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Synthesis and characterization of soluble polyphosphazenes having pendent Cp* Fe(dppe) groups

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Summary

The reaction of $HOC_6H_4CH_2CN$, $N_3P_3(O_2C_{12}H_8)_2(OC_6H_4CH_2CN)_2$ and

- $[\{NP(O_2C_{12}H_8)\}_{0.8}\ \{NP\ (OC_6H_4CH_2CN)_2\}_{0.18}\ ]_n$ with $Cp^*Fe(dppe)I$ in dichloromethane solution and in the presence of $TlPF_6$ affords the new compounds $[Cp^*Fe(dppe)NCCH_2C_6H_4OH][PF_6]$ **1** $Cp^* = C_5(CH_3)_5$

$[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4CH_2CN{\bullet}Cp^*Fe(dppe))_2]\ [PF_6]_2$ **2** and the copolymer $[\{NP\{(O_2C_{12}H_8)\}_{0.8}\ \{NP(OC_6H_4CH_2CN{\bullet}[Cp^*Fe(dppe)][PF_6])_2\}_{0.18}]_n$ **3** respectively. The σ coordination of the $Cp^*Fe(dppe)$ fragment toward the nitrile group is indicated by spectroscopic data. The copolymer **3** is soluble in several organic solvents with no significant cross-linking and has a Mw on the order of 1.260.000. Thermal effects of the incorporation of the organometallic fragment to the copolymer were investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Introduction

Among polymers, organometallics polymers have attracted interest due to their potential uses in material science, with considerable attention being given to their electrical, magnetic, optical, catalytic and redox properties [1,2]. An important class of organometallics polymers is the pendent type, where the metal moieties are anchored to the backbone of the polymer, see Figure 1 [3,4].

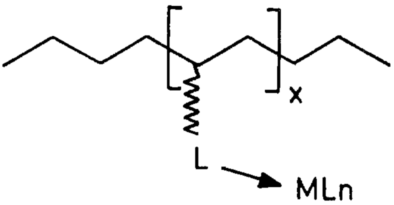

Figure 1. A linear polymer with a metal fragment anchored to the backbone

To this date, there are a limited number of reports dealing with these type of material with polyphozphazene as backbone [5]. We have previously investigated the reaction of the copolymer

- $[\{NP(O_2C_{12}H_8)\}_{0.8}\{NP\ (OC_6H_4CH_2CN)_2\}_{0.18}]_n$ with CpFe(dppe)I which affords an insoluble material which contains deprotonated iron fragments [6]. Although several ferrocene pendent polymers have been reported, [1-3] scarce half sandwich iron pendent containing polymers have been reported [1-3,7]. Although it is well known that the introduction of bulky substituents into the cyclopentadienyl(ring)iron fragments increases the solubility of the respective derivatives, few organometallic polymers with pendent η^5-C_5R_5-Fe moieties have been reported [8]. With the purpose to obtain more soluble polyphosphazenes with pendent iron organometallic fragments, here we report the incorporation of η^5-Cp*Fe(dppe) fragments to the copolymer having pendent benzylcyanide spacers. As models the complex **1** and the oligomer **2** containing the same fragment, were also synthesized, see Figure 2.

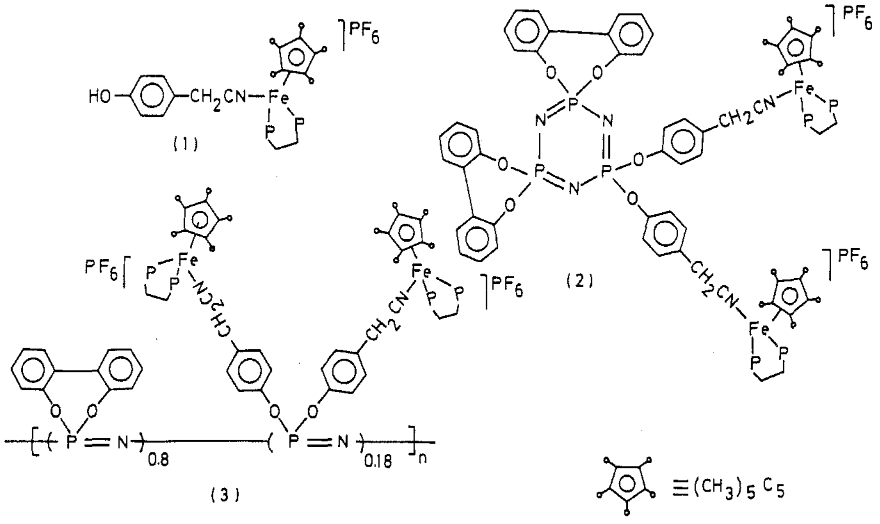

Figure 2. Schematic structures of the compounds **1**,**2** and approximate representation of the copolymer **3**.

Experimental

Measurements

The IR spectra were recorded with a FT-IR Perkin-Elmer 2000 spectrophotometer. The NMR spectra were recorded on a Brucker AMX 300 Instrument. Visible absorption spectra were measured with a Varian DMS-90 Spectrophotometer in 1cm length cuvettes. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on a Netzsch STA 409 instrument.

The polymer samples were heated at a rate of 10°C/min from ambient temperature to 1000°C under constant flow of nitrogen. The average molecular weight of the copolymer **3** was calculated by the Mark-Houwink Equation .The intrinsic viscosity was measured at 25 °C using a typical glass viscometer. The polymer was dissolved in chloroform at 25 °C (K= 3.45 10^3 , a= 0.17). A calibration for several polyphospazenes, using molecular weights determined by GPC, was used.

Materials

The ligand $HOC_6H_4CH_2CN$ (Aldrich) was used as purchased. The organometallic $Cp^*Fe(dppe)I$ was prepared starting from $[Cp^*Fe(CO)_2]_2$ [9]. The spiro derivative $N_3P_3(O_2C_{12}H_8)_2(OC_6H_4CH_2CN)_2$ and the copolymer $[\{NP(O_2C_{12}H_8)\}_{0.8}$ $\{NP(OC_6H_4CH_2CN)_2\}_{0.18}]_n$ were prepared using the alkaline carbonate method as previously reported [13]. (A small fraction of the polymer with composition $[\{NP(OC_6H_4CH_2CN)(OC_6H_5)\}]_{0.02}$ was also identified and omitted for simplify in the formula). Purification of this copolymer was achieved by dissolving the solid in THF and reprecipitation in water.The procedure was repeated dissolving in THF/2-propanol and THF/petroleum ether. The solvents, tetrahydrofuran (THF), CH_2Cl_2, and diethyl ether were dried and purified by standard methods.

Reaction of $HOC_6H_4CH_2CN$ with $Cp^*Fe(dppe)I$

To a solution of Cp*Fe(dppe)I (0.11 g, 0.15 mmol) in CH_2Cl_2 (25 ml) and in the presence of $TlPF_6$ (0.11g, 0.33 mmol) was added $HOC_6H_4CH_2CN$ (0.03g, 0.24 mmol) . The mixture was stirred for 20h. The solution was filtered through Celite and the solvent was evaporated under vacuum. The resulting red brown solid was washed with a n-hexane/diethylether (1/1) mixture and dried under vacuum to give **1** (25%) as red-brown solid. Elemental Analysis, Found: C, 59.2; H, 5.07; N, 1.68; Calcd for $C_{44}H_{44}ONF_6P_3Fe$: C, 60.84; H, 5.3; N, 1.6. ^1H NMR($CDCl_3$,δ ppm): 7.68(m),7.46(m) 20 H, C_6H_5,dppe ; 7.18(d), 6.86(d), 4 H -C_6H_4O ; 3.67(s), 2H CH_2CN, 2.52(m) 2H, CH_2-P ; 1.56(s), 15H, CH_3 . $^{13}C\{H\}$($CDCl_3$, δ ppm): 132.37,130.83, C_6H_5,dppe ; 129.07 -C_6H_4O ; 116.26 CN ; 23.1 CH_3 ; 21.8 CH_2CN.

Reaction of $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4CH_2CN)_2$ with $Cp^*Fe(dppe)I$

To a solution of $N_3P_3(O_2C_{12}H_8)_2$ $(OC_6H_4CH_2CN)_2$ (0.055 g, 0.071 mmol) in CH_2Cl_2 (25 ml)) was added Cp*Fe(dppe)I (0.12 g, 0.28 mmol) in the presence of $TlPF_6$ (0.1g, 0.28 mmol) and this solution was stirred for 22 h. A similar procedure to isolation and purification to **1** affords **2** (30%) as a brown dark powder . Elemental Analysis, Found: C, 56.18; H, 4.41; N, 3.33 ; Calc. for

$C_{76}H_{67}O_6N_{12}F_{12}P_9Fe_2 \bullet 2CH_2Cl_2$: C, 56.89; H, 5.07; N, 2.91.

^1H NMR($CDCl_3$,δ ppm): 7.718m),7.50(m) 40 H, C_6H_5,dppe ; 7.35(d), 7.0(d), 8H -C_6H_4O ;

5.3(s), 4H,CH_2Cl_2 ; 3.77(s),4H, CH_2CN ; 2.528(m) 4H, CH_2-P ; 1.59(s), 30H, CH_3 . $^{13}C\{H\}$($CDCl_3$, δ ppm): 132.16,130.83, 129.79,129.69,128.91 C_6H_5, dppe ; 150.54, 129.79, 121.77 -C_6H_4O ; 148.0, 130.83, 129.24, 126,94, 121,99, $OC_6H_4C_6H_4O$

117.72 CN ; 86.83(m) 85.78(m) $^*Cp$; 54.5(s) CH_2Cl_2 ; 23.13(s) ; CH_3, 21.5(s) CH_2CN.

Reaction of the copolymer $-[\{NP(O_2C_{12}H_8)\}_{0.8}\{NP(OC_6H_4CH_2CN)_2\}_{0.18}]_n-$ with $Cp^*Fe(dppe)I$

A solution of $-[\{NP(O_2C_{12}H_8)\}_{0.8}\{NP(OC_6H_4CH_2CN)_2\}_{0.18}]_n-$ (0.06 g, 0.246 mmol based on the molecular weight of the polymer repeat unit) and $Cp^*Fe(dppe)I$ (0.12 g, 0.16 mmol) in CH_2Cl_2 (25 ml) in presence of $TlPF_6$ (0.12g, 0.57 mmol) were stirred at room temperature for 24 h. A procedure similar to that described for the isolation of **1** was used except the precipitate was filtered twice, affording **3**(40%) as a brown dark powder. Elemental Analysis, Found: C, 50.93; H, 4.00; N, 2.02. Calcd. $C_{25.4}H_{22.6}O_{1.96}N_{1.34}F_{2.16}P_{2.06}Fe_{0.36} \bullet 1.5CH_2Cl_2$: C, 51.29; H, 4.06; N, 2.89.

^1H NMR($CDCl_3$,δ ppm): 7.7(m),7.46(m), C_6H_5,dppe ; 7.198(d), 6.87(d), -C_6H_4O ;

5.3(s), CH_2Cl_2 ; 3.18(s), CH_2CN ; 2.75(m), CH_2-P ; 1.52(s), CH_3 . $^{13}C\{H\}$($CDCl_3$, δ ppm): 132.15, 131.6, 130.86, C_6H_5, dppe ; 150.83, 129.67, 120.0 -C_6H_4O ; 149.5m, 130.84, 129.67, 120.5, $OC_6H_4C_6H_4O$; 115, CN ; 86.83(m) 85.78(m) $^*Cp$; 54.0(s) CH_2Cl_2 ; 22.14(s) CH_3 ; 21.5(s) CH_2CN.

Results and Discussion

As a source to incorporate the iron fragment to the polymer we have used $Cp^*Fe(dppe)I$ prepared by a new route starting from the commercial $[Cp^*Fe(CO)_2]_2$ [9]. Incorporation of the fragment $Cp^*Fe(dppe)^+$ was achieved by reaction of the respective ligand with $Cp^*Fe(dppe)I$ in a dichloromethane solution in the presence of $TlPF_6$ as halide abstractor . From the reactions products **1**, **2** and **3** were isolated as dark brown, solids. They were characterized by IR, ^1H , ^{31}P and ^{13}C NMR and UV-visible spectroscopy techniques. The organometallic co-polymer was also characterized by DTA/DSC and molecular weigh measurement.

Mononuclear complex 1

Single coordination of the ligand $HOC_6H_4CH_2CN$ to the mononuclear complex **1** was established by the ν(CN) IR band, at 2249 cm^{-1} shifted from free ligand, to 2318 cm^{-1} [10], as well as by the ^{13}C NMR signal of methyl, from the Cp* and the signal of CN group which appears at 23,1 and 116,2 respectively. In their IR spectrum, the ν(OH) band was observed at 3400 cm^{-1} which is near its free value [10]. Typical ^1H signal of Cp* [8] appears at 1.56 ppm while the typical doublets of phenyl ring in CH_2-C_6H_4-OH appear at 7.18 and 6.85 ppm.

Oligomer complex 2

Similarly, the coordination of the Cp*Fe(dppe) fragment to the bis-spirocyclophosphazene model was evidenced by IR; typical bands of ν(CN) at 2251 cm^{-1}, ν(P = N) at 1231, 1184, 1165 cm^{-1} [11,12] were observed among others. NMR data also confirmed the proposed structure for **2**. As found for another bis-spiro cyclophosphazene [13] the ^{31}P-NMR spectrum exhibits the expected signal of the N_3P_3 ring : a doublet at 21.34 ppm and a triplet at 5.79 ppm. These signals compare well with those of the free ligand [13], slightly shifted by coordination. Their ^{13}C - NMR spectrum exhibits the typical signal of the ligands; 117 ppm for CN group, and 29.7 ppm for CH_2 group. On the other hand signals for the Cp*Fe(dppe) fragment are: 23.13 ppm for CH_3 and 86.37 ppm for the carbons of the cyclopentadienyl ring. In the ^1H-NMR spectrum the methyl signal of the Cp* group appears at 1.49 ppm, while the two doublets corresponding to the phenyl NC-C_6H_4O group appear at 7.0 and 7.3 ppm.

Organometallic co-polymer 3

Reaction of Cp*Fe(dppe)I with the copolymer copolymer $[\{NP(O_2C_{12}H_8)\}_{0.8}\ \{NP(OC_6H_4CH_2CN)_2\}_{0.18}]_n$ in CH_2Cl_2 and in the presence of $TlPF_6$ affords the new soluble organometallic polymer **3**. Coordination of the iron fragment to the copolymer backbone was evidenced by IR as well as by ^1H, ^{31}P and ^{13}C NMR spectroscopy. Two weak IR bands appear at 2252 and 2217 cm^{-1} slightly shifted respect to the free ligand indicate the coordination of the organometallic fragment to the polymer. On the other hand the expected νPF_6 band was observed at 842 cm^{-1}. ν(P = N) bands appear normally at 1247, 1192 and 1181 cm^{-1}[11,12]. In the ^1H NMR spectrum, the signal of the methyls of the Cp* were observed at 2.52 ppm, while in the ^{13}C NMR, the carbon methyl signal appears at 30.9 ppm.

UV-visible spectra

Owing to the ligands $HOC_6H_4CH_2CN$, the bis-spirophosphazene and their polymer do not absorb in the zone above 400nm , UV-visible provides a valuable information about the coordination of the fragment Cp*Fe(dppe)I to these compounds. In fact compounds **1**,**2** and **3** exhibit the typical absorptions of the fragments $Cp^*M(P_1P_2)$, M= Fe , Ru and P_1,P_2= mono and diphosphines [14], namely d-d transitions located around 650,530 and 460 nm. The two former were observed as shoulders.

Physical Properties of the Polymer

Molecular Weight

Owing to the insolubility of polyphosphazenes with anchored organometallic fragments, few molecular weight have been reported [5]. The average molecular weight (Mw) calculated by viscometry gave a value of 1.260.000, which compares well with values for other organometallic polyphosphazene. For instance the polymer $\{[NP(O_2C_{12}H_8)]_{0.65}[NP(OC_6H_4PPh_2.\ W(CO)_5)_2]_{0.35}\}_n$ has a Mw = 1.700.000 [5], although this polymer being obtained by a slight different route.

Thermal Properties

The Tg/DSC curve for the organometallic complex **3** is shown in Figure 3.The organometallic polymer undergoes an initial loss of 11.8% weight, as observed for other similar polyphosphazenes [15]. This can be attributed to loss of the organometallic residues. The thermolysis pattern above 340°C exhibits a sudden loss of weight due to volatilization of the previously formed cyclo0phosphazenes. Theses processes are in agree- ment with the endothermic peaks exhibits by the DSC curve (see Figure 3).

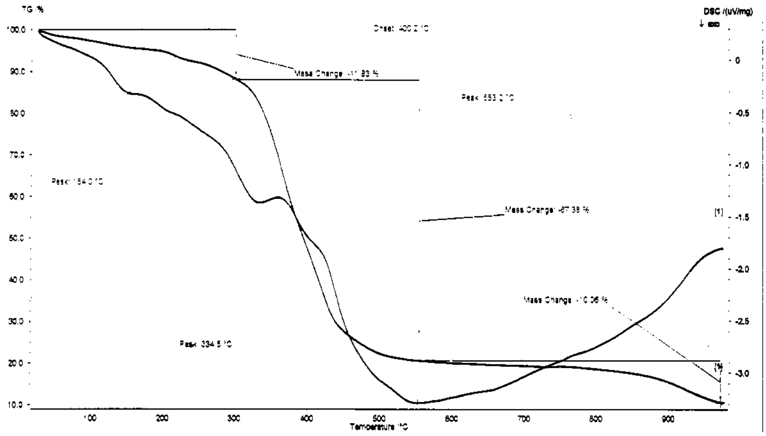

Figure 3. Tg/DSC curve for the organometallic polymer **3** (heat- rate of 10 °C/min flowing He)

The percentage of nonvolatile residue at 900°C was somewhat low, 21%, compared with the values observed for others organometallic polymers [16,17]. The cross-linking of polyphosphazenes by metal or organometallic fragments appears to be an important factor in the preparation of ceramic materials [17]. Then, the low pyrolitic residue of the polymer 3 could be due to the low capacity of the Cp*Fe(dppe) organometallic fragment to crosslinks the polymer chains. The glass transition temperature (Tg) of polymers was 123°C for the polymer without metal and 149°C for the organometallic polymer derivative. The higher Tg may be a result of the increased steric bulk of the Cp*Fe(dppe) group.

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