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# Synthesis, spectroscopy, structure and photophysical properties of dinaphthylmethylarsine complexes of palladium(II) and platinum(II)

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#### Abstract

Dinaphthylmethylarsine complexes of palladium(II) and platinum(II) with the formulae  $[MX_2L_2]$  (M = Pd, Pt; L = di(1-naphthylmethylarsine = Nap<sub>2</sub>AsMe and X = Cl, Br, I),  $[M_2Cl_2(\mu-Cl)_2L_2]$ ,  $[PdCl(S_2CNEt_2)L]$ ,  $[Pd_2Cl_2(\mu-OAc)_2L_2]$  and  $[MCl_2(PR_3)L]$  (PR<sub>3</sub> = PEt<sub>3</sub>, PPr<sub>3</sub>, PBu<sub>3</sub>, PMePh<sub>2</sub>) have been prepared. These complexes have been characterized by elemental analyses, IR, Raman, NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) and UV-vis spectroscopy. The stereochemistry of the complexes has been deduced from the spectroscopic data. The crystal structures of *trans*-[PdCl<sub>2</sub>(PEt<sub>3</sub>)(Nap<sub>2</sub>AsMe)] and of [Pd(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>], a follow-up product, were determined. The UV-vis spectra of  $[MX_2L_2]$  complexes show a red shift on going from X = Cl to X = I. The complexes [PdX<sub>2</sub>L<sub>2</sub>] and [PtX<sub>2</sub>L<sub>2</sub>] are strongly luminescent in fluid solution and in the solid at ambient temperature. © 2005 Elsevier B.V. All rights reserved.

Keywords: Organoarsenic compounds; Palladium complexes; Platinum complexes; Crystal structures; Photoluminescence

#### 1. Introduction

During the last decade, the chemistry of organoarsenic compounds has witnessed extensive growth due to the development of new ligands and due to the search for molecular precursors for CVD [1–4]. Arsines containing a 1-naphthyl group could be of interest because the facile cleavage of the M–C(naphthyl) linkage should render them as ideal components for molecular precursors. Besides, coordinated naphthylarsines in metal complexes may cause steric crowding, thus facilitating, e.g., the ortho metallation of the aromatic carbon atom [5,6]. In view of this and in pursuance of our work on organoarsines, we have now examined the chemistry of di(1-naphthyl)methylarsine (Nap<sub>2</sub>AsMe = L) with palladium(II) and platinum(II).

#### 2. Experimental

### 2.1. General procedures

The compounds Na<sub>2</sub>PdCl<sub>4</sub>, [PdCl<sub>2</sub>(MeCN)<sub>2</sub>] and [PtCl<sub>2</sub>(PhCN)<sub>2</sub>] were prepared according to the literature procedures [7]. All reactions were carried out under a nitrogen atmosphere in dry and distilled analytical grade solvents. Microanalyses were carried out in the Analytical Chemistry Division, BARC. The <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H}NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300, 75.47 and 121.49 MHz, respectively. Chemical shifts are relative to internal chloroform peak [ $\delta$  = 7.26 ppm

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for <sup>1</sup>H;  $\delta$  = 77.0 ppm for <sup>13</sup>C] and external H<sub>3</sub>PO<sub>4</sub> (85%) for <sup>31</sup>P{<sup>1</sup>H} NMR. IR spectra were recorded as Nujol mulls using CsI plates on a Bomen-102 FT IR spectrometer in the range 200–4000 cm<sup>-1</sup>. UV–vis absorption spectra were recorded on a JASCO V-530 spectrophotometer. The fluorescence spectra were recorded on Hitachi F-4014 Fluorescence spectrophotometer. Raman spectra were recorded on Labram I (ISA make) Raman spectrometer using an excitation wavelength of 488 nm (Ar<sup>+</sup>) with a resolution of 2 cm<sup>-1</sup>. Thermogravimetric analyses were carried on a Setaram 92–16.18 instrument (calibrated with CaC<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O) under an N<sub>2</sub> atmosphere at a heating rate of 10 °C/min.

## 2.2. Crystallography

Suitable crystals of  $[PdCl_2(PEt_3)(Nap_2AsMe)]$  and  $[Pd(S_2CNEt_2)_2]$  were obtained from saturated solutions in CH<sub>2</sub>Cl<sub>2</sub>. Data collection was performed at T = 293(2) ( $[PdCl_2(PEt_3)(Nap_2AsMe)]$ ) or 100(2) K ( $[Pd(S_2CNEt_2)_2]$ ) on a KappaCCD device (Mo K $\alpha$ :  $\lambda = 0.71073$  Å; horizontally mounted graphite crystal; 95mm CCD camera on  $\kappa$ -goniostat) using Collect (Nonius BV, 1997–2000) software. All structures were solved by direct methods using the SHELXTL package [8] and refinement was carried out with SHELXL-97 [9], employing full-matrix least-squares methods on  $F^2$  with  $F_o^2 \ge 2\sigma(F_o^2)$  with the results shown in Table 2. All non-hydrogen atoms were treated anisotropically, hydrogen atoms were included by using appropriate riding models.

## 2.3. Syntheses

## 2.3.1. Di(1-naphthyl)methylarsine (Nap<sub>2</sub>AsMe or L)

To an ice cold ethereal solution of 1-naphthylmagnesiumbromide (9.3 g, 40.3 mmol), freshly distilled (88 °C/4 mmHg) MeAsI<sub>2</sub> (6.51 g, 18.9 mmol) [10] in diethyl ether (200 cm<sup>3</sup>) was added slowly with vigorous stirring. The reactants were brought to room temperature and then refluxed for 2 h. After cooling to 0 °C, the mixture was treated with an aqueous NH<sub>4</sub>Cl solution (300 cm<sup>3</sup>). The diethyl ether layer was separated through a *canula*. The ethereal extract was dried over sodium sulfate, filtered, and the filtrate was concentrated to dryness. The residue was washed with *n*-hexane (40 cm<sup>3</sup>) and dried to yield a white crystalline solid (2.8 g; 43%). A previously reported synthetic procedure involved the reaction of Nap<sub>2</sub>AsCl with RMgX in diethyl ether [11].

## 2.3.2. $[PdCl_2L_2]$

To a stirred acetone solution of  $[PdCl_2(MeCN)_2]$  (303 mg, 1.17 mmol), a solution of Nap<sub>2</sub>AsMe (810 mg, 2.34 mmol) was added with stirring whereupon a yellow precipitate formed. The mixture was stirred for 3 h. The precipitate was separated using a G-3 filter, washed

with *n*-hexane and dried in vacuo (948 mg; 93%). Pertinent data are given in Table 1. Attempts to recrystallize the title complex from pyridine gave yellow  $[PdCl_2(pyridine)_2]$ .

## 2.3.3. $[PdBr_2L_2]$

To a stirred acetone solution of  $[PdCl_2L_2]$  (130 mg, 0.15 mmol), an excess of KBr (683 mg, 5.7 mmol) was added. The mixture was stirred for 48 h and the solvent was dried in vacuo. The product was extracted with benzene and filtered. The filtrate was evaporated in vacuo to yield the title compound (110 mg; 77%).

Similarly,  $[PdI_2L_2]$  was prepared in 73% yield (69 mg) as orange-red crystals from  $[PdCl_2L_2]$  (80 mg, 0.09 mmol) and an excess of KI (650 mg, 3.9 mmol).

#### 2.3.4. $[Pd_2Cl_2(\mu-Cl)_2L_2]$

To a stirred benzene (60 cm<sup>3</sup>) solution of  $[PdCl_2L_2]$ (410 mg, 0.47 mmol)  $[PdCl_2(MeCN)_2]$  (130 mg; 0.49 mmol) was added. The mixture was stirred with refluxing for 3 h. The orange precipitate thus formed was filtered through a G-3 glass filter, washed with *n*-hexane and dried in vacuo to give an orange powder (450 mg; 92%). Attempts to recrystallize the product from pyridine gave  $[PdCl_2(pyridine)_2]$ . Calc. for  $[PdCl_2(pyridine)_2]$ : C, 35.8; H, 3.0; N, 8.3. Found: C, 35.5; H, 3.2; N, 8.3%. <sup>1</sup>H NMR in CDCl<sub>3</sub>  $\delta$ : 7.31–7.38 (m, 2*H*); 7.77–7.82 (m, 1*H*); 8.83–8.87 (m, 2*H*).

## 2.3.5. $[PdCl(S_2CNEt_2)L]$

To a stirred CH<sub>2</sub>Cl<sub>2</sub> solution of  $[Pd_2Cl_2(\mu-Cl)_2L_2]$  (89 mg, 0.085 mmol), NaS<sub>2</sub>CNEt<sub>2</sub> · 3H<sub>2</sub>O (40 mg, 0.18 mmol) was added and the reactants were stirred for 3 h. This mixture was filtered through a Florisil column and dried in vacuo to yield an orange compound which was rapidly recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–hexane (90 mg; 87%). When the complex is left in solution for a few days or reaction is carried out with an excess of NaS<sub>2</sub>CNEt<sub>2</sub> · 3H<sub>2</sub>O, yellow orange single crystals of  $[Pd(S_2CNEt_2)_2]$  were separated. m.p. 221°C. Calc. for  $[Pd(S_2CNEt_2)_2]$ : C, 29.8; H, 5.0; N, 7.0. Found: C, 29.7; H, 4.9; N, 6.9%. <sup>1</sup>H NMR in CDCl<sub>3</sub>  $\delta$ : 1.27 (t, 7.1 Hz, NCH<sub>2</sub>Me); 3.71 (q, 7.1 Hz, NCH<sub>2</sub>).  $\lambda_{max}$ : 300 (86815), 344 (11195) nm ( $\varepsilon$  in M<sup>-1</sup>cm<sup>-1</sup>).

## 2.3.6. $[PdCl_2(PEt_3)L]$

To a stirred CH<sub>2</sub>Cl<sub>2</sub> solution of  $[Pd_2Cl_2(\mu-Cl)_2(PEt_3)_2]$  (41 mg, 0.069 mmol), a solution of L = Nap<sub>2</sub>AsMe (48 mg, 0.14 mmol) was added. The colour changed instantaneously from orange red to yellow. The mixture was stirred for 2 h and the solvent was evaporated in vacuo. The product was recrystallized from an acetone–hexane mixture (56 mg; 67%).

Similarly,  $[PdCl_2(PMePh_2)L]$  and  $[PtCl_2(PR_3)L]$ (R = Pr, Bu) were prepared from  $[M_2Cl_2(\mu-Cl)_2(PR_3)_2]$ (M = Pd or Pt) and Nap<sub>2</sub>AsMe (Table 1).

Complex	Solvents of recrystallization (% yield) (colour)	m.p. (°C)	Analyses % found (calc.)		<sup>1</sup> H NMR data in CDCl <sub>3</sub> ( $\delta$ in ppm)
			С	Н	
Nap <sub>2</sub> AsMe $(=L)^{a}$	diethyl ether (43) (colourless)	146–148	72.2 (73.3)	4.7 (5.0)	1.64 (s, As <i>Me</i> ); 8.42–8.45 (m, H-2/or H-4); 7.82–7.89 (m, H-5, 8 + H-4 or 2); 7.36–7.53 (m, H-6, 7, H-3)
[PdCl <sub>2</sub> L <sub>2</sub> ]	acetone-hexane (93) (yellow)	162	57.7 (58.3)	4.1 (4.0)	2.16 (small), 2.22 (large) (each s) (As <i>Me</i> ); 7.32 (td, 8.1 Hz (t), 0.9 (d)); 7.40 (td, 8.0 Hz, 1.4 (d)); 7.54 (td, 8.0 Hz (t), 1.0 (d)); 7.75 (dd, 7.1 Hz, 1.0 Hz); 7.93 (t, 7.5 Hz) (2 protons); 8.58 (d, 8.4 Hz)
[PdBr <sub>2</sub> L <sub>2</sub> ]	CHCl <sub>3</sub> -hexane (77) (orange)	255	53.0 (52.8)	3.7 (3.6)	2.33, 2.43 (each s, As <i>Me</i> 1:2 ratio); 7.31 (t, 7.3 Hz); 7.43 (t, 7.8 Hz); 7.54 (t, 7.4 Hz); 7.75 (d, 7.0 Hz); 7.92 (d, 7.7 Hz); 8.57 (d, 8.0 Hz)
$[PdI_2L_2]^b$	CHCl <sub>3</sub> -hexane (73) (orange-red)	165-167 (deco)	48.6 (48.1)	3.7 (3.3)	2.76 (s, As <i>Me</i> ); 7.34 (t, 7.5 Hz); 7.48 (t, 8.1); 7.57 (t, 7.0 Hz); 7.77 (d, 6.5 Hz); 7.94 (dd, 7.6, 4.8 Hz); 8.52 (d, 8.3 Hz)
$[Pd_2Cl_2(\mu\text{-}Cl)_2L_2]^c$	benzene-hexane (92) (orange)	chars 225-230	48.5 (48.4)	3.4 (3.3)	2.49 (s, AsMe); 7.48 (t, 8.4 Hz); 7.62 (br,); 8.09 (d, d); 8.60 (br)
$\left[\text{PdCl}(S_2\text{CNEt}_2)L\right]^d$	CH <sub>2</sub> Cl <sub>2</sub> -hexane (87) (orange)	212 (deco)	48.8 (49.2)	4.2 (4.3)	1.08 (t, 7.1 Hz), 1.24 (t, 7.1 Hz) (Et); 2.34 (s, As <i>Me</i> ); 3.43 (q, 7.1 Hz), 3.65 (q, 7.1 Hz) (CH <sub>2</sub> ); 7.42–7.55 (m); 7.90–7.98 (m); 8.38, d, 7.9 Hz
$\left[PdCl_2(PEt_3)L\right]^e$	acetone-hexane (67) (yellow)	119	50.3 (50.7)	5.2 (5.0)	1.21 (dt, 17 (d), 7.5 (t) Hz, PCH <sub>2</sub> CH <sub>3</sub> ); 1.96 (m, PCH <sub>2</sub> ); 2.15 (s, As <i>Me</i> ); 7.39 (t, 7.3 Hz); 7.53 (m); 7.67 (d, 7.1 Hz); 7.90–7.95 (m); 8.64 (d, 8.4 Hz)
[PdCl2(PMePh2)L]f	acetone-hexane (82) (yellow)	113	56.0 (56.6)	4.4 (4.2)	2.08 (d, 11.5 Hz); 2.21 (s, AsMe); 2.25 (s, small signal); 7.34–7.97 (m,); 8.65 (d, 8.6 Hz)
$[PtCl_2(PPr_3)L]^g$	CH <sub>2</sub> Cl <sub>2</sub> -hexane (58) (colourless)	153	46.8 (46.5)	5.2 (5.0)	1.06 (t, 7.2 Hz); 1.62–1.75 (m); 1.86–1.95 (m); 2.19 (s, As <i>Me</i> ); 7.40 (t, 7.3 Hz); 7.49– 7.57 (m); 7.76 (d, 7.1 Hz); 7.93 (t, Hz); 8.69 (d, 8.4 Hz)
$[PtCl_2(PBu_3)L]^h \\$	CH <sub>2</sub> Cl <sub>2</sub> -hexane (62) (colourless)	153	50.7 (48.8)	5.6 (5.5)	0.71 (t, 7 Hz); 1.00–1.18 (m, PCH <sub>2</sub> C $H_2H_2$ ); 1.39–1.48 (m, PCH <sub>2</sub> ); 2.64 (s, As $Me$ , <sup>3</sup> $J$ (Pt–H) = 19 Hz); 7.41–7.64 (m); 7.96–8.08 (m); 8.20 (d, 6.8 Hz); 8.36 (d, 8.0 Hz)
$[Pd_2Cl_2(\mu\text{-OAc})_2L_2]$	CHCl <sub>3</sub> -hexane (73) (orange)	130	51.2 (50.7)	3.8 (3.7)	2.17 (s, As <i>Me</i> ); 2.25 (s, OAc); 6.93 (d, 6.8 Hz); 7.01 (d, 6.8 Hz); 7.15 (t, 7.7 Hz); 7.29 (t, 7.2 Hz); 7.53 (m); 7.74 (d, 8.3 Hz); 7.80 (8 Hz); 8.46 (8 Hz)
[PtCl <sub>2</sub> L <sub>2</sub> ]	CH <sub>2</sub> Cl <sub>2</sub> -hexane (91) (cream)	253	52.7 (52.8)	3.7 (3.6)	2.22 (small, s, As <i>Me</i> ), 2.24 (large, s, As <i>Me</i> , <sup>3</sup> <i>J</i> (Pt–H) = 12 Hz); large: 7.33 (t, 7.4 Hz); 7.43 (t, 7.1 Hz); 7.54 (t, 7 Hz); 7.83 (dd, 7.1, 0.9 Hz); 7.93 (t, 7 Hz); 8.67 (d, 8.4 Hz) small: 7.05 (t, 7.5 Hz); 7.39 (d, 7.3 Hz); 7.74 (t, 7.3 Hz); 8.28 (d, 7.9 Hz)
[PtBr <sub>2</sub> L <sub>2</sub> ]	acetone-hexane (57) (orange)	225	49.9 (48.3)	4.1 (3.3)	2.31 (very small As <i>Me</i> ); 2.39 (s, As <i>Me</i> , <sup>3</sup> <i>J</i> (Pt–H) = 15 Hz); 7.33 (t, 8 Hz); 7.45 (t, 8.0 Hz); 7.55 (t, 7 Hz); 7.85 (d, 7 Hz); 7.93 (d, 8 Hz); 8.63 (d, 8.5 Hz)
$[PtI_2L_2]^i$	CHCl <sub>3</sub> -hexane (60) (orange)	265	43.2 (44.3)	3.2 (3.0)	2.71 (s, As <i>Me</i> , <sup>3</sup> <i>J</i> (Pt–H) = 21 Hz); 7.34 (t, 7.9 Hz); 7.47 (t, 8 Hz); 7.56 (t, 7 Hz); 7.86 (7.1 Hz); 7.92 (dd, 8, 3.4 Hz); 8.55 (d, 8.3 Hz)

Physical, analytical and <sup>1</sup>H NMR data of dinaphthylmethylarsine complexes of palladium and platinum

<sup>a</sup> <sup>13</sup>C{<sup>1</sup>H} NMR in CDCl<sub>3</sub>  $\delta$ : 10.0 (s, AsMe); 125.7 (C-3,7); 126.1 (C-2); 126.9 (C-6); 128.9 (C-5,8); 130.5 (C-4); 133.8 (C-9); 136.1 (C-10); 139.7 (As–C). <sup>b</sup> <sup>13</sup>C{<sup>1</sup>H} NMR in CDCl<sub>3</sub>  $\delta$ : 19.9 (s, AsMe); 124.8, 126.1, 126.4, 128.5, 129.3, 131.4, 133.6, 133.7, 134.2.

<sup>c 1</sup>H NMR in DMSO-d<sup>6</sup>.

Table 1

<sup>d</sup> % N: 1.9 (2.2); <sup>13</sup>C{<sup>1</sup>H} NMR in CDCl<sub>3</sub>  $\delta$ : 10.4 (s, NCH<sub>2</sub>Me); 12.2 (s, AsMe); 43.7 (s, NCH<sub>2</sub>); 125.2, 126.2, 126.7, 127.1, 129.0, 130.5, 131.3, 133.2, 133.7, 134.2, 206.9 (s, N-CS<sub>2</sub>).

<sup>e</sup> <sup>31</sup>P{<sup>1</sup>H} in CDCl<sub>3</sub>: 29.7 ppm, <sup>13</sup>C{<sup>1</sup>H} NMR in CDCl<sub>3</sub> & 8.1 (s, PCH<sub>2</sub>CH<sub>3</sub>); 9.2 (s, AsMe); 15.2 (d, J(P-C) = 28 Hz, PCH<sub>2</sub>); 125.3, 126.2, 126.4, 128.2, 130.9, 132.9, 134.4, 134.4.

 $f^{-31}P\{^{1}H\}$  in CDCl<sub>3</sub>: 11.2 ppm.

 $g^{-31}P{^{1}H}$  in CDCl<sub>3</sub>: 3.4 ppm,  ${}^{1}J(Pt-P) = 3013$  Hz.

<sup>h 31</sup>P{<sup>1</sup>H} in CDCl<sub>3</sub>: -4.5 ppm, <sup>1</sup>*J*(Pt-P) = 3362 Hz. <sup>i 13</sup>C{<sup>1</sup>H} NMR in CDCl<sub>3</sub>  $\delta$ : 17.5 (s, AsMe); 124.7, 126.0, 126.3, 128.3, 129.2, 131.0, 131.4, 131.7, 132.6, 133.6, 134.3, 134.7.

#### 2.3.7. $[Pd_2Cl_2(\mu - OAc)_2L_2]$

To a stirred CH<sub>2</sub>Cl<sub>2</sub> solution of  $[Pd_2Cl_2(\mu-Cl)_2L_2]$ (100 mg, 0.1 mmol), 36 mg of AgOAc (0.21 mmol) was added and the mixture was stirred for 3 h. Filtering through a Florisil column and drying of the residue *in vacuo* yielded an orange solid which was recrystallized from CHCl<sub>3</sub>-hexane (80 mg; 73%).

## 2.3.8. $[PtCl_2L_2]$

To a stirred CH<sub>2</sub>Cl<sub>2</sub> solution of [PtCl<sub>2</sub>(PhCN)<sub>2</sub>] (217 mg, 0.46 mmol), 320 mg of Nap<sub>2</sub>AsMe (0.93 mmol) was added. The reactants were stirred for 3 h whereupon a white precipitate formed which was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub>-hexane (1:2 v/v) and dried in vacuo (400 mg; 91%).

Similarly,  $[PtBr_2L_2]$  and  $[PtI_2L_2]$  were prepared from  $[PtCl_2L_2]$  and excess KBr and KI, respectively (see Table 1).

#### 3. Results and discussion

## 3.1. Synthesis and spectroscopic analyses

Treatment of  $[MCl_2(RCN)_2]$  (M = Pd or Pt; R = Me or Ph) with two equivalents of di(1-naphthyl)methylarsine (L) readily gave  $[MCl_2L_2]$  (Scheme 1). The chloride ligands in the latter can be substituted with Br or I by the reaction of  $[MCl_2L_2]$  with an excess of KBr or KI in acetone. The reaction of  $[PdCl_2L_2]$  with  $[PdCl_2(MeCN)_2]$  in refluxing benzene afforded sparingly soluble binuclear complexes  $[Pd_2Cl_2(\mu-Cl)_2L_2]$ . Attempts



Fig. 1. Raman spectrum of [PdCl<sub>2</sub>(Nap<sub>2</sub>AsMe)<sub>2</sub>].

to recrystallize  $[Pd_2Cl_2(\mu-Cl)_2L_2]$  and  $[PdCl_2L_2]$  from pyridine result in bridge cleavage and ligand substitution with the formation of yellow  $[PdCl_2(pyridine)_2]$ . The IR and Raman spectra of the complexes  $[MCl_2L_2]$  display strong single absorptions at 304 (Fig. 1) or 316 cm<sup>-1</sup> for M = Pd or Pt, respectively, assigned to M–X stretching modes (v(M-X)). Similarly, the Raman spectrum of  $[PdBr_2L_2]$  shows a resonance at 200 cm<sup>-1</sup>. The presence of a single absorption due to v(M-X) suggests that these complexes adopt a *trans* configuration in the solid state. The IR spectrum of  $[Pd_2Cl_2(\mu-Cl)_2L_2]$  exhibits three absorptions at 360, 325 and 305 cm<sup>-1</sup>, attributable to v(Pd-Cl(terminal)), v(Pd-Cl(bridging,*trans*to Cl)) and<math>v(Pd-Cl(bridging,*trans*to arsine)) [1,12]. <sup>1</sup>H NMR spectra of these complexes display AsMe proton resonances



Scheme 1. Preparation of Nap<sub>2</sub>AsMe complexes.

which are considerably deshielded from the corresponding signals for free Nap<sub>2</sub>AsMe. The naphthyl protons, which are also deshielded, appear as multiplets (Table 1). For the complexes  $[MX_2L_2]$  (X = Cl or Br) two singlets, attributable to the AsMe protons, were found presumably due to the occurrence of trans and cis isomers in solution. For [PdI<sub>2</sub>L<sub>2</sub>], we found only one resonance at 2.76 ppm after dissolving the complex. When leaving the solution for a longer time we observed two singlets at  $\delta$  2.16 and 2.76 ppm (in a 3:2 ratio). Assuming a *trans* conformation for the solid material (see IR spectroscopy), we can assign the low field signal to the *trans* isomer and the upcoming high field signal to the *cis* form. In an analogous way (low-field = trans, high-field = cis), we can conclude for the whole series of complexes that in fluid solution slow trans/cis isomerization occurs with trans being the initial isomer from the preparation procedures. This is remarkable in view of the recently rebenzyldimethylarsine complexes ported  $[MX_2]$  $(BzAsMe_2)_2$  (M = Pd or Pt) [2] which have been found exclusively in *cis* conformation for X = Cl and in *trans* conformation for X = Br or I and also in view of the reported triallylarsine complexes  $[MX_2(allyl_3As)_2]$ (M = Pd or Pt) [3] where only for M = Pd and X = Clboth trans and cis conformers were obtained after preparation. However, the *cis* form quickly isomerizes to the trans form, which is found exclusively for all other complexes in this series. The reason for this peculiarity can be found in the high lability of the di(1-naphthyl)methylarsine ligand. Ligand lability is a prerequisite for the isomerization and was found to be much higher for the Nap<sub>2</sub>AsMe ligand than for related BzAsMe<sub>2</sub> or allyl<sub>3</sub>As ligands (see, e.g., the formation of  $[Pd(S_2CNEt_2)_2]$ ).

The thermal behaviour of  $[PdCl_2(Nap_2AsMe)_2]$  was studied by thermogravimetric analysis. The TGA curve (Fig. 2) shows two steps of decomposition. These steps can be characterized by arsine loss, leaving behind PdCl<sub>2</sub>



Fig. 2. TGA curve of [PdCl<sub>2</sub>(Nap<sub>2</sub>AsMe)<sub>2</sub>].

at  $\sim$ 270 °C. The transition from first step to second stage is poorly resolved.

The bridging chlorides in  $[Pd_2Cl_2(\mu-Cl)_2L_2]$  are readily substituted by bridging acetate ligands through treatment with AgOAc. The acetato-bridged complex  $[Pd_2Cl_2(\mu-OAc)_2L_2]$  shows a  $\nu(C=O)$  resonance at 1570 cm<sup>-1</sup>. This is comparable to other reported values for acetato bridged palladium or platinum complexes [13,14].

Reaction of  $[Pd_2Cl_2(\mu-Cl)_2L_2]$  with two equivalents of NaS<sub>2</sub>CNEt<sub>2</sub> · 3H<sub>2</sub>O yielded orange  $[PdCl(S_2CNEt_2)L]$ . The ethyl groups in the complex are anisochronous, two separate triplets and quartets are observed for the methyl and methylene protons in <sup>1</sup>H NMR spectroscopy. Such behaviour of the diethyldithiocarbamate ligand is not uncommon [15]. If the complex is left in solution for a few days or if the dimer  $[Pd_2Cl_2(\mu-Cl)_2L_2]$  is treated with an excess of NaS<sub>2</sub>CNEt<sub>2</sub> · 3H<sub>2</sub>O, yellow orange crystals of  $[Pd(S_2CNEt_2)_2]$  were separated which could be characterized by analytical, spectroscopic and structural analysis (see later).

Bridge cleavage of  $[M_2Cl_2(\mu-Cl)_2(PR_3)_2]$  with Nap<sub>2</sub>AsMe in dichloromethane gave the mixed ligand complexes  $[MCl_2(L)(PR_3)]$ . The complexes display single sets of resonances in the <sup>1</sup>H and <sup>31</sup>P NMR spectra, indicating the formation of only one isomer. The magnitude of <sup>1</sup>*J*(Pt–P) suggests a *trans* configuration which is confirmed by X-ray structural analysis (see later).

## 3.2. Photophysical studies

Despite the isomerization reaction described above, we can assume that all the compounds  $[PdX_2L_2]$  exhibit initially a trans configuration. This is important for the photophysical properties discussed here. The compounds exhibit colours that range from colourless to red in the solid as well as in solution. The electronic spectra (Table 2) reveal that the long-wavelength absorption maxima are lower in energy for the palladium derivatives as compared to the platinum analogues. Furthermore, the energy decreases along the series Cl > Br > I. In view of recent results on related benzyldimethylarsine complexes  $[MX_2(BzAsMe_2)_2]$  [2] and triallylarsine complexes  $[MX_2(allyl_3As)_2]$  [3], we tentatively assign the long-wavelength absorptions to mixed ligand(pX)-to-ligand (s/p\*As)/metal(d)-to-ligand (s/p\*As) charge transfer (L'LCT/MLCT) transitions. Strong evidence for this assignment comes from the clear separation of the longwavelength absorption into two bands for the iodide derivatives (see Fig. 3). Iodide is the best donor in this respect and should provide the highest contribution to the starting orbital (HOMO) of the electronic transition. Further support for the role of arsine in providing the acceptor orbitals comes from recent investigations on related complexes of the type [MCl(TeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)  $(PR_3)$ ] (M = Pt or Pd; R = alkyl or aryl) where the

Table 2
Photophysical data of the dinaphthylmethylarsine complexes of Pd(II) and Pt(II) <sup>a</sup>

Compound	$\lambda_{\max}/nm \ (\varepsilon/M^{-1} \ cm^{-1})^a$	Emission maxima $\lambda_{max}$	$\varDelta^{\mathbf{b}}$
Naphthalene	248 (2180), 257 (3700), 266 (3128), 275 (6044), 286 (3993)	321, 334°	
$[Nap_2AsMe] (= L)$	291 (15322)	345, 370	7340
[PdCl <sub>2</sub> L <sub>2</sub> ]	285 (37083), 368 (20025)	415(sh), 438, 463(sh)	4340
[PdBr <sub>2</sub> L <sub>2</sub> ]	286 (48 551), 380 (19745)	417(sh), 440, 461(sh)	3590
$[PdI_2L_2]$	287 (45669), 364 (14619), 434 (6036)	445	5000 <sup>e</sup>
$[Pd_2Cl_2(\mu-Cl)_2L_2]$	286 (19086), 398(br)		
$[Pd_2Cl_2(\mu-OAc)_2L_2]$	234 (28571), 292 (13966), 333(sh)		
[PdCl(S <sub>2</sub> CNEt <sub>2</sub> )L]	282 (24431), 368 (3611)		
[PdCl <sub>2</sub> (PEt <sub>3</sub> )L]	288 (13710), 340 (13042)		
[PdCl <sub>2</sub> (PMePh <sub>2</sub> )L]	284 (16359), 350 (13312)		
[PtCl <sub>2</sub> (PPr <sub>3</sub> )L]	290 (24144)		
[PtCl <sub>2</sub> (PBu <sub>3</sub> )L]	289 (23900)		
[PtCl <sub>2</sub> L <sub>2</sub> ]	298 (28257)	349	4900
$[PtBr_2L_2]$	292 (19335), 309 (16277)	359	4510
[PtI <sub>2</sub> L <sub>2</sub> ]	290 (22738), 353 (3658)	405	3640

<sup>a</sup> As measured in CH<sub>2</sub>Cl<sub>2</sub> solution.

<sup>b</sup>  $\Delta$  = Stokes shift = v(abs,max) - v(em,max) in wavenumbers (cm<sup>-1</sup>).

<sup>c</sup> Measured in cyclohexane, emission originating from the singlet <sup>1</sup>IL state = fluorescence.

<sup>d</sup>  $\Delta$  was calculated from the second maximum at 364 nm. Taking the lowest maximum,  $\Delta$  calculates to 570 cm<sup>-1</sup>.



Fig. 3. UV-vis spectra of [PdX<sub>2</sub>(Nap<sub>2</sub>AsMe)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub>.

long-wavelength absorptions were assigned to ligand(Te)-to-ligand(P) charge transfer transitions, based on spectroscopic and theoretical evidence [16].

Compared to the above cited benzyl- or (methyl)allyl complexes, the dinaphthyl derivatives carry the additional naphthyl chromophore for relatively long-wavelength absorptions and, even more importantly, strong emissions (see later). Therefore, we assign the partially structured bands around 290 nm to intra-ligand  $\pi$ - $\pi$ \*(naphthyl) (IL) transitions for the complexes [MX<sub>2</sub>(Nap<sub>2</sub>AsMe)<sub>2</sub>], they occur in the free ligand Nap<sub>2</sub>AsMe as well as in naphthalene (Table 2, Fig. 4). For the Pt(II) complexes, these bands partly overlap with the long-wavelength CT bands.

The absorption spectra of the complexes  $[PdCl_2(L)(PR_3)]$  are very similar to the ones described above. The long-wavelength bands (L'LCT/MLCT) are shifted to somewhat higher energies and are lower in intensity. This supports our assignment since arsines



Fig. 4. Absorption and emission spectrum of Nap<sub>2</sub>AsMe in CH<sub>2</sub>Cl<sub>2</sub>.

are better acceptors compared to phosphine ligands, which has been conclusively shown for related palladium complexes with ER<sub>3</sub> ligands (E = P, As or Sb) where the lowest absorption maxima show a red-shift when going from E = P to E = Sb [17]. The bands around 290 nm are also present here albeit with markedly lower intensity when compared to the [MX<sub>2</sub>(L)<sub>2</sub>] derivatives, which is in excellent agreement to the IL assignment outlined above.

The complexes  $[MX_2L_2]$  (M = Pd or Pt; X = Cl, Br, I) have been found to exhibit bright luminescence in fluid solution (Fig. 5) as well as in the solid. The highest maxima of the partly structured bands shift to lower energy with decreasing electronegativity of the halide or substituting platinum by palladium (Table 2). The values for the bromide and chloride derivatives differ only slightly in this respect, the iodide analogues deviate much stronger, connected to an obvious loss of the partial



Fig. 5. Emission spectra of [PdX<sub>2</sub>(Nap<sub>2</sub>AsMe)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub>.

structuring (Fig. 5) and a mismatch of the Stokes shifts  $\varDelta$  calculated from the difference between the long-wavelength absorption maxima and the main maxima of the emission bands. Both naphthalene [18] and Nap<sub>2</sub>AsMe (Fig. 4) are emissive in fluid solution, however, their emission maxima do not coincide with those of the complexes (Table 2). The broad emission of the free ligand Nap<sub>2</sub>AsMe (Fig. 4) is assumed to originate from a  $\pi$ - $\pi^*$  IL excited state. Presumably, the transition has triplet character (<sup>3</sup>IL) due to the heavy element influence of arsenic, with its relatively high spin-orbit coupling. Similarly, the emissions of the complexes  $[MX_2(L)_2]$  are assumed to originate from corresponding <sup>3</sup>CT states (L'LCT/MLCT). The Stokes shifts ⊿ support the different character of the emission. The complexes all exhibit  $\Delta$  values of about 3000–5000 cm<sup>-1</sup> which are typical for CT states in platinum(II) complexes, whereas  $\Delta$  is much higher for the ligand indicating an IL state [19]. Comparing the iodide with the bromide or chloride analogues, the emission behaviour suggests a marked change for the excited state which we tentatively ascribe to a shift from mainly MLCT for X = Cl or Br to mainly L'LCT for X = I. In view of the fact that the naphthylarsine complexes exhibit much stronger luminescence than the above-mentioned benzyldimethyl- or (methyl)allylarsine analogues, we suspect that the naphthyl chromophore not only provides the high energy IL states but may also contribute to the lowest transitions and the corresponding excited states. Detailed spectroscopic experiments (time-resolved experiments, quantum yield determination, resonance Raman spectroscopy) combined with theoretical calculations could help to gain a better insight.

## 3.3. Crystal structures

Unfortunately, the complexes  $[MX_2(Nap_2AsMe)_2]$  failed to give reasonable crystals for an XRD analysis to confirm the isomers observed by IR and NMR spec-

Table 3 Crystallographic and refinement data for [PdCl<sub>2</sub>(PEt<sub>3</sub>)(Nap<sub>2</sub>AsMe)] and [Pd(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>]

Compound	[PdCl <sub>2</sub> (PEt <sub>3</sub> )	$[Pd(S_2CNEt_2)_2]$
	(Nap <sub>2</sub> AsMe)]	
Empirical formula	C27H32AsCl2PPd	$C_{10}H_{20}N_2PdS_4$
Formula weight	639.72	402.92
T (K)	293(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	tetragonal
Space group	$P2_1/c$	$P4_2/n$
a (Å)	13.2660(2)	16.2435(3)
b (Å)	14.3565(2)	16.2435(3)
c (Å)	14.8659(2)	6.1746(2)
β (°)	109.8824(9)	90.0
$V(Å^3)$	2662.50(7)	1629.18(7)
Ζ	4	4
$\rho_{\rm calc} \ ({\rm g \ cm^{-3}})$	1.596	1.643
$\mu (\mathrm{mm}^{-1})$	2.205	1.634
F(000)	1288	816
Data/restraints/ parameters	6082/0/305	1859/0/120
Final R indices	$R_1 = 0.0267;$	$R_1 = 0.0235;$
$[I > 2\sigma(I)]$	$wR_2 = 0.0587$	$wR_2 = 0.0554$
R indices (all data)	$R_1 = 0.0316;$	$R_1 = 0.0270;$
	$wR_2 = 0.0606$	$wR_2 = 0.0577$
Goodness-of-fit on $F^2$	1.091	1.103
Largest difference in	0.567 and -0.661	0.607 and
peak and hole (e $Å^{-3}$ )		-0.636

troscopy. From the series of  $[MX_2(PR_3)(Nap_2AsMe)]$  complexes, a representative example could be examined (Table 3). The structure of  $[PdCl_2(PEt_3)(Nap_2AsMe)]$  shows that the palladium atom is in a distorted square planar environment with the neutral donors (P and As) in a *trans* arrangement (Fig. 6). The two Pd–Cl distances (which are very similar), the Pd–P, Pd–As and the As–C bond lengths (Table 4) are in agreement with the literature values for related complexes [1,20–23]. At



Fig. 6. Molecular structure of *trans*-[PdCl<sub>2</sub>(PEt<sub>3</sub>)(Nap<sub>2</sub>AsMe)] in the crystal, showing 30% thermal ellipsoids.

Table 4 Selected bond lengths (Å) and bond angles (°) of palladium(II) complexes

[PdCl <sub>2</sub> (PEt <sub>3</sub> )(Nap <sub>2</sub> AsMe)]		[Pd(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ]		
Bond lengths $(\mathring{A})$				
Pd–P	2.2863(6)	Pd-S(2)	2.3214(4)	
Pd–Cl(1)	2.2970(5)	Pd-S(2)#1	2.3214(4)	
Pd–Cl(2)	2.3055(5)	Pd-S(1)#1	2.3263(4)	
Pd–As	2.4560(3)	Pd-S(1)	2.3263(4)	
As-C(1)	1.946(2)	S(1)–C(1)	1.7257(18)	
As-C(8)	1.947(2)	S(2)-C(1)	1.7267(19)	
As-C(18)	1.952(2)	N–C(1)	1.317(2)	
		N–C(2)	1.474(2)	
		N–C(4)	1.476(2)	
Bond angles (°)				
P-Pd-Cl(1)	86.34(2)	S(2)-Pd-S(2)#1	180.00(2)	
P-Pd-Cl(2)	94.59(2)	S(2)-Pd-S(1)#1	104.325(15)	
Cl(1)-Pd-Cl(2)	178.81(2)	S(2)#1-Pd-S(1)#1	75.675(15)	
P-Pd-As	176.218(16)	S(2)-Pd-S(1)	75.675(16)	
Cl(1)–Pd–As	90.585(16)	S(2)#1-Pd-S(1)	104.325(15)	
Cl(2)-Pd-As	88.451(15)	S(1)#1–Pd–S(1)	180.00(2)	
C(1)-As-C(8)	101.60(10)	C(1)–S(1)–Pd	86.42 (6)	
C(1)-As-C(18)	101.57(10)	C(1)–S(2)–Pd	86.55 (6)	
C(8)-As-C(18)	101.94(9)	N-C(1)-S(1)	124.50 (14)	
C(1)–As–Pd	112.60(8)	N-C(1)-S(2)	124.15 (14)	
C(8)–As–Pd	121.60(6)	S(1)-C(1)-S(2)	111.35 (10)	
C(18)-As-Pd	114.89(6)			

2.4560(3) Å, the Pd–As distance is, however, longer than that reported for  $[Pd_2Me_2(\mu-Cl)_2(As^iPr_3)_2]$  (2.3495(7) Å) [1] or  $[PdCl_2{PhAs(CH_2CH_2CH_2CH_2CH_2)}_2]$  (2.3999(6) Å) [24]. The coordination around arsenic shows a typical trigonal pyramidal AsC<sub>3</sub> skeleton with C–As–C angles of ~101.6°, which do not differ significantly from those reported for other coordinated arsines. The individual naphthyl rings are planar and point away from the coordination plane of the palladium atom.

The structure (Fig. 7) of the product  $[Pd(S_2CNEt_2)_2]$ from the reaction involving  $[PdCl(S_2CNEt_2)L]$  shows discrete molecules with the palladium atom in distorted square planar geometry defined by the two symmetrically chelated dithio ligands. Similar symmetrical binding of that dithiocarbamate ligand had been reported for  $[Pd(SMe)(S_2CNEt_2)(PEt_3)]$  [25], in contrast to dithiophosphate ligands of analogous complexes which show asymmetrical chelate binding, e.g., in  $[Pd(2-Spy)-{S_2P(O'Pr)_2}(PPh_3)]$  [26] or  $[PdCl{S_2P(OEt)_2}(PPh_3)]$ [27]. The four Pd–S distances are essentially identical and are in agreement with the values (2.2–2.5 Å) reported for a variety of palladium complexes containing dithio ligands [25–28]. The strain imposed by the four membered PdS\_2C chelate ring is reflected by a compression in those S–Pd–S angles (~75.7°), while the adjacent angles S–Pd–S(#) have opened to 104.3°. The mutually *trans* sulfur atoms exhibit an S–Pd–S angle of 180°.

The N–C(1) distance (Table 4) is significantly reduced compared to a single N–C bond length, reflecting partial double bond character. The S–C distances lie between the values reported for single or double bonds, e.g.,  $[RAs(S_2CNEt_2)_2]$  (R = Me: C–S = 1.769(9), 1.675(9); R = Ph: C–S = 1.745(7), 1.691(7) Å) [29]. The observed N–C (1) and S–C distances indicate an effective delocalization in the S<sub>2</sub>–C–N core. The ethyl groups of the NEt<sub>2</sub> moiety lie above and below the central NCS<sub>2</sub>PdS<sub>2</sub>CN plane.

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#### Appendix A. Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic



Fig. 7. Molecular structure of [Pd(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>] in the crystal, showing 30% thermal ellipsoids.

Data Centre, CCDC Nos. 247069 ( $[PdCl_2(PEt_3)(Nap_2AsMe)]$ ), 247070 ( $[Pd(S_2CNEt_2)_2]$ ). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (int. code) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.03.026.

Four figures illustrating the crystal structures (unit cell and intermolecular interactions) and perspective views as well as full structural data of both complexes are available from the author on request.

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