

Note

Platinum (II) phosphine complexes with acetylene ligands containing 1,4,5,8-naphthalenediimide: Synthesis, crystal structure and electrochemistry

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Abstract

A new acetylene ligand modified with the electron-accepting 1,4,5,8-naphthalenediimide group and its Pt(II) phosphine complexes are reported. The Pt(II) complexes incorporate optical properties of the imide group, and display two reversible imide-centred reduction processes.

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1. Introduction

The aromatic acid imides are chemically- and photo-stable compounds that combine efficient absorption and fluorescence [1] with strong electron-accepting properties [2]. These compounds can be used in the synthesis of metal complexes by attachment of the imide group to a suitable neutral [3–5] or anionic [6,7] ligand to give materials with tuneable optical and electrochemical properties.

Herein, we report a simple approach to imide-modified acetylene ligands and illustrate it by the synthesis of acetylene with attached 1,4,5,8-naphthalenediimide (NDI) group and its Pt(II) phosphine complexes. Acetylene ligands containing various functional groups, such as metallocene [8], metal-arene [9], metal-carbonyl [10], porphyrin [11], organic radical [12] or imide [6] have been used previously to prepare Pt(II) complexes. The Pt(II) phosphine acetylides have been developed for application as molecular wires [13], luminescent [14], NLO [15] or charge-transport [16] materials, and solar cell dyes [17].

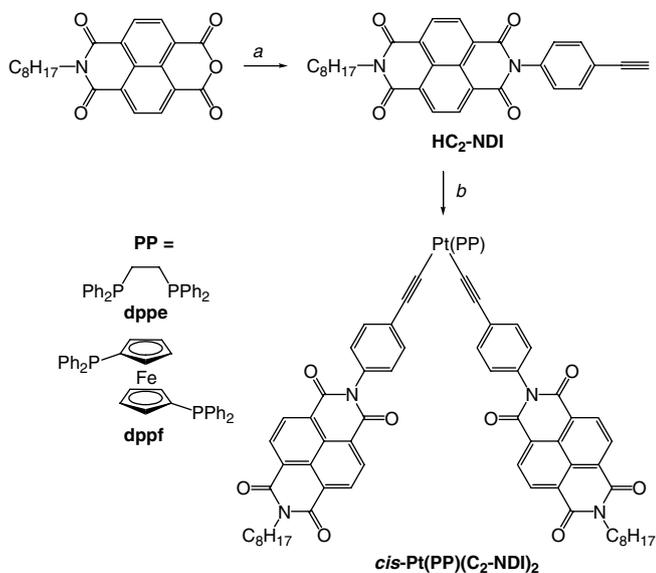
It should be noted that McAdam et al. and Robinson et al. recently reported 1,8-naphthalimide substituted acetylene and its metal complexes; however these authors prepared the acetylene ligand by a synthetic approach [6] different to the one reported here.

2. Results and discussion

The acetylene ligand HC₂-NDI was obtained by the reaction of 4-ethynylaniline with *N*-octyl-1,4,5,8-naphthalenetetracarboxylic monoanhydride in DMF at reflux (Scheme 1). The Pt(PP)Cl₂ precursor complexes (PP = dppe or dppf) were prepared in quantitative yield by the reaction of the PP ligand with PtCl₂(DMSO)₂ in dichloromethane. The target acetylides Pt(PP)(C₂-NDI)₂ were synthesised by the reaction of HC₂-NDI with Pt(PP)Cl₂ in dichloromethane in the presence of *i*-Pr₂NH as a base and CuI as a catalyst [18]. All compounds were purified by column chromatography and were identified by EI mass-spectrometry, elemental analysis and ¹H and ³¹P NMR spectroscopy.

The acetylene proton C≡CH was observed as a singlet at 3.16 ppm in the ¹H NMR spectra of the HC₂-NDI ligand. This signal was not present in the ¹H NMR spectra

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Scheme 1. Synthesis and structures of the ligand HC₂-NDI and Pt(PP)(C₂-NDI)₂ complexes: (a) 4-ethynylaniline, DMF, reflux, N₂, 24 h; (b) Pt(PP)Cl₂, CuI (catalyst), *i*-Pr₂NH (excess), CH₂Cl₂, N₂, r.t., 48 h.

of the corresponding Pt(II) acetylide complexes, confirming coordination of the ligand to the metal centre.

The absorption spectra of the new compounds are shown in Figs. 1S–3S and are summarized in Table 1. The acetylene HC₂-NDI was obtained as a pale yellow solid; its solutions in organic solvents do not have absorption bands above 400 nm. The complexes Pt(PP)(C₂-NDI)₂ were obtained as pale pink or brown solids. Their colour in solution was determined by the broad and weak unresolved absorption shoulder $\epsilon < 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in the visible region that stretched to 500 nm. The absorption of the ferrocene chromophore at 426 nm was observed in the spectra of both the precursor Pt(dppf)Cl₂ and the acetylide Pt(dppf)(C₂-NDI)₂ complexes. The absorption spectra of the new acetylene and its Pt(II) phosphine complexes in the UV region (300–400 nm) were dominated by the intense structured bands of the 1,4,5,8-naphthalenediimide chromophore [2].

The HC₂-NDI ligand and Pt(PP)(C₂-NDI)₂ complexes do not show luminescence in degassed CH₂Cl₂ solutions at r.t. (the upper limit of the luminescence quantum yield would be 0.01%).

Table 1
Absorption spectra of acetylene HC₂-NDI and Pt(II) phosphine complexes in CH₂Cl₂

Complex	$\lambda_{\text{max}}/\text{nm}$ ($10^{-3} \epsilon/\text{M}^{-1} \text{ cm}^{-1}$)
Pt(dppe)Cl ₂	298 (2.4), 256 (18)
Pt(dppf)Cl ₂	426 (0.27)
HC ₂ -NDI	380 (30), 359 (25), 342 (15)
Pt(dppe)(C ₂ -NDI) ₂	380 (74), 359 (61), 340 (43), 322 (41), 274 (42), 257 (49)
Pt(dppf)(C ₂ -NDI) ₂	426 (0.47, sh), 380 (73), 359 (61), 340 (42), 316 (43), 271 (41)

The solutions of Pt(PP)(C₂-NDI)₂ in freshly distilled and degassed dry CH₂Cl₂ or CH₃CN underwent a facile photochemical decomposition under laser irradiation in the flash-photolysis experiments (laser wavelength 355 nm, pulse duration 9 ns, pulse energy 5 mJ), which precluded investigations of excited state processes.

The Pt(II) complexes show several redox processes in the potential window between 1.5 and –2 V (all potentials are quoted vs. Fc/Fc⁺). The relevant cyclic voltammograms and electrochemical data are presented in Fig. 1 and Table 2, respectively.

A single electrochemically irreversible oxidation was observed for the Pt(dppe)(C₂-NDI)₂ complex at ~1.1 V and is likely to be associated with a Pt(II)/Pt(III) couple [19]. The first oxidation of the Pt(dppf)(C₂-NDI)₂ complex at ~0.6 V is electrochemically irreversible and is followed by a second, electrochemically reversible, oxidation at 0.83 V. A similar redox behaviour was reported for Pt(dppf)C≡CPh₂ complex in which an irreversible oxidation at 0.52 V was followed by a reversible one at 0.83 V [20]. These processes might be assigned *either* as an irreversible Pt(II)-centred oxidation, followed by a reversible oxidation of Pt(dppf) unit (for comparison, the reversible oxidation of ferrocene in Pt(dppf)Cl₂ is observed at

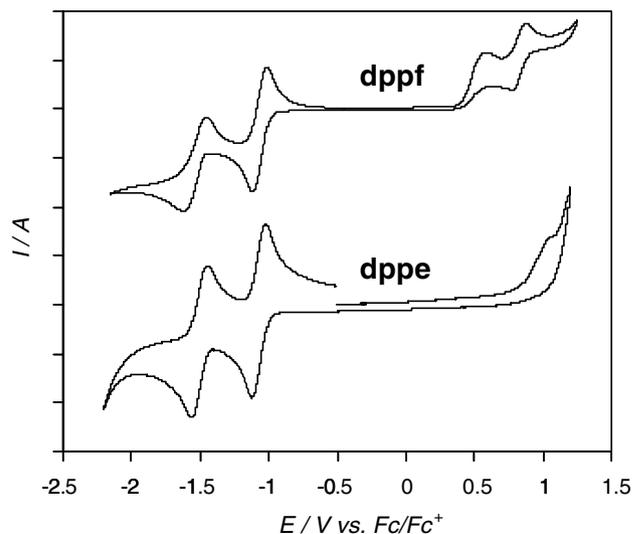


Fig. 1. Cyclic voltammograms of Pt(dppe)(C₂-NDI)₂ (200 mV/s) and Pt(dppf)(C₂-NDI)₂ (50 mV/s) in CH₂Cl₂ containing 0.1 M (NBu₄)PF₆. The unit on the vertical axis is 5 μA .

Table 2
Electrochemical data (in V vs. Fc/Fc⁺) for Pt(II) complexes in CH₂Cl₂ containing 0.1 M (NBu₄)PF₆^a

Complex	Reduction	Oxidation
Pt(dppe)(C ₂ -NDI) ₂	–1.07, –1.50	~1.1 ^b
Pt(dppf)(C ₂ -NDI) ₂	–1.07, –1.55	~0.6 ^b , 0.83

^a Anodic/cathodic peak separations for reversible processes were in the range 80–115 mV at scan rate 50 mV/s; for Fc/Fc⁺ couple used as an internal standard these values were in the range 80–100 mV.

^b Irreversible process; the anodic peak potential is reported.

0.57 V [21a]), [20,21] or as an irreversible oxidation of Pt(dppf) unit followed by a reversible oxidation of the chemical product formed in the first step [22].

Both complexes undergo two reversible reductions, at -1.07 V and ~ -1.5 V. Comparison with the literature data [2] allows us to assign these processes as two consecutive one-electron reductions of the NDI group. The two NDI groups present in the complex are being reduced at the same potentials, indicating a lack of electronic communication between them. The reduction potentials of the NDI group are not sensitive to the change of the Pt(PP) group, indicating that these two units are decoupled.

The crystal structure of Pt(dppe)(C₂-NDI)₂ is shown in Fig. 2. The Pt(II) centre is in a distorted square planar coordination environment. The Pt–C≡C fragment is not linear, but bent, with angles of 162–165°. The shortest Pt...Pt distance is 8.054 Å indicating the absence of metal–metal interaction. The bond lengths and angles around the Pt(II) centre, as well as the non-linearity of the Pt–C≡C fragment in Pt(dppe)(C₂-NDI)₂ are similar to the previously reported structures of *cis*-Pt(dppe) acetylide complexes [14c].

The NDI groups are planar and are almost orthogonal to the attached phenylacetylene group with dihedral angles of $\sim 80^\circ$. The molecule lacks elements of symmetry in the solid state structure. As a result, each NDI group in the molecule is unique, and is involved in *one* intermolecular aromatic π – π interaction with the NDI group of another molecule, with the inter-planar distances of 3.356 Å and 3.359 Å, respectively. The net result is the formation of an infinite chain of molecules connected through π – π interactions and arranged in a head-to-head fashion.

In conclusion, we have shown that an acetylene ligand can be easily modified with an electron-accepting 1,4,5,8-naphthalenediimide group and consequently used to prepare stable metal complexes. The Pt(dppf)(C₂-NDI)₂ complex which combines ferrocene and imide groups can be considered as a Pt(II)-based donor–acceptor system.

The synthetic approach to modified acetylenes described in this ‘Note’ could potentially be extended to incorporate any imide group. A simple variation of the attached imide is expected to fine-tune the optical and electrochemical properties of the acetylene ligand and its metal complexes.

3. Experimental

All reactions were carried out in the dark under N₂, using general grade solvents that were degassed by bubbling N₂ for 10 min. Purification, crystal growth and handling of all compounds were carried out under air with a minimum exposure to light. All products were air- and moisture-stable solids which were stored in the dark when not used.

3.1. Synthesis of *N*-octyl-1,4,5,8-naphthalenetetracarboxylic monoanhydride

The synthesis is based on the reported procedure [1a] which was significantly modified. *n*-Octylamine (2 ml, 1.56 g, 12 mmol, excess) was added to a suspension of 1,4,5,8-naphthalenetetracarboxylic dianhydride (1 g, 3.73 mmol) in a mixture of water (10 ml) and *n*-propanol (10 ml) at r.t. under N₂. The suspension dissolved in 10 min, and the resulting solution was heated at 50 °C (important) for 24 h to give a white precipitate. The reaction mixture was cooled down to r.t., acidified to pH 1 with HCl to give more precipitate, and was then further stirred for 1 h at r.t. The solid was filtered off and stirred in acetic acid (50 ml or more) at reflux for 1 h or longer, producing first a suspension and then a clear yellow solution. It was cooled to r.t. (a precipitate is formed on cooling), diluted with CH₂Cl₂ (200 ml) and extracted with water (200 ml) to give clear organic and aqueous layers (the formation of an inseparable emulsion at this stage can be avoided by addition of more acetic acid). The organic layer was dried if necessary (MgSO₄) and then reduced in volume. Addition of ethanol (50 ml) and evaporation of CH₂Cl₂ gave a suspension of the product in ethanol that was filtered off, washed with ethanol, hexane and small amount of ether.

The product was obtained as a 1:12 molar mixture of the bis- and mono-imide and was used without further purification (the bis-imide is an inert impurity which is easily removed in the next reaction step). It should be noted that the amount of bis-imide impurity increases if the reaction is carried out at temperatures higher than 50 °C. Crude yield – 0.99 g, contains 0.90 g (2.38 mmol, 64%) of mono-imide.

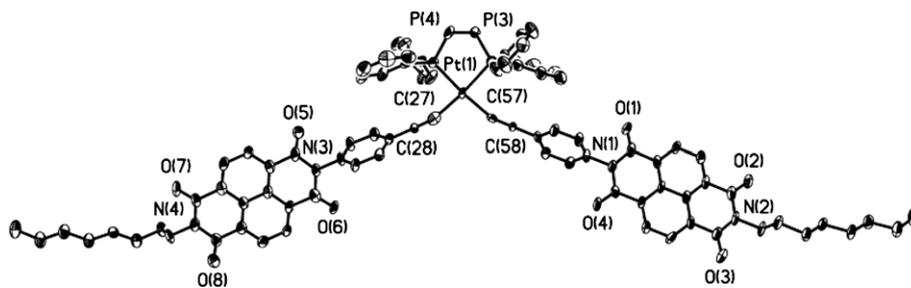


Fig. 2. Molecular structure of Pt(dppe)(C₂-NDI)₂ (50% probability ellipsoids, H atoms omitted). Selected bond lengths (Å): Pt(1)–C(27) 2.024(11), Pt(1)–C(57) 2.042(9), Pt(1)–P(3) 2.262(2), Pt(1)–P(4) 2.263(2). Selected angles (°): C(27)–Pt(1)–C(57) 97.9(3), P(3)–Pt(1)–P(4) 86.49(9), C(57)–Pt(1)–P(3) 88.2(2), C(27)–Pt(1)–P(4) 87.4(3), C(27)–Pt(1)–P(3) 173.9(3), C(57)–Pt(1)–P(4) 174.6(3), C(28)–C(27)–Pt(1) 164.5(8), C(58)–C(57)–Pt(1) 162.0(8). The dihedral angle between the planes defined by P(3) Pt(1) P(4) and C(27) Pt(1) C(57) atoms is 1.05°.

The product was obtained as a white or pale pink solid; $C_{22}H_{21}NO_5$ (MW 379.41); soluble in CH_2Cl_2 and acetone, insoluble in ethanol and hexane. Characteristic 1H NMR ($CDCl_3$) signals were observed in aromatic region for the mono-imide at 8.81 ppm (s) and for the bis-imide at 8.75 ppm (s).

3.2. Synthesis of the acetylene HC_2 -NDI

4-Ethynylaniline (131 mg, 1.12 mmol) and *N*-octyl-1,4,5,8-naphthalenetetracarboxylic monoanhydride (424 mg, 1.12 mmol) were refluxed in dry degassed DMF (5 ml) for 24 h. Cooling the reaction mixture to r.t. followed by addition of a mixture of hexane and ether precipitated the crude product that was filtered and purified by column chromatography (SiO_2 , 0–0.2% CH_3OH in CH_2Cl_2). Yellow solid – 183 mg (0.38 mmol, 34%). Anal. Calc. for $C_{30}H_{26}N_2O_4$ (MW 478.54): C, 75.30; H, 5.48; N, 5.85. Found: C, 75.50; H, 5.54; N, 5.80%. EI MS m/z : 478 (100%, M^+). 1H NMR ($CDCl_3$): 0.82–0.92 (m, 3H), 1.2–1.5 (m, 10H), 1.68–1.82 (m, 2H), 3.16 (s, 1H), 4.20 (t, J 7.6, 2H), 7.29 (d, J 8.9, 2H), 7.69 (d, J 8.9, 2H), 8.80 (s, 4H).

3.3. General synthesis of $Pt(PP)(C_2\text{-NDI})_2$ complexes

$Pt(PP)Cl_2$ (PP = dppe or dppf), HC_2 -NDI (excess) and CuI (catalyst) in a degassed mixture of dry CH_2Cl_2 (10 ml) and dry *i*-Pr₂NH (1 ml) under N_2 were sonicated for 1 h and stirred for 48 h at r.t. to give yellow or orange solution. The reaction mixture was diluted with CH_2Cl_2 and extracted with water. The organic phase was separated, dried ($MgSO_4$) and evaporated to dryness. Purification by column chromatography (SiO_2 , 0.5% CH_3OH in CH_2Cl_2) gave the product as a first major yellow fraction. It was reduced in volume and the product was precipitated with ether. The complexes are highly soluble in CH_2Cl_2 .

$Pt(dppe)(C_2\text{-NDI})_2$: $Pt(dppe)Cl_2 \cdot (CH_2Cl_2)_{0.5}$ (49 mg, 0.069 mmol), HC_2 -NDI (75 mg, 0.157 mmol, excess) and CuI (5 mg, catalyst) gave 65 mg (0.042 mmol, 61%) of the product as a pink solid. Anal. Calc. for $C_{86}H_{74}N_4O_8P_2Pt$ (MW 1548.56): C, 66.70; H, 4.82; N, 3.62. Found: C, 66.42; H, 4.67; N, 3.51%. 1H NMR (CD_2Cl_2): 0.82–0.92 (m, 6H), 1.2–1.5 (m, 20H), 1.68–1.8 (m, 4H), 2.50 (d, J 19, 4H, br Pt sat), 4.16 (t, J 7.6, 4H), 7.06 (d, J 8.9, 4H), 7.26 (d, J 8.9, 4H), 7.45–7.54 (m, 12H), 7.9–8.03 (m, 8H), 8.74 (s, 8H). ^{31}P NMR: 42.09 (s, J_{Pt-P} 2273).

$Pt(dppf)(C_2\text{-NDI})_2$: $Pt(dppf)Cl_2 \cdot (CH_2Cl_2)_{0.4}$ (60 mg, 0.07 mmol), HC_2 -NDI (75 mg, 0.157 mmol, excess), CuI (5 mg, catalyst) gave 60 mg (0.035 mmol, 50%) of the product as a pale-brown solid. Anal. Calc. for $C_{94}H_{78}FeN_4O_8P_2Pt$ (MW 1704.52): C, 66.24; H, 4.61; N, 3.29. Found: C, 66.00; H, 4.44; N, 3.01%. 1H NMR (CD_2Cl_2): 0.81–0.91 (m, 6H), 1.20–1.46 (m, 20H), 1.62–1.78 (m, 4H), 4.15 (t, br, 4H), 4.23 (m, 4H), 4.36 (m, 4H), 6.88–7.00 (m, 8H), 7.35–7.50 (m, 12H), 7.83–7.95 (m, 8H), 8.73 (s, 8H). ^{31}P NMR: 14.91 (s, J_{Pt-P} 2377).

3.4. X-ray crystallography

Single crystals of the $Pt(dppe)(C_2\text{-NDI})_2$ complex were obtained by slow evaporation of a CH_2Cl_2 -heptane solution.

$Pt(dppe)(C_2\text{-NDI})_2$: $C_{86}H_{74}N_4O_8P_2Pt$: MW 1548.52; pink plates; size (mm): $0.18 \times 0.07 \times 0.03$; $T = 150(2)K$; $\lambda = 0.71073 \text{ \AA}$; triclinic; space group $P\bar{1}$ (C_i^1 , no.2); $a/b/c$ (\AA) = $8.0541(7)/18.5909(19)/24.538(2)$; $\alpha/\beta/\gamma$ ($^\circ$) = $98.279(8)/90.059(5)/102.383(6)$; $V = 3549.3(6) \text{ \AA}^3$; $Z = 2$; $\rho_{calc} = 1.449 \text{ g cm}^{-3}$; $\mu = 2.085 \text{ mm}^{-1}$; $F(000) = 1580$; θ range ($^\circ$) = $0.84\text{--}25.00$; min/max transmission = $0.7054/0.9401$; reflections collected/ R_{int} = $48203/0.1002$; data/restraints/parameters = $12051/0/910$; GOF on $F^2 = 1.052$; $R(I > 2\sigma_I)$: $R_1 = 0.0588$, $wR_2 = 0.1206$; $R(\text{all data})$: $R_1 = 0.1264$, $wR_2 = 0.1563$; $\Delta\rho_{min/max}$ ($e \text{ \AA}^{-3}$) = $-2.717/2.123$.

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Appendix A. Supplementary material

CCDC 623168 contain the supplementary crystallographic data for $Pt(dppe)(C_2\text{-NDI})_2$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article (additional experimental details and absorption spectra) can be found, in the online version, at [doi:10.1016/j.jorgchem.2006.10.060](https://doi.org/10.1016/j.jorgchem.2006.10.060).

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