6H_4) 1.63, 1.43(s, CH_2). ^{13}C NMR ($CDCl_3$): 129.73, 125.63, 121.79, 118.54 (OC_6H_4X): 117.36 (CN), 24.43 (CH_2). UV/Vis(CH_2Cl_2): $\lambda = 234$ nm.

3.2.1.3. Synthesis of $N_3P_3(OC_6H_5)_5N(CH_3)(CH_2)_2CN$ (L_2). A mixture of $N_3P_3(O–C_6H_5)_5Cl$ 1.05 g, (1.65 mmol); $HN(CH_3)(CH_2)_2CN$ 0.154 ml; (1.65 mmol), NEt_3 0.229 ml; (1.65 mmol) were refluxed in benzene (35 ml) for 72 h. The solution was evaporated in vacuo and the yellow pale oil residue was poured into water and was extracted with dichloromethane. The extract was dried over sodium sulphate and filtered trough celite and the same solvent evaporated under vacuum to give a white solid. *Anal*. Calc. for $C_{34}H_{27}O_5N_5P_3$: C, 59.76; H, 4.68; N, 10.25; P, 13.01. Found: C, 57.67; H, 4.25; N, 6.96; P, 13.61%. ^{1}H NMR (CD_2Cl_2): 7.3–7.0 (m, C_6H_5), 2.56 (d, CH_3 $J_{PNH} = 11$ Hz), 2.99 (m, CH_2), 2.03 (t, CH_2). ^{13}C NMR ($CDCl_3$, ppm): 150.59, 129.82, 125.49, 121.35 (P-OC_6H_5), 118.54(CN), 45.56(CH_2), 34.158CH_2), 17.14(CH_3).). UV/Vis(CH_2Cl_2): $\lambda = 261$ nm.

3.2.1.4. Synthesis of $N_3P_3(N(CH_3)(CH_2)_2CN)_6$ (L_5). A mixture of $N_3P_3Cl_6$ 5 g, (14.38 mmol); $HN(CH_3)(CH_2)_2CN$ 8.068 ml (86.31 mmol), in NEt_3 11.96 ml; (86.31 mmol) were refluxed in bencene (50 ml) for 10 h. The pale yellow solution was filtered and the solvent evaporated in vacuo. The oil residue was redissolved in a n-hexane/dichloromethane mixture. Purification of the product mixture was made by chromatography using neutral alumna. Elution with a n-hexane/dichloromethane mixture and collection of the transparent fraction followed by evaporation under vacuum afford a ligth yellow oil, which was dried under reduce pressure. *Anal*. Calc. for $C_{24}H_{42}N_{15}P_3$; C, 45.51; H, 6.63; N, 33.18; P, 14.30. Found: C, 43.24; H, 6.71; N, 28.03; P, 14.69%. ^{1}H NMR ($CDCl_3$): 2.78 (m CH_2CN), 2.69(s, CH_3), 2.6(m CH_2N). ^{13}C NMR ($CDCl_3$): 118.47 (CN), 45.71 (CH_2), 33.58 (CH_2), 17.60(CH_3).

3.2.1.5. Synthesis of $N_3P_3(O–C_6H_5)_5(O–C_6H_4–PPh_2)$ (L_3). A mixture of $N_3P_3(O–C_6H_5)_5Cl$ 0.3052 g, (0.48 mmol); $HO–C_6H_4–PPh_2$ 0.1214 g; (0.849 mmol), Cs_2CO_3 0.294 g; (0.9 mmol) were refluxed in acetone (30 ml) for 2 h. The solution was filtered through celite and the solvent evaporated in vacuo. The yellow pale oil residue was extracted with toluene to give a red solution. n-Hexane was added to obtain a ligth red oil, which was washed with n-hexane and dried under reduce pressure. *Anal*. Calc. for $C_{48}H_{39}O_6N_3P_4$: C, 65.67; H, 4.78; N, 4.78; P, 13.9. Found: C, 64.28; H, 4.26; N, 4.26; P, 14.14%. ^{1}H NMR (CD_3Cl): 7.1–7.3 (m OC_6H_5), 7.0–6.9 (m, C_6H_4), 3.75 (s, CH_2). ^{13}C NMR ($CDCl_3$, ppm): 151.06, 134.96, 133.47, 125.2, 121.22, 115.87 (OC_6H_4X) 135.74, 133.47, 129.46, 128.76 (–PPh_2), 150.17, 128.41, 124.88, 120.97 (P–OC_6H_5). UV/Vis(CH_2Cl_2): $\lambda = 230$ nm.

3.2.2. Complexes

3.2.2.1. Synthesis of $[N_3P_3(O–C_6H_5)_5(O–C_6H_4–CH_2–CN)\cdot Fe(Cp)dppe]PF_6$ (1). A mixture of $N_3P_3(O–C_6H_5)_5(O–C_6H_4–CH_2–CN)$ 0.23 g (0.31 mmol), and

CpFe(dppe)I 0.2 g (0.31 mmol) in methanol (20 ml), in presence of NH_4PF_6 0.2 g (1.23 mmol) was stirred for 21 h at room temperature. The solvent was removed under reduced pressure and the residue extracted with CH_2Cl_2 and filtered through celite and concentrated to ≈10 ml. A n-hexane/diethylether 4:1 mixture was added and the red powdered precipitate was twice washed with the same solvent mixture and dried under reduced pressure.

Yield: 0.25 g, 49%. *Anal*. Calc. for $C_{69}H_{60}F_6O_6N_4$-P_6Fe: C, 61.99; H, 5.00; N, 4.01; P, 13.32. Found: C, 62.9; H, 4.7; N, 3.9; P, 12.32%. ^1H NMR (CD_3Cl): 7.73(m), 7.75(m), 7.35(m), 7.26(m), 7.18(m OC_6H_5), 6.98(m), 6.77(m OC_6H_4), 4.3 (s, C_5H_5), 3.7 (CH_2P), 1.27 (CH_2C). ^{13}C NMR ($CDCl_3$): 156.7, 129.95, 125.3, 121.3, 116.45 (OC_6H_4X), 156.7; 129,6, 120.18, 116.45 $P(OC_6H_5)$, 137, 133.19, 133.13, 132.56, 131.68, 131.55 131.55, 127.97 ($P(C_5H_5)$), 79.3 (C_5H_5), 29.26 (CH_2CN), 20.13.3 (CH_2P). UV/Vis(CH_2Cl_2): $\lambda = 366$ and 466 nm.

3.2.2.2. Synthesis of $[N_3P_3(O-C_6H_5)_5(O-C_6H_4-CH_2-CN)\cdot Ru(Cp)(PPh_3)_2]PF_6$ (2). A solution of CpRu-$(PPh_3)_2$Cl 0.14 g (0.19 mmol) in CH_3OH (20 ml) was stirred with $[N_3P_3(O–C_6H_5)_5(O–C_6H_4–CH_2–CN)$ 0.22 g (0.3 mmol) in the presence of NH_4PF_6 0.2 g (1.22 mmol) at room temperature for 23 h. The solvent was removed under reduced pressure and the residue extracted with CH_2Cl_2 (15 ml) and filtered through celite. Then reduced in volume and n-hexane/dithylether 4:1 mixture was added. The yellow solid precipitate was twice washed with the same mixture and dried.

Yield: 0.41 g, 97%. *Anal*. Calc. for $C_{79}H_{66}F_6O_6N_4P_6$-Ru: C, 60.46; H, 4.20; N, 3.0. Found: C, 60.5; H, 6.3; N, 3.57%. ^1H NMR (CD_3Cl): 7.3, 7.42 ($P(C_5H_5)$), 6.94–6.83, 6.72, 6.64, (OC_6H_4X), 4.43 (s, C_5H_5), 1.13(CH_2). ^{13}C NMR ($CDCl_3$): 156, 133.58, 129.14, 123.38, 121.44 (OC_6H_4X), 156, 128.7, 119.44, 116.44 ($P(OC_6H_5)$), 134.11, 133.58, 130.56, 130.38, 129.73, 127.33 ($P(C_5H_5)$). 115.22 CN; 81.47 (C_5H_5); 24,12 (CH_2CN); 19.99,13.66 CH_2P.

3.2.2.3. Synthesis of $[N_3P_3(O–C_6H_4–CH_2–CN)_6\cdot(Fe-(Cp)dppe)_6][PF_6]_6$ (3). A mixture of $N_3P_3(O–C_6H_4–CH_2–CN)_6$ 0.21 g (0.23 mmol), and CpFe(dppe)I 0.17 g (0.26 mmol) in methanol (30 ml), in presence of NH_4PF_6 0.2 g (1.23 mmol) was stirred for 24 h at room temperature. The solvent was removed under reduced pressure and the residue extracted with CH_2Cl_2 and filtered through celite and concentrated to ≈10 ml. n-Hexane was added and the red powdered precipitate was twice washed with the same solvent and dried under reduced pressure.

Yield: 0.25, g. 49%. *Anal*. Calc. for $C_{234}H_{210}$$F_{36}O_6N_9P_{21}Fe_6$: C, 54.37; H, 4.03; N, 2.05. Found: C,

54.76; H, 5.7; N, 2.64%. ^1H NMR (CD_3Cl): 7.3(m), 7.25(m), 7.13(m), 6.97(m), (OC_6H_4X /PC_6H_5), 5.33(sC_5H_5), 1.01(CH_2). ^{13}C NMR($CDCl_3$): 156, 129.96, 125.49; 121.73 129.54, 121.73 (OC_6H_4X): 133.13, 133.07, 131.63, 130.91 ($P(OC_6H_5)$), 79.54 (C_5H_5); 24.22 (CH_2CN), 20.45, 23.66 (CH_2P). UV/Vis(CH_2Cl_2): $\lambda = 340$ and 440 nm.

3.2.2.4. Synthesis of $[N_3P_3(O–C_6H_4–CH_2–CN)_6\cdot(Ru-(Cp)(PPh_3)_{26}][PF_6]_6$ (4). A solution of CpRu(PPh_3)_2-Cl 0.2 g (0.27 mmol) in CH_3OH (30 ml) was stirred with $[N_3P_3(O–C_6H_4–CH_2–CN)_6$ 0.085 g. (0.09 mmol) in the presence of NH_4PF_6 0.25 g (1.5 mmol) at room temperature for 74 h. The solvent was removed under reduced pressure and the yellow–orange residue extracted with CH_2Cl_2 (15 ml) and filtered through celite. Then reduced in volume and n-hexane/dithylether 4:1 mixture was added. The yellow solid precipitate was twice washed with the same mixture and dried.

Yield: 0.41 g, 97%. *Anal*. Calc. for $C_{102}H_{86}F_{36}O_6$-$N_9P_{21}Ru_6$; C, 59.34; H, 4.34; N, 2.0. Found: C, 58.79; H, 4.48; N, 2.12%. ^1H NMR (CD_3Cl): 6.6–7.68(m C_6H_4), 4.36 (s,C_5H_5). ^{13}C NMR ($CDCl_3$):156, 129.13, 127,85 (OC_6H_4X): 134.14, 133.57, 132.38, 132.25, 128.96, 128.80, 127.85 ($P(OC_6H_5)$), 81.04 (C_5H_5), 24.0 (CH_2).

3.2.2.5. Synthesis of $[N_3P_3(O–C_6H_5)_5(O–C_6H_4–PPh_2)\cdot Fe(Cp)dppe]PF_6$ (5). A mixture of $N_3P_3(O–C_6H_5)_5$-$(O–C_6H_4–PPh_2)$ 0.2478 g (0.28 mmol), and CpFe(dppe)I 0.182 g (0.254 mmol) in methanol (20 ml), in presence of NH_4PF_6 0.0937 (0.575 mmol) was stirred for 19 h at room temperature. The solvent was removed under reduced pressure and the residue extracted with CH_2Cl_2 and filtered through celite and concentrated to ≈10 ml. A n-hexane/diethylether 4:1 mixture was added and the red powdered precipitate was twice washed with the same solvent mixture and dried under reduced pressure.

Yield: 0.25 g, 49%. *Anal*. Calc. for $C_{79}H_{68}F_6O_6N_3$-$P_6Fe\cdot CH_2Cl_2$; C, 58.68; H, 4.28; N, 2.3; P, 13.9. Found: C, 58.81; H, 4.53; N, 1.9, P, 14.14%. ^1H NMR (CD_3Cl): 8.6–8.3 (m PC_6H_5), 7.4,7.8 (m OC_6H_5), 7.25–7.18 ($P(C_6H_5)_3$), 6.93, 6.91 (mOC_6H_4P)4. 9(sC_5H_5), 3.5(m.b.CH_2). UV/Vis(CH_2Cl_2): 239, 268, 448 and 526 nm(sh), 602 nm(sh).

3.2.2.6. Synthesis of $[N_3P_3(O–C_6H_5)_5(O–C_6H_4–PPh_2)\cdot(Ru(Cp)(PPh_3)_2)]PF_6$ (6). A mixture of $N_3P_3(O–C_6H_5)_5(O–C_6H_4–PPh_2$ 0.2478 g (0.28 mmol) and (Ru-(Cp)(PPh_3)_2Cl 0.182 g (0.254 mmol) in methanol (20 ml), in presence of NH_4PF_6 0.0937 (0.575 mmol) was stirred for 19 h at room temperature. The solvent was removed under reduced pressure and the residue extracted with CH_2Cl_2 and filtered through celite and

concentrated to ≈10 ml. A *n*-hexane/diethylether 4:1 mixture was added and the red powdered precipitate was twice washed with the same solvent mixture and dried under reduced pressure.

Yield: 0.25 g, 49%. *Anal*. Calc. for $C_{89}H_{74}F_6O_6N_3P_6$-Ru; C, 62.38; H, 4.73; N, 4.32; P, 10.50. Found: C, 63.05; H, 4.73; N, 2.16; P, 10.86%. ^1H NMR (CD$_3$Cl): 7.8–7.7 (OC$_6$H$_5$), 7.2–7.0 (P(C$_6$H$_5$)$_3$), 6.94–6.88 (OC$_6$H$_4$P), 4,9(s, C$_5$H$_5$).). UV/Vis(CH$_2$Cl$_2$): $\lambda = 239$ nm, 268 nm (sh), 302 nm(sh), 353 nm.

3.2.2.7. Synthesis of [HO–C$_6$H$_4$–PPh$_2$·Fe(Cp)dppe]-PF$_6$ (7). A mixture of HO–C$_6$H$_4$–PPh$_2$ 0.2478 g (0.28 mmol), and CpFe(dppe)I 0.182 g (0.254 mmol) in methanol (20 ml), in presence of NH$_4$PF$_6$ 0.0937 (0.575 mmol) was stirred for 19 h at room temperature. The solvent was removed under reduced pressure and the residue extracted with CH$_2$Cl$_2$ and filtered through celite and concentrated to ≈10 ml. A *n*-hexane/diethylether 4:1 mixture was added and the red powdered precipitate was twice washed with the same solvent mixture and dried under reduced pressure.

Yield: 0.25 g, 49%. *Anal*. Calc. for $C_{49}H_{44}F_6$-OP$_2$Fe.CH$_2$Cl$_2$: C, 58.68; H, 4.28; N, 2.3. Found: C, 58.81; H, 4.53; N, 1.9%. ^1H NMR (CD$_3$Cl): 6.6–6.7 (m C$_6$H$_4$) 4.27(s, C$_5$H$_5$). 3.04 (CH$_2$). ^{13}C NMR (CDCl$_3$): 156.7, 129.6 129.95 (OC$_6$H$_4$X) 133.13, 131.62, 130.95, 127.97, 125.3, 121.3 (P(C$_6$H$_5$)$_2$), 120.18 (CN), 79.3 (C$_5$H$_5$), 24.2 (CH$_2$). UV/Vis(CH$_2$Cl$_2$): $\lambda = 255$, 476 and 617 nm.

3.2.2.8. Synthesis of [N$_3$P$_3$(OC$_6$H$_5$)$_5$N(CH$_3$)(CH$_2$)$_2$-CNFe(Cp)dppe]PF$_6$ (8). A mixture of N$_3$P$_3$(OC$_6$H$_5$)$_5$-N(CH$_3$)(CH$_2$)CN 0.20 g (0.29 mmol) and CpFe(dppe)I 0.195 g (0.295 mmol) in methanol (20 ml), in presence of NH$_4$PF$_6$ 0.097 (0.67 mmol) was stirred for 19 h at room temperature. The solvent was removed under reduced pressure and the residue extracted with CH$_2$Cl$_2$ and filtered through celite and concentrated to ≈10 ml. A *n*-hexane/diethylether 4:1 mixture was added and the red powdered precipitate was twice washed with the same solvent mixture and dried under reduced pressure.

Yield: 0.25 g, 49%. *Anal*. Calc. for $C_{65}H_{56}F_6O_5N_5P_6$-Fe: C, 61.99; H, 5.00; N, 5.19; P, 13.8. Found: C, 62.9; H, 4.7; N, 5.0; P, 13.0%. ^1H NMR (CD$_3$Cl): 7.3–6.9 (m) 6.4 (PC$_6$H$_5$) 4.32 (s, C$_5$H$_5$), 1.54(m CH$_3$), 1.25 (CH$_2$). ^{13}C NMR (CDCl$_3$): 156.7, 129.95, 125.3 121.3 (P(OC$_6$H$_5$)), 133.13, 131.62, 130.95, 129.6, 127.97 (P(C$_5$H$_5$)), 120.18 (CN) 79.3 (C$_5$H$_5$), 24.2 (CH$_2$). UV/Vis(CH$_2$Cl$_2$): $\lambda = 233$, 467 and 623 nm.

3.2.2.9. Synthesis of [N$_3$P$_3$(O–C$_6$H$_5$)$_5$(N(CH$_3$)(CH$_2$)$_2$CN)·Ru(Cp)(PPh$_3$)$_2$]PF$_6$ (9). A solution of CpRu(PPh$_3$)$_2$Cl 0.2155 g (0.297 mmol) in CH$_3$OH (20 ml) was stirred with [N$_3$P$_3$(O–C$_6$H$_5$)$_5$(O–C$_6$H$_4$–CH$_2$–CN) 0.2 g (0.29 mmol) in the presence of NH$_4$PF$_6$ 0.098 g (0.67 mmol) at room temperature for 23 h. The solvent was removed under reduced pressure and the residue extracted with CH$_2$Cl$_2$ (15 ml) and filtered through celite. Then reduced in volume and *n*-hexane/dithylether 4:1 mixture was added. The yellow solid precipitate was twice washed with the same mixture and dried.

Yield: 0.41 g, 97%. *Anal*. Calc. for $C_{75}H_{62}F_6O_5N_5$-P$_6$Ru: C, 60.46; H, 4.20; N, 4.6; P, 12.12. Found: C, 60.5; H, 6.3; N, 3.5; P, 11.08%. ^1H NMR (CD$_3$Cl): 7.8–7.0 (OC$_6$H$_5$), 4.1 (s, C$_5$H$_5$) 1.55 CH$_3$. ^{13}C NMR (CDCl$_3$): 129.14, 128.70, 121.44 P(OC$_6$H$_5$), 133.58; 130.56; 129.14 128.70 (P(C$_5$H$_5$)), 121.44 (CN), 84.5 (C$_5$H$_5$), 24.12 (CH$_2$). UV/Vis (CH$_2$Cl$_2$): $\lambda = 233$ and 350 nm.

3.2.2.10. Synthesis of [N$_3$P$_3$(N(CH$_3$)(CH$_2$)$_2$CN)$_6$·(Fe(Cp)dppe)$_6$][PF$_6$]$_6$ (10). A mixture of [N$_3$P$_3$(O–C$_6$H$_4$–CH$_2$–CN)$_6$ 0.0235 g (0.037 mmol) and CpFe(dppe)I 0.1207 g (0.18 mmol) in methanol (20 ml), in presence of NH$_4$PF$_6$ 0.1123 g (0.77 mmol) was stirred for 12 h at room temperature. The solvent was removed under reduced pressure and the residue extracted with CH$_2$Cl$_2$ and filtered through celite and concentrated to ≈10 ml. *n*-Hexane was added and the red powdered precipitate was twice washed with the same solvent and dried under reduced pressure.

Yield: 0.25 g, 49%. *Anal*. Calc. for $C_{210}H_{216}F_{36}O_5$-N$_9$P$_{18}$Fe$_6$: C, 54.37; H, 4.03; N, 5.19; P, 13.79. Found: C, 54.76; H, 5.7; N, 4.07; P, 13.90%. ^1H NMR (CD$_3$Cl): 7.81(m), 7.74(m), 7.58(m), 7.42(m)(PC$_6$H$_5$), 4.36 (s,C$_5$H$_5$), 2.16 (CH$_3$), 0.1 (CH$_2$). UV/Vis(CH$_2$Cl$_2$): $\lambda = 230$ and 451 nm.

3.2.2.11. Synthesis of [N$_3$P$_3$(N(CH$_3$)(CH$_2$)$_2$CN)$_6$·(Ru(Cp)(PPh$_3$)$_2$)$_6$][PF$_6$]$_6$ (11). A solution of CpRu(PPh$_3$)$_2$Cl 0.1569 g (0.27 mmol) in CH$_3$OH (30 ml) was stirred with [N$_3$P$_3$(O–C$_6$H$_4$–CH$_2$–CN)$_6$ 0.02182 g (0.034 mmol) in the presence of NH$_4$PF$_6$ 0.6741 g (0.41 mmol) at room temperature for 1 h. The solvent was removed under reduced pressure and the yellow–orange residue extracted with CH$_2$Cl$_2$ (15 ml) and filtered through celite. Then reduced in volume and *n*-hexane/dithylether 4:1 mixture was added. The yellow solid precipitate was twice washed with the same mixture and dried.

Yield: 0.41g, 97%. *Anal*. Calc. for $C_{270}H_{252}F_{36}N_{15}P_{18}Ru_6$: C, 59.34; H, 4.34; N, 4.46; P, 11.53. Found: C, 58.79; H, 4.48; N, 2.31; P, 11.9%. ^1H NMR (CD$_3$Cl): 7.8–7.0 (m PC$_6$H$_5$), 4.5 (s, C$_5$H$_5$), 1.6 (CH$_3$) 1.3, 0.8 (CH$_2$). ^{13}C NMR (CDCl$_3$): 134.14, 133.57, 132.38, 132.25, 129.13, 128.96, 128.80(P(C$_5$H$_5$)), 127.85 (CN),

81.8 (C_5H_5), 24.2 (CH_2). UV/Vis(CH_2Cl_2): $\lambda = 235$ and 349 nm.

Acknowledgements

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