

Note

Probing delocalisation across highly ethynylated mono and dinuclear Pt(II) tethers containing nitro groups and organic models as redox active probes: X-ray crystal structure of *trans*-[Pt(C≡C–C₆H₄NO₂)₂(PPh₃)₂]

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Abstract

The electrochemical study on Pt(II) organometallic and organic ethynylated compounds bearing nitro substituents in the phenyl groups has been performed, demonstrating that the presence of severe chemical irreversibility accompanying the electron transfer, preclude an evaluation of the electronic communication between redox active centres. The X-ray structure of the complex *trans*-[Pt(C≡C–C₆H₄NO₂)₂(PPh₃)₂] is showed.

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1. Introduction

Polymers and oligomers containing metal centres bound to acetylide groups have emerged as efficient "molecular wires", because of the possibility of charge transfer along the conjugated backbone [1]. The research related to electronic communications in these ethynylated compounds shows some intriguing aspects, related to the chemical nature either of the organic ligand and of the transition metal [2], and to geometric arrangement, that would hinder conjugation, if twisted from planarity [3]. Previous investigation on bis(ferrocenylethynyl) Pt(II) complexes showed a moderate electronic communication between ferrocenyl moieties [4]. Electrochemical studies performed on heterotrimetallic Ru/Pt/Ru complexes connected by –C≡C–C₆H₄–C≡C– bridges, indicate that the platinum centre transfers electron density to

the ruthenium [5]. On the other hand, investigations on a series of aryl-acetylide bridged diruthenium complexes came to the conclusion that there is almost no electronic interaction between the two Ru moieties [6].

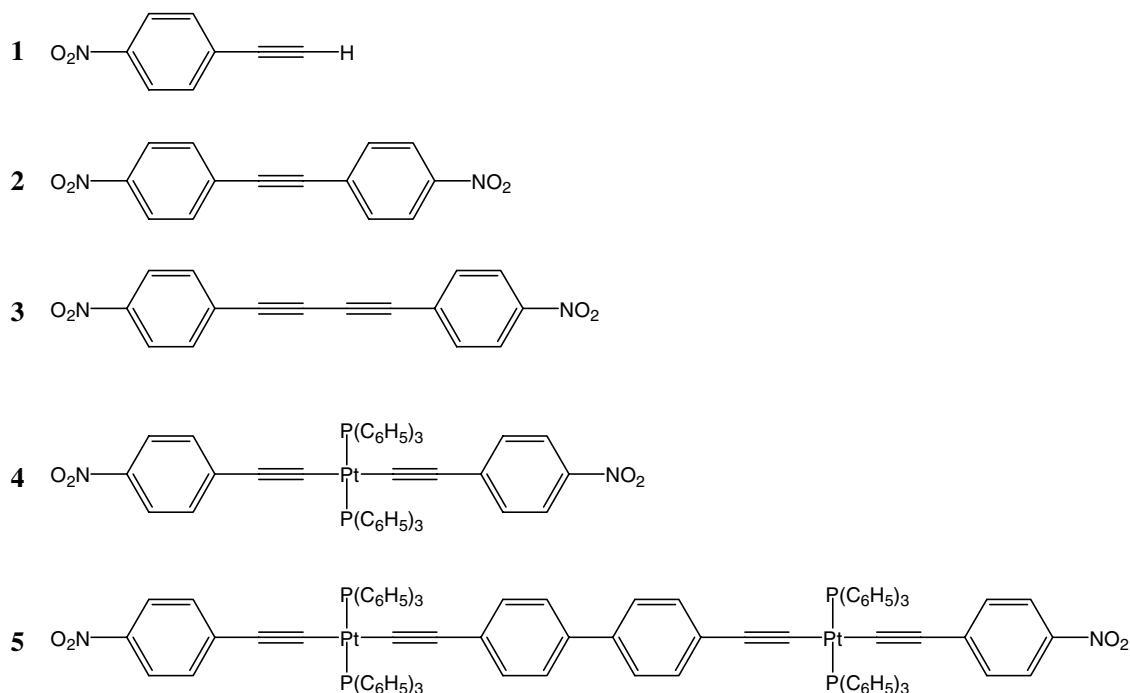
In this Note we report the investigation on the electrochemical behaviour of the pure organic nitrophenyl acetylides 1–3 (Scheme 1) and their organometallic derivatives 4–5, containing one or two platinum centres coordinated to acetylene moieties. In addition the X-ray crystal structure of the complex *trans*-[Pt(C≡C–C₆H₄NO₂)₂(PPh₃)₂] (4) has been determined.

2. Results and discussion

2.1. Electrochemical properties

Fig. 1 shows the cyclic voltammetric (CV) response of a THF solution of 1. A Nernstian, electrochemically

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Scheme 1.

quasi-reversible and chemically reversible reduction process (peak system A/B), followed by a further reduction process (peak C) are observed (Table 1). If peak C is traversed, peak system A/B becomes chemically irreversible and two small peaks, D and E, due to reoxidation of electrogenerated fragments, appear in the reverse scan. The electrochemical features for the reduction peak C are compatible with a Nernstian electrochemically quasi-reversible and chemically irreversible two independent 1e reduction processes taking place at the same potential (for a true 2e reduction $i_p(C)$ should be ca. 2.8 times $i_p(A)$; in our case this ratio is only 2).

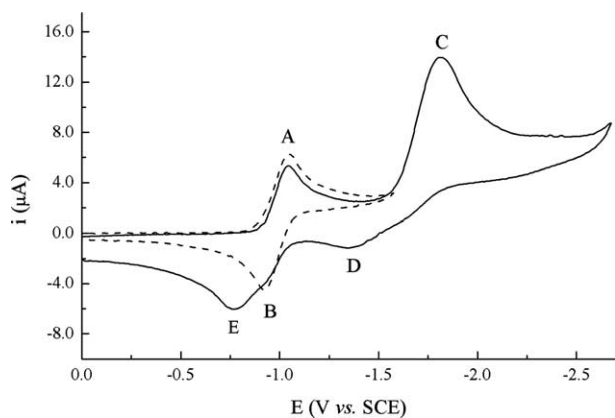


Fig. 1. Cyclic voltammetric response of $\text{HC}\equiv\text{C}-\text{C}_6\text{H}_4\text{NO}_2$ (**1**) in THF.

The electrochemical behaviour of compound **2** is identical to that of **1**; while compound **3** shows two almost overlapped waves, C and C', with $i_p(C) \cong i_p(C') \cong i_p(A)$ (Table 1). No oxidation processes are observed in the anodic scan (0 ± 1.7 V).

The overall CV results could be explained as the reversible reduction of the NO_2 group to the radical anion and, at a more negative potential, to the dianion [7]. In our experimental conditions, the latter species is not stable and generates fragments electroactive at the potential employed, increasing the current of peak C (ECE process).

By adding ferrocene, Fc, as internal standard in equimolar concentration, $i_p(A)$ is always equal to the 1e oxidation peak of Fc, also when lowering the temperature (from 25 to -60 °C), while $i_p(B)/i_p(A)$ and $i_p(A)/i_p(C)$ ratios increase, as a consequence of the quench of the

Table 1
Electrochemical data for **1–5** compounds

Compound	$E^{\circ}(A/B)$ (V vs. SCE)	$E_p(C)$ (V vs. SCE)
1	-0.990 (110–150)	-1.81
2	-0.938 (110–150)	-1.88
3	-0.874 (120–150)	-1.72; -1.87
	$E^{\circ}(F/G)$ (V vs. SCE)	$E_p(H); E_p(I)$ (V vs. SCE)
4	-1.14 (120–150)	-2.04; -2.41
5	-1.15 (120–160)	-1.95; -2.29

In the case of chemically reversible processes, ΔE_p in the scan rate range $0.05\text{--}1.50$ V s^{-1} is reported in parenthesis (in mV).

chemical reaction in the ECE process. In compounds **2** and **3**, $i_p(\text{A})$ is higher than $i_p(\text{Fc})$, as expected for the reduction of two independent redox active groups, even if $i_p(\text{A})/i_p(\text{Fc}) < 2$. Then the reduction of two independent and non-interacting nitro-groups can be assessed and work is in progress to find an explanation to this topic.

In Fig. 2 we report the CV response of complex **4**. The overall electrochemical behaviour is quite similar to that of **1–3**, with the addition of a new chemically irreversible peak reduction I (Table 1). On the basis of the similarities of the CVs, we can associate peaks F/G and H to ligand reductions, while peak I may be related to a Pt(II) \rightarrow Pt(I) chemically irreversible reduction. The Pt(I) \rightarrow Pt(0) process is likely located beyond the solvent discharge. In the case of **5**, an electron transfer between the two Pt centres, if any, may not be observed because of the chemical irreversibility of the electrogenerated intermediates.

Electrochemistry represents a simple tool to evaluate the extent of the electronic interaction between two redox centres. When there is charge delocalisation *through-bond* or *through-space* over the two centres, the $E^{\circ'}$ values for the redox processes differ up, giving two, more or less resolved, peaks. On the other hand, when there is no electronic interaction between them, the $E^{\circ'}$ values differ only by a small statistical factor [8] ($\Delta E^{\circ'}$ ca. 36 mV) and in CV a single peak is observed. The absence of two peaks may indicate that all **1–5** systems display virtually no delocalisation of the radical anion species. However, very recently, Jones et al. [9] reported for a Pt(II)-bridged triarylamine species, having a structure quite similar to that of **4** with two $-\text{NAr}_2^+$ groups instead of $-\text{NO}_2$, the presence of two very close reversible oxidations due to the triarylamine group ($\Delta E^{\circ'} = 65$ mV), resolvable only by differential techniques. In our case, both the CV study and the use of differential techniques, were not able to shed light in

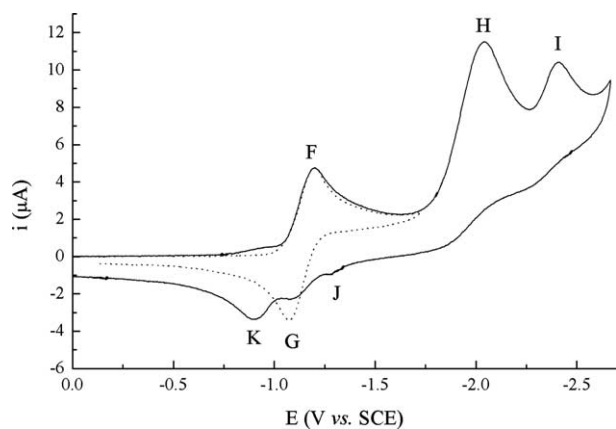


Fig. 2. Cyclic voltammetric response of $[\text{Pt}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{NO}_2)_2(\text{PPh}_3)_2]$ (**4**) in THF.

the problem due the severe chemical irreversibility. Moreover, in the radical anion of an aliphatic nitro compound, the charge of the nitro-group is virtually unity, whereas in the radical anion from nitrobenzenes a certain delocalisation of the charge occurs according to EPR measurements [10]. Since the Pt centre increases the electron density on the ring ($E^{\circ'}$ for $\text{NO}_2 \rightarrow \text{NO}_2^{\cdot-}$ in **4–5** is 190 mV more negative than in simple organic ligands), such unit could be responsible of a poor charge delocalisation of $\text{NO}_2^{\cdot-}$ on the overall structure, giving a $\Delta E^{\circ'}$ separation below the recognisable limits.

2.2. Crystal structure

The X-ray crystal structure of $[\text{Pt}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{NO}_2)_2(\text{PPh}_3)_2]$ (**4**) is determined. Suitable crystals for structural determination of complex **4** were obtained from a slow diffusion of EtOH into a CHCl_3 solution.

The complex **4** (Fig. 3) has a high degree of symmetry, in fact the platinum ion lies on an inversion center. The metal ion has the expected square planar coordination geometry, slightly distorted as provided by the value of the *cis* angle $87.0(2)^\circ$. Both bond lengths and angles of the coordination sphere are comparable with those of similar structures retrieved in the Cambridge Structural Database [11] (CSD) v.5.25. The coordination plane and that containing the nitrophenyl moiety are almost coplanar (the angle is $3.8(2)^\circ$) at variance with similar structures, featuring the same *trans*-bis(ethynyl-*p*-nitrophenyl) ligand [12]. The ethynyl moiety is essentially linear being the angles Pt(1)–C(1)–C(2) and C(1)–C(2)–C(3), respectively, $176.7(7)^\circ$ and $176.0(8)^\circ$.

An intermolecular interaction C–H– π type exists between the aromatic hydrogen atom H(14) and the ethynyl $\text{C}\equiv\text{C}$ bond of a symmetry related metal complex ($-x - 1, -y, -z + 1$). The distance between

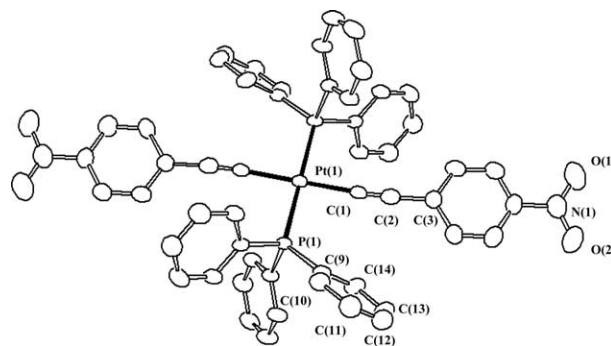


Fig. 3. X-ray crystal structure of **4** ellipsoids drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Pt(1)–P(1), 2.321(1); Pt(1)–C(1), 2.044(8); C(1)–C(2), 1.107(9); C(2)–C(3), 1.48(1); C(6)–N(1), 1.46(1); C(1)–Pt(1)–P(1), $87.0(2)$; C(1)–Pt(1)–P(1'), $93.0(2)$; Pt(1)–C(1)–C(2), $176.7(7)$; C(1)–C(2)–C(3), $176.0(8)$. C(1)' is reported by the symmetry operation $-x, -y, -z + 1$.

the hydrogen atom and the centre of mass (Cm) of the two carbon atoms is 2.61 Å and the angle C(14)–H(14)–Cm 158.39°. In addition it can be pointed out a weak stacking interaction between the aromatic ring C(9)–C(14) of the triphenylphosphine moiety with the same aromatic ring of a metal complex reported by the symmetry operation $-x - 1, -y, -z + 1$, being the distance between the centroids of the two rings 4.07 Å. Due to the high degree of symmetry of the molecule this interaction propagates into the crystal giving rise to a ribbon of molecules developing along the *x*-axis.

The crystal structure of compound **3** was previously reported [13] and exhibits the two nitrophenyls plane twisted almost perpendicular each other: this structure seems to be the preferred one for the substituted benzene derivatives [14].

In conclusion, the presence of Pt centres in ethynylated compounds promotes the planar structure and then may facilitate the conjugation between the termini of the molecule, even if the irreversible nature of the electrochemical processes in the selected molecules renders speculation regarding electronic communication unwarranted and precludes further comments.

3. Experimental

3.1. Syntheses

FT-IR and Raman spectra were recorded on a Perkin–Elmer-1700X spectrophotometer. UV–Vis spectra were recorded on a Perkin–Elmer-Lambda-5 instrument. ¹H and ¹³C NMR spectra were recorded on a Varian-XL300 MHz spectrometer using solvent as reference signal (7.24 and 77 ppm for CDCl₃, respectively). Elemental analyses were determined by Servizio di Microanalisi of University of Rome “La Sapienza”.

Materials and solvents were purified by standard procedures. *p*-Nitrophenylacetylene (*p*NPA) (**1**) [15], complex **4** [16], complex **5** [17] were synthesised according to previously reported procedures. 1,2-Bis(*p*-nitrophenyl)acetylene (**2**) and 1,4-bis(*p*-nitrophenyl)butadiyne (**3**) were prepared by novel synthetic routes.

3.1.1. 1,2-bis(*p*-nitrophenyl)acetylene (**2**)

p-Nitrophenylacetylene (**1**) (400 mg, 2.7 mmol) and *p*-bromonitrobenzene (1.6 g, 8 mmol) were mixed in 60 mL of NH₄Et₂ with 101 mg (0.14 mmol) of *trans*-[Pd(PPh₃)₂Cl₂] and a catalytic amount (10 mg) of CuI. The reaction solution was stirred under argon atmosphere, at room temperature for 12 h, then the solvent was removed and the solid residue was purified by column chromatography (silica gel, 1:1 chloroform/toluene eluent). Compound **2** was eluted in the second fraction and was purified by crystallisation with chloroform, leading to yellow crystals (yield 60%). M.p. 198 °C. Elemental

analysis: Calc. for C₁₄H₈N₂O₄: C, 62.7; H, 3.0; N 10.4. Found: C, 62.1; H, 2.8; N, 10.2%. FT-IR (nujol, cm⁻¹): 1510 (ν_{as} NO₂), 1344 (ν_s NO₂). Raman (cm⁻¹): 2200 (ν C≡C). ¹H NMR (CDCl₃), δ(ppm): 7.71 (d, 4H aromatic), 8.27 (d, 4H aromatic). ¹³C NMR (CDCl₃), δ(ppm): 147.5, 132.5, 128.7, 123.6, (C aromatic) 91.0 (C≡C). UV (CHCl₃) (nm): λ_{max} 344.

3.1.2. 1,4-bis(*p*-nitrophenyl)butadiyne (**3**)

p-Nitrophenylacetylene (**1**) (400 mg, 2.7 mmol) were dissolved in 30 mL of NH₄Et₂ in the presence of CuI (10 mg); the yellow solution turned to red while the reaction run. After 1 h, a precipitate (crude compound **3**) was formed that had to be separated from the reaction solution, in order to let the reaction continue. To the cleared solution 5 mg of CuI were added again, and this procedure was repeated for six times during 24 h. The batches of **3** were collected and purified by chromatography (silica gel, 1:1 chloroform/toluene eluent). Yellow crystalline needles were obtained by crystallisation with chloroform. (yield 40%). M.p. 282 °C. Elemental analysis: Calc. for C₁₆H₈N₂O₄: C, 65.8; H, 2.8; N 9.6. Found: C, 66.1; H, 2.9; N, 9.5%. FT-IR (nujol, cm⁻¹): 1510 (ν_{as} NO₂), 1344 (ν_s NO₂). Raman (cm⁻¹): 2200 (ν C≡C). ¹H NMR (CDCl₃), δ(ppm): 7.70 (d, 4H aromatic), 8.24 (d, 4H aromatic). ¹³C NMR (CDCl₃), δ(ppm): 147.3, 132.9, 129.7, 123.3 (C aromatic); 99.3, 81.4 (C≡C). UV (CHCl₃) (nm): λ_{max} 344.

3.2. Electrochemistry

Electrochemical measurements were performed using an EG&G-PAR-273 electrochemical analyser interfaced to a PC, employing EG&G-PAR-M270 Electrochemical Software. A standard three-electrode cell was designed to allow the tip of the reference electrode to closely approach the working electrode. All measurements were carried out at room temperature (25 °C) under Ar in anhydrous deoxygenated THF; solutions were 1 × 10⁻³ M with respect to the compounds under study (for the less soluble compounds the solutions were saturated) and 2 × 10⁻¹ M for the supporting electrolyte [Bu₄N][PF₆]. The working electrode was a glassy carbon. The reference electrode was an aqueous SCE, to which all data are referred. Scan rate was 0.2 V s⁻¹. Ferrocene was used as an internal standard; E^o(Fc/Fc⁺) = +0.56 V vs. SCE in THF.

3.3. Crystal structure determination

Crystallographic data for **4** were collected on a Siemens-SMART diffractometer equipped with a rotating anode and controlled using the SMART [18] software. The radiation used was Cu Kα (λ = 1.5418 Å). Data reduction were performed with the SAINT-4.0 [19] program, an absorption correction was performed with

the program SADABS [20]. Structure was solved using the SIR97 program [21] and the structure was refined by means of SHELX [22]. Geometrical calculations were performed by PARST97 [23] and molecular plots were produced by the program ORTEP3 [24]. Details of the crystal data, data collection, structure solution and refinement are reported in [Supplementary Materials](#).

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Appendix A. Supplementary data

Crystallographic data for the structural analysis of **4** have been deposited with the Cambridge Crystallographic Data Center; publication numbers CCDC 246218. Supplementary data associated with this article can be found, in the online version at [doi:10.1016/j.jorganchem.2005.02.014](https://doi.org/10.1016/j.jorganchem.2005.02.014).

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