

Synthesis of highly ethynylated mono and dinuclear Pt(II) tethers bearing the 4,4'-bis(ethynyl)biphenyl (debp) unit as central core

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Abstract

Mono and bisubstituted bis(ethynyl)biphenyl Pt(II) complexes, i.e. *trans*-[(R-C≡C-)Pt(PPh₃)₂-(C≡C-*p*-C₆H₄-*p*-C₆H₄-C≡C-H)], R = *p*-NO₂C₆H₄ (**3b**), (η⁵-C₅H₅)Fe(η⁵-C₅H₄) (**3c**), and *trans*-[(R-C≡C-)Pt(PPh₃)₂-(C≡C-*p*-C₆H₄-*p*-C₆H₄-C≡C-)Pt-(PPh₃)₂-(C≡C-R)], R = C₆H₅ (**4a**), *p*-NO₂C₆H₄ (**4b**), (η⁵-C₅H₅)Fe(η⁵-C₅H₄) (**4c**), have been synthesized by the dehydrohalogenation reaction from the appropriate Pt monochloro acetylides *trans*-[(R-C≡C-)Pt(PPh₃)₂Cl], R = C₆H₅ (**1a**), R = *p*-NO₂C₆H₄ (**1b**), R = (η⁵-C₅H₄)Fe(η⁵-C₅H₅) (**1c**) and HC≡C-*p*-C₆H₅-*p*-C₆H₅-C≡CH, (4,4'-bis-ethynylbiphenyl), (DEBP) (**2**). In order to make possible a direct evaluation of the role of Pt centers on the properties of these highly ethynylated complexes, the corresponding species without Pt were prepared, i.e. C₆H₅-C≡C-C≡C-C₆H₄-C₆H₄-C≡C-C≡C-C₆H₅, (4,4'-(bis-phenylethynyl)-diethynylbiphenyl) (**7**), and (η⁵-C₅H₅)Fe(η⁵-C₅H₄)-(C≡C-C≡C-C₆H₄-C₆H₄-C≡C-C≡C)-(η⁵-C₅H₄)Fe(η⁵-C₅H₅), (4,4'-(bis-ferrocenylethynyl)-diethynylbiphenyl) (**8**). Preparation of the latter compounds was only achieved by the use of the palladium catalyzed Stille coupling reaction, since the dehydrohalogenation route afforded only homocoupled and polymeric products. The electron-donor or electron-withdrawing ligands coordinated to Pt were chosen for the purpose of tuning the optical properties of the complexes through the different charge distribution along the π-electron conjugation. Characteristic spectroscopic features (UV-vis, FT-IR and NMR) of these complexes are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

A great deal of interest has grown recently in the scientific community, towards organometallic oligomers and polymers in which transition metals are bound to organic spacers [1]. Since the pioneering work of Hagi-hara's group [2] who developed the dehydrohalogenation reaction pathway, an alternative reaction route proposed by Lewis and co-workers [3], based on bis-SnMe₃ derivatives of dialkynes, has been widely used for the synthesis of mono- and poly-nuclear σ-bonded acetylides. These materials show a wide domain of properties useful for application in modern technology. For example Pt-containing poly-ynes exhibit promising

photoluminescence, optical and photoinduced absorption effects, which can be successfully used in light emitting diodes (LEDs) [4]. Similar organometallic polymers containing group 10 transition metals, with a rigid rod conjugated backbone, show interesting properties of alignment in a magnetic and electrical field [5], fast and reproducible response to relative humidity variations in SAW (surface acoustic wave) sensors [6], and molecular orientation even when spin deposited in thick layers [7]. Moreover Group 10 metal alkynyls and related polymers have been studied in view of their second- and third-order non-linear optical (NLO) properties, which depend on the transition metal, on the organic ligand, on the spacer in the polymer chain and on the symmetry of the molecules [8].

Within this frame, it is interesting the study of organometallic oligomers and complexes, which can be considered the molecular models and the building blocks of long chain organometallic polymers.

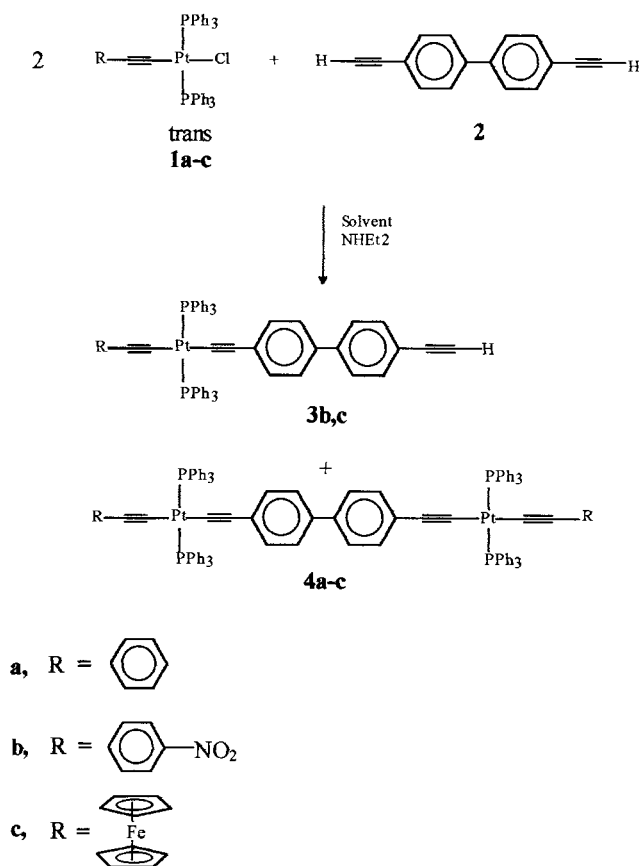
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A good deal of excellent research has been performed on this topic. Mixed-metal oligomers and complexes containing Ru and Pd, Fe and Pd, Fe and Ru, Pt and Ru, Os and Ru coordination centers linked by unsaturated carbon-rich bridges have been synthesized, and their electron communication between the metal centers was recently investigated [9]. Bimetallic complexes show intramolecular electronic communication through the metal centers that can act as electron donors or acceptors depending on the nature of the redox active transition metal and on the organic bridge connecting the terminal organometallic fragments [9b,c]. Heterobimetallic complexes containing ferrocenyl ligands as typical donor fragments and $M(\text{CO})_5$ ($M = \text{Cr}, \text{Mo}, \text{W}$) as electron accepting moiety have been recently synthesized, and they exhibit higher first hyperpolarizability β values [10], compared to those reported for other organometallic based materials. A wide series of homo-, bi- and poly-nuclear σ -acetylide complexes with $\text{Fe}(\text{dppe})\text{Cp}^*$ and $\text{Fe}(\text{CO})_2\text{Cp}^*$ linked to π -electron delocalized carbon bridges, have been prepared and characterized by Lapinte and coworkers [11]; investigation of the redox processes involving metal-acetylide complexes indicate a significant electronic communication between the metal centers [11b,c]. The synthesis and electrochemistry of dinuclear metal (Fe, Ru, Os) σ -

acetylide and allenylidenes has been recently investigated by Friend and co-workers [12], who present evidence for the presence of mixed valence species and elucidate the presence of quinoid structure with the aid of theoretical calculations. Homo and hetero-dinuclear acetylene and (*Z*)-1,3-enyne bridged bis(cyclopentadienyl) metal complexes, where the transition metals are Fe, W, Mo, Mn, and Re have been prepared, in the framework of an extensive project, using the palladium-catalyzed coupling reaction (Stille reaction) between organic electrophiles and organostannanes [13]. Recently this synthetic procedure has been also extended to the coupling of metal halides and alkynylstannanes, allowing an easy access to metal acetylides (homo and heterobimetallic) with the acetylenic moiety σ -bound to the metals [14].

In this paper we describe the procedures which allow the formation of model molecules with π -electron conjugation extended through ethynyl bonds of organometallic and pure organic highly ethynylated molecules. The presence of electron-donor or electron-withdrawing ligands linked to Pt(II) are expected to produce a tuning of the NLO properties of these materials, which are representative building blocks of highly ethynylated organometallic polymers with promising NLO response, that is one of the ultimate goals for advanced materials.



Scheme 1.

2. Results and discussion

The feasibility of obtaining Pt-acetylene σ -bonds is well known, and allowed us to prepare some model molecules for the polymeric materials which have been already studied [6,7] and for organometallic polymers whose synthesis is in progress. The synthetic procedures proposed here are suitable for the preparation of asymmetric Pt-bisacetylides [15], starting from monochloroacetylides [16]. The reactivity of monochloroacetylides requires mild and easy reaction conditions, but it is not trivial; in fact it depends on the *trans* influence of the acetylenic ligand σ -bonded to Pt(II) [16b]. The preparation of Pt(II) acetylides linking electron-donor or electron-withdrawing ligands was performed by the dehydrohalogenation reaction of the corresponding $[(\text{R}-\text{C}\equiv\text{C}-)\text{Pt}(\text{PPh}_3)_2\text{Cl}]$ complexes ($\mathbf{1a-c}$) and DEBP ($\mathbf{2}$) (Scheme 1).

General conditions to perform the dehydrohalogenation reaction are similar to those reported earlier [2,3a], that is the use of CuI as the catalyst and NHEt₂ as the base; however some modifications have been introduced for the purpose of obtaining better yields. The presence of organic solvents (CHCl_3 , $\text{C}_6\text{H}_5\text{CH}_3$) allows the solubility of the monochloroacetylides in the reaction medium. With the purpose of forming the disubstituted DEBP derivatives $\mathbf{4a-c}$, we initially tried the reaction

Table 1

Compound	UV-vis λ_{\max} (nm)	FT-IR (cm^{-1})
<i>trans</i> -[Pt(PPh ₃) ₂ (-C≡C-C ₆ H ₄ NO ₂)(-C≡C- <i>p</i> -C ₆ H ₄ - <i>p</i> -C ₆ H ₄ -C≡C-H)] (3b)	388	3266 ($\nu_{\text{H-C-C}}$) 2105 ($\nu_{\text{C=C}}$)
<i>trans</i> -[Pt(PPh ₃) ₂ (-C≡C-Fc)(-C≡C- <i>p</i> -C ₆ H ₄ - <i>p</i> -C ₆ H ₄ -C≡C-H)] (3c) ^a	351	3276 ($\nu_{\text{H-C-C}}$) 2109 ($\nu_{\text{C=C}}$)
<i>trans-trans</i> -[(PPh ₃) ₂ (Ph-C≡C-)Pt-C≡C- <i>p</i> -C ₆ H ₄ - <i>p</i> -C ₆ H ₄ -C≡C-Pt(-C≡C-Ph) (PPh ₃) ₂] (4a)	373	2112 ($\nu_{\text{C=C}}$)
<i>trans-trans</i> -[(PPh ₃) ₂ (<i>p</i> -NO ₂ -C ₆ H ₄ -C≡C-)Pt-C≡C- <i>p</i> -C ₆ H ₄ - <i>p</i> -C ₆ H ₄ -C≡C-Pt(-C≡C-C ₆ H ₄ - <i>p</i> -NO ₂)(PPh ₃) ₂] (4b)	397	2105 ($\nu_{\text{C=C}}$)
<i>trans-trans</i> -[(PPh ₃) ₂ (Fc-C≡C-)Pt-C≡C- <i>p</i> -C ₆ H ₄ - <i>p</i> -C ₆ H ₄ -C≡C-Pt(-C≡C-Fc)(PPh ₃) ₂] (4c) ^a	380	2115 ($\nu_{\text{C=C}}$)
Ph-C≡C-C≡C- <i>p</i> -C ₆ H ₄ - <i>p</i> -C ₆ H ₄ -C≡C-C≡C-Ph (7)	350	2213 ($\nu_{\text{C=C}}$) 2191 ($\nu_{\text{C=C}}$)
Fc-C≡C-C≡C- <i>p</i> -C ₆ H ₄ - <i>p</i> -C ₆ H ₄ -C≡C-C≡C-Fc (8) ^a	337	2141 ($\nu_{\text{C=C}}$)

^a Fc = (η^5 -C₅H₄)Fe(η^5 -C₅H₅).

between the Pt-monochloroacetylides **1a–c** and DEBP (**2**) in the molar ratio 2:1. Surprisingly, under these conditions only **1a** straightforwardly afforded the corresponding dinuclear derivative **4a**, while in the reaction of complexes **1b** and **1c** with **2** in the 2:1 stoichiometric ratio, formation of the dinuclear derivatives **4b** and **4c** was always accompanied by formation of a variable amount of the mononuclear complexes **3b** and **3c**.

Since mononuclear DEBP derivatives **3b–c** represent interesting intermediates which could be used to prepare more elaborate metallaacetylide oligomers, conditions that could favor their formation were searched. For this purpose the stoichiometric ratio between Pt-monochloroacetylides **1a–c** and DEBP was first reverted to 1:1 and then to 1:2. However, despite these modifications the reaction of **1a** and **2**, independently from the stoichiometric ratio between the reactants, always afforded the sole dinuclear derivative **4a**, while only using the most unbalanced stoichiometric ratio 1:6 and 1:2 between the Pt monochloroacetylides **1b** and **1c** versus DEBP, respectively, it was possible to orient the reaction toward the prevalent formation of **3b** and **3c**. Trying to order these results in a rationale, we can suppose that formation of the dinuclear derivatives **4a–c** is occurring through the previous formation of the mononuclear derivatives **3a–c**. Then in the case of **1a**, following the first attack of the Pt-monochloroacetylide on DEBP, the mononuclear complex **3a** is much more reactive toward the remaining Pt-monochloroacetylide **1a** than the unreacted DEBP, thus formation of dinuclear derivative **4a** is always preferred. On the contrary, in the case of **1b** and **1c**, the reactivity of unreacted DEBP can compete with the intermediates **3b** and **3c** versus the remaining monochloroacetylides **1b–c**; thus with the help of a favorable stoichiometry, an appreciable amount of the mononuclear derivatives **3b–c** can be obtained.

2.1. Mono substituted organometallic DEBP derivatives

The FT-IR spectra of the asymmetric (bis)acetylides, *trans*-[(*p*-NO₂C₆H₄-C≡C)Pt(PPh₃)₂(C≡C-*p*-C₆H₄-*p*-C₆H₄-C≡C-H)] (**3b**) and *trans*-[(Fc-C≡C)Pt(PPh₃)₂(C≡C-*p*-C₆H₄-*p*-C₆H₄-C≡C-H)] (**3c**) (Table 1) show sharp signals at 3266 and 3276 cm^{-1} , respectively, due to $\equiv\text{C-H}$ stretching of the DEBP ligand and at 2105 and 2109 cm^{-1} , attributed to C≡C stretching vibration; no bands at 540 cm^{-1} appear, suggesting a *trans* structure of the complexes by comparison with literature reports [16b][17].

UV spectra in CHCl₃ of **3b** show three absorption maxima at 314, 345 and 388 nm, this last one the more intense, while **3c** shows a single broad absorption at 351 nm. It is worth noting the comparison of values of the UV maximum observed for compounds **3b** and **3c** and those of compounds **4a** and **4c** (vide infra), with those of the corresponding constituting units, *p*-nitrophenylacetylene ($\lambda_{\max} = 289$ nm), ethynylferrocene ($\lambda_{\max} = 262$ nm) and DEBP ($\lambda_{\max} = 290$ nm). The strong variations of the UV shift observed when the constituting units are joined to form the metallaacetylide assembly, is accounting for the larger π delocalization probably occurring through the p orbitals of Pt. Nowadays there is still a large debate ongoing in the scientific community on whether electron mobility may be promoted or inhibited when a transition metal is bound into a poly-yne backbone. Molecular calculations of the extended Hückel type performed on metal (Fe, Rh, Pt) oligo-yne polymers indicate that Pt containing molecules, with a square planar configuration around the metal, present a larger conduction bandwidth than the molecules where the metal is in octahedral configuration [18]. However, electrochemical studies performed on heterotrimetallic Ru/Pd/Ru and Fe/Pd/Fe complexes connected by -C≡C-C₆H₄-C≡C- bridges, indicate that the insertion of the palladium moiety inhibits

the communication between the two ruthenium centers [19], while analogous measurements made on a Ru/Pt/Ru trinuclear mixed metal complex showed that the platinum moiety transfers electron density to the ruthenium center [9d]. Our results seem to suggest that there is at least a fairly good electronic communication flowing through the platinum centers and the organic spacer.

2.2. Disubstituted organometallic DEBP derivatives

The binuclear complex *trans-trans*-[(Ph-C≡C)Pt(PPh₃)₂(C≡C-*p*-C₆H₄-*p*-C₆H₄-C≡C)Pt(PPh₃)₂(C≡C-Ph)] (**4a**) has been obtained in good yield (80%) by the general reaction route described in Scheme 1. An alternative approach based on the condensation of **1a** and 4,4'-bis(trimethyltin)ethynylbiphenyl (**11**) gave a lower yield (54%) (vide infra). Using the dehydrohalogenation route, the corresponding mononuclear (bis)acetylide [(Ph-C≡C)Pt(PPh₃)₂(C≡C-*p*-C₆H₄-*p*-C₆H₄-C≡C-H)] (**3a**) was never found in the reaction mixture. The FT-IR spectrum of complex **4a** shows no bands in the range 3200–3300 cm⁻¹, characteristic of ≡C–H stretching vibration, thus confirming that the DEBP spacer is capped by two Pt moieties via σ bonds. The ν_{C≡C} stretching mode appears at 2112 cm⁻¹ as a sharp single band. The absorption at 540 cm⁻¹ (overtone of the deformation mode of P–C bonds in the PPh₃ ligands for *cis* square planar complexes) is absent, as well as bands around 320 cm⁻¹, due to Pt–Cl stretching vibrations. The UV spectrum shows an absorption band at 373 nm, close to the values found for mixed metal acetylide complexes with Pt and Ru centers bridged by (bis)ethynylbenzene, attributed to charge transfer transitions, i.e. ligand–metal charge transfer (LMCT) for Pt moiety and metal–ligand (MLCT) for Ru moiety [9d].

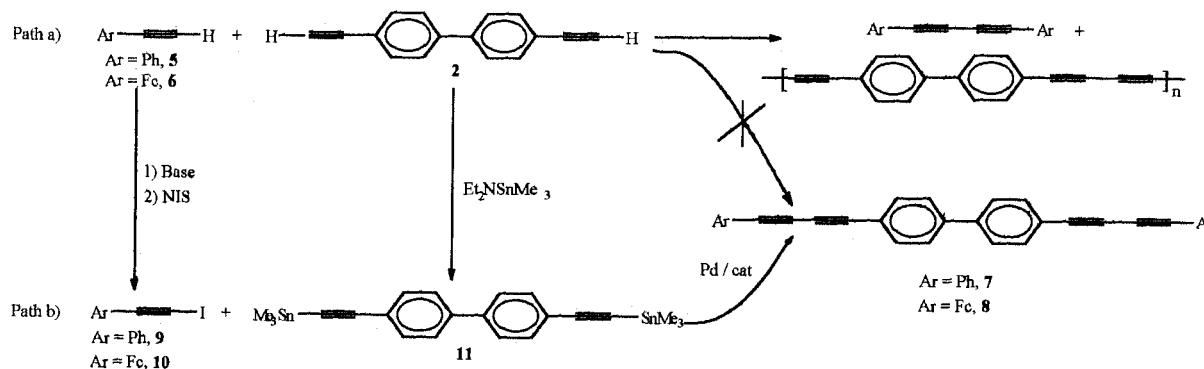
The binuclear complex *trans-trans*-[(*p*-NO₂-C₆H₄-C≡C)Pt(PPh₃)₂(C≡C-*p*-C₆H₄-*p*-C₆H₄-C≡C)Pt(PPh₃)₂(C≡C-C₆H₄-*p*-NO₂)] (**4b**), containing two electron withdrawing groups, is obtained in basic conditions, without the use of CuI, in a mixture containing the mononuclear (bis)acetylide **3b** as a minor product when the reactants are in 1:1 stoichiometric ratio; we surprisingly found that, running the reaction in the absence of CuI, the reaction is slower, but the yield is not affected and the reaction is much cleaner. The pattern of the FT-IR spectrum is quite similar to that of the complex **3b**, apart from the absence of the band at 3266 cm⁻¹ (ν_{≡C-H}); this results indicates that the DEBP moiety is bridge-linked to the two Pt atoms. The *trans* structure is again confirmed by the absence of the band at 540 cm⁻¹. In the optical spectrum of **4b** an absorption maximum at 398 nm is found indicating an enhancement of π conjugation in comparison with **3b** (λ_{max} = 388 nm). The tetranuclear complex *trans-trans*-[(Fc-C≡C)Pt(PPh₃)₂(C≡C-*p*-C₆H₄-*p*-C₆H₄-C≡C)-

Pt(PPh₃)₂(C≡C-Fc)] (**4c**), which contains the electron-donor ethynylferrocene (Fc) groups at the terminal ends of the molecule, has been prepared in view of the expected opposite behavior in charge transfer activity in comparison with **4b**. The FT-IR spectrum of complex **4c** shows a strong ν_{C≡C} at 2115 cm⁻¹, no bands in the range 3300–3200 cm⁻¹ (≡C–H stretching mode) and no bands at 540 and 320 cm⁻¹. Since the FT-IR spectra of **4c** and **3c** are exactly the same apart from the ν_{≡C-H} stretching, the two molecules must be quite similar in their coordination around Pt. These results are in agreement with the proposed *trans* structure, with no Pt–Cl bonds and no free acetylenic hydrogens. The UV spectrum of **4c** exhibits a broad maximum absorption band at 379 nm, which again suggests an increase of conjugation and electronic interaction between metal centers with respect to the related asymmetric bis-acetylide **3c** (λ_{max} = 351 nm), thus confirming the role of Pt centers in the increase of electron density in the conjugated system (compare also the UV absorptions of the molecules **7** and **8** with no Pt atoms). The electron donor property of the ligand (ferrocene) induces a little but detectable opposite effect on electron density and mobility with respect to the electron withdrawing –NO₂ group (Table 1).

2.3. Synthesis and characterization of 4,4'-(bis-phenylethynyl)-diethynylbiphenyl (**7**) and 4,4'-(bis-ferrocenylethynyl)-diethynylbiphenyl (**8**)

As mentioned before, there is still a controversial discussion in the scientific community on whether the electronic communication through π-conjugated carbon bonds is favored or inhibited by (i) the insertion of σ-bonded transition metal into the conjugation path [4a,9a,b,c,d], and/or (ii) the nature of the inserted metal (for example Pd) and the structure of the organometallic complex [9b]. Compounds **7** and **8** were prepared in order to form with compounds **4a** and **4c** two pairs of molecules differentiating only for the presence of the platinum-bis(triphenylphosphine) moiety into the conjugation path. In this way a direct evaluation of the role of a metal center on the properties of conjugated compounds might be elucidated.

In a first series of experiments we attempted the preparation of compounds **7** and **8** by the use of the Glaser–Hay oxidative coupling of C₆H₅–C≡C–H (**5**) and (η⁵-C₅H₅)Fe(η⁵-C₅H₄-C≡C–H) (**6**) with DEBP (**2**) (Path *a* of Scheme 2). However, although operating under a variety of experimental conditions, a complex mixture of products were invariably obtained: among the others biphenylbutadiene and polymeric materials of type [–C≡C–*p*-C₆H₄-*p*-C₆H₄-C≡C–]_n were found without any traces of the desired products **7** and **8**. Evidently homocoupling is always favored with respect to cross coupling. A different synthetic approach was



Scheme 2.

then accomplished by using the palladium catalyzed Stille coupling reaction [13,19,20], as outlined in Path *b* of Scheme 2. Although this synthetic path required the previous conversion of phenylacetylene and ferrocenylacetylene into the corresponding iodo derivatives **9** and **10** and the conversion of DEBP into the corresponding bis-trimethyltin derivative **11**, this route remains a unique path to achieve the otherwise inaccessible compounds **7** and **8**.

The characteristic features of the FT-IR spectrum of **7** are the bands at 2213 and 2191 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$); the high frequency band is shown only by compound **7** and is characteristic of disubstituted aromatic alkynes [21]. The absence of this band in the corresponding Pt containing complexes indicates that probably the coordination of a metal atom to the triple bonds causes the vanishing of this band (Table 1). The intensity of the two bands is low because a pseudo center of symmetry is established, about which the stretching of the triple

bond is symmetrical. The high energy of the $\text{C}\equiv\text{C}$ bands also suggests that there is no contribution to partial cumulenic linkages $\text{C}=\text{C}=\text{C}=\text{C}$ in the molecule [9c]. Compound **7** revealed to be very air and light sensitive either in the pure form and/or in solution. The FT-IR spectrum of complex **8** shows a strong absorbance and low resolution in the high energy region (4000–2000 cm^{-1}), which is a characteristic of conducting properties [22]. However, the stretching vibration of the $\text{C}\equiv\text{C}$ bonds is still detectable at 2141 cm^{-1} and the bands of the ferrocene unit at 821 and 1027 cm^{-1} are also present.

Having in hand compound **11**, an alternative approach to the synthesis of compound **4a** could be performed. Coupling of **11** and **1a** was carried out by the procedure described by Lewis [3c]; following work up, the binuclear complex **4a** was isolated in 52% yield.

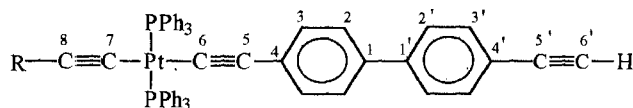
Despite the fact that the present route affords **4a** in lower yield than the dehydroalogenation procedure

Table 2
 $^1\text{H-NMR}$ data (δ , ppm) for compounds **3b,c**

R	$\text{H}_{\text{C,D}(\alpha,\alpha',\beta-\beta',\text{Cp})}$	PPh_3	$\text{H}_{\text{A-B}}$	$\text{H}_{\text{A}'\text{B}'}$	$-\text{C}\equiv\text{C}-\text{H}$
 3b	H_{C} 6,28,d,J=8,89 Hz,2H H_{D} 7,85-7,71,m,2H*	7,85-7,71,m,12H*	H_{A} 7,15,d,J=8,42 Hz,2H H_{B} 6,31,d,J=8,42 Hz,2H	$\text{H}_{\text{A}'\text{B}'}$ 7,51-7,29,m,4H*	3,08,s,1H
 3c	$\text{H}_{\alpha,\alpha'}$ 3,36-3,32,m,2H $\text{H}_{\beta,\beta'}$ 3,75-3,71,m,2H H_{Cp} 3,69,s,5H	7,85-7,75,m,12H 7,49-7,32,m,18H*	H_{A} 7,15,d,J=8,15 Hz,2H H_{B} 6,35,d,J=8,15 Hz,2H	$\text{H}_{\text{A}'\text{B}'}$ 7,49-7,32,m,4H*	3,08,s,1H

* Into those multiplets are cumulated signals of PPh_3 and $\text{H}_{\text{A}'\text{B}'}$ protons

Table 3

 ^{13}C -NMR data (δ , ppm) for compounds **3b,c**

R	12,11,10,9 α - α' , β - β' , <i>ipso</i> ,Cp	8,7	6,5	4,3,2,1	6',5'	4',3',2',1'	PPh ₃
 3b	12 144,17 11 122,72 10 131,29 9 135,68	8 112,53,t J=2,25 Hz 7 123,49,t J=14,44 Hz	6 111,27,t J=15,28 Hz 5 114,03,t J=2,58 Hz	4 128,20 3 131,22 2 126,42 1 136,26	6' 77,20 5' 83,65	4' 120,36 3' 132,41 2' 125,72 1' 141,32	135,02,t,J=6.14 Hz 131,07,t,J=29,88 Hz 130,42 127,94,t,J=5,35 Hz
 3c	α 70,16 β 71,07 <i>ipso</i> Cp 69,20	8 114,86 7 124,53	6 109,40 5 110,13	4 128,43 3 130,39 2 126,39 1 136,01	6' 83,88 5' 83,88	4' 120,66 3' 132,38 2' 125,53 1' 141,70	135,16 130,19 127,76

(Scheme 1), it represents an alternative route to disubstituted DEBP derivatives, that in case of **4b** and **4c** might be prepared avoiding the concomitant formation of the mononuclear derivatives **3b** and **3c**.

2.4. NMR characterization

In Tables 2 and 3 are reported NMR data (^1H , and ^{13}C) of compounds **3b** and **3c**, and Table 4 reports ^1H -NMR data of compounds **4a–c**, **7** and **8**. The scarce solubility of compounds **4a–c** led to some difficulties for their complete ^{13}C -NMR characterization; however, the main signals could be detected and assigned (Table 5). The higher solubility of compounds **7** and **8** allowed their full ^{13}C -NMR characterization, and specific attribution of each signal of the carbon skeleton was possible (Table 5).

It is interesting to compare the ^1H - and ^{13}C -NMR data of compounds **3b** and **c**, bearing a unsymmetrical substituted 4,4'-diethynylbiphenyl (DEBP) unit (Tables 2 and 3), with those of compounds **4a–c**, **7** and **8** bearing a symmetrical substituted DEBP core (Tables 4 and 5). In the proton spectra of compounds **3b** and **3c** (Table 2) the signals of the two different aromatic rings of the DEBP units are clearly distinct. In both compounds the protons on the phenyl ring attacked next to the platinum moiety appear as two distinct doublets ($\text{H}_{\text{A,B}}$) at 7.1 and 6.3 ppm, while protons ($\text{H}_{\text{A',B'}}$) on the ring bearing the free acetylene moiety appear as multiplet overlapping the signals of the triphenylphosphine ligands. Proton resonances of the DEBP unit of compounds **4a–c** ($\text{H}_{\text{A,B}}$) (Table 4) appear almost identical to the $\text{H}_{\text{A,B}}$ proton of compounds **3b** and **3c**, thus evidencing that in all compounds the proximity to the platinum moiety impress the same spectroscopic features to the protons of the nearest DEBP ring. In fact

in compounds **7** and **8** not bearing the platinum substituted the $\text{H}_{\text{A,B}}$ resonances appear as a confused multiplet in the 7.7–7.4 ppm range, just like as signals of the $\text{H}_{\text{A',B'}}$ protons of compounds **3b** and **3c**. The ^{13}C -NMR spectroscopic features of either the unsymmetrical compounds **3b** and **3c** (Table 3) and the symmetrical compounds **7** and **8** (Table 5) show some very impressive features. In particular in the ^{13}C -NMR spectra of compound **3b** (Fig. 1(a)) it has been possible to detect and assign five of the six nonequivalent acetylenic carbons 8, 7, 6, 5, and 5' (carbon marked as 6' is overlapping with the CDCl_3 triplet).

Of particularly interest are the signals of the acetylenic carbons 7 and 8. Because of the ^{13}C and ^{31}P coupling, both signals appear as a triplet. Carbon 7 closer to the platinum-bistriphenylphosphine moiety shows a coupling constant of 14 Hz, while the more distant carbon 8 shows a lower coupling constant of $J=2.5$ Hz. In compound **3c** this fine splitting was not observed because of the presence of the iron center which induces signal broadening, while the scarce solubility of compounds **4a–c** did not allow detection of signals for alkyne carbons.

Another remarkable feature seen in the ^{13}C spectra of compound **3b** bearing the platinum-bistriphenylphosphine moiety, is the splitting of the signal observed for the carbon resonances of the phenyl ring of the triphenylphosphine ligand (Fig. 1(b)). Four distinct signals, are observed for the *ipso*, *ortho*, *meta* and *para* carbons. While the latter appears as a singlet, the other three appear as triplets, whose different coupling constant (29, 6 and 5 Hz, respectively) reflects the progressive distance from the phosphorous center. As before in compound **4c** this fine splitting was not observed because of the presence of the iron center which induces signal broadening.

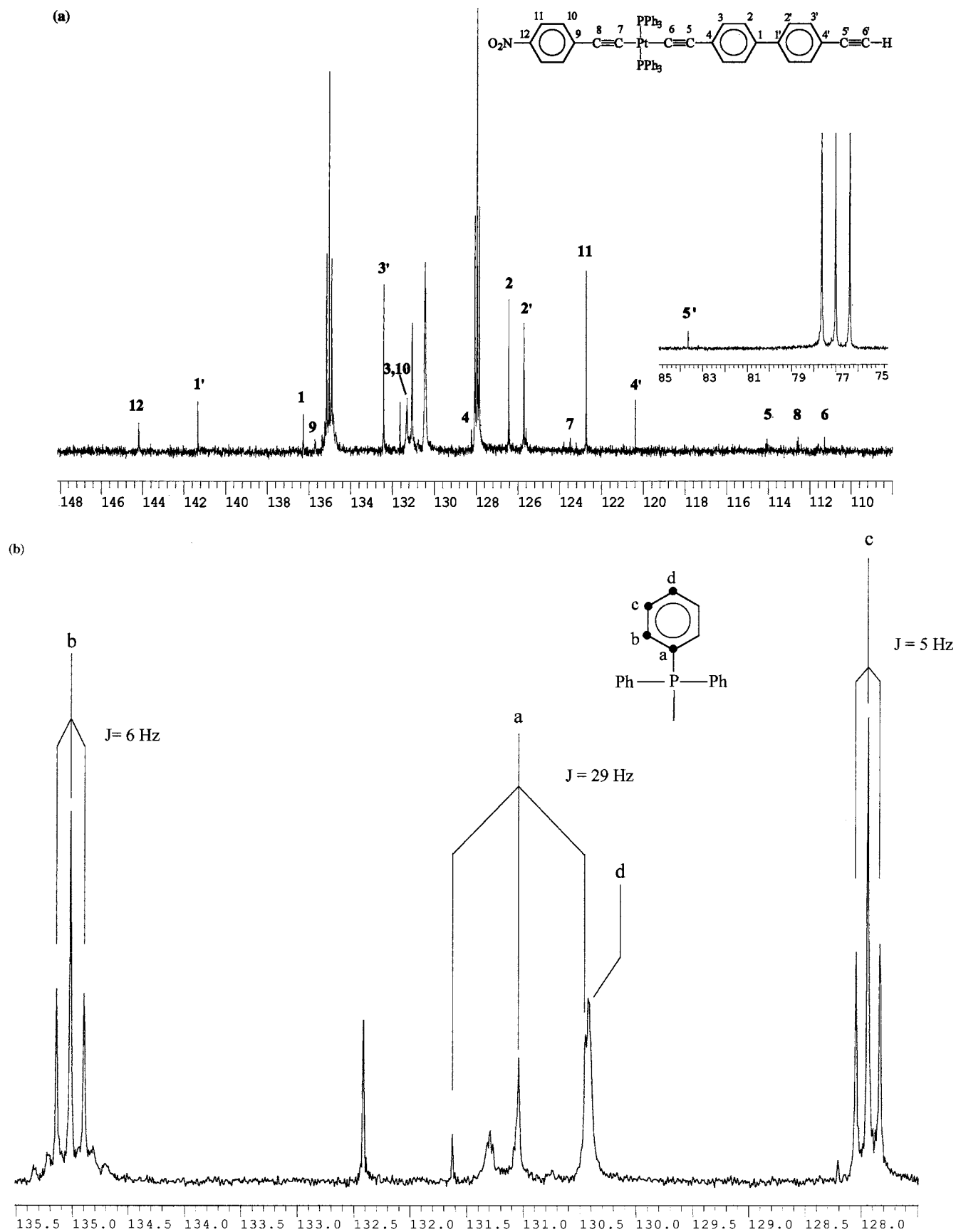
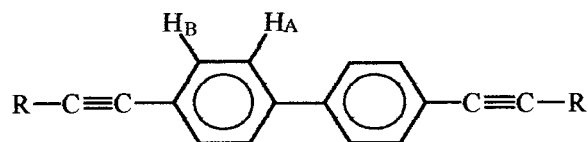


Table 4

¹H-NMR data (δ , ppm) for compounds 4a–c, 7 and 8

R	H _{C,D,E(α,α',β-β',Cp)}	PPh ₃	H _{A-B}
 4a	H _C 6,46-6,29,m,4H H _D 6,92-6,84,m,4H H _E 6,92-6,84,m,2H	7,94-7,76,m,24H 7,42-7,26,m,36H	H _A 7,05,d,J=7,55 Hz,4H H _B 6,46-6,29,m,4H
 4b	H _C 6,27,d,J=9,03 Hz,4H H _D 7,82-7,72,m,4H	7,82-7,72,m,24H 7,43-7,30,m,36H	H _A 7,02,d,J=8,55 Hz,4H H _B 6,24,d,J=8,55 Hz,4H
 4c #	H _{α-α'} 3,49-3,44,m,4H H _{β-β'} 3,84-3,30,m,4H H _{Cp} 3,79,s,10H	8,01-7,81,m,24H 7,63-7,43,m,36H	H _A 7,14,d,J=8,54 Hz,4H H _B 6,40,d,J=8,54 Hz,4H
 7	H _C 7,39-7,29,m,4H H _D 7,63-7,48,m,4H H _E 7,39-7,29,m,2H		H _{A,B} 7,63-7,48,m,8H
 8	H _{α-α'} 4,32-4,20,br,4H H _{β-β'} 4,56-4,48,br,4H H _{Cp} 4,32-4,20,br,10H		H _{A,B} 7,65-7,47,m 8H

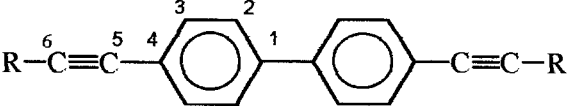
Spectra recorded in DMF-d₇ at 343 K

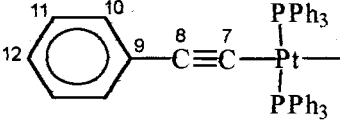
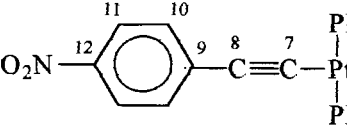
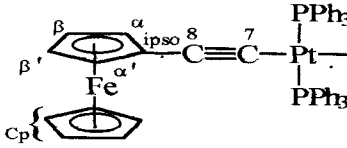
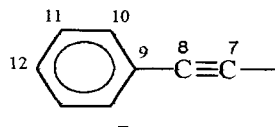
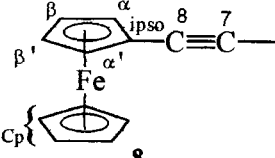
The ³¹P-NMR spectra show resonances with chemical shifts and $J(^{195}\text{Pt}-^{31}\text{P})$ values in agreement with those found for square planar Pt(II) *trans* isomers [23] (Section 3).

Finally it is worth noting that an interesting characteristic has been revealed upon observing the NMR data of compounds reported in Tables 3 and 5. We found that from the ¹³C-NMR data of the overall

series of compounds, it is possible to deduct a systematic and additive effect of substituents on the chemical shift of each carbon of the different benzene moieties. As consequence the ¹³C-NMR chemical shift of each carbon of the benzene moieties of an hypothetical compound made by combination of any of the moieties of compounds 3–6 is fully predictable [24].

Table 5

¹³C-NMR data (δ , ppm) for compounds 4a–c, 7 and 8


R	12,11,10,9 α - α' , β - β' ,ipso,Cp	8,7	PPh ₃	6,5	4,3,2,1
 4a	12 124,72 11 127,06 10 130,92 9 128,29	8 113,68 7 124,72	135,20,t,J=6,51 Hz 130,23 127,89,t,J=5,30 Hz	6 5	4 126,49 3 131,18 2 125,69 1 137,29
 4b	12 144,13 11 122,71 10 131,10 9 135,71	8 7	135,00,t,J=6,35 Hz 131,04,t,J=29,67 Hz 130,38 127,90,t,J=5,30 Hz	6 5	4 126,83 3 130,38 2 125,26 1 137,12
 4c	α 70,55 β 67,12 ipso * Cp 69,83	8 7	135,6 131,13 128,64	6 111,15 5 112,03	4 128,20 3 131,18 2 125,29 1 137,29
 7	12 129,27 11 128,45 10 132,50 9 121,69	8 81,26 7 73,88		6 74,98 5 82,11	4 121,23 3 133,04 2 126,99 1 140,67
 8	α 72,28 β 69,48 ipso 73,46 * Cp 70,24	8 78,62 7 62,98		6 75,91 5 82,76	4 121,62 3 132,89 2 126,93 1 140,40

* Spectra recorded in DMF-d₇ at 343 K

2.5. Conclusions

Several mono and dinuclear Pt(II) complexes were obtained and characterized by using different synthetic approaches. The complexes contain the 4,4'-bis(ethynyl)biphenyl (DEBP) unit as the common ligand, which is the central core bridging the metal units of the bimetallic compounds. Electron withdrawing and

electron donor ligands were bound to Pt, with the aim of tuning the electron delocalization along the highly ethynylated sequence of the organic moieties. Related molecules with no Pt inserted were also synthesized and characterized with the purpose of doing a comparative study on the role of the metals on the electronic and optical properties of highly ethynylated materials.

3. Experimental

3.1. General procedure

FT-IR spectra were recorded on a Perkin–Elmer 1700 X spectrophotometer: the samples were prepared as Nujol mulls using CsI cells.

UV–vis spectra were recorded on a Perkin–Elmer Lambda 16 instrument. ^1H -, ^{13}C - and ^{31}P -NMR spectra were recorded on a Bruker AC 300P spectrometer at 300, 75 and 121 MHz, respectively. The ^1H -NMR chemical shifts (ppm) are assigned considering the reference Me_4Si signal at 0 ppm and the residual ^1H impurity signal in the solvent at 7.24 ppm (CDCl_3). The ^{13}C -NMR chemical shifts are calibrated to the ^{13}C triplet of CDCl_3 at 77 ppm. The ^{31}P -NMR chemical shifts are relative to 85% H_3PO_4 . Low resolution mass spectra (FAB, *m*-nitrobenzyl alcohol) was obtained with a VG-Quattro Instrument, at the Università di Tor Vergata, Roma.

Elemental analyses were determined by Servizio di Microanalisi of the Department of Chemistry, University of Rome, La Sapienza.

Solvents including those used for chromatography, were distilled over standard drying agents and degassed before use. Chromatographic separations were performed with 70–230 mesh silica gel (Merck). All reactions were performed under Argon atmosphere, using standard glassware and equipment. $\text{Et}_2\text{NSnMe}_3$ was prepared according to a published method [25].

Preparations of *trans*- $[(\text{C}_6\text{H}_5-\text{C}\equiv\text{C})\text{Pt}(\text{PPh}_3)_2\text{Cl}]$ (**1a**), *trans*- $[(p\text{-NO}_2\text{C}_6\text{H}_4-\text{C}\equiv\text{C})\text{Pt}(\text{PPh}_3)_2\text{Cl}]$ (**1b**) and *trans*- $\{\text{ClPt}(\text{PPh}_3)_2[(\text{C}\equiv\text{C}-\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}$ (**1c**) were performed by reacting *cis*- $[\text{Pt}(\text{PPh}_3)_2\text{Cl}_2]$ and the corresponding alkynes, according to the synthetic routes reported in the literature, references [15,16b], respectively. DEBP (**2**) was obtained by the reaction reported in the literature [26]. Phenylacetylene (**5**) was a commercial product (Aldrich) dry distilled before use. Ethynylferrocene (**6**) was prepared according to a published method [27].

4. Syntheses

4.1. Formation of

trans-*trans*- $[(\text{C}_6\text{H}_5-\text{C}\equiv\text{C})\text{Pt}(\text{PPh}_3)_2-$
 $(-\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4-p\text{-C}_6\text{H}_4-\text{C}\equiv\text{C}-)\text{Pt}(-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)-$
 $(\text{PPh}_3)_2]$ (**4a**)

4.1.1. Reaction of *trans*- $[\text{Cl}-\text{Pt}(\text{PPh}_3)_2(-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)]$ (**1a**) with 4,4'-bis(ethynyl)biphenyl (**2**)

Complex **1a** (0.170 g, 0.2 mmol) and DEBP (**2**) (0.02 g, 0.1 mmol) were dissolved in 20 ml of CHCl_3 and 1.6 ml of NHET_2 and CuI (0.007 g) was added immediately after. The reaction mixture was warmed at reflux under

argon atmosphere for 5 h. The reaction solution was filtered and by addition of EtOH the product precipitated as yellow powder. The powder was dissolved in the minimum volume of 1:1 dichloromethane–toluene and submitted to column chromatography (1:2 dichloromethane–toluene); further purification was achieved by crystallization (CHCl_3 –EtOH) (0.147 g, yield 80%).

4.1.2. Reaction of *trans*- $[\text{Cl}-\text{Pt}(\text{PPh}_3)_2(-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)]$ (**1a**) with 4,4'-bis(trimethyltin)ethynylbiphenyl (**11**)

Complex **1a** (0.106 g, 0.1 mmol) and **11** (0.033 g, 0.06 mmol; a little excess of **11** improves the reaction yield) were added into 30 ml of toluene with 0.008 g of CuI . The reaction mixture was heated at 60°C for 6 h and then a pale yellow powder was obtained by precipitation with EtOH. The crude powder was then purified as above reported in method (4.1.1), yielding pure **4a** (yield 52%). Elemental analysis: Found: C, 68.05; H, 4.28. Calc. for $\text{C}_{120}\text{H}_{78}\text{P}_4\text{Pt}_2$: C, 67.82; H, 4.27%. FT-IR (cm^{-1}): 2112 ($\nu_{\text{C}\equiv\text{C}}$). ^{31}P -NMR (CDCl_3): δ (ppm) 17.31, $J(\text{Pt}-\text{P}) = 2646$ Hz.

4.2. Formation of *trans*- $[(p\text{-NO}_2\text{-C}_6\text{H}_4-\text{C}\equiv\text{C}-)$ $\text{Pt}(\text{PPh}_3)_2(-\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4-p\text{-C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{H})]$ (**3b**) and *trans*-*trans*- $[(p\text{-NO}_2\text{-C}_6\text{H}_4-\text{C}\equiv\text{C}-)\text{Pt}(\text{PPh}_3)_2-$ $(-\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4-p\text{-C}_6\text{H}_4-\text{C}\equiv\text{C}-)\text{Pt}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-p\text{-NO}_2)$ $(\text{PPh}_3)_2]$ (**4b**)

4.2.1. Reaction of *trans*- $[\text{Cl}-\text{Pt}(\text{PPh}_3)_2(-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-p\text{-NO}_2)]$ (**1b**) with 4,4'-bis(ethynyl)biphenyl (**2**)

This reaction can be orientated toward the prevalent formation of (i) **3b** or (ii) **4b** depending on the reaction conditions. (i) Compound **2** (0.500 g, 2.47 mmol) was dissolved in the minimum amount of CHCl_3 and to this solution 10 ml of NHET_2 were added. Another solution, containing complex **1b** (0.400 g, 0.44 mmol) dissolved in a mixture of solvents, (i.e. 25 ml of CHCl_3 and 100 ml of EtOH), was prepared and poured dropwise into the former one; the final mixture was stirred for 15 h at r.t. The reaction mixture was then filtered through a glass frit ($\neq 4$) to separate traces of **4b** and the solvent was reduced to a small volume (20 ml); by addition of EtOH a crude material precipitated as brown powder that was dissolved in the minimum amount of 1:1 dichloromethane–toluene and then further purified by chromatography (1:1 dichloromethane–toluene eluent). The eluted fraction containing **3b** was dry evaporated and the residue crystallized with CHCl_3 , giving pure **3b** in 50% yield. Elemental analysis: Found: C, 67.40; H, 4.05; N, 1.30. Calc. for $\text{C}_{60}\text{H}_{43}\text{NO}_2\text{P}_2\text{Pt}$: C, 67.54; H, 4.06; N, 1.31%. FT-IR (cm^{-1}): 3266 ($\nu_{\text{C}-\text{H}}$), 2105 ($\nu_{\text{C}\equiv\text{C}}$). ^{31}P -NMR (CDCl_3): δ (ppm) 19.40, $J(\text{Pt}-\text{P}) = 2618$ Hz.

(ii) The complex *trans*- $[\text{Cl}-\text{Pt}(\text{PPh}_3)_2(-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{NO}_2)]$ (**1b**) (0.260 g, 0.28 mmol) and DEBP (**2**) (0.03 g,

0.14 mmol) were dissolved in 30 ml of CHCl_3 . NHET_2 (5 ml) was added to the solution and the reaction mixture was warmed at reflux for 48 h. The progress of the reaction was monitored by TLC performed on periodical checks. The final solution was concentrated to small volume and by addition of EtOH, a crude red–brown precipitate was obtained. The solid residue was dissolved in a mixture of 1:1 dichloromethane–toluene and purified by column chromatography using the same solvents mixture as the eluent. Following a first band constituted by unreacted DEBP (0.0169, 50%) a second fraction showing UV absorption at $\lambda = 390$ nm was collected and the pure complex (**3b**) was obtained after evaporation of the solvent (0.045 g, 15%). A further fraction eluted from the chromatographic column, showing $\lambda_{\text{max}} = 397$ nm, contains the dinuclear complex (**4b**), that is recovered after evaporation under vacuum as a bright yellow powder (0.27 g, 50%). Elemental analysis: Found: C, 64.70; H, 3.99; N, 1.46. Calc. for $\text{C}_{104}\text{H}_{76}\text{N}_2\text{O}_2\text{P}_4\text{Pt}$: C, 64.66; H, 3.97; N, 1.45%. FT-IR (cm^{-1}): 2104 ($\nu_{\text{C}=\text{C}}$), 1101. ^{31}P -NMR (CDCl_3): δ (ppm) 19.36, $J(\text{Pt}–\text{P}) = 2620$ Hz.

4.3. Formation of trans- $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-C}\equiv\text{C-})]\text{-Pt}(\text{PPh}_3)_2(-\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-H})\}$ (3c**) and trans–trans- $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-C}\equiv\text{C-})]\text{Pt}(\text{PPh}_3)_2(-\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-})\text{Pt}[(-\text{C}\equiv\text{C-}\eta^5\text{-C}_5\text{H}_4\text{-Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{PPh}_3)_2\}$ (**4c**)**

4.3.1. Reaction of trans- $\{\text{Cl-Pt}(\text{PPh}_3)_2[(-\text{C}\equiv\text{C-}\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\}$ (1c**) with 4,4'-bis(ethynyl)biphenyl (**2**)**

(i) DEBP (**2**) (0.200 g, 1 mmol) and the monochloroacetylide Pt complex (**1c**) (0.450 g, 0.5 mmol) were mixed in 700 ml of THF with 18 ml of NHET_2 . The reaction was run at reflux for 48 h under argon atmosphere, giving a brown powder (**4c**) that was filtered off and washed with ethanol (yield 10%). The remaining reaction solution was evaporated to dryness, under vacuum, and the solid residue was dissolved in the minimum volume of the 1:2 dichloromethane–toluene mixture and submitted to chromatography (1:2 dichloromethane–toluene eluent). Pure complex (**3c**) was obtained from the eluted fractions by precipitation with EtOH (yield 40%). The characterization of **3c** is the following: Elemental analysis: Found: C, 68.31; H, 4.27. Calc. for $\text{C}_{64}\text{H}_{48}\text{FeP}_2\text{Pt}$: C, 68.03; H, 4.28%. FT-IR (cm^{-1}): 3276 ($\nu_{\text{H-C}}$), 2109 ($\nu_{\text{C}=\text{C}}$). ^{31}P -NMR (CDCl_3): δ (ppm) 19.59, $J(\text{Pt}–\text{P}) = 2660$ Hz.

(ii) DEBP (**2**) (0.080 g, 0.40 mmol) was dissolved in 45 ml of previously degassed toluene with complex **1c** (0.750 g, 0.80 mmol), and 4 ml of Et_2NH were added to the solution. The reaction mixture was heated at reflux for 36 h, yielding a deep red solution and a white precipitate (ammonium salt) that was filtered off. The volume was reduced to 20 ml with a rotary evaporator

and by addition of EtOH a solid yellow product was obtained. The crude product was dissolved in the minimum volume of 1:1 dichloromethane–toluene and then purified by column chromatography (2:1 dichloromethane–toluene eluent). Complex **4c** was further purified by crystallization with CHCl_3 –EtOH (yield 40%). Elemental analysis: Found: C, 65.67; H, 4.23. Calc. for $\text{C}_{112}\text{H}_{86}\text{Fe}_2\text{P}_4\text{Pt}_2$: C, 65.38; H, 4.21%. FT-IR (cm^{-1}): 2115 ($\nu_{\text{C}=\text{C}}$); 1101 (PPh_3) 804, 818 ($\nu_{\text{C-H Ar}}$), ^{31}P -NMR ($\text{DMF-}d_7$ at 343 K): δ (ppm) 19.56, $J(\text{Pt}–\text{P}) = 2652$ Hz.

4.4. Preparation of phenylacetylene iodide (**9**)

A solution of phenylacetylene (**5**) (7.2 mmol, 0.8 ml) in methanol (40 ml) was cooled to 0°C and treated with solid KOH (18 mmol, 1 g). After 20 min of stirring at a low temperature solid *N*-iodosuccinimide (8.6 mmol, 1.940 g) was added to the mixture, and the stirring continued at 0°C for 15 min. The cold bath was then removed and the stirring continued at r.t. for an additional 20 min. Then 200 ml of Et_2O was added and the mixture extracted three times with brine. The organic layer was separated, dried over MgSO_4 , filtered, and evaporated. The product was isolated in quantitative yield as brown oil. FT-IR (neat film, cm^{-1}): 2171 ($\nu_{\text{C}=\text{C}}$); 1070, 1026, 754 ($\nu_{\text{C-H Ar}}$); 3080, 3056, 3031 ($\nu_{\text{C-H Ar}}$); 1489, 1443 ($\nu_{\text{C-H Ar}}$). UV–vis (THF): $\lambda_{\text{max}} = 257$ nm. ^1H -NMR: δ (ppm) 7.26–7.34 (*m*, 3H), 7.39–7.45 (*m*, 2H), aromatic protons. Elemental analyses: Found: C, 41.98; H, 2.20. Calc. for $\text{C}_8\text{H}_5\text{I}$: C, 42.14; H, 2.21%. A different reaction route was already proposed for the synthesis of **9** [28].

4.5. Preparation of ethynylferrocene iodide (**10**)

Using the procedure described above, ethynylferrocene (**6**) (3.0 mmol, 0.63 g) in methanol (40 ml) was first treated with KOH (7.9 mmol, 0.44 g) at 0°C and then with *N*-iodosuccinimide (3.6 mmol, 0.820 g). Subsequent Et_2O –brine extraction, drying over MgSO_4 , filtration and evaporation afforded quantitative product as brown solid. FT-IR (cm^{-1}): 2176 ($\nu_{\text{C}=\text{C}}$). UV–vis (CHCl_3): $\lambda_{\text{max}} = 269$ nm. ^1H -NMR: δ (ppm) 4.15–4.19 (*m*, 2H), 4.20 (*s*, 5H), 4.40–4.45 (*m*, 2H). Elemental analysis: Found: C, 43.04; H, 2.71. Calc. for $\text{C}_{12}\text{H}_9\text{FeI}$: C, 42.90; H, 2.70%.

4.6. Preparation of 4,4'-bis(trimethyltin)ethynylbiphenyl (**11**)

A 100 ml Schlenk tube was loaded with 4,4'-bis(ethynyl)biphenyl (**2**) (1 mmol, 0.20 g) and capped with a rubber septum. The side arm was then connected with a vacuum–argon manifold and several evacuation–argon filling cycles were performed. With the use of a

syringe $\text{Et}_2\text{NSnMe}_3$ (2.1 mmol, 0.65 g) was introduced through the septa and the resulting mixture was stirred at r.t. for 1 h. After this time, the mixture was exposed to the vacuum, and the diethylamine side product formed during the reaction was removed. The product was thus isolated in quantitative yield as a pale yellow solid. FT-IR (cm^{-1}): 2136 ($\nu_{\text{C}=\text{C}}$); 1917; 825 ($\nu_{\text{C}-\text{H}}$ Ar). $^1\text{H-NMR}$: δ (ppm) 0.35 (*s*, $J(^{117}\text{Sn}-^1\text{H}) = 29.0$, $J(^{119}\text{Sn}-^1\text{H}) = 30.3$ Hz, 18H), 7.49 (*m*, 8H). $^{13}\text{C-NMR}$: δ (ppm) -7.65 (*t*, $J(^{117}\text{Sn}-^{13}\text{C}) = 192.5$ Hz), -7.65 (*t*, $J(^{119}\text{Sn}-^{13}\text{C}) = 202.5$ Hz) (CH_3); 94.55 (*t*, $J(^{117}\text{Sn}-^{13}\text{C}) = 202$ Hz) (C of the alkyne). UV-vis (CHCl_3): $\lambda_{\text{max}} = 300$ nm. Elemental analysis: Found: C, 49.96; H, 4.95. Calc. for $\text{C}_{22}\text{H}_{26}\text{Sn}_2$: C, 50.06; H, 4.96%.

4.7. Preparation of 4,4'-(bis-phenylethynyl)-diethynylbiphenyl (7)

Phenylacetyleneiodide (**9**) (1.1 g, 4.9 mmol) was added into the reaction vessel, where 4,4'-bis(trimethyltin)ethynyl-biphenyl (**11**) (1.3 mmol) was previously prepared, with 40 ml of dry THF and $\text{Pd}(\text{PPh}_3)_4$ (0.015 g, 0.013 mmol) as the catalyst. The reaction was performed at 50°C overnight (16 h). Then the reaction solvent and the $\text{Sn}(\text{CH}_3)_2\text{I}$ by-product were removed under vacuum pumping. To the brown residue THF (50 ml) was added and the solution was passed through a celite filter. Then dry, degassed *n*-pentane (30 ml) was added and the mixture stirred overnight at -30°C. Compound **7** (very air sensitive) was thus precipitated and recovered by filtering under argon atmosphere (yield 50%). Because of its sensitivity the compound must be stored under argon at ca. 2°C. FT-IR (cm^{-1}): 2186 ($\nu_{\text{C}=\text{C}}$), 821, 755 ($\nu_{\text{C}-\text{H}}$ Ar). MS (FAB) $m/e = 403$ [$\text{M} + \text{H}$] $^+$

4.8. Preparation of 4,4'-(bis-ferrocenylethynyl)-diethynylbiphenyl (8)

Using the same procedure for the preparation of (**7**), ethynylferrocene iodide (**10**) (2.7 mmol, 0.905 g) and (**11**) (1.34 mmol, 0.70 g) were added to a solution of $\text{Pd}(\text{PPh}_3)_4$ (0.13 mmol, 0.156 g) in 30 ml of THF and the resulting mixture was stirred at 70°C for 16 h. Then the reaction solvent and the $(\text{CH}_3)_2\text{SnI}$ side product were removed under vacuum pumping and a crude powder was obtained. The powder was dissolved in the minimum amount of a 1:3 THF-*n*-hexane mixture and was purified by chromatography using the same solvent mixture as the eluent. Following evaporation of the solvent, compound (**8**) was obtained as a red-orange solid (yield 10%). An analytical sample was prepared by crystallization with CHCl_3 -EtOH. FT-IR (cm^{-1}): 2141 ($\nu_{\text{C}=\text{C}}$), 1027, 821 ($\nu_{\text{C}-\text{H}}$ ferrocene). UV-vis (CHCl_3): $\lambda_{\text{max}} = 337$ nm. Elemental analysis: Found: C, 78.01; H, 4.22. Calc. for $\text{C}_{40}\text{H}_{26}\text{Fe}_2$: C, 77.70; H, 4.24%.

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