Organometallic Platinum(II) and Palladium(II) Polymers Containing 2,6-Diethynyl-4-nitroaniline Bridging Spacer and Related Dinuclear Model Complexes

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The metal−carbon coupling in dehydrohalogenation conditions between Pt(II) or Pd(II) square planar bisphosphine dichloride complexes and 2,6-diethynyl-4-nitroaniline (DENA) yielded organometallic polymers, i.e., $-[M(PTol_3)_2(-C{\equiv}C-R-C{\equiv}C-)]_n-$ with R = p-NH₂C₆H₂-NO₂ and M = Pt(II) or Pd(II). Dinuclear platinum complexes were also synthesized as geometrical models. The polymers and complexes were fully characterized by means of spectroscopic techniques. Accurate investigations with 2D nuclear magnetic resonance (NMR) spectroscopy were used to define the chemical and spatial structure of the polymeric chains as a helical conformation for both Pt(II)- and Pd(II)-based organometallic polymers. Optical absorption studies and X-ray photoelectron spectroscopy measurements revealed the extent of conjugation and the nature of the ending groups.

Introduction

In the past decade a great deal of research work has been devoted to the synthesis of organometallic polymers.[1,2] Polymers containing in the main chain transition metals σ bonded to conjugated alkynes $-C{\equiv}C-R-C{\equiv}C-$ have been largely investigated,[3,4] being stable materials with interesting electrical[5] and linear and nonlinear optical[6] properties. Owing to their rigid rod linear structure, they also behave as liquid crystals.[7,8] Photoelectron spectroscopy measurements and theoreti-

cal calculations[9] have demonstrated that there is a significant overlap between the π system of the acetylene spacer and the d orbitals of the metal centers. As a consequence, a good deal of back-bonding between the metal orbitals and the π^* alkynyl orbitals, leading to an extended delocalization along the polymer chain throughout the ML$_n$ groups, is expected. Optical absorption and photoluminescence studies revealed relatively low band gaps, associated with metal to ligand charge transfer (MLCT) transitions. The optical band gaps are dependent on the nature of the organic spacer,[10] which also exerts an influence on the delocalization of π electrons throughout the polymer backbone. Therefore these materials are of potential interest for the development of new semiconductor organic devices, which can be realized using their thin films. Field effect transistors, electroluminescent diodes, and photoconductive devices have also been implemented by using organometallic polymers.[11]

Polymers with third-order NLO properties need an extended π delocalization and organometallic *rigid-rod* ones belong to this class.[12] Organometallic polymers in which donor−acceptor interactions can occur, resulting

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from charge transfer between electron-donor and electron-withdrawing groups, exhibit second-order NLO properties.[13]

In this framework, we have prepared and characterized new polymers using 2,6-diethynyl-4-nitroaniline (DENA) and bis-phosphine Pt and Pd dihalides as the precursors. To achieve a better characterization, Pt and Pd model complexes were also synthesized by using DENA and 2,5-diethynylthiophene (DET) as bridging ligands between metal centers.

Experimental Section

Instrumentation. IR spectra were recorded with a Perkin-Elmer 1700 FTIR spectrophotometer, in Nujol mulls, in CH_2Cl_2 solutions or KBr pellets. Spectra in the range $200-500$ cm^{-1} were run on a Perkin-Elmer 1700X interferometer. Raman spectra were run on a NIR FT Raman 1700X interferometer (laser Nd:YAG $\lambda = 1064$ nm) on samples mixed with $BaSO_4$.

UV spectra were measured on a Perkin-Elmer Lambda 5 UV/vis spectrophotometer in CHCl$_3$, *N,N*-dimethylformamide (DMF), or tetrahydrofuran (THF) solutions, in quartz cells. Photoluminescence spectra were registered on a Perkin-Elmer LS 50 spectrofluorimeter in CHCl$_3$ solutions. The molar extinction coefficient ϵ_o (with respect to the repeating unit) and the relative quantum yield η of chloroform solutions were also determined. We adopted as the standard a solution of coumarine in ethanol ($c = 0.0028$ g/L), with a quantum yield equal to 51%, calculated by comparison with a rhodamine 6G solution ($c = 0.016$ g/L, $\eta = 90\%$).[14] All data were corrected by taking into account the photomultiplier efficiency of the fluorescence spectrometer.

NMR spectra were collected with a Varian XL 300 spectrometer in CDCl$_3$. ^{1}H and ^{13}C spectra were calibrated with internal standards and ^{31}P spectra with H$_3$PO$_4$ (85%) probe. NMR measurement conditions: ^{1}H pulse width 7.5 μs (30°), acquisition time 2 s, repetition time 0.5 s, spectral width 4000 Hz, number of data points 32K, number of scans 128; ^{31}P pulse width 10 μs (45°), acquisition time 2 s, repetition time 1 s, spectral width 30 000 Hz, number of data points 32K, number of scans 2000; ^{13}C pulse width 4.3 μs (30°), acquisition time 1.815 s, repetition time 1.2 s, spectral width 19 000 Hz, number of data points 64K, number of scans 20 000. 2D COSY spectra were recorded on a Bruker AM-500 instrument, by using the pulse sequence available in the routine of the instrument. Measurement conditions: spectral width 8000 Hz, data matrix 4K × 512K points, 512 fid's were collected for each value of t_1. 2D NOESY spectra were obtained in the TPPI mode. The acquisition parameters were the following: time domain 8K mF2, 512 mF1 dimension, spectral width 8000 Hz in both dimensions, resolution 0.98 and 15.65 Hz/pt mF2 and F1, respectively. Number of scans 64, relaxation delay 1.5 s, mixing time 150 ms.

Elemental analyses were performed at the "Laboratorio Servizio Microanalisi, Dipartimento di Chimica" University "La Sapienza" of Rome. TG and DTA measurements were carried out on a Stanton Redcroft Rheometrics STA 1500 apparatus in air or in N$_2$ atmosphere, with a heating rate of 10 °C/min.

Molecular weights were determined by a Perkin-Elmer GPC-HPLC apparatus with a LC250 pump, LC oven, PL GEL 10 μm MIX analytical column, UV–vis LC 90 J detector, and CHCl$_3$ as eluent. Polystyrene standard samples were used for the calibration curve.

X-ray photoelectron spectroscopy (XPS) investigations were performed with a custom designed XPS spectrometer. Typical vacuum in the analysis chamber during the measurements was in the $10^{-9}-10^{-10}$ Torr range. The analysis chamber is equipped with a 150 mm mean radius hemispherical electron analyzer with a five-lens input system combined with a 16-channel detector. Al Kα nonmonochromatized X-ray radiation ($h\nu = 1486.6$ eV) was used during the measurements; the resolution is 1.0 eV as measured for the Ag 3d$_{5/2}$ line. The samples were spin deposited onto polished stainless steel substrates in the form of thin films obtained from chloroform solutions. All the spectra were energy referenced to the C 1s signal of aromatic carbons, i.e., at 284.7 eV binding energy (BE) value. Quantitative evaluation of the atomic ratios was obtained by using the well-known Scofield atomic cross-section values.

Materials. Standard techniques, with Schlenk type equipment for the manipulation of air-sensitive materials under argon atmosphere, were used. Reagent grade (Carlo Erba) solvents were freshly distilled under argon before use. The precursor complexes *cis*-[Pt(PTol$_3$)$_2$Cl$_2$] (**1**) and *trans*-[Pd-(PTol$_3$)$_2$Cl$_2$] (**2**) were prepared according to literature methods.[15] 2,5-[(Trimethylsilyl)ethynyl]thiophene, TSET (**3**), was obtained following a reported procedure.[16]

Syntheses. 2,6-Diethynyl-4-nitroaniline (4). The procedure followed a modified pathway with respect to that reported for the preparation of similar products.[17] 2,6-Diiodo-4-nitroaniline (4 g, 10.26 mmol, Sigma-Aldrich commercial product purified with acetone, acetic acid and diethyl ether) was dissolved in 33.3 mL of freshly distilled diisopropylamine in the presence of 0.10 g (0.50 mmol) of copper(II) acetate monohydrate and 0.35 g (0.49 mmol) of *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] crystallized from chloroform. The solution was degassed by passing a rapid stream of nitrogen through it, and then 3.1 mL (21.93 mmol) of trimethylsilylacetylene (TMSA) was added. An insoluble reaction product was formed, which was filtered off, dissolved in dichloromethane, and washed with HCl (5%) and successively with water. The organic layer was dried over sodium sulfate and the solvent removed at reduced pressure. The yellow-brown solid obtained was first column chromatographed (silica gel, hexane/diethyl ether, 20:1, as eluent) and then crystallized from ethanol. The solid was dissolved in 80 mL of methanol, and KOH was added to hydrolyze the trimethylsilyl groups. After 20 min of reaction, the volume of the yellow solution was reduced, diluted with water, and extracted with chloroform, and the organic layer was dried over sodium sulfate and evaporated under reduced pressure. The obtained solid was chromatographed on a SiO$_2$ column, by using isopropyl ether/hexane, 2:1, as eluent. The second eluted fraction contained 2,6-diethynyl-4-nitroaniline (DENA) as a yellow solid. Yield: 75%. Mp: $213-214$ °C. Anal. (calcd values in parentheses): C 64.57 (64.52); H 3.15 (3.25); N 15.11 (15.05). Raman: 2107 cm^{-1}. FTIR (KBr mull, cm^{-1}): 3481, 3371 (νNH$_2$), 3293 ($\nu \equiv$CH), 1619 (ν NO$_2$), 1288 (ν CN). UV (CHCl$_3$, nm): $\lambda_{max} = 350$. Luminescence emission (CHCl$_3$, nm): $\lambda_{max} = 484$. Quantum yield: $\eta = 0.04\%$. ^{1}H NMR (CDCl$_3$, δ ppm): 3.48 (s, $\equiv$C*H*), 5.51 (s, N*H*$_2$), 8.21 (s, *H* aromatics). ^{13}C NMR (CDCl$_3$, δ ppm): 78.5 ($C\equiv$), 85.5 ($\equiv C$H), 106.5 ($C-C\equiv$), 129.5 (CH aromatics), 138.4 ($C-$NO$_2$), 155.1 ($C-$NH$_2$).

***trans*-[Bis(tri-*para*-tolylphosphine)(ethynylbenzene)-platinum chloride] (5) and *trans*-[Bis(tri-*para*-tolylphosphine)bis(ethynylbenzene)platinum] (6).** Complexes **5** and **6** were prepared using a modified synthetic method already proposed for the analogous complexes containing the PPh$_3$

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ligand.[18] *cis*-[Pt(PTol)$_3$$_2Cl_2$] (0.601 g, 0.689 mmol) was dissolved in 40 mL of CHCl$_3$, and 0.1 mL (0.093 g, 0.912 mmol) of phenylacetylene and 1.6 mL of diethylamine were added. The mixture was stirred for 3 h at 70 °C, and the solvent was then removed. The solid product was a mixture of the monochloro-acetylide (**5**) and the diacetylide (**6**) complexes, which were separated on a SiO$_2$ column, using a mixture of CHCl$_3$/toluene (3:1) as eluent. In the first eluted fraction *trans*-[Pt(PTol$_3$)$_2$-(C≡C−C$_6$H$_5$)$_2$] (**6**) was present. From the second fraction, *trans*-[Pt(PTol$_3$)$_2$(C≡C−C$_6$H$_5$)Cl] (**5**) was obtained. The products were further purified and crystallized from CHCl$_3$/EtOH.

Characterization of Complex 5. Yield: 54%. Mp: 211−212 °C. Anal. (calcd): C 63.74 (63.86); H 5.28 (5.04). FTIR (Nujol mull, cm^{-1}): 315 (ν Pt−Cl), 2130 (ν C≡C). UV (CHCl$_3$, nm): λ_{max} = 313. NMR (CDCl$_3$, δ ppm): ^{1}H, 2.36 (s, CH_3), 6.09−6.87 (m, C$_6$H$_5$), 7.17−7.66 (qt, *p*-C$_6$H$_4$Me of PTol$_3$ ligand); ^{13}C, 21.4 (CH$_3$), 88.0−106.0 (−C≡C−), 124.4, 126.8, 127.7, 131.0 (C$_6$H$_5$), 127.3, 128.6, 135.0, 140.3 (C$_6$H$_4$Me of PTol$_3$ ligand); ^{31}P, 20.23 (J_{Pt-P} = 2620 Hz).

Characterization of Complex 6. Yield: 40%. Mp: 213-215 °C. Anal. (calcd): C 70.20 (69.24); H 5.64 (5.21). FTIR (Nujol mull, cm^{-1}): 2110 (ν C≡C). UV (CHCl$_3$, nm): λ_{max} = 348. NMR (CDCl$_3$ δ ppm): ^{1}H, 2.40 (s, CH_3), 6.95−6.32 (m, ≡C−C$_6$H$_5$), 7.76−7.21 (dd, C$_6$H$_4$Me of PTol$_3$ ligand); ^{13}C, 21.25 (CH$_3$), 111.57−112.68 (−C≡C−), 124.20, 126.81, 128.32, 130.94 (C$_6$H$_5$), 128.37, 128.49, 134.90, 139.91 (C$_6$H$_4$Me of PTol$_3$ ligand); ^{31}P, 15.5 (J_{Pt-P} = 2625 Hz).

The data for **6** are in agreement with a literature report.[19]

***trans,trans*-[Diethynylbenzenedibis(tri-*para*-tolylphosphine)diplatinum(II)-2,6-diethynyl-4-nitroaniline] (7).** *trans*-[Pt(PTol$_3$)$_2$(C≡C−C$_6$H$_5$)Cl] (0.166 g, 0.19 mmol) was dissolved, under argon, in 20 mL of degassed diethylamine, and 0.19 g (0.095 mmol) of DENA and 0.013 g (0.07 mmol) of CuI as catalyst were added. The solution was warmed at 40 °C for 4 h. After removal of the solvent, the solid residue was dissolved in CHCl$_3$ and washed with water in a separatory funnel. From the CHCl$_3$ solution, yellow crystals were obtained by addition of EtOH. Yield: 85%. Mp: 228−230 °C (dec). Anal. (calcd): C 65.92 (66.26); H 5.24 (4.95); N 1.34 (1.40). FTIR (Nujol mull, cm^{-1}): 3479, 3363 (ν NH$_2$); 2101 (ν C≡C); 1287 (ν C−N). UV (CHCl$_3$, nm): λ_{max} = 360. Luminescence emission (CHCl$_3$, nm): λ_{max} = 500. Quantum yield: η = 0.02%. NMR (CDCl$_3$, δ ppm): ^{1}H, 2.26 (s, CH_3), 3.50 (s, NH_2), 6.20−6.95 (m, C$_6$H$_5$), 6.58 (s, NH$_2$C$_6$H$_2$NO$_2$), 7.00−7.58 (qt, resonances of PTol$_3$ ligand); ^{13}C, 21.2 (CH$_3$), 106.2, 111.8, 112.8, 118.1 (−C≡C−), 124.3, 126.9, 128.4, 131.3 (C$_6$H$_5$), 127.0, 128.8, 134.8, 140.4 (C$_6$H$_4$Me of PTol$_3$ ligand), 110.7, 128.0, 136.0, 152.5 (NH$_2$C$_6$H$_2$NO$_2$); ^{31}P, 17.48 (J_{Pt-P} = 2600 Hz).

***trans,trans*-[Diethynylbenzenedibis(tri-*para*-tolylphosphine)diplatinum(II)-2,5-diethynylthiophene] (8).** TSET was used to perform the reaction, because this silyl derivative is more stable and easy to handle than the corresponding 2,5-diethynylthiophene, that is highly sensitive to oxygen and reactive. TSET (0.292 g, 1.05 mmol) was dissolved in 40 mL of deoxygenated methanol, to which 4 mL of a KOH solution (0.5 M) was added. The reaction was carried out at room temperature for 1 h, to obtain the 2,5-diethynylthiophene revealed by means of ^{1}H NMR spectra. To this reaction mixture, 0.198 g (2.11 mmol) of *trans*-[Pt(PPTol$_3$)$_2$(C≡C−C$_6$H$_5$)Cl], dissolved in 45 mL of deoxygenated CH$_2$Cl$_2$, and 0.05 g of CuI as the catalyst were added under argon atmosphere. The reaction was stirred at 25 °C for 25 h, and then the solvent volume was reduced to 10 mL in a vacuum and the residue chromatographed on a silica gel column (eluent CHCl$_3$/petroleum ether, 40−70, 3:2). The dinuclear complex **8** was separated from the side products in 31% yield. Mp: 145−147

°C. Anal. (calcd): C 66.12 (66.85); H 4.80 (4.99); S 1.59 (1.65). FTIR (CHCl$_3$ solution, cm^{-1}): 1441 (ν C≡C of thiophene) 2101 (ν C≡C). UV (CHCl$_3$, nm): λ_{max} = 409. NMR (CDCl$_3$, δ ppm): ^{1}H, 2.29 (s, CH_3), 6.17, 6.87 (m, phenyl), 6.90 (s, thiophene), 7.11, 7.61 (qt, resonances of PTol$_3$ ligand); ^{13}C, 21.4 (CH$_3$), 124.4, 126.8, 128.8, 130.9 (C$_6$H$_5$), 127.2, 128.0 (C$_4$H$_2$S), 126.9, 128.5, 134.9, 140.0 (C$_6$H$_4$Me); ^{31}P, 16.67 (J_{Pt-P} = 2605 Hz).

Poly[2,6-diethynyl-4-nitroanilinebis(tri-*para*-tolylphosphine)platinum(II)] (9). *cis*-[Pt(PTol$_3$)$_2$Cl$_2$] (0.611 g, 0.07 mmol) was dissolved in 40 mL of degassed diethylamine, and 0.127 g (0.7 mmol) of DENA and 0.013 g (0.07 mmol) of CuI as catalyst were added. The mixture was warmed at 45 °C for 24 h. A yellow-brown solid separated gradually. The solid was filtered off, thoroughly washed with EtOH, and dried under vacuum. Yield: 75%. Mp: 245 °C (dec). Anal. (calcd for the repeating unit PtP$_2$O$_2$N$_2$C$_{52}$H$_{46}$): C 63.11 (63.24); H 4.41 (4.68); N 2.69 (2.85). FTIR (Nujol mull, cm^{-1}): 3468, 3357 (ν NH$_2$), 2101 (ν C≡C), 1288, 1310, 1344 (ν C−N). UV (CHCl$_3$, nm): λ_{max} 390. Luminescence emission (CHCl$_3$, nm): λ_{max} = 500. Quantum yield: η = 0.02%. NMR (CDCl$_3$, δ ppm): ^{1}H, 2.18, 2.26 (s, CH_3), 3.40 (s, NH$_2$), 6.60 (s, C$_6$H$_2$ NH$_2$ NO$_2$), 7.02, 7.09, 7.52 (m, resonances of PTol$_3$ groups); ^{13}C, 21.5, (CH$_3$), 107.5, 124.0 (C≡C), 110.5 128.2, 135.5, 153.0 (NH$_2$C$_6$H$_2$NO$_2$), 127.9, 128.9, 135.0, 141.1 (C$_6$H$_4$Me); ^{31}P, 17.62 (J_{Pt-P} = 2589 Hz), 20.38 (J_{Pt-P} = 2605 Hz). GPC: molecular weight, M_w = 14600 amu (n = 16 repeat units), polydispersity p = 2.4.

Poly[2,6-diethynyl-4-nitroanilinebis(tri-*para*-tolylphosphine)palladium(II)] (10). DENA (0.20 g, 1.07 mmol) was dissolved in 50 mL of degassed diethylamine under argon, and 0.841 (1.07 mmol) of *trans*-[Pd(PTol$_3$)$_2$Cl$_2$], 0.065 g (0.214 mmol) of tri-*para*-tolylphosphine (used to stabilize the resulting polymer), and 0.010 g (0.053 mmol) of CuI were added. The reaction was carried out for 7 h at room temperature under argon. At the end of the reaction, the solid product was filtered off and washed with MeOH. The reaction product was dissolved in CHCl$_3$ and flash chromatographed on Florisil, using CHCl$_3$ and CH$_3$OH as gradient eluents to remove the byproducts NHEt$_2$Cl and cuprous salts. After evaporation of the solvent from the eluted fraction, a yellow-brown powder was obtained. Yield: 69%. Mp: 187 °C (dec). Anal. (calcd for the repeating unit PdP$_2$O$_2$N$_2$C$_{52}$H$_{46}$): C 66.99 (69.48); H 5.38 (5.12); N 3.11 (3.67). FTIR (in Nujol mull, cm^{-1}): 3468, 3357 (ν NH$_2$), 2095 (ν C≡C), 1288, 1310, 1344 (ν C−N). UV (CHCl$_3$, nm): λ_{max} = 390. Luminescence emission (CHCl$_3$, nm): λ_{max} = 500. Quantum yield: η = 0.02%. NMR (CDCl$_3$, δ, ppm): ^{1}H, 2.24 (m, CH_3), 3.65 (s, NH_2), 6.90 (s, NH$_2$C$_6$H$_2$NO$_2$), 7.10, 7.65 (m, resonances of PTol$_3$ groups); ^{13}C, 21.4 (CH$_3$), 107.0, 124.0 (C≡C), 110.2, 129.0, 134.6, 152.3 (NH$_2$C$_6$H$_2$NO$_2$), 127.9, 128.6, 132.0, 140.2 (C$_6$H$_4$Me); ^{31}P, 25.70. GPC: molecular weight, M_w = 6000 amu (n = 8 repeat units), polydispersity p = 2.3.

Results and Discussion

Synthesis and Characterization. The monomer DENA was chosen for the presence of NH$_2$ and NO$_2$ groups in *p*-nitroaniline, which are suitable for the formation of materials with second-order nonlinear optical (NLO) properties, and because the two alkynyl moieties are able to link transition metals (mainly Pt and Pd) to form organometallic, highly ethynylated polymers. The IR spectrum of DENA is characterized by three bands in the 3500−3000 cm^{-1} region; two bands at 3481 and 3371 cm^{-1}, due to the stretching vibrations of the NH$_2$ group; and a band at 3293 cm^{-1}, due to the stretching vibrations of the ≡C−H groups. In the IR spectrum no bands are present in the 2200−2000 cm^{-1} region, where the C≡C stretching vibrations should be observable, while a band at 2107 cm^{-1} is present in the Raman spectrum of DENA, confirming the presence of the symmetric triple C≡C bond.

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Table 1. Collection of Spectroscopic Data for Compounds 4, 5, and 7−10

sample	yield (%)	IR (cm^{-1})	elemental analyses C% (C% $_{calc}$) H% (H% $_{calc}$) N% (N% $_{calc}$)			^{1}H NMR δ (ppm)	^{31}P NMR δ $J_{31P-195Pt}$ (ppm) (Hz)	^{13}C NMR δ (ppm)
4	75	3481, 3371ν(NH$_2$) 1619 ν(NO$_2$)	64.57 (64.52)	3.15 (3.25)		3.48 (s *H*−C≡C) 5.51(s −N*H$_2$*)		78.5, 85.5 (*C*≡*C*) 106.5, 129.5, 138.4, 155.1 (NH$_2$*C$_6$*H$_2$NO$_2$)
		3293 ν(≡CH) 1288, 1310, 1344 ν(CN) 2107 ν(C≡C) Raman	15.11 (15.05)			8.21 (s −Ar*H*)		
5	54	2130 ν(C≡C) 315 ν (Pt−Cl)	63.74 (63.86)	5.28 (5.04)		2.36 (s C*H$_3$*) 6.09, 6.87 (m Ph) 7.17, 7.66 (qt PTol$_3$)	20.23 (2620)	21.4 (*C*H$_3$) 88.0, 106.0 (*C*≡*C*) 124.4, 126.8, 127.7, 131.0 (*C$_6$*H$_5$) 127.3, 128.6, 135.0, 140.3 (*C$_6$*H$_4$Me)
7	85	3479, 3363 ν(NH$_2$) 2101 ν(C≡C)	65.92 (66.26)	5.24 (4.95)		2.26 (s C*H$_3$*) 3.50 (s −N*H$_2$*)	17.48 (2600)	21.2 (*C*H$_3$) 106.2, 111.8, 112.8, 118.1 (*C*≡*C*)
		1287 ν(CN)	1.34 (1.40)			6.58 (s −Ar*H*)		124.3, 126.9, 128.4, 131.3 (*C$_6$*H$_5$)
						6.20, 6.95 (m Ph)		110.7, 128.0, 136.0, 152.5 (NH$_2$*C$_6$*H$_2$NO$_2$)
						7.00, 7.58 (qt PTol$_3$)		127.0, 128.8, 134.8, 140.4 (*C$_6$*H$_4$Me)
8	31	2101 ν(C≡C) 1441 ν(C=C Th)	66.12 (66.85)	4.80 (4.99)		2.29 (s C*H$_3$*) 6.17, 6.87 (m Ph)	16.67 (2605)	21.4 (*C*H$_3$) 124.4, 126.8, 128.8, 130.9 (*C$_6$*H$_5$)
					S 1.59 (1.65)	6.90 (s Th) 7.11, 7.61 (qt PTol$_3$)		127.2, 128.0 (*C$_4$*H$_2$S) 126.9, 128.5, 134.9, 140.0 (*C$_6$*H$_4$Me)
9	75	3468, 3357ν(NH$_2$) 2101 ν(C≡C) 1288, 1310, 1344 ν(CN)	63.11 (63.24)	4.41 (4.68)	2.69 (2.85)	2.18, 2.26 (s C*H$_3$*) 3.40 (s −N*H$_2$*) 6.60 (s −Ar*H*)	17.62 (2589) 20.38 (2605)	21.5 (*C*H$_3$) 107.5, 124.0 (*C*≡*C*) 110.5, 128.2, 135.5, 153.0 (NH$_2$*C$_6$*H$_2$NO$_2$)
						7.02, 7.09, 7.52 (m PTol$_3$)		127.9, 128.9, 135.0, 141.1 (*C$_6$*H$_4$Me)
10	69	3468, 3357ν(NH$_2$) 2095 ν(C≡C) 1288, 1310, 1344 ν(CN)	66.99 (69.48)	5.38 (5.12)	3.11 (3.67)	2.24 (m C*H$_3$*) 3.65 (s −N*H$_2$*) 6.90 (s −Ar*H*)	25.70	21.4 (*C*H$_3$) 107.0, 124.0 (*C*≡*C*) 110.2, 129.0, 134.6, 152.3 (NH$_2$*C$_6$*H$_2$NO$_2$)
						7.10, 7.65 (m PTol$_3$)		127.9, 128.6, 132.0, 140.2 (*C$_6$*H$_4$Me)

The ^{1}H NMR spectrum of DENA shows the aromatic protons signal at 8.21 ppm, owing to the high influence of the NO$_2$ group in *ortho* position, a signal at 3.48 ppm assigned to the ≡C−H proton, and the resonance at 5.51 ppm assigned to the NH$_2$ group. The ^{13}C NMR spectrum exhibits the resonances of the C≡C group at 85.5 and 78.5 ppm and the resonances of the aromatic carbons at 106.5 (C linking the triple bond), 129.5 ppm (aromatic C−H), 138.4 ppm (C bonded to NO$_2$), and 155.1 ppm (C bonded to NH$_2$); these values are consistent with correlation chart values. The experimental data are collected in Table 1.

The polarizability of this molecule is confirmed by UV measurements. As a general statement, an optical excitation induces a different electronic distribution between the donor and the acceptor groups in the polarizable molecules and the dipole moment of the ground and the excited state are largely different. The position of the intramolecular charge transfer (ICT) transition bands of these molecules is dependent on the polarity of the solvent, and the solvatochromic effect is characteristic of molecules that exhibit second-order NLO properties.[20] The UV spectra of DENA recorded in CHCl$_3$ and in *N,N*-dimethylformamide, solvents with quite different polarity, show a shift of the absorption maximum from 350 to 360 nm, supporting the fairly extended ICT occurring for this molecule.
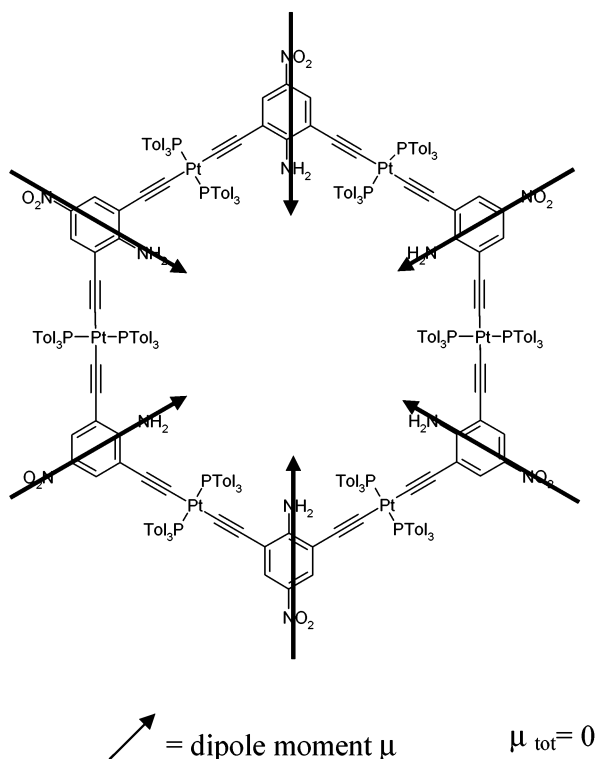
If we look at the geometry of DENA and of the square planar Pt(II) and Pd(II) precursor complexes, the coupling reaction that leads to the formation of rodlike organometallic poly-ynes would produce in this case a six-membered ring with total dipole moment $\mu = 0$ if the *p*-nitroaniline moiety maintains the original conformation, i.e., if no turn around the −C≡C− bonds in *meta* position occurs (Scheme 1).

Looking at the recent literature on analogous systems, cyclic complexes with diethynyl bridging spacers between the square planar metal centers have been recently utilized to construct metallosupramolecular assemblies,[21] and the synthesis of organometallic macrocycles consisting of a nearly planar and symmetric structure composed of metal acetylides has been reported.[22] However, in our case, we can suppose that the total dipole moment would be $\mu \neq 0$ if a free rotation were possible, and a random sequence of the differently oriented nitroaniline might result. In this way an

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(21) (a) Bunz, U. H. F.; Roidl, G.; Altmann, M.; Enkelmann, V.; Shimizu, K. D. *J. Am. Chem. Soc.* **1999**, *121*, 10719. (b) Lee, S. J.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 4554.

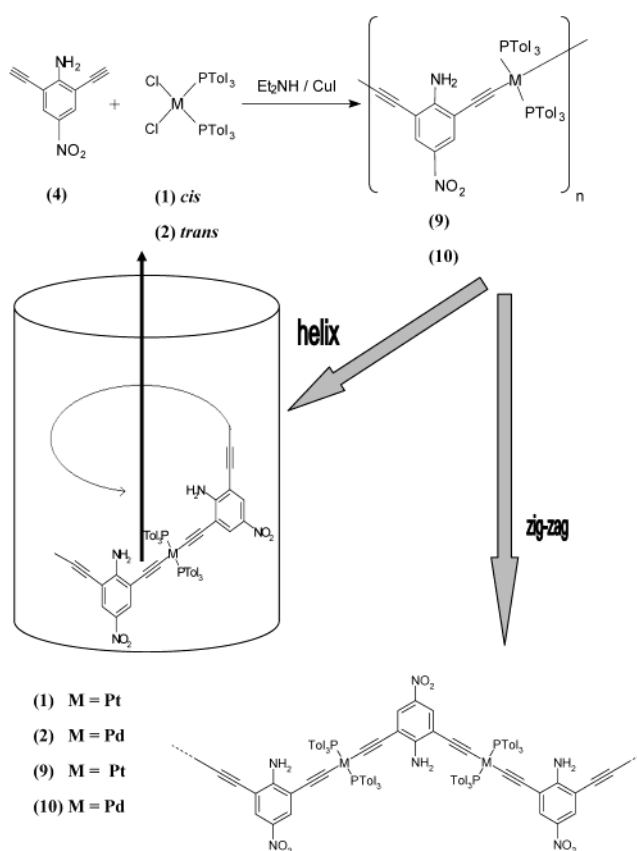(22) Onitsuka, K.; Yamamoto, S.; Takahashi, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 174.

Scheme 1.   Hypothesis of Hexanuclear Hexagonal Structure

$\nearrow$ = dipole moment μ $\mu_{tot} = 0$

Scheme 2.   Helical and Zigzag Structures for Pt(II) and Pd(II) Poly-ynes

(1) M = Pt
(2) M = Pd
(9) M = Pt
(10) M = Pd

asymmetric complex with expected second-order NLO properties would be synthesized. In our case the formation of an organometallic cyclic compound was observed as a side product of the polymerization reaction based on the Pt(II) complex. The structure of the cyclic complex was assessed by X-ray crystal structure, and it will be the subject of a forthcoming paper.[23] If distortion from planarity occurs, a metal poly-yne with helical structure can be formed in analogy with the results reported by Takahashi et al.[24] Otherwise, zigzag polymer structures are likely obtained, as depicted in Scheme 2, in analogy with the structure of organometallic polymers formed by chelate Pt and Pd centers bridging diethynylbiphenyl spacers.[25]

As model molecules of the metal poly-ynes, the dinuclear platinum complexes **7** and **8** were synthesized from DENA and TSET in reaction with the monochloro complex **5**, which shows a *trans* configuration, as determined from the J_{Pt-P} coupling constant (2620 Hz). The synthesis of the dinuclear complexes **7** and **8** follows the pathway reported in Scheme 3, where the chemical structure of the complexes is depicted.

High yields of product **7** (85%) are found. The IR spectrum of **7** shows a band centered at 2101 cm^{-1}, suggesting a loss of symmetry in the dinuclear model complex; the absence of the band at 315 cm^{-1}, present in the far-IR spectrum of the precursor **5**, indicates the performance of the coupling reaction. ^{1}H NMR of **7** exhibits the same pattern as the precursor complex **5** in the range of the phosphine resonances, the resonance of the $-NH_2$ group at $\delta = 3.50$ ppm, and the resonance

of the protons of the nitroaniline ring at 6.58 ppm. The double doublet typical pattern of the ending phenyl ligand is detected at 6.20–6.95 ppm. In the ^{13}C NMR spectrum the resonances of the phosphine and ending phenyl ligands are nearly the same as those of the precursor **5**, and those of the nitroaniline moiety are nearly the same as those of DENA, while a shift toward low field of the resonances of the carbon–carbon triple bonds is found (Table 1), suggesting that the main effect of charge transfer is induced on this moiety of the complex. The ^{31}P NMR spectrum of **7** is characterized by a signal at 17.48 ppm, with two symmetrical signals due to the ^{195}Pt–^{31}P coupling ($J_{Pt-P} = 2600$ Hz), in agreement with a *trans* configuration of the ligands around the Pt atoms.

The reaction leading to complex **8** is performed by producing in situ diethynylthiophene from the silyl derivative TSET, because the protected bisacetylene is stable and easy to handle. The FTIR and NMR characterizations of **8** confirm the proposed structure, which is analogous to the structure of **7** and is deduced also by comparison with the spectroscopic characterizations of related diethynylthiophene Pd complexes and oligomers prepared with two different reaction routes, i.e., dehydrohalogenation and Stille-EOP (extended one pot).[16] The thiophene spacer is recognized from the presence of a singlet at 6.90 ppm in the ^{1}H NMR spectrum and of two resonances at 127.2 and 128.0 ppm in the ^{13}C NMR spectrum; the signals of the carbon atoms linked by triple bonds are not detectable because of the low solubility of the sample. The *trans* configuration of complex **8** is confirmed by the ^{195}Pt–^{31}P

(23) Hursthouse M., private communication.
(24) Takahashi, S.; Onitsuka, K.; Takei, F. *Macromol. Symp.* **2000**, *156*, 69.
(25) Iucci, G.; Infante, G.; Polzonetti, G. *Polymer* **2002**, *43*, 665.

Scheme 3.   Dinuclear Model Molecules
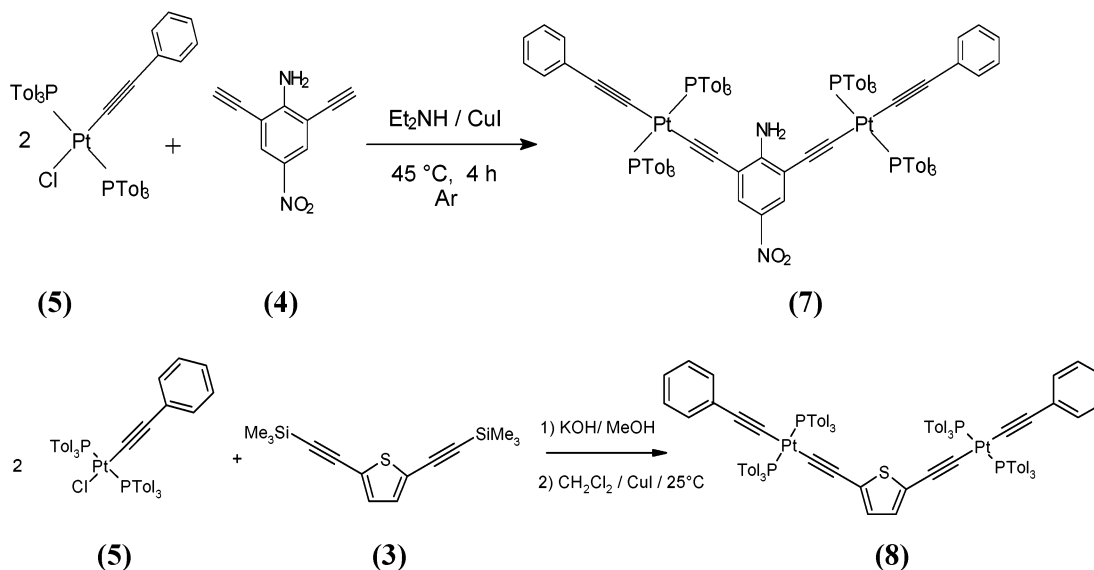
coupling constant J_{Pt-P} = 2605 Hz, in analogy with complex **7** (see Table 1).

The reaction between DENA and complex **1** was performed by the dehydrohalogenation procedure,[26] which leads to the organometallic polymer **9**. The IR spectrum of the polymer shows the signal of the C≡C stretching mode at 2101 cm^{-1}, and it is noteworthy that this signal does not appear in the IR spectrum of DENA, suggesting for polymer **9** a loss of symmetry; moreover, the signal is sharp and this feature is considered to be consistent with a low dispersion of polymer chain lengths, as reported for rigid-rod organometallic platinum-ethynyl polymers containing ferrocenyl phosphine ligands.[27]

The palladium-containing polymer **10** has been obtained under similar reaction conditions (Scheme 2). An excess of PTol$_3$ was added to avoid the release of the phosphine by the Pd centers, which are more reactive than Pt ones and can form new bonds with the unsaturated carbon–carbon bonds or with the amino groups, as reported in the case of poly(monosubstituted)acetylenes.[28] In the synthesis of **10** it was found that the optimum ratio between the free phosphine and CuI, used as catalyst, is 1:4; these reaction conditions lead to the organometallic polymer **10**, avoiding side reactions with the chain backbone or with the functional groups of DENA.

In general, palladium-containing polymers are less stable than the analogous platinum polymers. In fact, a decomposition may occur on a chromatographic column; however, the crude reaction product, which gave nonsatisfactory elemental analyses, was purified by using flash chromatography performed in mild conditions. The FTIR spectrum of **10** is quite similar to that of **9**, suggesting the same structure for both polymers, apart from the nature of the transition metal.

The molecular weights of polymers **9** and **10**, 14.600 and 6000 amu, respectively, as determined by GPC

measurements, indicate that the number of repeat units is probably underestimated, according to previous reports for rodlike organonickel polymers[29] and recent studies on Pt(II) poly-ynes.[30]

Interesting features are observed in the ^{1}H NMR spectra. The resonances of the amine hydrogens, found at 5.51 ppm in DENA, are shifted in the range 3.40–3.65 ppm upon coordination to the metal center in polymers **9** and **10**. The univocal assignment of the NH$_2$ signal has been performed by the exchange reaction with increasing amounts of D$_2$O, which showed the decrease of the resonance at about 3.5 ppm. The time of the exchange was low for the polymer solutions, probably due to the base characteristic of the NH$_2$ group. Moreover, this result supports the hypothesis of a helical structure for both the polymers, because of the difficult access of the water molecules to the hindered NH$_2$ group. The resonances of the two hydrogens of the *p*-nitroaniline moiety are found in the range 6.60–7.28 ppm (8.21 ppm in DENA) and are low-field shifted. The resonances of the PTol$_3$ ligand are not affected by coordination in long polymer chains and show almost the same chemical shift value (7.00–7.61 ppm), with a pattern quite similar to those of the model complex **7**.

The Pt and Pd organometallic polymers show analogous features in the ^{13}C NMR spectra. The resonances of the C≡C atoms are found at about 107 and 124 ppm, and those of the *p*-nitroaniline ring are nearly coincident in the range 110–153 ppm and close to those of the monomer DENA, indicating the negligible influence of the different transition metals on the polymer chemical structure.

Two resonances are detected in the ^{31}P NMR spectrum of **9**, at 17.62 and 20.38 ppm, corresponding to internal and terminal Pt centers, respectively. The ^{195}Pt–^{31}P coupling constant J_{Pt-P} = 2605 Hz indicates a *trans* configuration of the ligands around the Pt centers. The ^{31}P NMR spectrum of **10** shows only one

(26) Sonogashira, K. *J. Organomet. Chem.* **2002**, *65*, 46.
(27) Long, N. J.; White, A. J. P.; Williams, D. J.; Younus, M. *J. Organomet. Chem.* **2002**, *649*, 94.
(28) Russo, M. V.; Furlani, A.; Altamura, P.; Fratoddi, I.; Polzonetti, G. *Polymer* **1997**, *38*, 3677.

(29) Guo, X. A.; Sture, K. C.; Hunter, A. D.; Williams, M. C. *Macromolecules* **1994**, *27*, 7825.
(30) Fratoddi, I.; Battocchio, C.; Furlani, A.; Mataloni, P.; Polzonetti, G.; Russo, M. V. *J. Organomet. Chem.* **2003**, *674*, 10.
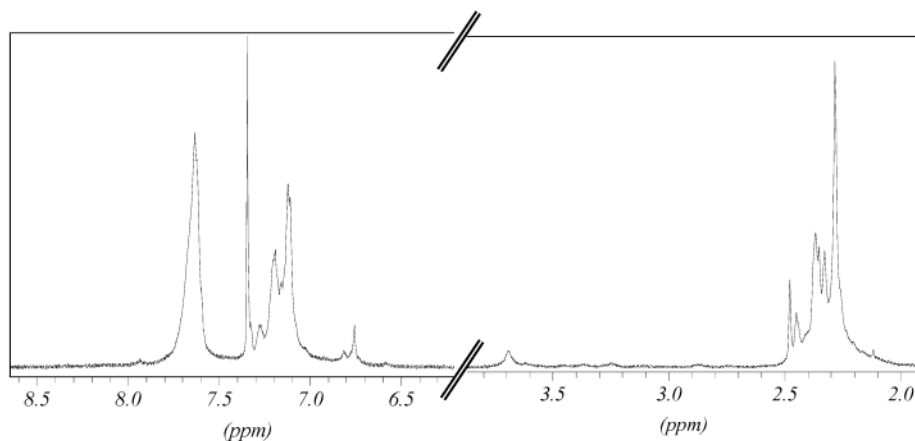
Figure 1. ¹H NMR of compound **10**.

signal at 25.70 ppm, indicating that a polymer with relatively high molecular weight was obtained.

With the aim of achieving a deeper insight into the chemical structure of our organometallic polymers, COSY and NOESY NMR investigations have been performed. COSY spectra do not exhibit scalar correlations, except for the expected ones between *ortho* aromatic protons. NOESY spectra give more interesting information. Dipolar correlations between *ortho* aromatic protons (7.18:7.65; 7.35:6.95, and 7.50:7.10 ppm) and between aromatic and aliphatic protons in polymer **10** (2.30:7.20; 2.30:7.60 ppm) are clearly detected as shown in Figure 1 and in Figure 2.

These latter correlations look less intense for polymer **9** than those found for polymer **10** and suggest that the aromatic and aliphatic protons are more far away in polymer **9**. Moreover, in both polymers dipolar correlations are found for NH_2 (3.65 ppm) and aromatic protons of phosphine (7.20 and 7.60 ppm), with a higher intensity for the signal at 7.60 ppm, indicating a close spatial proximity, confirmed on the basis of simple geometrical models and in analogy with literature reports on pyrimidine-dicarbaldeyde-based polymers.[31] Further information on the polymer structure can be deduced from the NOESY spectra, which suggest a chain entanglement that may be due either to helical structure or to interchain stacking. To elucidate this aspect, NMR spectra have been recorded for samples at different concentrations; no modification of the spectral features either in chemical shift or in peak intensity was detected, and thus the interchain correlations can be ruled out. Considering the steric hindrance of the phosphine ligands and simple molecular models based on the structure of Pt(II) and Pd(II) square planar complexes, which show little distortions from planarity, it can be deduced that the observed interactions are due to phosphine groups bound to metallic centers probably arranged in a helical configuration.

Thermogravimetric (TG) and differential thermal analyses (DTA) were carried out on the organometallic polymers, to investigate the range of stability in air of the metal poly-ynes, in view of their applications in NLO devices.

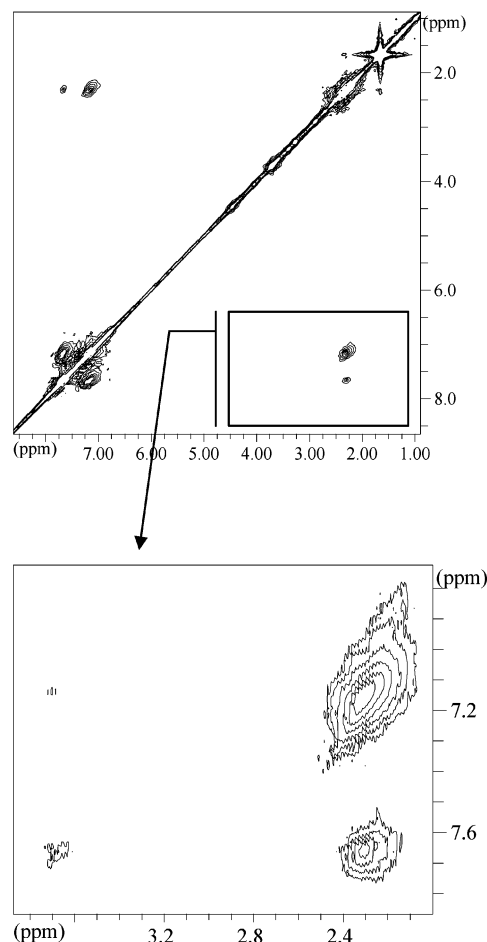The precursor monomer **4** was also investigated as a comparison. The TG and DTA curves of DENA (**4**) show

(31) Schmitt, J. L.; Stadler A. M.; Kyritsakas N.; Lehn J. M. *Helv. Chim. Acta* **2003**, *86* 1598.

Figure 2. NOESY spectrum of compound **10** and in the inset a magnification of the correlations.

that at the decomposition temperature (227 ± 3 °C) an exothermic explosive reaction occurs with a weight loss of about 50%. The total combustion occurs at higher temperature, and a total weight loss is achieved at about 600 °C. The TG and DTA curves of polymer **9** indicate that the polymer is stable until about 267 ± 3 °C, with a negligible weight loss probably due to some solvent. The following weight loss (34%) occurs with exothermic reactions up to 500 °C, and further decomposition occurs up to 800 °C (weight loss 10%). Over 800 °C the residue is about 55%, due to the presence of the metal atoms of the starting material. The TG and DTA curves of

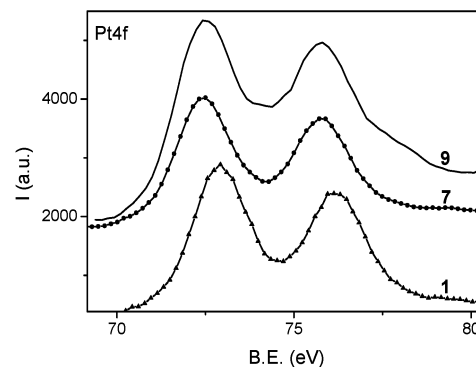**Table 2. Optical Absorption and Emission Properties of Compounds of Model Molecules and Metal-Polyynes**

sample	absorption		emission	
	λ_{max} (nm)	ϵ_0 (L mol cm^1)	λ_{max} (nm)	η (%)
4	350	9200	484	0.04
5	313	15 875	365	
6	348	26 600	413	
7	360	41 335	410−505	
9	360	25 000	520	0.02
	390	18 800	520	
	420	10 900	520	
10	330	9810	520	0.02
	390	7975	520	
	420	6380	520	

Figure 3. Pt 4f core level spectra of compounds **1**, **7**, and **9**.

polymer **10** showed a lower thermal stability in comparison with polymer **9**, with a first loss of weight (8%) at 210 ± 3 °C, exothermic peak. The total combustion leaves about 45% of material, probably the transition metal oxide. These experimental data are in agreement with the expected behavior of Pd-containing polymers compared with those containing Pt; a higher stability is achieved when DENA is bonded between two Pt atoms in the polymer chain.

Absorption and emission spectra of the organometallic polymers **9** and **10** have been recorded in order to investigate the influence of the metal centers on the position of absorption and emission. The results are collected in Table 2. The UV−vis spectra of the polymers show broad absorptions at higher wavelength in comparison with DENA, with a new tail band at about 420 nm. The maximum of absorption shifts from $\lambda = 350$ to $\lambda = 360$ and to $\lambda = 390$ nm on going from the monomer DENA to the Pt dinuclear complex **7** and to polymers **9** and **10**, respectively, indicating some enhancement of effective conjugation through the metal centers by increasing the chain length; the data concerning complexes **5** and **6,** reported in Table 2 as a comparison, support this statement. It is noteworthy that the values of the absorption maxima of **9** and **10** are quite similar, as well as the quantum yields (0.02), thus suggesting that the emission peaks are not due to d−d transitions of the metal, but related to the chemical nature of the organic spacer.

The positions of the luminescence maxima are shifted with respect to the absorption maxima, but there is however an overlap between the absorption and the emission spectra, which probably is the reason for the

low light emission efficiency of the investigated polymers, despite their π-conjugation characteristics.

XPS Investigations. The chemical and electronic structure of the organometallic polymers **9** and **10** was further investigated by means of XPS. As a comparison and aid for the assessment of the polymer structure, XPS measurements were performed on the precursor **4** and related model molecule **7**. The C 1s, Pt 4f, Pd 3d, P 2p, Cl 2p, and N 1s core level spectra were acquired, and a summary of the core level BE and fwhm (full width at half-maximum) values is reported in Table 3.

The C 1s spectra for all our samples exhibit one main feature positioned at 284.7 eV on the BE scale assigned to aromatic carbons (phosphine and DENA). For the polymer samples the C 1s contribution at lower BE values is more evident (i.e., about 283.5 eV) due to the C−M carbons (M = Pd, Pt), and shake-up features, due to π−π* transitions associated with the aromatic moiety, occur at nearly 7 eV higher energy from the main line for all the samples. The P 2p spectra show binding energy values in the range 131.1−131.6 eV, consistent with those measured for metal-bonded phosphine groups, in agreement with the values reported in the literature.[32]

The Pt 4f spectra shown in Figure 3 have been informative on the effect of the conjugation leading to charge distribution in the organometallic system. Comparison between the BE values of Pt 4f$_{7/2}$ core level spin−orbit component, measured for the inorganic precursor complex *cis*-[Pt(PTol$_3$)Cl$_2$] (**1**), the model complex **7**, and the polymer **9**, shows values of 72.9, 72.4, and 72.5 eV, respectively.

Table 3. XPS Data Collection of Spectroscopic Data for Compounds 1, 2, 4, 7, 9, 10, and *p*-Nitroaniline

sample	C 1s BE (fwhm) (eV)	Pd 3d$_{5/2}$ BE (fwhm) (eV)	Pt 4f$_{7/2}$ BE (fwhm) (eV))	P 2p$_{3/2}$ BE (fwhm) (eV)	Cl 2p$_{3/2}$ BE (fwhm) (eV)	N 1s BE (fwhm) (eV)
1	284.7 (2.0)		72.9 (1.8)	131.6 (2.0)	197.8 (2.0)	
2	284.7 (1.7)	337.8 (1.7)		131.3 (1.9)	197.9 (1.8)	
p-nitroaniline^b	284.7					399.4 (−NH$_2$)
						405.0 (−NO$_2$)
						406.9 (NO$_2$ shake up)
4^a	284.7(2.4)					399.3 (2.0) (−NH$_2$)
						405.5 (2.0) (−NO$_2$)
7	284.7 (1.8)		72.4 (1.9)	131.4 (1.9)		399.7 (2.8) (−NH$_2$)
						405.1 (4.8) (−NO$_2$)
9	284.7 (1.9)		72.47 (2.0)	131.3 (1.8)	198.3^c (2.0)	399.6 (3.2) (−NH$_2$)
						406.1 (4.8) (−NO$_2$)
10	284.7 (1.9)	337.9 (1.8)		131.1 (2.0)	198.0^c (2.0)	399.4 (2.2) (−NH$_2$)
						406.0 (4.2) (−NO$_2$)

^{a} Decomposes under X-rays, measurements performed at −95 °C. ^{b} Data from literature, referred to solid-state measurements (ref 33). ^{c} Ending groups.
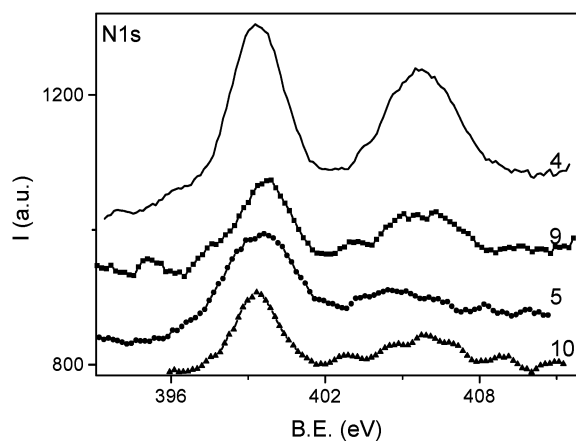
Figure 4. N 1s core level spectra of compounds **4**, **5**, **9**, and **10**.

The observed trend is indicative of a limited increase of the charge at the Pt atoms on changing from the complex to the polymer, correlated to a delocalized distribution through the organic spacer. In the effective conjugation length of the rodlike molecules the metal center is involved in the conjugation through the organo-metallic system (d and p atomic orbitals of the metal and π electrons of the organic spacer), although this effect seems to occur in this case to a lesser extent in comparison with other reported macromolecules[30] that have a rodlike structure.

As for the palladium-containing molecules, we have analyzed the polymer **10** and the *trans*-[Pd(PTol$_3$)Cl$_2$] (**2**) complex, and the Pd 3d BE measured values show strong similarity, being 337.8 and 337.9 eV, respectively. The observed trend differs from that of the already discussed Pt systems; the electronic communication that should occur through the polymeric system seems to be confined on the organic spacer. Probably the push−pull substituents of the nitroaniline moiety provoke a dipole moment that opposes the charge flow along the organo-metallic chain, and this effect is more evident in the case of Pd polymer **10**.

The N 1s spectra of the investigated samples exhibit interesting features related to the chemical structure of the polymers and are shown in Figure 4.

DENA (**4**), which can be considered the building block of the polymer backbone, gives a N 1s spectrum with two mains features, whose BE values are found at 399.3 eV (NH$_2$ group) and 405.5 eV (NO$_2$ group). Ågren et al.[33] investigated *para*-nitroaniline in the solid state and reported values of 399.4 eV for the amino (NH$_2$), 405.0 eV for the nitro (NO$_2$) groups, and 406.9 eV for the shake-up features. Our results are in good agreement with these data, but considering that the N 1s doublet of NO$_2$ is not resolved, we probably overestimate the band position for NO$_2$ and attribute this effect also to a small charge perturbation induced by the triple bond toward the NO$_2$ group.

As the DENA molecule undergoes insertion between metal complexes, some charge variation at the nitrogens occurs. The XPS spectrum of the dinuclear complex **7**

shows the N 1s BE value of NH$_2$ 0.5 eV higher than that of DENA, while an opposite trend on the NO$_2$ group gives rise to a decrease of the N 1s BE value from 405.5 to 405.1 eV. These data should be considered together with the changes detected at the platinum site of complex **1** compared with the dinuclear system **7** (see Table 3); a BE decrease of Pt 4f from 72.9 to 72.4 eV is indicative of charge density increase at the metal. Overall, the charge flows through the system toward the metal, affecting both the metal center and the substituents of the organic spacer, becoming more positively charged (NH$_2$) and more negatively charged (NO$_2$) (Figure 4). As far as the polymers are concerned, considering the platinum-containing system **9** we detect no variations for the nitrogen of the NH$_2$ group, while the nitro group gives a BE value (406.1 eV) that is higher than that of sample **7**; the BE value found for platinum shows nearly the same value observed for the dinuclear sample. Completely similar N 1s BE values are measured for the palladium-containing polymer **9** (see Table 3), and the Pd 3d$_{5/2}$ core level does not show any significant variation compared with the precursor complex **2**. These data suggest that for both polymers the variations at the organic spacer substituents are nearly the same. However, there is evidence for a relatively small charge perturbation on the platinum site (Table 3, Figure 3); the role of the different transi-tion metals seems to be detectable, although not dra-matic. It is noteworthy to point out that there is still a disagreement in the scientific community on whether the transition metals favor or inhibit the charge flow through conjugated bridges, and this topic needs further studies. Photoelectron spectroscopy measurements pro-vided information for the characterization of terminal groups in polymers **9** and **10**, which, according to GPC measurements, have chain lengths corresponding to about 8−16 repeat units. The analysis of the Cl 2p spectra identified the presence of chlorine ending groups. The Cl 2p BE values of the polymers are quite similar, consistent with chlorine bonded to a metal atom, since almost the same values are found for the precursor Pt and Pd complexes reported in Table 3.

The XPS data provided results in good agreement with the molecular structures suggested by other tech-niques used for the chemical characterization and evidenced the difference in charge distribution depend-ing on the nature of the transition metal bound to the same organic spacer, despite the expected same extent of electron delocalization.

Conclusions

Organometallic polymers containing Pt and Pd cen-ters in a square planar configuration linked through 2,6-diethynyl-4-nitroaniline bridging units, namely, Pt-DENA and Pd-DENA, were synthesized by the building block approach. The polymer structure is a sequence of organic spacers bound to metal centers, likely arranged in a helical configuration, with chain length correspond-ing to about 16 repeat units in the case of Pt-DENA and about 8 repeat units in the case of Pd-DENA. The polymer structure, which could be elucidated by means of accurate NMR studies, allows only a moderate charge delocalization through the metal centers along the chain, as determined by means of optical and photo-

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electron spectroscopy studies. Model dinuclear Pt complexes were prepared and characterized, with the aim of comparing the spectral features with those of the polymers. The results confirm that the repeat unit of the organometallic macromolecules has the same structure as the dinuclear complex.

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