ELSEVIER

Journal of Organometallic Chemistry 627 (2001) 13–22

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Synthesis, characterisation and optical properties of symmetrical and unsymmetrical Pt(II) and Pd(II) bis-acetylides. Crystal structure of *trans*-[Pt(PPh_3)$_2$(C≡C–C_6H_5)(C≡C–$C_6H_4NO_2$)]

R. D'Amato [a,*], A. Furlani [a], M. Colapietro [a], G. Portalone [a], M. Casalboni [b], M. Falconieri [c], M.V. Russo [a]

[a] *Dipartimento di Chimica, Università di Roma 'La Sapienza', Piazzale Aldo Moro 5, 00185 Rome, Italy*
[b] *Dipartimento di Fisica ed Istituto Nazionale di Fisica della Materia, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 1-00133 Rome, Italy*
[c] *ENEA, C.R. Casaccia, Via Anguillarese, 301-00060 Rome, Italy*

Received 3 August 2000; received in revised form 3 September 2000; accepted 10 October 2000

Abstract

Symmetric *trans*-[Pt(PPh_3)$_2$(C≡CR)$_2$] and unsymmetrical *trans*-[Pt(PPh_3)$_2$Cl(C≡CR)], (R = C_6H_4–*p*NO_2, C_6H_4–*p*OCH_3), Pt(II) acetylides were prepared and characterised, as well as unsymmetrical Pt(II) bis-acetylides, *trans*-[Pt(PPh_3)$_2$(C≡CR)(C≡CR′)], (R = C_6H_4–*p*NO_2, R′ = C_6H_5; R = C_6H_4–*p*OCH_3, R′ = C_6H_5; R = C_6H_4–*p*OCH_3, R′ = C_6H_4–*p*NO_2; R = C_6H_4–*p*NO_2, R′ = [(η^5-C_5H_4)Fe(η^5-C_5H_5)]). Also symmetric Pd(II) bis-acetylides, *trans*-[Pd(PPh_3)$_2$(C≡CR)$_2$] (R = C_6H_4–*p*NO_2, C_6H_5) were synthesised and characterised by IR, NMR, and UV–vis spectroscopies. The optical properties of the new complexes were compared within a series of known Pt(II) complexes containing different phosphines and *cis–trans* configuration. The absorption and photoluminescence spectra indicate that the emission is found in the range 355–600 nm, depending on the nature of the acetylide ligand bound to Pt. Measurements of SHG for the unsymmetrical bis-acetylides dispersed in polymethylmethacrylate (PMMA) show that the second-order nonlinear optical (NLO) properties depend on the strength of the donor–acceptor substituent of the acetylide ligand. Third-order NLO properties (in particular the nonlinear absorption coefficient α_2) were measured by the Z-scan technique; strong push–push and pull–pull substituents on the Pt(II) symmetric bis-acetylides induce electronic delocalisation and tuning of the NLO properties. The single crystal X-ray structure of *trans*-[Pt(PPh_3)$_2$(C≡C–C_6H_5)(C≡C–$C_6H_4NO_2$)] shows that the unsymmetrical molecule crystallised in the *Pbca* centric space groups.

Keywords: Pt, Pd acetylides; Optical properties; Crystal structures

1. Introduction

A great deal of interest has been devoted to the synthesis of new π-conjugated polymers, in view of their third-order non-linear optical properties (NLO) [1,2]. The most investigated systems have been metal containing polyynes, showing high π-electron delocalisation, increased by the dπ–pπ* interactions between the metal centres and the polyyne ligands [3–5]. Numerous investigations have been also carried out on acetylide complexes, mainly on dinuclear complexes, and electron transfer between the metallic centres has been confirmed [6–9]. Although a great number of organometallic complexes have been studied, some examples have only recently been reported on complexes in which electron withdrawing and electron donor fragments had been combined in order to obtain high first order hyperpolarisabilities [10–12]. New ferrocenyl hetero-bimetallic compounds have been recently synthesised [13], for which large β values, as determined by the hyper Rayleigh scattering method, have been found.

Preliminary investigations performed a few years ago on unsymmetrical Pt acetylides evidentiated second order NLO properties of these materials [3], but no further studies were carried out. On the basis of our experience in the synthesis of Pt acetylides [14–16], we

---

* Corresponding author. Tel.: +39-06-49913347; fax: +39-06-490324.

E-mail address: rosaria.damato@uniroma1.it (R. D'Amato).

0022-328X/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(00)00791-9

have now prepared and characterised a series of symmetrical and unsymmetrical Pt and Pd complexes. We hereby report on the synthesis of some of these complexes, and the characterisation of their NLO properties. The unsymmetrical bis-acetylides were prepared in order to investigate the influence of the electron attracting and electron releasing substituents of the acetylenic ligands on the second order NLO properties. The effect of substituents on the third order NLO properties of unsymmetrical and symmetrical complexes has been also investigated by the *Z*-scan technique and a correlation between chemical structure and NLO response is proposed. The X-ray crystal structure of the unsymmetrical bis-acetylide $[Pt(PPh_3)_2(C{\equiv}C{-}C_6H_5)(C{\equiv}C{-}C_6H_4NO_2)]$ is also reported.

2. Experimental

2.1. Instruments

IR and FIR spectra were recorded as Nujol mulls or KBr mixture on a Fourier Transform Perkin–Elmer 1700 spectrometer. Laser Raman spectra were observed on a Fourier Transform Perkin–Elmer 1700 spectrometer, using Nd:YAG laser light, at 1064 nm. UV spectra were recorded on a Perkin–Elmer Lambda 5 spectrometer, using 1-cm optical fused quartz cells, and $CHCl_3$ as the solvent. Photoluminescence measurements were carried out using a fluorescence spectrophotometer Perkin Elmer PL50 on $CHCl_3$ solutions at room temperature, using 1-cm optical fused quartz cells. ^1H-, ^{13}C- and ^{31}P-NMR spectra were run on a Varian XL300 instrument in $CDCl_3$ solutions; the solvent was used as a reference ($\delta = 7.24$ and 77 ppm) for ^1H and ^{13}C spectra; 85% H_3PO_4 was used as a reference ($\delta = 0$) in ^{31}P spectra. Elemental analyses were carried out at the Laboratorio di Microanalisi, University of Pisa and at Department of Chemistry, University of Rome 'La Sapienza'. Fast Atom Bombardment (FAB) analyses were performed with a VG Quattro instruments, using 3-nitrobenzyl-alcohol as matrix and the reported molecular weights. were determined by this technique. The second order nonlinear optical measurements were performed using the second harmonic generation technique (SHG). The complexes were dispersed in polymethylmethacrilate (PMMA) and the films were poled by high temperature corona-poling [17]. The third order nonlinear optical properties of complexes have been studied with the *Z*-scan set-up reported by M. Falconieri et al. [18,19]. The laser source was a self-mode-locked Ti-sapphire delivering 130 fs linearly polarised pulses with 76 MHz repetition rate at laser wavelength of 770 nm.

2.2. Materials

All the solvents and products (reagent-grade Carlo Erba) were dried according to conventional methods before use. The complexes *cis*-$[Pt(PPh_3)_2Cl_2]$ [20], *cis*-$[Pt(PTol_3)_2Cl_2]$ ($PTol_3$ = tri *para*-tolylphosphine), *cis*-$[Pt(PMePh_2)_2Cl_2]$ [21], and *trans*-$[Pd(PPh_3)_2Cl_2]$ [22] were prepared following the procedures reported in the literature. The synthesis of *cis*-$[Pt(dppe)Cl_2]$ (dppe = 1,2-diphenylphosphinoethane) reported by Westland [23] was modified according to Leviston et al. [24]. Phenylacetylene (PA) (Fluka-purum) was distilled under vacuum prior to use; *p*-nitrophenylacetylene (pNPA) was prepared following a published method [25]; ethynylferrocene (Efc) was obtained with modifying the method reported by Doisneau et al. [26]; the synthesis of *p*-methoxyphenylacetylene (pMOPA) was performed with the literature procedure [27].

2.3. Syntheses of the complexes

The synthesis of the bis(acetylide) complexes *trans*-$[Pt(PMePh_2)_2(C{\equiv}C{-}C_6H_5)_2]$ (**14**) [28], *trans*-$[Pt(PPh_3)_2(C{\equiv}C{-}C_6H_5)_2]$ (**19**) [14], *trans*-$[Pt(PPh_3)_2(C{\equiv}C{-}C_6H_5)(C{\equiv}C{-}\{\eta^5\text{-}C_5H_4\}Fe\{\eta^5\text{-}C_5H_5\})]$ (**18**) [29], and of the monochloroacetylides *trans*-$[Pt(PPh_3)_2(C{\equiv}C{-}C_6H_5)Cl]$ [16] and *trans*-$[Pt(PPh_3)_2(C{\equiv}C{-}\{\eta^5\text{-}C_5H_4\}Fe\{\eta^5\text{-}C_5H_5\})Cl]$ [29] were already reported. Also the reaction procedures for the synthesis of some symmetric complexes i.e. *trans*-$[Pt(PTol_3)_2(C{\equiv}C{-}C_6H_5)_2]$ (**12**), *trans*-$[Pt(PTol_3)_2(C{\equiv}C{-}\{\eta^5\text{-}C_5H_4\}Fe\{\eta^5\text{-}C_5H_5\})_2]$ (**13**), *trans* - $[Pt(PMePh_2)_2(C{\equiv}C{-}\{\eta^5\text{-}C_5H_4\}Fe\{\eta^5\text{-}C_5H_5\})_2]$ (**15**), *cis*-$[Pt(dppe)(C{\equiv}C{-}C_6H_5)_2]$ (**16**) and *cis*-$[Pt(dppe)(C{\equiv}C{-}\{\eta^5\text{-}C_5H_4\}Fe\{\eta^5\text{-}C_5H_5\})_2]$ (**17**) were reported elsewhere [30].

2.3.1. Symmetric bis(acetylide) bis(phosphine) Pt complexes

Complexes **1** and **2** were prepared using the proper Pt(II) precursors and acetylenic monomers, following a well established reaction route. The basis for the assignment of *cis* and *trans* structures of the complexes is given in next session.

*2.3.1.1. trans-$[Pt(PPh_3)_2(C{\equiv}C{-}C_6H_4NO_2)_2]$ (**1**).* *cis*-$[Pt(PPh_3)_2Cl_2]$ (0.500 g, 0.63×10^{-3} mol) was treated with $HC{\equiv}C{-}C_6H_4NO_2$ (0.500 g, 3.4×10^{-3} mol) in Et_2NH (20 ml) in the presence of a catalytic amount of CuI (5 mg) at reflux for 2 h. A crude material was obtained, insoluble in the reaction solvent. After filtration and washing with Et_2NH, H_2O and EtOH a yellow product was obtained that was crystallised from $CHCl_3$–EtOH (0.450 g, 70% yield). M.W. (a.m.u.) = 1012. Elemental analysis (%): Calc. for $C_{52}H_{38}N_2O_4P_2Pt$: C, 61.72; H 3.79; N 2.77. Calc. for

$C_{52}H_{38}N_2O_4P_2Pt\cdot1/3CHCl_3$: C, 59.71; H, 3.64; N, 2.66. Found: C, 59.53; H, 3.59; N, 2.77. IR (cm^{-1}): 2107 ($\nu_{C\equiv C}$).

2.3.1.2. trans and cis-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$OCH$_3$)$_2$] ***(2** and **3)***. The reaction procedures were the same reported for complex **1**. The crude product contained both *trans* and *cis*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$OCH$_3$)$_2$], as was evidentiated from ^{31}P-NMR spectrum, and they were separated by crystallisation from CHCl$_3$–EtOH. The first precipitate is the *trans* product (0.300 g, 50% yield), while the *cis* complex was obtained as yellow crystals by dry evaporation of crystallisation solvents (0.060 g, 10% yield). *trans*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$OCH$_3$)$_2$]: *M.W.* (a.m.u.) = 982. Elemental analysis (%): Calc. for $C_{54}H_{44}O_2P_2Pt$: C, 66.05; H, 4.52. Calc. for $C_{54}H_{44}O_2P_2Pt\cdot1/5CHCl_3$: C, 64.72; H, 4.43. Found: C, 64.66; H, 4.57. IR (cm^{-1}): 2109 ($\nu_{C\equiv C}$). *cis*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$OCH$_3$)$_2$]: *M.W.* (a.m.u.) = 982. Elemental analysis (%): Found: C 65.84; H 4.70. IR (cm^{-1}): 2122 ($\nu_{C\equiv C}$).

2.3.2. Monochloro(acetylide) bis(triphenylphosphine) Pt complexes

The novel monochloro-acetylides **4** and **5** were obtained through similar procedures, reported in detail for complex **4**. The synthesis of complex **5** is reported concisely in Table 1.

*2.3.2.1. trans-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$NO$_2$)Cl] (**4**)*. A mixture of *cis*-[Pt(PPh$_3$)$_2$Cl$_2$] (0.500 g, 0.63 × 10^{-3} mol) and pNPA (0.670 g, 4.5 × 10^{-3} mol) in CHCl$_3$ (40 ml) with 0.8 ml of Et$_2$NH was refluxed for 2 h. Upon addition of absolute ethanol the yellow product precipitated. The pure, crystalline product was obtained by recrystallisation from CHCl$_3$–EtOH (0.230 g, 40% yield). *M.W.* (a.m.u.) = 901. Elemental analysis (%): Calc. for $C_{44}H_{34}ClNO_2P_2Pt$: C, 58.64; H, 3.80; Cl, 3.93; N, 1.55; Found: C, 58.55; H, 3.72; N, 1.53. IR (cm^{-1}): 2118 ($\nu_{C\equiv C}$), 320, 280 (ν_{Pt-Cl}).

*2.3.2.2. trans-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$OCH$_3$)Cl] (**5**)*. 0.400 g, 80% yield. *M.W.* (a.m.u.) = 886. Elemental analysis (%): Calc. for $C_{45}H_{37}ClOP_2Pt$: C, 60.39; H,

Table 1
Comprehensive data for the synthesis of Pt and Pd complexes

No.	Complex	Reference	Reactions conditions	Cryst. solvent	Yield (%)	M.p. (°C)
1	*trans*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$NO$_2$)$_2$]		Et$_2$NH–CuI, reflux, 2 h	CHCl$_3$–EtOH	70	> 350(dec.)
2	*trans*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$OCH$_3$)$_2$]		Et$_2$NH–CuI, reflux, 2 h	CHCl$_3$–EtOH	50	247–248
3	*cis*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$OCH$_3$)$_2$]		Et$_2$NH–CuI, reflux, 2 h	CHCl$_3$–EtOH	10	> 200(dec.)
4	*trans*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$NO$_2$)Cl]		CHCl$_3$–Et$_2$NH, reflux, 2 h	CHCl$_3$–EtOH	40	235–238
5	*trans*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$OCH$_3$)Cl]		CHCl$_3$–Et$_2$NH, reflux, 2 h	CHCl$_3$–EtOH	80	214–215
6	*trans*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_5$)-(C$\equiv$C–C$_6$H$_4$NO$_2$)]		From Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_5$)Cl, CHCl$_3$–Et$_2$NH, reflux, 3 h	CHCl$_3$–EtOH	55	234–236
			From **4**, CHCl$_3$–Et$_2$NH reflux, 3h	CHCl$_3$–EtOH	85	234–236
7	*trans*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_5$)-(C$\equiv$C–C$_6$H$_4$OCH$_3$)]		From **5**, Et$_2$NH, reflux, 2 h, chrom. silica gel–toluene	CHCl$_3$–EtOH	60	225–226
8	*trans*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$NO$_2$)-(C$\equiv$C–C$_6$H$_4$OCH$_3$)]		From **5**, Et$_2$NH, reflux, 3 h, chrom. silica gel–toluene	CHCl$_3$–EtOH	65	222–223
9	*trans*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$NO$_2$)-(C$\equiv$C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})]		From Pt(C$\equiv$C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})Cl, CHCl$_3$–Et$_2$NH, reflux, 3 h	CHCl$_3$–EtOH	85	246–248
10	*trans*-[Pd(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_5$)$_2$]		Et$_2$NH–CuI, r.t., 1 h	C$_6$H$_6$–EtOH	80	126–128
			MeOH–NaOH–CuI, r.t., 24 h	Toluene–MeOH	93	126–128
11	*trans*-[Pd(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_4$NO$_2$)$_2$]		Et$_2$NH–CuI, r.t., 6 h	C$_6$H$_6$–EtOH	86	143–145
12	*trans*-[Pt(PTol$_3$)$_2$(C$\equiv$C–C$_6$H$_5$)$_2$]	[30]	Et$_2$NH–CuI, reflux, 18 h	Toluene–EtOH	90	213–215
13	*trans*-[Pt(PTol$_3$)$_2$-(C$\equiv$C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})$_2$]	[30]	Et$_2$NH–CuI, reflux, 3 h	CH$_2$Cl$_2$–EtOH	90	226–228
14	*trans*-[Pt(PMePh$_2$)$_2$(C$\equiv$C–C$_6$H$_5$)$_2$]	[28]	Et$_2$NH–CuI, reflux, 30 min	CHCl$_3$–EtOH	55	193–194
15	*trans*-[Pt(PMePh$_2$)$_2$-(C$\equiv$C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})$_2$]	[30]	Et$_2$NH–CuI, reflux, 1 h	CHCl$_3$–EtOH	85	> 250(dec.)
16	*cis*-[Pt(dppe)(C$\equiv$C–C$_6$H$_5$)$_2$]	[30]	Et$_2$NH–CuI, reflux, 5 h	CHCl$_3$–hexane	85	> 200(dec)
17	*cis*-[Pt(dppe)-(C$\equiv$C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})$_2$]	[30]	Et$_2$NH–CuI, reflux, 5 h	C$_6$H$_6$–EtOH	25	> 250(dec.)
18	*trans*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_5$) (C$\equiv$C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})]	[29]	From Pt(C$\equiv$C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})Cl, CHCl$_3$–Et$_2$NH, reflux, 1 h	C$_6$H$_6$–EtOH	70	210–212
19	*trans*-[Pt(PPh$_3$)$_2$(C$\equiv$C–C$_6$H$_5$)$_2$]	[14]	Et$_2$NH–CuI, reflux, 2 h	CHCl$_3$–EtOH	85	220–222

4.21. Found: C, 60.84; H, 4.70. IR (cm^{-1}): 2125 ($\nu_{C\equiv C}$), 316, 280 (ν_{Pt-Cl}).

2.3.3. Unsymmetrical bis(acetylide) bis(triphenylphosphine) Pt complexes

The reaction route for the synthesis of the unsymmetrical complex **6** is reported in detail. Complexes **7**, **8**, **9** were prepared following the same procedure: the reaction conditions are summarised in Table 1.

*2.3.3.1. trans-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$)(C≡C–C$_6$H$_5$)] (**6**).* The unsymmetrical complex **6** was prepared in two ways: (i) 0.170 g (0.19 × 10^{-3} mol) of *trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$)Cl] (**4**) were dissolved in 10 ml of CHCl$_3$ with 0.1 ml (0.09 g, 1.0 × 10^{-3} mol) of PA and 0.8 ml of Et$_2$NH. The reaction mixture refluxed for 3 h and complex **6** was obtained as a yellow powder by addition of EtOH and crystallised from CHCl$_3$–EtOH (0.160 g, 85% yield). (ii) *trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_5$)Cl] and pNPA (molar ratio 1:1) were dissolved in CHCl$_3$ following the procedure described in point (i). The complex **6** was recrystallised from CHCl$_3$–EtOH (0.100 g, 55% yield). *M.W.* (a.m.u.) = 967. Elemental analysis (%): Calc. for $C_{52}H_{39}NO_2P_2Pt$: C, 64.59; H, 4.07; N, 1.45. Found: C, 64.18; H, 4.16; N, 1.61. IR (cm^{-1}): 2109 ($\nu_{C\equiv C}$).

*2.3.3.2. trans-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$OCH$_3$)(C≡C–C$_6$H$_5$)] (**7**).* Complex **7** was obtained from PA and *trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$OCH$_3$)Cl] (**5**) (60% yield). *M.W.* (a.m.u.) = 952. Elemental analysis (%): Calc. for $C_{53}H_{42}OP_2Pt$: C, 66.87; H, 4.45. Found: C, 66.62; H, 4.26%. IR (cm^{-1}): 2109 ($\nu_{C\equiv C}$).

*2.3.3.3. trans-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$OCH$_3$)(C≡C–C$_6$H$_4$NO$_2$)] (**8**).* Complex **8** was obtained from pNPA and *trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$OCH$_3$)Cl] (65% yield). *M.W.* (a.m.u.) = 997. Elemental analysis (%): Calc. for $C_{53}H_{41}NO_3P_2Pt$: C, 63.85; H, 4.15; N, 1.40. Anal. Calc. for $C_{53}H_{41}NO_3P_2Pt \cdot 1/4CHCl_3$: C, 62.29; H, 4.05; N, 1.36. Found: C, 62.57; H, 3.99; N, 1.35. IR (cm^{-1}): 2105 ($\nu_{C\equiv C}$).

*2.3.3.4. trans-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$)(C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})] (**9**).* Complex **9** was obtained from pNPA and *trans*-[Pt(PPh$_3$)$_2$(C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})Cl] (85% yield). *M.W.* (a.m.u.) = 1075. Elemental analysis (%): Calc. for $C_{56}H_{43}FeNO_2P_2Pt$: C, 62.58; H, 4.03; N, 1.30. Found: C, 61.58; H, 4.05; N, 1.24. IR (cm^{-1}): 2106 ($\nu_{C\equiv C}$).

2.3.4. Symmetrical bis(acetylide) bis(triphenylphosphine) Pd complexes

Complexes **10** and **11** were prepared according to the reaction procedures reported for complex **1** (Table 1). Complex **10** was also obtained using a new method:

*2.3.4.1. trans-[Pd(PPh$_3$)$_2$(C≡C–C$_6$H$_5$)$_2$] (**10**).* A mixture of 0.200 g (0.3 × 10^{-3} mol) of *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] and 0.1 ml (0.093 g, 0.9 × 10^{-3} mol) of PA in 4 ml of a 0.2 M solution of NaOH in MeOH with 5 mg of CuI were stirred magnetically for 18–20 h at $T = 20°C$. We observed formation of a snow-white powder that was filtered, washed with H$_2$O and MeOH and then crystallised from C$_6$H$_6$–EtOH (0.240 g, yield 95%). Elemental analysis (%): Calc. for $C_{52}H_{40}P_2Pd$: C, 74.96; H, 4.84. Found C, 75.79; H, 5.06. IR (cm^{-1}): 2108 ($\nu_{C\equiv C}$).

*2.3.4.2. trans-[Pd(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$)$_2$] (**11**).* Yield 85%. Elemental analysis (%): Calc. for $C_{52}H_{38}N_2O_4P_2Pd$: C, 67.65; H, 3.03; N, 4.15. Anal. Calc. for $C_{52}H_{38}N_2O_4P_2Pd \cdot C_6H_6$: C, 69.57; H, 4.39; N, 2.80. Found: C, 69.98; H, 4.42; N, 2.95. IR (cm^{-1}): 2103 ($\nu_{C\equiv C}$).

3. Results and discussions

3.1. Synthesis of the complexes

In order to obtain new complexes with second and third order nonlinear optical properties, a series of new Pt(II) and Pd(II) acetylides were synthesised. A summary of all the experimental procedures is shown in Table 1.

The use of Et$_2$NH as solvent, in the presence of CuI as catalyst, and with an excess of the appropriate acetylenes (ca. 1:5 ratio) led to the successful synthesis of a wide range of symmetrical Pt(II) bis(acetylide) complexes (see Refs. [14,30]). This result demonstrates the wide applicability of this synthetic approach. It is worth noting that, while we generally obtain the *trans* isomer of the complexes, a small amount of *cis* form of the *p*-methoxyphenylacetylide was also observed and subsequently isolated as illustrated in Section 2. A similar result was observed for the complex [Pt(PPh$_3$)$_2$C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})$_2$]. The insoluble *trans* isomer was isolated by filtration, and the *cis* form was crystallised from THF–EtOH [30].

In order to obtain the monochloro-acetylide species, we used CHCl$_3$ as the solvent and only a small amount of Et$_2$NH. This procedure avoided undesired formation of significant amounts of the corresponding symmetric bis(acetylide) complexes [16].

The unsymmetrical complexes were obtained reacting the monochloro-acetylides *trans*-[Pt(PPh$_3$)$_2$(C≡C–R)Cl] with the related alkyne HC≡C–R^1 in Et$_2$NH as solvent. It is noteworthy that complexes **7**, **8**, **9**, **18** can only be obtained from the monochloro-acetylide containing the OCH$_3$ or ferrocene groups, as shown in Fig. 1. The necessity for the presence of an electron-donating group on the reacting acetylide can be interpreted in terms of a charge repulsion effect towards the Cl ligand, and an

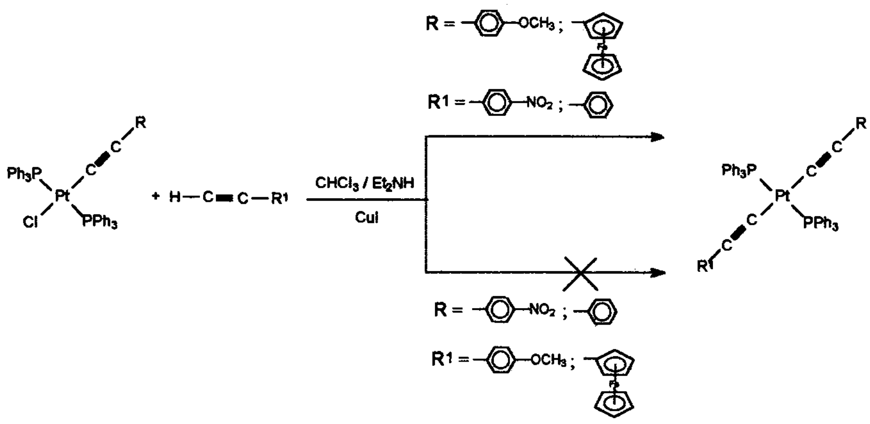

Fig. 1. Reaction scheme for the synthesis of asymmetric platinum complexes.

enhancement of the coordination of the entering acetylenic ligand (i.e. $-C{\equiv}C-C_6H_4NO_2$, or $-C{\equiv}C-C_6H_5$). Only the bis-acetylide **6** could be prepared in high yield either from complex **4** reacting with phenylacetylene or from complex $[Pt(PPh_3)_2(C{\equiv}C-C_6H_5)Cl]$ reacting with *p*-nitrophenylacetylene.

Pd(II) complexes were prepared at room temperature from *trans*-$[Pd(PPh_3)_2Cl_2]$ and the alkyne. New reaction conditions, with a solution of NaOH in MeOH as the reaction solvent, led to the successful synthesis of $[Pd(PPh_3)_2(C{\equiv}C-C_6H_5)_2]$ (**10**). This method gave very good results for the synthesis of Pd bis(acetylide)s, while lower yields were observed for Pt complexes. Palladium was more reactive and bis(acetylide) complexes were obtained with almost quantitative yields in milder conditions. However, this method required longer reaction times than with Et_2NH. Pd complexes were generally unstable, and decomposed in solution at temperature just higher than $T = 30$°C.

In order to obtain pure products, the crude complexes were chromatographed on a silica gel column with benzene, toluene, or $CHCl_3$ as the eluent. As already observed in similar cases [31], elemental analyses showed a tendency of some complexes to retain solvents in the crystal molecular lattice. By changing the crystallization solvents, different elemental analyses are obtained.

3.2. Spectroscopic characterisation

The full characterisation of the organometallic compounds has been performed using traditional methodologies: elemental analysis, IR, UV–vis, ^1H-, ^{13}C- and ^{31}P-NMR spectroscopy and mass spectrometry.

The FAB spectrum of the complex $[Pt(PPh_3)_2(C{\equiv}C-C_6H_4NO_2)_2]$ (**1**) ($M.W. = 1011.91$) in the m/z range 350–1100 is discussed in detail as an example. The spectrum is characterised by platinum containing ions, which are identified readily by their characteristic pattern due to the natural isotopic abundance of platinum. The quasi-molecular ion $[M+H]^+$ ($m/z = 1013$) is present together with peaks resulting from fragmentations that are typical of nitro-aromatic compounds (elimination of one NO_2 radical $[M-NO_2]^+$ $m/z = 966$ and two NO radicals $[M-2NO]^+$ $m/z = 952$). The typical fragmentation peaks of bis-acetilides are also present. For example the peak due to loss of $C_6H_4NO_2$ and $C{\equiv}C-C_6H_4NO_2$ $[M+1-C_6H_4NO_2-C{\equiv}C-C_6H_4NO_2]^+$ ($m/z = 745$) is observed among the others.

The IR spectra of Pt and Pd complexes are characterised by the C≡C stretching vibrations in the range 2103–2125 cm^{-1}; the position of the band is shifted towards higher frequencies in the mono-acetylides. A band at 540 ± 5 cm^{-1}, characteristic of *cis*-bis(triphenylphosphine) acetylido–platinum complexes [32], is observed in the spectrum of *cis*-$[Pt(PPh_3)_2(C{\equiv}C-C_6H_4OCH_3)_2]$ (**3**). Its absence in the case of other Pt and Pd complexes suggests a *trans* configuration.

The NMR parameters of the eleven new compounds are listed in Table 2, and general trends are worth mentioning. The ^{31}P spectra of the platinum complexes show the expected signal, which consists of three lines in the ratio 17:66:17% because of the coupling with ^{195}Pt. The magnitude of ^1J ($^{195}Pt^{31}P$) is known to be very sensitive to the nature of the ligands in square planar platinum(II) complexes and can thus act as a useful probe of the geometry of any present isomer [33]. The ^1J ($^{195}Pt^{31}P$) values obtained for the compounds here reported are in agreement with the values found in other square planar platinum complexes, with the *trans* isomers showing larger platinum–phosphorus coupling constants than the *cis* analogues according to literature results (see for example complexes **2** and **3** of Table 2) [28,34,35].

The bis-triphenylphosphine ligand exhibits similar ^{13}C-NMR pattern in all the investigated complexes (Table 2). The resonance at 131.2 ppm is attributed to the *ipso* carbon (directly linked to the P atom), and the resonances at 134.8, 130.4 and 127.9 ppm correspond to the *ortho*, *para* and *meta* carbons, respectively. Some minor shifts from these values are observed depending on the different alkyne ligands. It is worth noting that the coupling constant increases with decreasing C–P distance, with the exception of the carbon in *para* position, which appears as a singlet. The signals of the benzene moiety of the alkyne ligand are detected in the range 144.4–112.0 ppm and have been identified by comparing the spectra of the new complexes of Table 2 with those of the precursors and of the free acetylenes. The attribution of the quaternary carbons is more difficult, because have low intensity and sometimes the low solubility of the material does not allow for an easy detection and assignment of these carbons. However, the resonances of the $C\equiv C$ carbons are found around 100–113 ppm for the carbon bound to the metal, and in the range 110–125 ppm for the carbon bound to the aromatic ligand R of the $C\equiv C{-}R$ moiety. A doublet of doublets at 101.0 ppm and a doublet at 110.0 ppm was detected only in the case of the *cis* complex **3**. These two signals were unambiguously assigned to the C^1 and C^2 atoms, respectively, of the ligand $-C^1\equiv C^2-C_6H_4-OCH_3$, as previously reported in the literature [30]. For the other complexes, the poor resolution of the spectra prevented a similar rigorous assignment.

The ^{1}H chemical shifts of $C\equiv C-C_6H_4NO_2$, $C\equiv C-C_6H_4OCH_3$, $C\equiv C-C_6H_5$, and $C\equiv C-\{\eta^5\text{-}C_5H_4\}Fe\{\eta^5\text{-}C_5H_5\}$ are independent of the nature of the phosphine, but they are influenced by *cis* and *trans* complex configuration; in fact the ^{1}H-NMR signals are shifted toward higher fields in the spectrum of the *cis* complex. Further proof of the *cis* configuration is given by the different pattern of phosphine signals for complex **3**.

Table 2
NMR data for complexes **1**–**11** [a]

No.	Complex	^{1}H (ppm)	^{13}C [b] (ppm)	^{31}P (ppm) J (Hz)
1	*trans*-$[Pt(PPh_3)_2(C\equiv C-C_6H_4NO_2)_2]$	7.73–7.38 (m, 34H, $P(C_6H_5)$ and $C_6H_4NO_2$), 6.27 (d, 4H, $C_6H_4NO_2$)	144.3, 135.0, 131.0, 122.7 ($C_6H_4NO_2$), 113.1, 97.4 ($C\equiv C$)	19.5 ($^1J_{PtP} = 2592$)
2	*trans*-$[Pt(PPh_3)_2(C\equiv C-C_6H_4OCH_3)_2]$	7.80–7.30 (m, 30H, $P(C_6H_5)$), 6.45–6.16 (dd, 8H, C_6H_4OMe), 3.65 (s, 6H, OCH_3)	131.9–112.6 (C_6H_4OMe), 55.0 (OCH_3) [c]	19.2 ($^1J_{PtP} = 2662$)
3	*cis*-$[Pt(PPh_3)_2(C\equiv C-C_6H_4OCH_3)_2]$	7.51–7.10 (m, 30H, $P(C_6H_5)$), 6.70–6.52 (dd, 8H C_6H_4OMe), 3.68 (s, 6H, OCH_3)	157.1, 132.7, 120.9, 112.5 ($C_6H_4OCH_3$), 110.0 (d, $\equiv C-Ph$), 101.0 (dd, $\equiv C-Pt$), 55.0 (OCH_3)	17.0 ($^1J_{PtP} = 2323$)
4	*trans*-$[Pt(PPh_3)_2(C\equiv C-C_6H_4NO_2)Cl]$	7.73–7.38 (m, 32H, $P(C_6H_5)$ and $C_6H_4NO_2$), 6.11 (d, 2H, $C_6H_4NO_2$)	144.3, 135.4, 131.0, 122.6 ($C_6H_4NO_2$), 105.6, 98.3 ($C\equiv C$)	20.3 ($^1J_{PtP} = 2617$)
5	*trans*-$[Pt(PPh_3)_2(C\equiv C-C_6H_4OCH_3)Cl]$	7.79–7.33 (m, 30H, $P(C_6H_5)$), 6.41–6.00 (dd, 4H C_6H_4OMe), 3.63 (s, 3H, OCH_3)	157.2, 132.2, 121.0, 112.5 (C_6H_4OMe), 115.9, 114.5 ($C\equiv C$), 55.0 (OCH_3)	22.1 ($^1J_{PtP} = 2664$)
6	*trans*-$[Pt(PPh_3)_2(C\equiv C-C_6H_5)(C\equiv C-C_6H_4NO_2)]$	7.78–7.37 (m, 32H, $P(C_6H_5)$ and $C_6H_4NO_2$), 6.89–6.27 (m, 7H, $C_6H_4NO_2$ and C_6H_5).	144.1, 135.4, 131.0, 122.7 ($C_6H_4NO_2$), 130.8, 128.2, 127.1, 124.8 (C_6H_5), 124.8, 112.2, 97.4 ($C\equiv C$)	19.2 ($^1J_{PtP} = 2613$)
7	*trans*-$[Pt(PPh_3)_2(C\equiv C-C_6H_5)(C\equiv C-C_6H_4OCH_3)]$	7.81–7.31 (m, 30H, $P(C_6H_5)$), 6.89–6.18 (m, 9H, C_6H_5 and C_6H_4OMe), 3.65 (s, 3H, OCH_3)	156.9, 132.0, 121.7, 112.6 ($C_6H_4OCH_3$), 130.8, 128.6, 127.0, 124.5 (C_6H_5), 112.9, 112.8, 111.0, 108.0 ($C\equiv C$), 55.0 (OCH_3)	19.2 ($^1J_{PtP} = 2656$)
8	*trans*-$[Pt(PPh_3)_2(C\equiv C-C_6H_4NO_2)(C\equiv C-C_6H_4OCH_3)]$	7.75–7.26 (m, 32H, $P(C_6H_5)$ and $C_6H_4NO_2$), 6.41–6.15 (td, 6H, $C_6H_4NO_2$ and C_6H_4OMe), 3.59 (s, 3H, OCH_3)	144.1, 135.8, 131.0, 122.7 ($C_6H_4NO_2$), 157.1, 132.0, 122.4, 112.7 (C_6H_4OMe), 124.0, 121.0, 113.2, 112.4 ($C\equiv C$), 55.0 (OCH_3)	19.2 ($^1J_{PtP} = 2619$)
9	*trans*-$[Pt(PPh_3)_2(C\equiv C-C_6H_4NO_2)(C\equiv C\text{-}\{\eta^5\text{-}C_5H_4\}Fe\{\eta^5\text{-}C_5H_5\})]$	7.80–7.37 (m, 32H, $P(C_6H_5)$ and $C_6H_4NO_2$), 6.32–6.29 (d, 2H, $C_6H_4NO_2$), 3.68 (s, 5H, $\eta^5\text{–}C_5H_5$), 3.74–3.35 (t, 4H, $\eta^5\text{-}C_5H_4$)	144.3, 135.0, 131.2, 122.7 ($C_6H_4NO_2$), 108.2–99.8 ($C\equiv C$), 70.1, 66.6 ($\eta^5\text{-}C_5H_4$), 69.2 ($\eta^5\text{-}C_5H_5$)	19.0 ($^1J_{PtP} = 2638$)
10	*trans*-$[Pd(PPh_3)_2(C\equiv C-C_6H_5)_2]$	7.81–7.33 (m, 30H, $P(C_6H_5)$), 6.90–6.31 (m, 10H, C_6H_5)	130.7, 128.1, 127.1, 124.7 (C_6H_5), 115.0, 113.5 ($C\equiv C$)	26.58
11	*trans*-$[Pd(PPh_3)_2(C\equiv C-C_6H_4NO_2)_2]$	7.76–7.35 (m, 34H, $P(C_6H_5)$ and $C_6H_4NO_2$), 6.33 (d, 4H, $C_6H_4NO_2$)	144.4, 130.8, 128.3, 122.8 ($C_6H_4NO_2$), 125.0, 114.2 ($C\equiv C$)	27.03

[a] The spectra were run in $CDCl_3$ solutions.

[b] The ^{13}C resonances of the $P(C_6H_5)$ ligand are found at 134.8 (t, $J_{PC} = 6.3$Hz, *ortho*), 131.2 (t, $J_{PC} = 27$Hz, *ipso*), 130.4 (s, *para*), 127.9 (t, $J_{PC} = 5.3$Hz, *meta*). These values are almost the same for the series of Pt and Pd complexes, with little differences (ca. 0.2 ppm) depending on the bound acetylide ligands.

[c] Due to the low solubility, the quaternary carbon resonances could not be detected.

Table 3
UV–vis data for complexes **1**–**19** [a]

No.	Complexes	λ_{max} (nm) absorb.	ε_0 (l mol cm^{-1})	λ_{max} (nm) emission
1	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$)$_2$]	402	49 000	475–600
2	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$OCH$_3$)$_2$]	358	24 700	400
4	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$)Cl]	385	26 600	515
5	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$OCH$_3$)Cl]	321	12 610	355–429
6	*trans*-Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_5$)(C≡C–C$_6$H$_4$NO$_2$)	390	32 200	500–600
7	*trans*-Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_5$)(C≡C–C$_6$H$_4$OCH$_3$)	354	22 600	425
8	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$OCH$_3$)(C≡C–C$_6$H$_4$NO$_2$)]	390	25 600	510
9	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$) (C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})]	390	24 700	510
10	*trans*-[Pd(PPh$_3$)$_2$(C≡C–C$_6$H$_5$)$_2$]	305	36 870	385
11	*trans*-[Pd(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$)$_2$]	381	39 470	490
12	*trans*-[Pt(PTol$_3$)$_2$(C≡C–C$_6$H$_5$)$_2$]	348	26 600	413
13	*trans*-[Pt(PTol$_3$)$_2$(C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})$_2$]	332, 368	14 200, 11 700	410, 410
14	*trans*-[Pt(PMePh$_2$)$_2$(C≡C–C$_6$H$_5$)$_2$]	343	28 700	380
15	*trans*-[Pt(PMePh$_2$)$_2$(C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})$_2$]	331, 363	10 600, 8190	407, 407
16	*cis*-[Pt(dppe)(C≡C–C$_6$H$_5$)$_2$]	315	21 200	387
17	*cis*-[Pt(dppe)(C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})$_2$]	315, 363	9200, 5160	400–428, 409–442
18	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_5$) (C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})]	340	16 500	409
19	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_5$)$_2$]	350	29 700	421

[a] CHCl$_3$ was used as the solvent.

Table 4
Absorption peak wavelength in films (λ_{max} PMMA), order parameter (Φ), SH coefficients (d_{33} and β)

No.	Chromophore	λ_{max} PMMA (nm)	Φ	d_{33} (10^{-9} esu)	β (10^{-30} esu)
	DR1	490	0.30	20	22 [39]
6	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_5$)(C≡C–C$_6$H$_4$NO$_2$)]	387	0.07	7	16
7	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_5$)(C≡C–C$_6$H$_4$OCH$_3$)]	354	0.12	1.5	3
8	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$OCH$_3$) (C≡C–C$_6$H$_4$NO$_2$)]	391	0.08	5.5	12
9	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$) (C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})]	384	0.18	11	16
18	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_5$) (C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})]	341	0.10	$<$0.1	$<$0.2

UV–vis characterisation was carried out on all the complexes. The values of λ_{max} are reported in Table 3. All the coordination compounds show no absorption bands over 420 nm, so they are transparent in a very large visible region, and this is a great advantage for optical applications. The absorption bands are only slightly influenced by the presence of the chromophore and by the different environment (different phoshines). The absorption peaks in the optical spectra are attributed to metal → ligand charge transfer [3], and their position moves to longer wavelengths due to coordination of acetylide ligands. The highest red shift observed for our acetylides is recorded for the bis(*p*-nitrophenylacetylide) complex **1**.

3.3. Photoluminescence

Preliminary measurements concerning the luminescence properties were also performed. The photoluminescence spectra recorded for the solutions of the complexes under excitation at the wavelength of the absorption maximum ($\lambda = 315–400$ nm) show emission peaks in the range 355–600 nm (Table 3). It is noteworthy that complex **1** exhibits emission at 475 nm (blue–green emission colour) and another emission signal at 600 nm (yellow–orange colour). Quite similar emission spectra (blue region) were found recently for a copolymer consisting of thiophene-based and uretane spacer units [36] and similar features were observed in the photoluminescence spectra of platinum-containing polyynes with aromatic and heteroaromatic spacers [4].

3.4. SHG measurements

A full discussion on the second order nonlinear characteristics of organometallic platinum complexes has been reported recently [17]. For purpose of completeness, here we will briefly report on the optical characterisation of the unsymmetrical bis(acetylides) bis(triphenylphosphine)Pt complexes **6**–**9**, **18**. The measurements were carried out on PMMA films as the host matrix, by the SHG technique. The molecular hyperpolarisability β and the order parameter Φ could be determined and the results are collected in Table 4. The most promising molecule seems to be complex **9** containing both ferrocene (push) and nitro (pull) groups, as expected.

3.5. Third-order nonlinear optical measurements

Measurements on different Pt(II) and Pd(II) complexes were carried out in order to relate their structure (different phosphines and different acetylides) to their third order nonlinear optical properties. The results concerning 11 selected complexes are reported in Table 5.

The nonlinear refractive index n_2 was in most cases too low to be detectable (complexes **2**, **10**, **12**, **14**, **19**). An uncertainty of one order of magnitude affected the determination of n_2 in all the other cases. It can be seen that the nonlinear absorption coefficient α_2 is strictly related to the presence of linear absorption feature at/or near the half wavelength ($\lambda = 380$ nm) of the laser light used for nonlinear measurements ($\lambda = 770$ nm). In particular, all complexes showing detectable absorption around 380 ± 20 nm also exhibit nonlinear absorption, pointing out for a two-photon absorption mechanism.

The values of the nonlinear constants reported in Table 5 are calculated for a single molecule, in order to normalise the results obtained at different concentrations. Non substituted bis(phenylacetylide)s do not show measurable nonlinear optical constants. Appropriate substituents at the sides of the molecule are needed to give large nonlinearities. The molecules containing the donor ferrocene group show appreciable nonlinearities confirming the high polarisability of this group, in agreement with previous results reported in the literature [3,13]. The highest value for α_2, 1.2×10^{-38} cm W^{-1}, was found for [Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$)$_2$] (**1**), which is a pull–pull (acceptor groups at either sides) molecule, while the value for the push–pull complex **8** is intermediate. The donor methoxy group in [Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$OCH$_3$)$_2$] (**2**), does not give large nonlinearities. Different phosphines do not seem to dramatically change the values of the nonlinear optical constants. The central metal atom affects the α_2 values as can be seen by comparing the values of sample **1**, where the metal centre is platinum, and sample **11** which contains palladium. This is an interesting effect which deserves, however, further investigation.

These results are in agreement with studies reported by Humphrey et al. on ruthenium bis-acetylene systems [37]. Although being preliminary, our results show the possibility of tailoring the molecular structure in order to optimise a material for different nonlinear properties and ultimately for different applications. Also, these results could be used as a mean to study the electronic polarisability, i.e. the delocalisation of the electrons in coordination compounds.

Table 5
Third-order nonlinear optical coefficients for the complexes

No.	Complex	α_2 (cm W^{-1}) [a] $\lambda = 770$ nm
1	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$)$_2$]	1.2×10^{-38}
2	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$OCH$_3$)$_2$]	/
8	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$)(C≡C–C$_6$H$_4$OCH$_3$)]	2.0×10^{-39}
9	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$)(C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})]	6.8×10^{-39}
10	*trans*-[Pd(PPh$_3$)$_2$(C≡C–C$_6$H$_5$)$_2$]	/
11	*trans*-[Pd(PPh$_3$)$_2$(C≡C–C$_6$H$_4$NO$_2$)$_2$]	4.3×10^{-39}
13	*trans*-[Pt(PTol$_3$)$_2$(C≡C–C$_6$H$_5$)$_2$]	/
14	*trans*-[Pt(PTol$_3$)$_2$(C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})$_2$]	6.8×10^{-39}
15	*trans*-[Pt(PMePh$_2$)$_2$(C≡C–C$_6$H$_5$)$_2$]	/
16	*trans*-[Pt(PMePh$_2$)$_2$(C≡C–{η^5-C$_5$H$_4$}Fe{η^5-C$_5$H$_5$})$_2$]	1.1×10^{-38}
19	*trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_5$)$_2$]	/

[a] The reported values are calculated for molecule.

Table 6
Summary of crystal data, data collection [a], structure solution and refinement [b]

Crystal data	
Empirical formula	PtP$_2$C$_{52}$H$_{39}$NO$_2$
Molar mass	966.923
Color, habit	Colorless, prismatic
Crystal size (mm)	0.3 × 0.2 × 0.2
Crystal system	Orthorombic
a (Å)	9.591(3)
b (Å)	3.036(15)
c (Å)	38.422(46)
V (Å^3)	8489(12)
Space group	*Pbca*
Z	4
F(0,0,0)	3856.0
D_{calc} (g cm^{-3})	1.513
μ (cm^{-1})	34.235
Data collection	
Temperature (K)	298
Unit-cell reflections (θ range (°))	10 (6–10)
Maximum value of θ (°) for reflections	25
hkl range of reflections	0–11; 0–27; 0–45
Variation in three standard reflections	<3%
Reflections measured	9269
Unique reflections	4879
Reflections with $\lvert F_o/ > 6\sigma \lvert F_o\rvert$	3251
R of merged reflections	0.0527
Structure solution and refinement	
Refinement on	F_o
Solution method	Direct methods
Variables refine	523
Weighting scheme, $1\lvert(a+b\lvert F_o\rvert+c\lvert F_o\rvert^2)$	54.34320, 1.00000, 0.00227
R, wR, GOF	0.0560, 0.0790, 0.704
Density range in final Δ-map (e Å^{-3})	−1.72, 1.32 (16)
Final shift/error ratio	0.000

[a] Data were collected using ω scan. The intensities were corrected for Lorentz-polarization effects, and for absorption.

[b] All calculations were done on a Pentium PC with SIR CAOS [40], PARST [41], CRYSTALS [42], ORTEP-3 [43] packages. Atomic form factors were taken from Ref. [44].

3.6. X-ray structure of trans-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_5$)(C≡C–C$_6$H$_4$NO$_2$)]

It is well known that π-electron conjugated molecules with charge asymmetry are suitable for second-order NLO properties. Moreover, for a bulk material, a non centrosymmetric arrangement is also required. In order to investigate the symmetry of complex **6** in its crystal arrangement, the single crystal X-ray molecular structure was determined.

Crystals of complex **6** were grown by slow evaporation from toluene–methanol. A suitable crystal was mounted on Huber CS diffractometer [38] with graphite monochromatized Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å). Details of the crystal data, data collection, structure solution and refinement are given in Table 6. All the hydrogen atoms at calculated positions with thermal parameters arbitrarily fixed at 1.2 times that of attached C atoms were included in the final least-squares refinement.

The structure consists of discrete molecules (Fig. 2) in which phenylacetylene and *p*-nitrophenylacetylene moieties are σ-bonded to platinum in a *trans* configuration. Coordination around the platinum atoms is square planar, with small tetrahedral distortions (max 0.027(7) Å from the mean square plane passing through P(1), P(2), C(1) and C(3) atoms). The mean planes through phenylacetylene and *p*-nitrophenylacetylene form dihedral angles of 9.54 and 2.64°, respectively, with the coordination plane. The molecular geometry is that normally expected for *trans*-(Ph$_3$P)$_2$Pt(II) compounds, and no contacts other than those of van der Waals type are observed in the crystal.

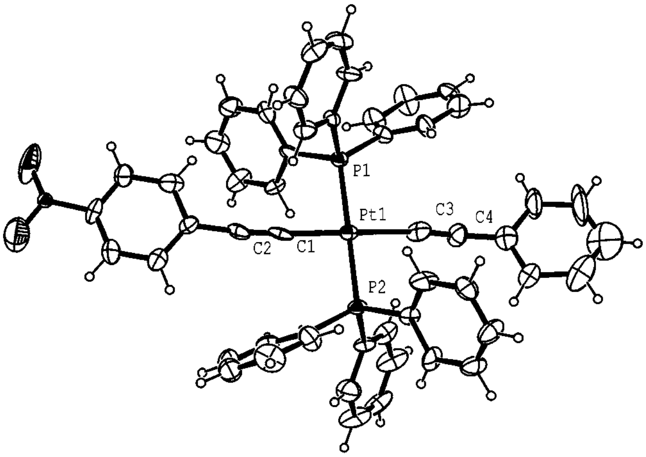

Fig. 2. Drawing of *trans*-[Pt(PPh$_3$)$_2$(C≡C–C$_6$H$_5$)(C≡C–C$_6$H$_4$NO$_2$)] showing the anisotropy of the thermal motion. The ellipsoids are scaled to the 30% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.325(5), Pt(1)–P(2) 2.321(5), Pt(1)–C(1) 1.98(2), Pt(1)–C(3) 2.05(2), P(1)–Pt(1)–P(2) 177.5(2), C(1)–Pt(1)–C(3) 179.7(9).

4. Conclusions

A series of Pt(II) and Pd(II) bis-acetylides has been prepared and characterised. The complexes show optical properties that can be finely modulated by the choice of the acetylide ligand. The UV absorption and emission spectra suggest that the complexes may be considered as precursors or models of related organometallic polymers with analogous properties. Among the unsymmetrical molecules, the SHG measurements indicate that the molecular hyperpolarisability β is correlated with the strength of the donor/acceptor acetylide ligand and is alike that of a typical azo-dye such as Disperse Red 1 (DR1) for complexes **6** and **9**.

Investigations on the third order nonlinear optical properties show that a strong acceptor group like NO$_2$ in the acetylide ligand σ-bound to Pt(II) (complex **1**) induces the highest value of nonlinear absorption coefficient α_2. A strong donor group (ferrocene in complexes **13** and **15**) also leads to appreciable values of α_2, suggesting that push–push or pull–pull substituents modify the delocalisation of π electrons involving the central Pt atom. The Pd complexes here investigated show third-order properties to a lesser extent.

The results so far obtained for the reported series of Pt and Pd bisacetylides suggest some general trends for the implementation of materials with the desired NLO properties.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 147478 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336003; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors wish to gratefully acknowledge MURST (Italy) for financial support to this research.

References

[1] N. Hagihara, K. Sonogashira, S. Takahashi, Adv. Polym. Sci. 41 (1981) 149.
[2] C.C. Frazier, S. Guha, W.P. Chen, M.P. Cockerham, P.L. Porter, E.A. Chauchard, C.H. Lee, Polymer 28 (1987) 553.

[3] M.S. Khan, A.S. Kakkar, N.J. Long, J. Lewis, P.R. Raithby, P. Nguyen, T.B. Marder, F. Wittmann, R.H. Friend, J. Mater. Chem. 4 (1994) 1227.

[4] N. Chawdhury, A. Köhler, R.H. Friend, M. Younus, N.J. Long, P.R. Raithby, J. Lewis, Macromolecules 31 (1998) 722.

[5] W.E. Douglas, D.M.H. Guy, A.K. Kar, C. Wang, Chem. Commun. (1998) 2125.

[6] N. Le Narvor, L. Toupet, C. Lapinte, J. Am. Chem. Soc. 117 (1995) 7129.

[7] M.C.B. Colbert, J. Lewis, N.J. Long, P.R. Raithby, A.J.P. White, D.J. Williams, J. Chem. Soc. Dalton Trans. (1997) 99.

[8] A. Lavastre, J. Plass, P. Bachmann, S. Guesmi, C. Mainet, P.H. Dixneuf, Organometallics 16 (1997) 184.

[9] M.C.B. Colbert, J. Lewis, N.J. Long, P.R. Raithby, M. Younus, A.J.P. White, D.J. Williams, N.N. Payne, L. Yellowlees, D. Beljonne, N. Chawdhury, R.H. Friend, Organometallics 17 (1998) 3034.

[10] R.H. Naulty, A.M. McDonagh, I.R. Whittall, M.P. Cifuentes, M.G. Humphrey, S. Houbrechts, J. Maes, A. Persoons, G.A. Heath, D.C.R. Hockless, J. Organomet. Chem. 563 (1998) 137.

[11] R. Loucif-Saiba, J.A. Delaire, L. Bonazzola, G. Doisneau, G. Balavoine, T.F. Fillebeen-Khan, I. Ledoux, G. Puccetti, Chem. Phys. 167 (1992) 369.

[12] S. Houbrechts, K. Clays, A. Persoons, V. Cadierno, M.P. Gamase, J. Gimeno, Organometallics 15 (1996) 5266.

[13] J. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts, A. Persoons, J. Organomet. Chem. 562 (1998) 197.

[14] M.V. Russo, A. Furlani, J. Organomet. Chem. 165 (1979) 101.

[15] A. Furlani, S. Licoccia, M.V. Russo, A. Chiesi Villa, C. Guastini, J. Chem. Soc. Dalton Trans. (1982) 2449.

[16] A. Furlani, S. Licoccia, M.V. Russo, A. Chiesi Villa, C. Guastini, J. Chem. Soc. Dalton Trans. (1984) 2197.

[17] M. Casalboni, F. Sarcinelli, R. Pizzoferrato, R. D'Amato, A. Furlani, M.V. Russo, Chem. Phys. Lett. 319 (2000) 107.

[18] M. Falconieri, G. Salvetti, Appl. Phys. B 69 (1999) 133.

[19] M. Falconieri, J. Opt. A Pure Appl. Opt. 1 (1999) 662.

[20] K.A. Jensen, Z. Anorg. Allg. Chem. 229 (1936) 265.

[21] S.O. Grim, R.L. Keiter, W. McFarlane, Inorg. Chem. 6 (1967) 1133.

[22] F.R. Hartley, Organomet. Chem. Rev. A6 (1979) 119.

[23] A.D. Westland, J. Chem. Soc. (1965) 3060.

[24] P.G. Leviston, M.G.H. Wallbridge, J. Organomet. Chem. 110 (1976) 271.

[25] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, Synthesis (1980) 627.

[26] D. Doisneau, G. Balavoine, T. Fillebeen-Khan, J. Organomet. Chem. 425 (1992) 113.

[27] H. Takalo, J. Kankare, E. Hanninen, Acta Chem. Scand. Ser. B 42 (1988) 448.

[28] R.J. Cross, M.F. Davidson, J. Chem. Soc. Dalton Trans. (1986) 1987.

[29] M.V. Russo, A. Furlani, S. Licoccia, R. Paolesse, A. Chiesi Villa, C. Guastini, J. Organomet. Chem. 469 (1994) 245.

[30] D. Osella, R. Gobetto, C. Nervi, M. Ravera, R. D'Amato, M.V. Russo, Inorg. Chem. Commun. 1 (1998) 239.

[31] A. Chiesi Villa, A. Gaetani Manfredotti, C. Guastini, M.V. Russo, Cryst. Struct. Commun. 6 (1977) 313.

[32] A. Furlani, P. Carusi, M.V. Russo, J. Organomet. Chem. 116 (1976) 113.

[33] P.S. Pregosin, R.W. Kunz (Eds.), ^{31}P- and ^{13}C-NMR of Transition Metal Phosphine Complexes, Springer-Verlag, Berlin, 1976.

[34] C.R. Langrick, D.M. McEwan, P.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1983) 2487.

[35] P. Bhattachryya, R.N. Sheppard, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, J. Chem. Soc. Dalton Trans. (1993) 2393.

[36] S. Blumstengel, I. Sokolik, R. Dorsinville, D. Voloschenko, M. He, O. Lavrentovich, L.C. Chien, Synth. Met. 99 (1999) 85.

[37] A.M. McDonagh, M.P. Cifuentes, I.R. Whittall, M.G. Humphrey, M. Samoc, B. Luther-Davies, D.C.R. Hockless, J. Organomet. Chem. 526 (1996) 99.

[38] M. Colapietro, G. Cappuccio, C. Marciante, A. Pifferi, R. Spagna, J.R. Helliwell, J. Appl. Crystallogr. 25 (1992) 192.

[39] M.A. Pauley, C.H. Wang, Chem. Phys. Lett. 49 (1997) 248.

[40] (a) M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, D. Viterbo, J. Appl. Crystallogr. 22 (1989) 389. (b) M. Camalli, D. Capitani, G. Cascarano, C. Giacovazzo, R. Spagna, Italian Patent no. 3540c/86, SIR CAOS user guide, Istituto di Strutturistica Chimica CNR, Rome, Italy.

[41] M. Nardelli, Comput. Chem. 7 (1983) 95.

[42] D.J. Watkin, J.R. Carruthers, P.W. Betteridge, CRYSTALS User Guide, Chemical Crystallography Laboratory, Oxford, UK, 1985.

[43] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.

[44] International Tables for X-Ray Crystallography, vol. 4, Kynoch Press, Birmingham, 1974, p. 71.