

# Preparation and electrochemical behaviour of dinuclear platinum complexes containing NCN ligands (NCN = [C<sub>6</sub>H<sub>3</sub>(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2-2,6</sub>]<sup>-</sup>). The crystal structure of [C<sub>6</sub>H<sub>3</sub>(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2-1,3</sub>-(C≡C)-5]<sub>2</sub><sup>☆</sup>

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## Abstract

A series of homodinuclear Pt compounds containing the anionic, potentially terdentate NCN ligand (NCN = [C<sub>6</sub>H<sub>3</sub>(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2-2,6</sub>]<sup>-</sup>) or its 4-ethynyl derivative were prepared. The two platinum centres are linked together in two different fashions: (i) directly linked by an ethynyl or diethynylphenyl group (head-to-head) and (ii) indirectly bonded by a ethynyl- or butadiynyl-linked bis-NCN ligand (tail-to-tail). The reaction of the head-to-head σ,σ'-ethynylidene complex {Pt}C≡C{Pt} ({Pt} = [Pt(C<sub>6</sub>H<sub>3</sub>{CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-2,6</sub>]<sup>+</sup>) with [CuCl]<sub>n</sub> yields {Pt}Cl and [Cu<sub>2</sub>C<sub>2</sub>]<sub>n</sub>, while with [Cu(NCMe)<sub>4</sub>][BF<sub>4</sub>] a Cu(I) bridged complex was formed: [(η<sup>2</sup>-{Pt}C≡C{Pt})<sub>2</sub>Cu][BF<sub>4</sub>]. The results of cyclic voltammetry experiments reveal that both connection modes of the two platinum centres lead to electrochemically independent Pt–NCN units. The X-ray crystal structure analysis of the neutral, tail-to-tail bridging butadiyne bis-NCNH ligand [C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-1,3</sub>-(C≡C)-5]<sub>2</sub> is reported. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Organoplatinum complexes; Electrochemistry; Bimetallic compounds; Crystal structures; Acetylides

## 1. Introduction

Classical second-order non-linear optically (NLO) active organic molecules contain both a donor and an acceptor unit. These are usually connected by a π-conjugated system which facilitates electronic communication between them. This arrangement results in the formation of a molecular dipole [1]. However, the number of electrons involved in these processes is small. Therefore, bi- and oligometallic molecules have attracted considerable attention in the recent years be-

cause transition metal (TM) complex moieties can act as donor and/or acceptor units by changes in their oxidation state [2]. If the metal atoms present in such molecules are connected by π-conjugated systems, a bulk sample of this material may have potential application in the design of optical devices [2b]. Interesting work in this area has been reported on various homo- and heterometallic mono-, di- or oligonuclear assemblies [3].

The monoanionic, potentially terdentate NCN ligand (NCN = [C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-2,6</sub>]<sup>-</sup>) [4] and its 4-substituted derivatives [5] have been used for the preparation of a wide range of metal complexes, inter alia of Ni [6], Pd [7], Pt [8] and Ru [9]. It has been shown that these ligands maintain their η<sup>3</sup>-N,C,N coordination mode even when the imbedded metals are oxidised [6c,d,8d,9b]. These ligands also stabilise unusual oxida-

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tion states of these metals, e.g. a Ni(III) intermediate in the Kharasch addition [6c,d]. Recently, the 4-ethynyl Pt–NCN entity **A** (Chart 1) has been tested as a connectivity between two TM complex fragments [10]. **A** can be interpreted as subunit of chain molecules such as **B**, which have a high degree of directionality along the molecular vector as shown.

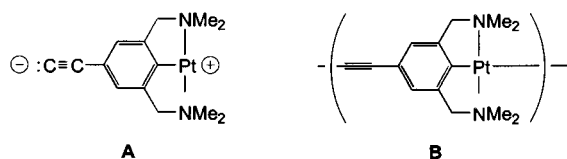


Chart 1.

It was found that an Au(I) complex fragment, attached to the ethynyl-substituent of a 4-ethynyl NCN–Pt complex, facilitates the oxidation of the Pt centre through the conjugated system offered by the 4-ethynyl NCN ligand [10]. The same effect was observed when  $C\equiv CFC$  [ $Fc = (\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)$ ] served as a  $\sigma$ -acetylide ligand on the Pt centre [10]. Also, recently it has been found that a biphenyl-type bis-NCN ligand shows an electrochemically detectable long-range interaction of two Ru-centres, which are held in the  $\eta^3$ -*N,C,N* coordination mode [9b].

In this context, we here report our attempts to assemble homodinuclear Pt-containing complexes in which NCN–Pt entities are either facing each other in a head-to-head fashion connected by a  $\sigma$ -acetylide bridge of variable length between the Pt-atoms, or point away from each other in a tail-to-tail mode imposed by 4-ethynyl- or butadiynyl-linked bis-NCN ligands (Chart 2).

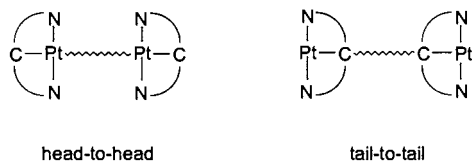


Chart 2.

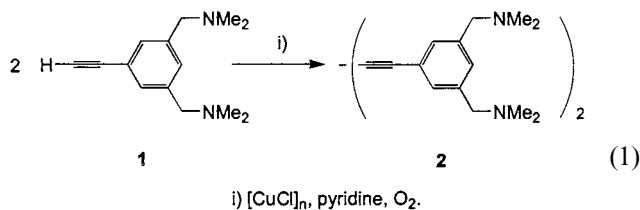
In addition, the synthesis and crystal structure analysis of a suitable butadiynyl bis-NCN ligand system is included. Furthermore, the assembly of two binuclear NCN–Pt  $\sigma$ -acetylides and the reactivity of the doubly substituted acetylene  $\{Pt\}C\equiv C\{Pt\}$  with Cu(I) compounds is described. The electrochemical behaviour of these homodinuclear complexes is reported.

## 2. Results and discussion

### 2.1. Synthesis and solid state structure of $[C_6H_3(Me_2NCH_2)_2-1,3-(C\equiv C)-5]_2$ (**2**)

Previously, it has been shown that it is possible to synthesise bis-NCN ‘pincer’ molecules which can be

used for the construction of homo- and heterobimetallic molecules [8d,11]. In these, the pincer ligands were directly attached to each other in a *para-para* fashion, i.e. forming biphenyl derivatives [8d]. The introduction of a single  $C\equiv C$  spacer and the subsequent synthesis of a bis-NCN–H acetylene has been described [12]. The coupling reaction of two units of the 4-ethynyl NCN–H molecule **1** was carried out following procedures described for the Glaser coupling (Eq. (1)). This reaction leads to the butadiyne derivative **2** in high yields.



The spectroscopic data of **2** (IR,  $^1H$ -NMR,  $^{13}C\{^1H\}$ -NMR) are consistent with a 1,4-NCN–H substituted butadiyne. The FAB MS spectrum of **2** exhibits the peak of the molecular ion  $[M]^+$  ( $m/z = 431$ ) as the parent peak.

Single crystals suitable for an X-ray crystal structure analysis were grown by cooling an *n*-pentane solution of **2** to  $-30^\circ C$ . Fig. 1 shows the molecular structure of **2** in the crystal. Representative bond lengths ( $\text{\AA}$ ), angles and torsion angles ( $^\circ$ ) are listed in Table 1.

In the solid state, compound **2** contains a crystallographic inversion centre on the midpoint of the single bond of the butadiyne unit. Therefore, only half of the molecule is independent. One of the *ortho*- $CH_2NMe_2$  substituents was refined with a disorder model, reflecting the high flexibility of the benzylamino group when it is not coordinated to a metal. The bond distances found for the butadiyne unit [C(14)–C(14E): 1.390(6)  $\text{\AA}$ , C(13)–C(14): 1.191(4)  $\text{\AA}$ ] resemble the distances found in other organic or organometallic butadiyne derivatives [13]. The distance between the butadiyne residue and the aromatic system [C(13)–C(4): 1.437(4)  $\text{\AA}$ ] is in good accordance with values reported recently, e.g. for the iodo NCN pincer compound  $C_6H_2I-1-(CH_2NMe_2)_2-2,6-(C\equiv CH)-4$  [14b]. The butadiyne unit is essentially linear [C(14)–C(13)–C(4):  $176.5(4)^\circ$ ; C(14E)–C(14)–C(13):  $179.5(4)^\circ$ ].

### 2.2. Homodinuclear Pt–NCN compounds

The tail-to-tail diplatinum complexes **4** and **5** have been assembled via a lithiation-transmetallation sequence (Eq. (2)). This reaction has been used earlier for the preparation of a variety of mono- and dinuclear Pt–NCN complexes [8a,d,11].

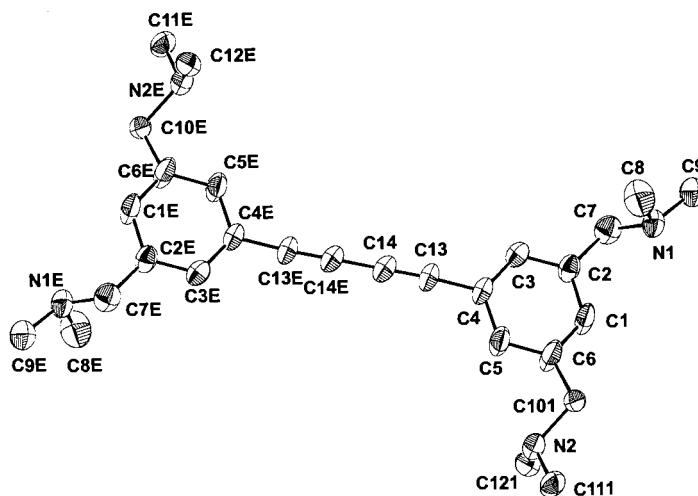
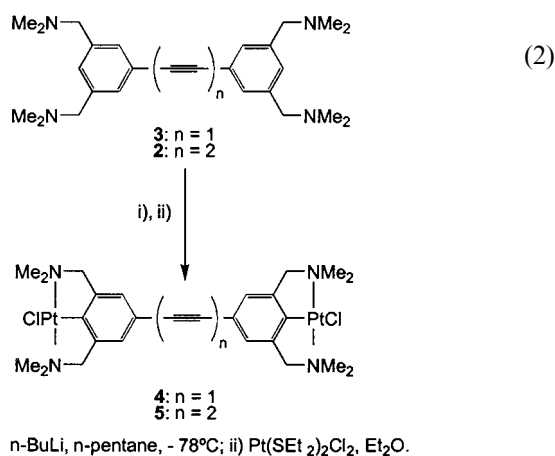
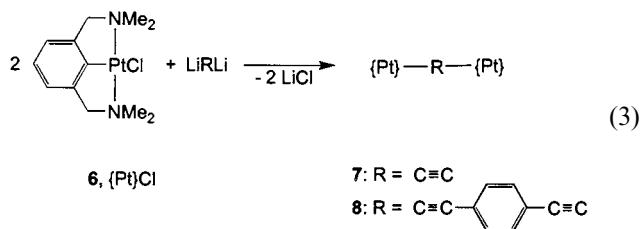


Fig. 1. Displacement ellipsoid plot of compound **2** at 50% probability level including our atom labelling scheme. Hydrogen atoms are omitted for clarity. Only one conformation of the disordered *ortho*-CH<sub>2</sub>NMe<sub>2</sub> at C(101) is shown (symmetry operation E: 1 - x, 2 - y, - z).



The homodinuclear head-to-head bis(Pt–NCN) ethyne {Pt}C≡C{Pt} (**7**) and butadiyne {Pt}C≡CC<sub>6</sub>H<sub>4</sub>C≡C{Pt} (**8**, Eq. (3)) have been synthesised by reacting the corresponding dilithium dianions (prepared in situ) with two equivalents of the monochloride {Pt}Cl (**6**, {Pt} = [Pt{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2-2,6</sub>}]<sup>+</sup>).



Both types of complexes are obtained as off-white air-stable solids. While **7** and **8** readily dissolve in C<sub>6</sub>H<sub>6</sub>, THF or CH<sub>2</sub>Cl<sub>2</sub>, complexes **4** and **5** have very low solubility in these solvents. A similar observation was made with bis-Pt or bis-Pd complexes containing a biphenyl type bis-NCN moiety ((like compound **4** in

Eq. (2) with n = 0) [8d]. Relevant spectroscopic data of complexes **4–8** are listed in Table 2.

The IR spectra of **4** and **5** are essentially identical to those of the free ligands. In contrast, the formation of the head-to-head complexes **7** or **8** can be monitored easily by the shift of the ν<sub>C≡C</sub> stretching frequency in the IR or Raman spectrum. In these complexes, the C≡C absorption band for monosubstituted acetylenes (between 2090 and 2120 cm<sup>-1</sup>) [15] or HC≡CH (1974 cm<sup>-1</sup>) [16] is found at lower wavenumbers (**7**: 1942 cm<sup>-1</sup>; **8**: 2081 cm<sup>-1</sup>). Due to its molecular symmetry, the ν<sub>C≡C</sub> vibration of complex **7** is Raman active only. The NMR spectra of **7** and **8** show that the <sup>1</sup>H-NMR signals of the chelating *ortho*-CH<sub>2</sub>NMe<sub>2</sub> substituents are shifted slightly (ca. 0.1 ppm) to lower field when compared to those of **6** (Table 2) [14]. This observation was made previously when the Cl ligand of {Pt}Cl (**6**) was replaced by acetylide entities [14]. In the <sup>13</sup>C{<sup>1</sup>H}-NMR spectra of **4** and **5**, it was found that the introduction of two Pt centres into one molecule does not lead to a different signal pattern of the NCN framework than reported, for example for **6** [14]. The signals of the sp-hybridised carbon skeleton are not influenced by the presence of the two Pt centres. The <sup>13</sup>C{<sup>1</sup>H}-NMR spectra of the head-to-head complexes **7** and **8**

Table 1  
Selected bond lengths (Å), angles and torsion angles (°) of **2**<sup>a</sup>

C(14)–C(14E)	1.390(6)	C(14E)–C(14)–C(13)	179.5(4)
C(13)–C(14)	1.191(4)	C(14)–C(13)–C(4)	176.5(4)
C(13)–C(4)	1.437(4)	C(5)–C(6)–C(101)–N(2)	43.3(6)
		C(1)–C(6)–C(101)–N(2)	–159.3(4)
		C(5)–C(6)–C(102)–N(2)	–44.3(6)
		C(1)–C(6)–C(102)–N(2)	159.6(4)

<sup>a</sup> Standard deviations in the unit of the last significant figure in parentheses. Symmetry operation E: 1 - x, 2 - y, - z. Occupancy C(101):C(102) = 0.49:0.51.

Table 2

Representative spectroscopic data (IR, Raman,  $^1\text{H-NMR}$ ,  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ) of complexes **4**, **5**, **7**, **8** and **6** [14] for comparison

Compound	IR, Raman <sup>a</sup>	$^1\text{H-NMR}$ <sup>b</sup>	$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ <sup>c</sup>				
		$\text{CH}_2\text{N}$ ( $J_{\text{HPt}}$ [Hz])	$\text{NMe}_2$ ( $J_{\text{HPt}}$ [Hz])	$\text{C}_{\text{ipso}}(\text{Pt})$	$\text{C}_{\text{ipso}}(\text{CH}_2)$ ( $J_{\text{CPt}}$ [Hz])	$\text{PtC}_\alpha=\text{C}_\beta$	$\text{C}\equiv\text{C}$
$\{\text{Pt}\}\text{Cl}$	<b>6</b> –	4.01 (45.9)	3.08 (38.0)	145.2	143.3 (76.4)	–	–
$[\text{PtCl}(\text{C}_6\text{H}_2\{\text{CH}_2\text{NMe}_2\}\text{-}2,6\text{-}\{\text{C}\}\text{-}4)_2]$	<b>4</b> 2152(IR)	4.00 (38.0)	3.08 (37.0)	146.6	143.4	–	89.3
$[\text{PtCl}(\text{C}_6\text{H}_2\{\text{CH}_2\text{NMe}_2\}\text{-}2,6\text{-}\{\text{C}\equiv\text{C}\}\text{-}4)_2]$	<b>5</b> 2134(IR)	4.01 (39.3)	3.09 (42.3)	148.6	143.5	–	73.0, 82.9
$\{\text{Pt}\}\text{C}\equiv\text{C}\{\text{Pt}\}$	<b>7</b> 1942(Raman)	4.10 (44.8)	3.19 (48.0)	166.2	146.2	91.2 ( $\text{C}_\alpha$ )	–
$\{\text{Pt}\}\text{C}\equiv\text{CC}_6\text{H}_4\text{CvC}\{\text{Pt}\}$	<b>8</b> 2081(IR)	4.13 (43.0)	3.22 (43.0)	166.6	146.1	107.8 ( $\text{C}_\beta$ ), 141.0 ( $\text{C}_\alpha$ )	–

<sup>a</sup> Recorded in KBr ( $\nu$  [ $\text{cm}^{-1}$ ]).<sup>b</sup> Recorded in  $\text{CDCl}_3$  with the solvent as the internal reference signal (rel. to  $\text{SiMe}_4$ : 0.00 ppm).<sup>c</sup> Recorded in  $\text{CDCl}_3$  with the solvent as the internal reference signal (rel. to  $\text{SiMe}_4$ : 0.00 ppm).

reveal that the signal of the two carbon atoms *ortho* to  $\text{C}_{\text{ipso}}$  is shifted by ca. 3 ppm downfield, while the signal of  $\text{C}_{\text{ipso}}$  itself is shifted by about 20 ppm to lower field [14]. The resonances of the acetylenic carbon atoms are found in regions which are characteristic for Pt acetylides [17]. Due to the low intensity of the  $\text{C}_{\text{ipso}}$  atoms of the aryl moiety [C(1)] and the acetylide ligands,  $^{195}\text{Pt}\text{-C}$  satellite resonances could not be detected. The FAB mass spectra of the new complexes **4**, **5**, **7** and **8** each exhibit the molecular ion  $[\text{M}]^+$  peak.

### 2.3. Reaction of $\{\text{Pt}\}\text{C}\equiv\text{C}\{\text{Pt}\}$ (**7**) with Cu(I) compounds

The ability of the Cu(I) cation to coordinate organic or organometallic acetylenes is well studied and a variety of coordination compounds have been reported [18], e.g. the trinuclear complex  $[(\eta^2\text{-}\{\text{Pt}\}\text{C}\equiv\text{CSiMe}_3)_2\text{M}][\text{BF}_4]$  ( $\text{M} = \text{Cu}, \text{Ag}$ ) [14]. The dinuclear Pt compound **7** was reacted with one equivalent of  $[\text{CuCl}]_n$  or with 0.5 equivalents of  $[\text{Cu}(\text{NCMe})_4][\text{BF}_4]$ , respectively, in order to form Cu(I)-bridged complexes with four Pt–NCN centres in one molecule (Scheme 1).

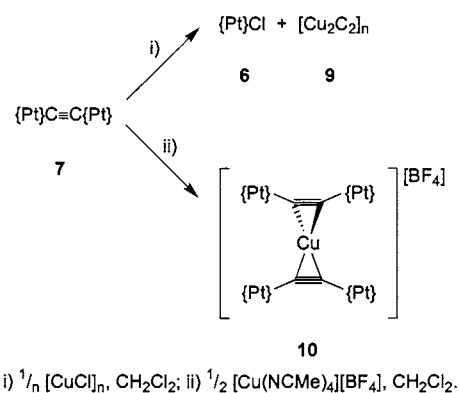
As observed previously for this type of Pt  $\sigma$ -acetylides, the Pt acetylide carbon bond was cleaved selectively by  $[\text{CuCl}]_n$  yielding the monochloride  $\{\text{Pt}\}\text{Cl}$  (**6**) and a reddish precipitate of  $[\text{Cu}_2\text{C}_2]_n$  (**9**). Compound **6** was identified by its  $^1\text{H-NMR}$  spectrum and the Cu(I)-acetylide **9** by IR spectroscopy [19]. However, the reaction of **7** with  $[\text{Cu}(\text{NCMe})_4][\text{BF}_4]$  yielded an off-white precipitate which was insoluble in common organic solvents and had a  $[(\eta^2\text{-}\{\text{Pt}\}\text{C}\equiv\text{C}\{\text{Pt}\})_2\text{Cu}][\text{BF}_4]$  (**10**) stoichiometry (Scheme 1). The IR spectrum of this material reveals an intense absorption at  $1941\text{ cm}^{-1}$  which can be assigned to the stretching vibration of a CC fragment coordinated to a Cu(I) cation [14,18]. The loss of all MeCN ligands from the Cu(I) centre is confirmed by the absence of stretching bands in the

region typical for nitriles (ca.  $2200\text{--}2300\text{ cm}^{-1}$ ) [19]. These results indicate that the  $\text{C}\equiv\text{C}$  unit of **7** is indeed accessible for coordination chemistry by cationic metal centres. However, it has already been shown that the Pt  $\sigma$ -acetylide bond is readily cleaved by the presence of halide sources, i.e. reacting with neutral copper(I) halides leads to cleavage of the  $\sigma\text{-Pt}\text{-C}(\text{acetylide})$  bond. These findings contrast with reports by Beck et al. concerning the coordination chemistry of the acetylenic unit of the bimetallic molecule  $(\text{CO})_5\text{ReC}\equiv\text{CRe}(\text{CO})_5$  [20].

### 2.4. Cyclic voltammetry studies

The dinuclear Pt–NCN complexes described in this work have been studied by cyclic voltammetry (CV) in order to detect communication between the two metal centres along the  $\pi$ -conjugated system. The results are presented in Table 3, along with data collected for mononuclear Pt–NCN compounds for comparison.

The cyclic voltammogram of the prototypical mononuclear complex **6** reveals an irreversible two-electron oxi-



i)  $1/n$   $[\text{CuCl}]_n$ ,  $\text{CH}_2\text{Cl}_2$ ; ii)  $1/2$   $[\text{Cu}(\text{NCMe})_4][\text{BF}_4]$ ,  $\text{CH}_2\text{Cl}_2$ .

Scheme 1.

Table 3  
Cyclic voltammetric data<sup>a</sup> of compounds **4–8** and {Pt}C≡CSiMe<sub>3</sub> [14] for comparison

Compound		$E_{\text{ox}}$ (V) Pt(II)/Pt(IV)
{Pt}Cl	<b>6</b>	+0.78
[PtCl(C <sub>6</sub> H <sub>2</sub> {CH <sub>2</sub> NMe <sub>2</sub> }-2,6-{C}-4)] <sub>2</sub>	<b>4</b>	+0.74
[PtCl(C <sub>6</sub> H <sub>2</sub> {CH <sub>2</sub> NMe <sub>2</sub> }-2,6-{C≡C}-4)] <sub>2</sub>	<b>5</b>	+0.80
{Pt}C≡CSiMe <sub>3</sub>	[14]	+0.58
{Pt}C≡C{Pt}	<b>7</b>	+0.57
{Pt}C≡CC <sub>6</sub> H <sub>4</sub> C≡C{Pt}	<b>8</b>	+0.59

<sup>a</sup> Cyclic voltammograms have been recorded in the presence of [n-Bu<sub>4</sub>N][PF<sub>6</sub>] (*c* = 0.1 mol dm<sup>-3</sup>) at 25°C under N<sub>2</sub>; scan-rate 100 mV s<sup>-1</sup>; potentials are referenced to the FcH/FcH<sup>+</sup> couple ( $E_{1/2}$  = 0.00 V).

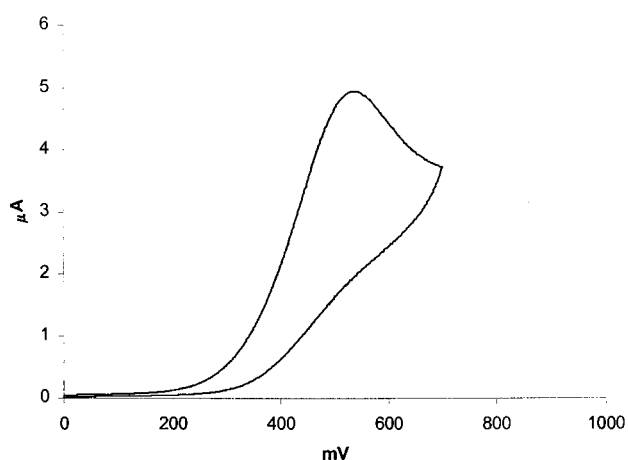


Fig. 2. Cyclic voltammogram of {Pt}C≡C{Pt} (**7**); in THF solution in the presence of [n-Bu<sub>4</sub>N][PF<sub>6</sub>] (*c* = 0.1 mol dm<sup>-3</sup>) at 25°C under N<sub>2</sub>; scan rate 100 mV s<sup>-1</sup>; potentials are referenced to FcH/FcH<sup>+</sup> as internal standard ( $E_{1/2}$  = 0.00 V).

dation at  $E_{\text{ox}} = +0.78$  V for the Pt(II)/Pt(IV) system. Although the presence of a second metal centre might be indicated by a second oxidative wave at higher potential than the first Pt(II)/Pt(IV) oxidation, this was not found. The dinuclear tail-to-tail complexes **4** and **5** as well as the head-to-head complexes **7** and **8** exhibit only one oxidative process corresponding to the removal of a total of four electrons in two simultaneous irreversible oxidation steps. As was previously reported [14], the exchange of a Cl (**6**,  $E_{\text{ox}} = +0.78$  V) by a  $\sigma$ -acetylide ligand leads to a shift of the irreversible Pt(II)/Pt(IV) oxidation by ca. 0.2 V to a more negative potential. The representative cyclic voltammogram for the head-to-head complex **7** is shown in Fig. 2 and clearly shows the irreversibility of the oxidative processes.

These findings suggest that both types of acetylide bridges between the two Pt(II) centres (head-to-head: **7** and **8**) and the aryl-acetylene-aryl backbone (tail-to-tail:

**4** and **5**) do not support electronic communication between the Pt centres. This contrasts with recent findings which were made in a diruthenium system. There, a fast electron exchange between the two remote Ru centres in the mixed-valence Ru(II)/Ru(III) species has been detected [9b].

### 3. Conclusions

A series of homodinuclear NCN–Pt complexes has been prepared in which two Pt(II) centres are connected either via a dianionic alkynediyl bridge (**7** and **8**) or a dianionic  $\alpha,\omega$ -diarylacetylene one (**4** and **5**). Reactions of {Pt}C≡C{Pt} (**7**) with Cu(I) salts revealed that the C≡C bond shows a coordinative behaviour typical of 1,2-disubstituted acetylenes despite its sterically congested environment. The cationic Cu(I) bridged dimer [( $\eta^2$ -{Pt}C≡C{Pt})<sub>2</sub>Cu][BF<sub>4</sub>] (**10**) was prepared. It contains four {Pt} units in one molecule. However, reaction with Cu(I) halide leads to cleavage of the Pt–C  $\sigma$ -acetylide bond and consequently to the formation of {Pt}Cl (**6**) and a Cu(I) acetylide. The electrochemical studies of the homodinuclear complexes suggest that in both types of alkynediyl bridged head-to-head (**7** and **8**) and tail-to-tail compounds (**4** and **5**), the two Pt centres do not communicate through the  $\pi$ -conjugated system.

### 4. Experimental

#### 4.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et<sub>2</sub>O) and *n*-pentane were purified by distillation from sodium/benzophenone ketyl; methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) was purified by distillation from calcium hydride. Acetylene was dried with KOH and traces of acetone were removed at –78°C. Infrared spectra were obtained with a Mattson Galaxy Series FTIR 5000. <sup>1</sup>H- and <sup>13</sup>C{<sup>1</sup>H}-NMR spectra were recorded on a Bruker AC 300 spectrometer. Chemical shifts are reported in  $\delta$  units (ppm) downfield from tetramethylsilane with the solvent as the internal reference signal. FAB mass spectra were recorded at the Department of Mass Spectrometry, Bijvoet Center, Utrecht University on a JEOL JMS SX/SX 102A four sector mass spectrometer operating at 10 kV accelerating voltage. Melting points (m.p.) were determined on a Büchi melting point apparatus. Microanalyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr, Germany. Electrochemical measurements were carried out by cyclic voltammetry in a solution of NBu<sub>4</sub>PF<sub>6</sub> (0.1 mol dm<sup>-3</sup>) in THF at 25°C, using a standard three-electrode cell on a Prince-

ton Applied Research EG&G 263A analyzer. All potentials were referenced to the ferrocene/ferrocenium couple which was defined to be  $E_{1/2} = 0.00$  V.

#### 4.2. General remarks

The starting materials **1** [5b], **3** [12], **6**, [21] and  $(\text{HC}\equiv\text{C})\text{C}_6\text{H}_4$ -1,4 [22] were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and used as received.

#### 4.3. Synthesis of $[5-(\text{C}\equiv\text{C})-1,3-(\text{Me}_2\text{N})_2\text{CH}_2\text{C}_6\text{H}_3]_2$ (**2**)

The experimental procedure and work-up were performed as described by Haim [23]. Experimental details: **1** (2 g, 9.3 mmol),  $[\text{CuCl}]_n$  (50 mg, 0.5 mmol), pyridine (50 ml), 25°C. Yield: 1.8 g, 90% based on **1**.

M.p.: [°C] 81°C. IR (KBr):  $[\text{cm}^{-1}]$  2137  $[\nu_{\text{C}\equiv\text{C}}]$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $[\delta]$  2.26 (s, 24 H,  $\text{NMe}_2$ ), 3.42 (s, 8 H,  $\text{CH}_2$ ), 7.32 (s, 2 H,  $\text{C}_6\text{H}_3$ ), 7.39 (s, 4 H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $[\delta]$  45.3 ( $\text{NMe}_2$ ), 63.7 ( $\text{CH}_2$ ), 73.9 ( $\text{C}\equiv\text{C}$ ), 81.5 ( $\text{C}\equiv\text{C}$ ), 121.7 ( $^i\text{C}/\text{C}_6\text{H}_3$ ), 130.8 ( $\text{CH}/\text{C}_6\text{H}_3$ ), 131.9 ( $\text{CH}/\text{C}_6\text{H}_3$ ), 139.2 ( $^i\text{C}/\text{C}_6\text{H}_3$ ). FAB-MS  $[m/z]$  (rel. int.): 431 (100)  $[\text{M} + \text{H}]^+$ , 58 (40)  $[\text{C}_3\text{H}_8\text{N}]^+$ . Anal. Calc. for  $\text{C}_{28}\text{H}_{38}\text{N}_4$  (430.64): C, 78.09; H, 8.89; N, 13.01. Found: C, 77.93; H, 8.96; N, 12.88%.

##### 4.3.1. Crystal structure determination of **2**

$\text{C}_{28}\text{H}_{38}\text{N}_4$ ,  $M = 430.62$  g mol $^{-1}$ , brown, plate,  $0.38 \times 0.25 \times 0.08$  mm $^3$ , monoclinic,  $P2_1/n$ ,  $a = 11.110(6)$ ,  $b = 7.8881(14)$ ,  $c = 14.786(6)$  Å,  $\beta = 90.08(2)^\circ$ ,  $V = 1295.8(9)$  Å $^3$ ,  $Z = 2$ ,  $\rho = 1.104$  g cm $^{-3}$ , 3691 measured reflections, 2269 unique reflections ( $R_{\text{int}} = 0.0685$ ),  $R$  [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0673$ ,  $wR_2 = 0.1279$ .  $R$  (all data):  $R_1 = 0.1530$ ,  $wR_2 = 0.1591$ .  $S = 1.008$ . Intensities were measured on an Enraf-Nonius CAD4T diffractometer with rotating anode ( $\text{Mo-K}\alpha$ ,  $\lambda = 0.71073$  Å) at a temperature of 150 K. The structure was solved with direct methods with the program SIR-97 [24] and refined with the program SHELXL-97 [25] against  $F^2$  of all reflections up to a resolution of  $(\sin \theta/\lambda)_{\text{max}} = 0.59$  Å $^{-1}$ . Absorption correction was based on Psi-Scans ( $\mu = 0.07$  mm $^{-1}$ , 0.91–0.97 transmission). Non-hydrogen atoms were freely refined with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups with fixed isotropic parameters  $U = 0.05$ . The disordered benzylamino group was refined with an occupancy of 0.49:0.51. Structure calculations and checking for higher symmetry were performed with the program PLATON [26].

#### 4.4. Synthesis of $[\text{PtCl}(\text{C}_6\text{H}_2\{\text{CH}_2\text{NMe}_2\}-2,6-\{\text{C}\}-4)]_2$ (**4**)

The synthesis was conducted according to the published procedure [8b]. Experimental details: **3** (430 mg,

1.1 mmol),  $n\text{-BuLi}$  (1.5 ml of a 1.6 molar soln. in  $\text{Et}_2\text{O}$ ; 2.2 mmol),  $\text{Pt}(\text{SEt}_2)_2\text{Cl}_2$  (940 mg, 2.2 mmol). Yield: 580 mg, 50% based on **3**.

M.p.: [°C]  $> 200^\circ\text{C}$ . Raman (KBr):  $[\text{cm}^{-1}]$  2152  $[\nu_{\text{C}\equiv\text{C}}]$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $[\delta]$  3.09 (s,  $^3J_{\text{PtH}} = 38.0$  Hz, 24 H,  $\text{NMe}_2$ ), 4.00 (s,  $^3J_{\text{PtH}} = 37.0$  Hz, 8 H,  $\text{CH}_2$ ), 6.95 (s, 4 H,  $\text{C}_6\text{H}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $[\delta]$  54.4 ( $\text{NMe}_2$ ), 77.4 ( $\text{CH}_2$ ), 89.2 ( $\text{C}\equiv\text{C}$ ), 118.2 ( $^i\text{C}/\text{C}_6\text{H}_2$ ), 122.2 ( $\text{CH}/\text{C}_6\text{H}_2$ ), 143.4 ( $^i\text{C}/\text{C}_6\text{H}_2$ ), 146.6 ( $^i\text{C}/\text{C}_6\text{H}_2$ ). FAB-MS  $[m/z]$  (rel. int.): 865 (20)  $[\text{M}]^+$ , 829 (40)  $[\text{M}-\text{Cl}]^+$ . Anal. Calc. for  $\text{C}_{26}\text{H}_{36}\text{Cl}_2\text{N}_4\text{Pt}_2$  (865.69): C, 36.07; H, 4.19; N, 6.47. Found: C, 36.31; H, 4.42; N, 6.78%.

#### 4.5. Synthesis of $[\text{PtCl}(\text{C}_6\text{H}_2\{\text{CH}_2\text{NMe}_2\}-2,6-\{\text{C}\}-4)]_2$ (**5**)

Experimental procedure and work-up were the same as for compound **4**. Experimental details: **2** (450 mg, 1.1 mmol),  $n\text{-BuLi}$  (1.5 ml of a 1.6 molar soln. in  $\text{Et}_2\text{O}$ ; 2.2 mmol),  $\text{Pt}(\text{SEt}_2)_2\text{Cl}_2$  (940 mg, 2.2 mmol). Yield: 630 mg, 65% based on **2**.

M.p.: [°C]  $> 200^\circ\text{C}$ . Raman (KBr):  $[\text{cm}^{-1}]$  2134  $[\nu_{\text{C}\equiv\text{C}}]$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $[\delta]$  3.09 (s,  $^3J_{\text{PtH}} = 42.3$  Hz, 24 H,  $\text{NMe}_2$ ), 4.01 (s,  $^3J_{\text{PtH}} = 39.3$  Hz, 8 H,  $\text{CH}_2$ ), 6.98 (s, 4 H,  $\text{C}_6\text{H}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $[\delta]$  54.3 ( $\text{NMe}_2$ ), 73.0 ( $\text{C}\equiv\text{C}$ ), 77.2 ( $\text{CH}_2$ ), 82.9 ( $\text{C}\equiv\text{C}$ ), 116.1 ( $^i\text{C}/\text{C}_6\text{H}_2$ ), 123.1 ( $\text{CH}/\text{C}_6\text{H}_2$ ), 143.5 ( $^i\text{C}/\text{C}_6\text{H}_2$ ), 148.6 ( $^i\text{C}/\text{C}_6\text{H}_2$ ). FAB-MS  $[m/z]$  (rel. int.): 889 (10)  $[\text{M}]^+$ , 853 (30)  $[\text{M}-\text{Cl}]^+$ . Anal. Calc. for  $\text{C}_{28}\text{H}_{36}\text{Cl}_2\text{N}_4\text{Pt}_2$  (889.71): C, 37.80; H, 4.08; N, 6.30. Found: C, 37.63; H, 4.14; N, 6.21%.

#### 4.6. Synthesis of $\{\text{Pt}\}\text{C}\equiv\text{C}\{\text{Pt}\}$ (**7**)

Through a solution of 1.6 ml of  $n\text{-BuLi}$  ( $\text{Et}_2\text{O}$ , 150 ml) was bubbled a stream of dried acetylene (30 min, 25°C). Then,  $\{\text{Pt}\}\text{Cl}$  (**6**) (680 mg, 1.6 mmol) was added in one portion. After stirring (24 h, 25°C) all volatiles were removed in vacuo and the residue was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 15$  ml). Evaporation of the combined  $\text{CH}_2\text{Cl}_2$  extracts gave **8** as amber solid (560 mg, 80% yield based on **3**).

M.p.: [°C]  $> 200^\circ\text{C}$ . Raman (KBr):  $[\text{cm}^{-1}]$  1942  $[\nu_{\text{C}\equiv\text{C}}]$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $[\delta]$  3.19 (s,  $^3J_{\text{PtH}} = 48$  Hz, 24 H,  $\text{NMe}_2$ ), 4.10 (s,  $^3J_{\text{PtH}} = 44.8$  Hz, 8 H,  $\text{CH}_2$ ), 7.2–7.6 (m, 6 H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $[\delta]$  55.9 ( $\text{NMe}_2$ ), 80.0 (s,  $^2J_{\text{PtC}} = 42$  Hz,  $\text{CH}_2$ ), 91.2 ( $\text{C}\equiv\text{C}$ ), 119.2 ( $\text{CH}/\text{C}_6\text{H}_3$ ), 123.3 ( $\text{CH}/\text{C}_6\text{H}_3$ ), 146.2 ( $^i\text{C}/\text{C}_6\text{H}_3$ ), 166.2 ( $^i\text{C}/\text{C}_6\text{H}_3$ ). FAB-MS  $[m/z]$  (rel. int.): 797 (15)  $\text{M}^+$ , 385 (100)  $[\text{C}_{12}\text{H}_{19}\text{N}_2\text{Pt}]^+$ . Anal. Calc. for  $\text{C}_{26}\text{H}_{38}\text{N}_4\text{Pt}_2$  (796.80): C, 39.19; H, 4.81; N, 7.04. Found: C, 39.34; H, 5.02; N, 6.85%.

#### 4.7. Synthesis of $\{\text{Pt}\}\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}\{\text{Pt}\}$ (**8**)

To a suspension of 1,4-( $\text{LiC}\equiv\text{C}$ ) $\text{C}_6\text{H}_4$  (150 mg, 1.1 mmol) in  $\text{Et}_2\text{O}$  (150 ml, 25°C) was added  $\{\text{Pt}\}\text{Cl}$  (**6**)

(930 mg, 2.2 mmol) in one portion. After stirring (24 h, 25°C) all volatiles were removed in vacuo. The residue was then washed with *n*-pentane (3 × 30 ml) and extracted with benzene (4 × 40 ml). After evaporation of the combined benzene extracts (vacuo), the resulting residue was washed with acetone (2 × 10 ml) and dried in vacuo. **9** (200 mg, 30% yield based on **3**) remained as off-white solid.

M.p.: [°C] > 200. IR (KBr): [cm<sup>-1</sup>] 2081 [ $\nu_{C=C}$ ]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): [δ] 3.22 (s, <sup>3</sup>J<sub>HPt</sub> = 43 Hz, 24 H, NMe<sub>2</sub>), 4.13 (s, <sup>3</sup>J<sub>HPt</sub> = 43 Hz, 8 H, CH<sub>2</sub>), 6.7–7.1 (m, 6 H, C<sub>6</sub>H<sub>3</sub>), 7.33 (s, 4 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): [δ] 56.0 (NMe<sub>2</sub>), 80.0 (CH<sub>2</sub>), 107.8 (PtC≡C), 118.7 (CH/C<sub>6</sub>H<sub>3</sub>), 123.5 (CH/C<sub>6</sub>H<sub>3</sub>), 127.9 (<sup>i</sup>C/C<sub>6</sub>H<sub>4</sub>), 131.7 (CH/C<sub>6</sub>H<sub>4</sub>), 141.0 (PtC≡C), 146.1 (<sup>i</sup>C/C<sub>6</sub>H<sub>3</sub>), 166.6 (<sup>i</sup>C/C<sub>6</sub>H<sub>3</sub>). FAB-MS [*m/z* (rel. int.):] 897 (10) M<sup>+</sup>, 798 (10) M<sup>+</sup>–[C<sub>8</sub>H<sub>4</sub>], 512 (20) M<sup>+</sup>–[C<sub>12</sub>H<sub>19</sub>N<sub>2</sub>Pt], 385 (50) [C<sub>12</sub>H<sub>19</sub>N<sub>2</sub>Pt]<sup>+</sup>. Anal. Calc. for C<sub>34</sub>H<sub>42</sub>N<sub>4</sub>Pt<sub>2</sub> (896.92): C, 45.53; H, 4.72; N, 6.25. Found: C, 45.29; H, 4.64; N, 6.34%.

#### 4.8. Reaction of **7** with [CuCl]<sub>*n*</sub>

Compound **7** (50 mg, 0.06 mmol) and [CuCl]<sub>*n*</sub> (10 mg, 0.1 mmol) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (20 ml, 25°C, 3 h). In the course of the reaction a reddish precipitate formed. Then the reaction mixture was centrifuged and the supernatant solution was separated from the solid. Evaporation of the CH<sub>2</sub>Cl<sub>2</sub> solution affords {Pt}Cl (**6**) as a colourless solid (45 mg, 100% yield based on **7**; <sup>1</sup>H-NMR). The precipitate was shown to be [Cu<sub>2</sub>C<sub>2</sub>]<sub>*n*</sub> (**9**, IR).

#### 4.9. Synthesis of [(η<sup>2</sup>-{Pt}C≡C{Pt})<sub>2</sub>Cu][BF<sub>4</sub>] (**10**)

Compound **7** (50 mg, 0.06 mmol) and [Cu(NCMe)<sub>4</sub>][BF<sub>4</sub>] (10 mg, 0.03 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). In the course of the reaction a precipitate was formed. After stirring (3 h, 25°C), the solution was centrifuged and the supernatant solution decanted. The residue was dried (vacuo) and yielded **10** (55 mg, 100% based on **7**) as an off-white solid.

Due to the insolubility of **10** in any common organic solvent, <sup>1</sup>H-NMR and <sup>13</sup>C{<sup>1</sup>H}-NMR spectroscopy could not be carried out. A mass spectrum could not be recorded.

M.p.: [°C] > 200. IR (KBr): [cm<sup>-1</sup>] 1941 [ $\nu_{C=C}$ ]. Anal. Calc. for C<sub>52</sub>H<sub>76</sub>BCuF<sub>4</sub>N<sub>8</sub>Pt<sub>4</sub> (1743.94): C, 35.81; H, 4.39; N, 6.36. Found: C, 35.66; H, 4.48; N, 6.36%.

## 5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data

Centre, CCDC no. 124698 for **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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