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Configurational selectivity in benzyldimethylarsine complexes of palladium(II) and platinum(II): synthesis, spectroscopy and structures

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Abstract

Benzyldimethylarsine complexes of palladium(II) and platinum(II) with the formulae $[MX_2(BZASMe_2)_2] (X = Cl, Br, I), [M_2Cl_2(\mu-Cl)_2(BZASMe_2)_2], [Pd_2Cl_2(\mu-OAc)_2(BZASMe_2)_2], [Pd_2Me_2(\mu-Cl)_2(BZASMe_2)_2] and [Pd_2X_2(\mu-N^N)_2(BZASMe_2)_2] (M = Pd or Pt; N^N = pyrazolate (pz) or 3,5-dimethylpyrazolate (dmpz)) have been prepared. All complexes have been characterised by elemental analysis, IR, UV–Vis absorption and NMR (¹H, ¹³C, ¹⁹⁵Pt) spectroscopy. The molecular structures of the complexes [MX_2(BZASMe_2)_2] (M = Pt or Pd; X = Cl, Br or I) have been established by NMR spectroscopy and single crystal X-ray diffraction analysis and reveal a clear dichotomy in solution and in the solid between the compounds with X = Cl in a$ *cis*configuration and the*trans*configured bromide and iodide complexes.

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1. Introduction

The chemistry of organoarsenic compounds has attracted considerable attention during the last decade due to their applications in several chemical vapour deposition (CVD) techniques for the preparation of semiconductor materials [1,2]. In these techniques alkyl derivatives show distinct advantages over the conventional arsine (AsH₃) source. The commercially available lower alkyls R_3As (R = Me or Et) have high decomposition temperatures and often yield poor quality films [3]. Efforts are continuously made to develop alternative clean and low decomposition temperature arsenic precursors [4,5]. Benzylarsines (I; $ER_2 = AsMe_2$) may prove successful precursors for CVD as the element (E)-benzyl bond is split more easily than analogous methyl and aryl linkages [6].



(E = N, P, As, Sb, Bi)

The reactions of **I** with metal salts show a pronounced dependence on the size of E. For example, N,N-dimethylbenzylamine (**I**, ER₂ = NMe₂) is readily cyclopalladated when treated with Pd(OAc)₂ or PdCl₄²⁻ to give binuclear complexes [Pd₂(μ -X)₂(C^{\wedge}N)₂] (X = Cl or OAc; C^{\wedge}N = cyclometallated dimethylbenzylamine) [7–10]. In contrast, reactions of benzylphosphines with metal salts readily yield complexes of the type '[M(PBz_nR_{3-n})]' [11–15] and orthometallation reactions are often base promoted [16,17]. Benzylphosphines are sterically more demanding and are stronger bases than PPh₃, consequently benzylphosphine complexes have shown different reactivities [15]. In view of the above and in pursuance of our work on organoarsenic compounds it was considered worthwhile to explore the

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chemistry of palladium and platinum complexes of a higher analogue, i.e. BzAsMe₂, although several tertiary arsine derivatives have been investigated earlier [18].

2. Experimental

2.1. Instrumentation

The ¹H, ¹³C{¹H} and ¹⁹⁵Pt{¹H} NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300 (¹H), 75.47 (¹³C) and 64.52 MHz (¹⁹⁵Pt), respectively. The chemical shifts are relative to internal CHCl₃ peak ($\delta = 7.26$ ppm for ¹H and $\delta = 77.0$ ppm for ¹³C) and external Na₂PtCl₆ in D₂O for ¹⁹⁵Pt. IR spectra were recorded as Nujol mulls using CsI plates on a Bomen-102 FTIR spectrometer in the range of 200– 4000 cm⁻¹. Microanalyses of the complexes were carried out in the Analytical Chemistry Division of Bhabha Atomic Research Centre.

2.2. Crystallography

For all six compounds $[MX_2(BzAsMe_2)_2]$ (M = Pt or Pd; X = Cl, Br, or I) data collection was performed at T = 173(2) K on a Siemens P4 diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å) employing $\omega - 2\theta$ scan technique. The structures were solved using the SHELXTL package [19] and refinement was carried out with SHELXL-97 employing full-matrix least-squares methods on F^2 [20] with $F_o^2 \ge -3\sigma(F_o^2)$ with the results shown in Table 4. All non-hydrogen atoms were treated anisotropically, hydrogen atoms were included by using appropriate riding models.

2.3. Reagents and general procedures

[PdCl₂(MeCN)₂] or [PtCl₂(PhCN)₂] were prepared as described in literature [21]. All reactions were carried out under a nitrogen atmosphere in dry and distilled analytical grade solvents.

2.4. Synthesis

2.4.1. BzAsCl₂

To a stirred Et₂O solution of AsCl₃ (36.3 g, 200 mmol) an ethereal solution of BzMgCl (36.2 g, 240 mmol) was added dropwise with vigorous stirring at -78 °C over a period of 4 h. After warming to room temperature (r.t.), stirring continued for an additional 2 h. The reaction mixture was filtered and the inorganic salts were washed with Et₂O (3 × 50 cm³). The filtrate was concentrated in vacuo and the residual oil was distilled twice in vacuo (118–120 °C/3 mmHg) as a faint greenish tinge liquid in 22% (10.3 g) yield. ¹H NMR spectrum in CDCl₃: δ 3.83 (s, CH₂); 7.34 (m, Ph). [Some

preparations also contained impurities of dibenzyl: δ 2.96 (CH₂); 7.16 (br, Ph)].

2.4.2. BzAsMe₂

To a stirred ethereal solution (70 cm³) of CH_3MgI (17.43 g, 105 mmol) BzAsCl₂ (10.3 g, 43.4 mmol) was added dropwise with vigorous stirring under nitrogen at 0 °C. The reaction mixture was heated to reflux for 3 h and then allowed to stand at r.t. To this a deoxygenated aq. solution of NH₄Cl (200 cm³) was added with constant stirring and cooling at 0 °C till the magnesium salts were completely dissolved in an aq. solution of NH₄Cl. The upper organic layer was separated and the aq. layer was washed with Et_2O (3 × 50 cm³) and all were combined. The Et₂O was distilled off and the residue was distilled twice in vacuo (44-45 °C/2 mmHg) to yield a colourless liquid in 41% (3.5 g) yield. ¹H NMR in CDCl₃: δ 0.91 (s, AsMe₂); 2.80 (s, AsCH₂); 7.11–7.30 (m, Ph). ${}^{13}C{}^{1}H{}$ in CDCl₃: δ 9.12 (s, AsMe₂); 34.40 (s, AsCH₂); 125.0 (C-4); 128.1 (C-2, 6 or C-3, 5); 128.3 (C-3, 5 or C-2, 6); 139.4 (s, C-1).

2.4.3. $[PdCl_2(BzAsMe_2)_2]$

To a stirred benzene solution (75 cm³) of [PdCl₂(MeCN)₂] (1.948 g, 7.51 mmol), BzAsMe₂ (2.95 g, 15.04 mmol) was added under a nitrogen atmosphere with stirring which was continued for 3 h. The solvent was evaporated in vacuo. The residue was recrystallised from CH₂Cl₂-hexane mixture as yellow crystals in 80% (3.44 g) yield. ¹³C{¹H} NMR in CDCl₃: δ 6.0 (s, AsMe₂); 30.8 (s, AsCH₂); 126.6 (C-4); 128.7 (C-2, 6 or C-3, 5); 129.4 (C-3, 5 or C-2, 6); 134.9 (C-1). UV–Vis (CH₂Cl₂): λ_{max} 364, 293 nm. Similarly [PtCl₂(BzAs-Me₂)₂] was prepared from [PtCl₂(PhCN)₂] (627 mg, 1.33 mmol) and BzAsMe₂ (528 mg, 2.69 mmol) as white crystals in 50% (435 mg) yield. UV–Vis (CH₂Cl₂): λ_{max} 298, 272 nm.

2.4.4. $[PdBr_2(BzAsMe_2)_2]$

To an acetone stirred solution (25 cm³) of $[PdCl_2(BzAsMe_2)_2]$ (125 mg, 0.22 mmol) a large excess of KBr (616 mg, 5.18 mmol) was added. It was stirred for 3 days. The solvent was evaporated and the product was recrystallised from acetone-hexane mixture as yellowish crystals in 72% (104 mg) yield. UV-Vis (CH₂Cl₂): λ_{max} 369, 286sh 255 nm. Similarly [PtBr₂-(BzAsMe₂)₂] was prepared from [PtCl₂-(BzAsMe₂)₂] (90 mg, 0.14 mmol) and a large excess of KBr (736 mg, 6.18 mmol) as yellowish crystals in 61% (62 mg) yield. UV-Vis (CH₂Cl₂): λ_{max} 300 nm.

2.4.5. $[PdI_2(BzAsMe_2)_2]$

To stirred acetone solution (30 cm^3) of $[PdCl_2(BzAsMe_2)_2]$ (126 mg, 0.22 mmol) a large excess of KI (642 mg, 3.87 mmol) was added. The whole was stirred for 2 days. The solvent was evaporated and the

product was recrystallised from acetone–hexane mixture as orange crystals in 70% (117 mg) yield. UV–Vis (CH₂Cl₂): λ_{max} 420 ($\varepsilon = 8240 \text{ M}^{-1} \text{ cm}^{-1}$), 345sh (7800), 307 (26010), 256 nm (24770). Similarly [PtI₂(BzAsMe₂)₂] was prepared from [PtCl₂(BzAsMe₂)₂] (100 mg, 0.15 mmol) and a large excess of KI (598 mg, 3.60 mmol) as orange crystals in 63% (80 mg) yield. UV–Vis (CH₂Cl₂): λ_{max} 344 ($\varepsilon = 6090 \text{ M}^{-1} \text{ cm}^{-1}$), 288 nm (6900 M⁻¹ cm⁻¹).

2.4.6. $[Pd_2Cl_2(\mu-Cl)_2(BzAsMe_2)_2]$

To a stirred benzene solution (50 cm³) of $[PdCl_2-(BzAsMe_2)_2]$ (534 mg, 0.94 mmol), $[PdCl_2(MeCN)_2]$ (235 mg, 0.91 mmol) was added and stirred for 1 h then refluxed for 3 h. The solvent was evaporated and the residue was recrystallised from benzene–hexane mixture as orange red crystals in 71% (498 mg) yield. Similarly $[Pt_2Cl_2(\mu-Cl)_2(BzAsMe_2)_2]$ was prepared from $[PtCl_2-(BzAsMe_2)_2]$ (210 mg, 0.32 mmol) and $PtCl_2$ (91 mg, 0.34 mmol), refluxing it in tetrachloroethane. The residue was recrystallised from benzene–hexane mixture in 34% (100 mg) yield.

2.4.7. $[Pd_2Me_2(\mu-Cl)_2(BzAsMe_2)_2]$

To an acetone solution (30 cm³) of $[Pd_2Cl_2(\mu-Cl)_2(BzAsMe_2)_2]$ (253 mg, 0.34 mmol), a slight excess of Me₄Sn (130 mg, 0.73 mmol) was added under a nitrogen atmosphere. Within a minute the colour faded. The whole was stirred for 20 min. Then the solvent was evaporated and the residue was washed with hexane to remove Me₃SnCl. The product was recrystallised from acetone-hexane mixture as a cream crystalline solid in 66% (157 mg) yield.

2.4.8. $[Pd_2Cl_2(\mu - OAc)_2(BzAsMe_2)_2]$

To a stirred CH₂Cl₂ solution (25 cm³) of [Pd₂Cl₂(μ -Cl)₂(BzAsMe₂)₂] (98 mg, 0.13 mmol), AgOAc (46 mg, 0.28 mmol) was added under a nitrogen atmosphere and the whole was stirred for 4 h and the solvent was evaporated and the product was recrystallised from toluene–hexane mixture as red crystals in 54% (56 mg) yield. ¹³C{¹H} in CDCl₃: δ 6.6 (s, AsMe₂); 23.4 (s, Me, OAc); 31.9 (s, AsCH₂); 127.2 (C-4); 129.0 (C-3, 5); 129.5 (C-2, 6); 133.4 (C-1) [Ph]; 182.2 (C=O).

2.4.9. $[PdMe_2(\mu - pz)_2(BzAsMe_2)]$

To a stirred CH₂Cl₂ solution (30 cm³) of [Pd₂Me₂(μ -Cl)₂(BzAsMe₂)] (105 mg, 0.15 mmol), a methanolic solution (10 cm³) of pyrazole (22 mg, 0.32 mmol) containing aq. NaOH (0.65 cm³, 0.49 N, 13 mg, 0.32 mmol) was added under a nitrogen atmosphere. The whole was stirred for 4 h and filtered. The solvent was evaporated in vacuo and the residue was recrystallised from CH₂Cl₂-hexane mixture as a white cubic crystals in 60% (69 mg) yield.

2.4.10. trans- $[Pd_2Cl_2(\mu-dmpz)_2(BzAsMe_2)]$

To a stirred CH₂Cl₂ solution (25 cm³) of [Pd₂Cl₂(μ -OAc)₂(BzAsMe₂)] (68 mg, 0.086 mmol) a slight excess of 3,5-dimethylpyrazole (18 mg, 0.19 mmol) was added under a nitrogen atmosphere and the whole was stirred for 3 h. The solvent was evaporated under vacuum and the residue was recrystallised from CH₂Cl₂-hexane mixture as pale yellow crystals in 70% (52 mg) yield. ¹³C{¹H} in CDCl₃: δ 6.0, 7.9 (each s, AsMe₂); 13.3, 13.6 (each s, Me₂-dmpz); 31.7 (s, AsCH₂); 104.3 (s, dmpz C-4); 126.9 (s, C-4); 128.8 (C-2, 6 or C-3, 5); 129.6 (s, C-3, 5 or C-2, 6); 134.7 (s, C-1) [Ph]; 147.2, 149.0 (each s, C-3, 5 dmpz).

2.4.11. $[Pd_2Me_2(\mu - dmpz)_2(BzAsMe_2)_2]$

To a stirred CH₂Cl₂ solution (30 cm³) of [Pd₂Me(μ -Cl)₂(BzAsMe₂)₂] (103 mg, 0.15 mmol) a slight excess of methanolic solution (10 cm³) of dmpzH (30 mg, 0.31 mmol) containing aq. NaOH (0.66 cm³, 0.47 N, 12 mg, 0.30 mmol) was added under a nitrogen atmosphere. The whole was stirred for 5 h and then filtered. The solvent was evaporated in vacuo and the compound was recrystallised from CH₂Cl₂–hexane mixture as white coloured compound in 79% (95 mg) yield. ¹³C{¹H} in CDCl₃: δ –13.2 (s, PdMe); 7.0, 7.9 (each s, AsMe₂); 13.7 (s, Me₂–dmpz); 32.2 (s, AsCH₂); 102.0 (s, C-4, dmpz); 126.3 (C-4); 128.5 (C-2, 6 or C-3, 5); 129.3 (C-3, 5 or C-2, 6); 135.8 (C-1) [Ph]; 145.4, 145.6 (each s, C-3, 5, dmpz).

3. Results and discussion

3.1. Synthesis and spectroscopic analyses

The syntheses of the palladium(II) and platinum(II) complexes with benzyldimethylarsine are depicted in Scheme 1 and their characterisation data are given in Tables 1 and 2. The reaction of $[MCl_2(RCN)_2]$ (R = Me, Ph) with 2 equiv. of BzAsMe2 readily gave [MCl2-(BzAsMe₂)₂]. The chloride in the latter can be substituted with Br or I by treating it with an excess of KBr or KI in acetone. The ¹H NMR spectra exhibited singlets each for the AsMe₂ and AsCH₂ protons which are deshielded relative to the free ligand. The deshielding of these resonances showed halogen dependence and increases with increasing size of the halogen atom. The signals for the platinum complexes were flanked by ¹⁹⁵Pt satellites. The ${}^{3}J(Pt-H)$ for the AsMe₂ resonance is approximately 17 Hz while the magnitude of ${}^{3}J(Pt-H)$ associated with AsCH2 decreases with increasing the size of halogen atom ${}^{3}J(Pt-H) = 20$ (Cl), 11 (Br), 7 (I) Hz). The ¹⁹⁵Pt NMR spectra display singlets (Table 2). The ¹⁹⁵Pt NMR chemical shifts for [PtCl₂(BzAsMe₂)₂] (δ -4320 ppm) can be compared with *cis*-[PtCl₂(AsR₃)₂] complexes (δ -4287 to -4363 ppm) [22,23]. The ¹⁹⁵Pt



Scheme 1. Preparation of the compounds (M = Pt or Pd; R = Me, Ph; pz = pyrazolate, dmpz = 3,5-dimethylpyrazolate).

NMR chemical shifts for the bromide (δ -4359 ppm) and iodide (δ -5496 ppm) are comparable to *trans*-[PtX₂(AsMe₃)₂] [X = Br (-4378), I (-5518)] [23] indicative of a *trans* configuration for [PtX₂(BzAsMe₂)₂] (X = Br, I). Indeed, different configurations for X = Cl (*cis*) as opposed to X = Br or I (*trans*) were unambiguously confirmed by X-ray structural analyses (vide infra).

The compounds exhibit colours that range from deep red to faint yellow in the solid as well as in fluid solution. An investigation of the absorption spectra revealed that the long-wavelength absorption maxima are lower in energy for the palladium derivatives when compared to the platinum analogues. Furthermore, the energy decreases along the series Cl > Br > I with the exception that for M = Pt the Br and Cl derivative exhibit their long-wavelength maximum at approximately the same energy (Table 3). We tentatively assign the long-wavelength absorptions to ligand (p_x) -to-li $gand(p_{As}^*)$ charge transfer transitions. This is supported by recent investigations on related complexes of the type $[MCl(TeCH_2CH_2NMe_2)(PR_3)]$ (M = Pt or Pd; R = alkyl or aryl) where the long-wavelength absorption were assigned to ligand(Te)-to-ligand(P) charge transfer transitions [24]. Further support comes from the comparison with related palladium complexes where in the series of ER_3 ligands (E = P, As, or Sb) the lowest absorption maxima show a red-shift when going along the series P < As < Sb [25].

We have reported earlier that tertiary arsines can be purified by thermolysis of their palladium adducts [26]. To assess whether BzAsMe₂ can be purified by thermolysis, a thermogravimetric (TG) analysis of [PdCl₂-(BzAsMe₂)₂] was carried out under a flowing nitrogen atmosphere. The TG curve shows that both arsine molecules are liberated at approximately 200 °C (from weight loss) leaving behind PdCl₂. This suggests that the arsine can be purified by thermolysis of [PdCl₂-(BzAsMe₂)₂].

Since the phosphine and amine analogues of benzyldimethylarsine easily undergo cyclometallation reactions mainly in cases where M = Pd [7,10–17], the present compounds were also examined in that respect. For none of the six derivatives [MX₂(BzAsMe₂)₂] did we observe any metallation reaction during the preparation of the compounds. To assess whether metallation of BzAsMe₂ is possible at all, the reactivity of [PdCl₂-(BzAsMe₂)₂] has been investigated in refluxing 2-ethoxvethanol in the presence and absence of Na₂CO₃. In both the cases, the starting material, as characterised by m.p., analysis and ¹H NMR, was recovered. The reluctance to metallation of BzAsMe2 under these reaction conditions indicates that there are only very weak agostic interactions, if any, between the o-phenyl proton and the vacant orbitals on palladium which is usually the pre-requisite for the metallation reaction. The absence of intra- or intermolecular agostic M-H interactions was further substantiated by the X-ray structural analyses of the complexes [MX₂(BzAsMe₂)₂] (vide infra).

The reaction of $[MCl_2(BzAsMe_2)]$ with $PtCl_2$ or $[PdCl_2(MeCN)_2]$ afforded the chloro-bridged complexes $[M_2Cl_2(\mu-Cl)_2(BzAsMe_2)_2]$ (M = Pd or Pt). The IR spectra displayed three M–Cl stretching bands at approximately 342 [ν M–Cl_(terminal)], approximately 260 cm⁻¹ [ν M–Cl_(bridging trans to arsine)], and 291 (Pd), 321 cm⁻¹ (Pt) [ν M–Cl_(bridging trans to Cl)] [26,27]. The ¹⁹⁵Pt NMR chemical shift for [Pt₂Cl₂(μ -Cl)₂(BzAsMe₂)₂] (δ – 3015 ppm) is well in agreement with that of [Pt₂Cl₂(μ -Cl)₂(AsMe₃)₂] (δ = –3034 ppm) [23]. The reaction of [Pd₂Cl₂(μ -Cl)₂(BzAsMe₂)₂] with silver ace-tate readily gave the acetato-bridged complex [Pd₂Cl₂(μ -Cl)₂(BzAsMe₂)₂]. Treatment of [Pd₂Cl₂(μ -Cl)₂(BzAsMe₂)₂] with tetramethyltin in dichloromethane

Table 1	
Physical, analytical and ¹ H NMR data for benzyldimethylarsine complexes of palladium(II) and plating	ım(II)

ComplexRecrystallisationL = BzAsMe2SolventYield (%)		m.p. (°C)	% Analysis Found (Calc.)	NMR data (δ in ppm)	$\frac{\text{IR}^{\text{a}}}{(\text{cm}^{-1})}$	
[PdCl ₂ (L) ₂]	CH ₂ Cl ₂ -hexane (80)	156	C 37.5 (37.9) H 4.2 (4.6)	1.24 (s, $AsMe_2$) 3.38 (s, $AsCH_2Ph$) 7.15–7.35 (m. $AsCH_2Ph$)	344	
$[PtCl_2(L)_2]$	CH ₂ Cl ₂ -hexane (50)	169	C 32.2 (32.8) H 3.8 (4.0)	1.25 (s, ${}^{3}J(Pt-H) = 17$ Hz, As Me_{2}) 3.35 (s, ${}^{3}J(Pt-H) = 20$ Hz, As $CH_{2}Ph$) 7.17–7.32 (m. As $CH_{2}Ph$)	273	
[PdBr ₂ (L) ₂]	acetone-hexane (72)	153	C 32.4 (32.8) H 3.6 (4.0)	1.45 (s, As Me_2) 3.64 (s, As CH_2Ph) 7.21–7.32 (m. As CH_2Ph)		
[PtBr ₂ (L) ₂]	acetone-hexane (61)	136	C 28.8 (28.9) H 3.3 (3.5)	1.33 (s, ${}^{3}J(Pt-H) = 17$ Hz, As Me_{2}) 3.44 (s, ${}^{3}J(Pt-H) = 11$ Hz, As $CH_{2}Ph$) 7.16–7.36 (m. As $CH_{2}Ph$)		
$[PdI_2(L)_2]$	acetone-hexane (70)	140	C 28.3 (28.7) H 3.3 (3.5)	1.58 (s, $AsMe_2$) 3.64 (s, $AsCH_2Ph$) 7.21–7.32 (m. $AsCH_2Ph$)		
$[PtI_2(L)_2]$	acetone-hexane (63)	124	C 25.7 (25.7) H 3.0 (3.1)	1.54 (s, ${}^{3}J(Pt-H) = 18$ Hz, As Me_{2}) 3.60 (s, ${}^{3}J(Pt-H) = 7$ Hz, As $CH_{2}Ph$) 7.17–7.35 (m. As $CH_{2}Ph$)		
$[Pd_2Cl_2(\mu\text{-}Cl)_2(L)_2]$	benzene-hexane (71)	213-216	C 28.0 (28.9) H 2.8 (3.5)	1.34 (s, As Me_2) 3.58 (s, As CH_2Ph) 7.18–7.36 (m. As CH_2Ph)	344 291 252	
$[Pt_2Cl_2(\mu\text{-}Cl)_2(L)_2]$	benzene-hexane (34)	123-125	C 22.6 (23.4) H 2.0 (2.8)	1.27 (s, ${}^{3}J(Pt-H) = 27$ Hz; As Me_2) 3.45 (s, base broadened As CH_2Ph) 7.17–7.36 (m, As CH_2Ph)	341 321 301 260	
$\left[Pd_2Cl_2(\mu\text{-}OAc)_2(L)_2\right]~^b$	toluene-hexane (54)	143-145	C 33.2 (33.3) H 3.7 (4.0)	1.28 (s, $AsMe_2$) 2.00 (s, $Pd-OAc$) 3.57 (s, $AsCH_2Ph$)	356	
$[Pd_2Me_2(\mu\text{-}Cl)_2(L)_2]$	acetone-hexane (66)	125	C 34.0 (34.0) H 4.8 (4.6)	7.18–7.33 (m, AsCH ₂ Ph) 0.54 (s,Pd Me) 1.18 (s, As Me_2) 3.25 (s, AsCH ₂ Ph) 7.18–7.25 (m AsCH ₂ Ph)	245	
$[Pd_2Me_2(\mu\text{-}pz)_2(L)_2]$	CH ₂ Cl ₂ -hexane (60)	125 °	C 40.4 (40.6)	 7.18-7.55 (m, AsCH₂Ph) 0.31 (s, Pd-Me); 0.94, 1.10 (each s, AsMe₂); 2.97 (AB pattern 12.8 Hz AsCH₂); 6.12 (s, CH, pz); 7.14-7.33 (Ph, CH, pz); 7.44 (d, 1.5 Hz, CH-pz) 		
$[Pd_2Me_2(\mu\text{-}dmpz)_2(L)_2]$	CH ₂ Cl ₂ -hexane (79)	122– 123 °	H 5.2 (5.0) N 7.5 (7.3) C 43.4 (43.7)	0.23 (s, Pd-Me); 0.89, 1.09 (each s, AsMe ₂); 1.98, 2.24 (each s, Me ₂ -dmpz); 2.98 (AB pattern 12.8 Hz AsCH ₂): 5.57 (s, CH, dmpz): 7.08–7.33 (m, Ph)		
$[Pd_2Cl_2(\mu\text{-}dmpz)_2(L)_2]$	CH ₂ Cl ₂ -hexane (70)	186–187	H 6.4 (5.6) N 6.6 (6.8) C 38.3 (38.8)	1.02, 1.27 (each s, AsMe ₂); 1.96, 2.34 (each s, Me ₂ , dmpz); 3.34 (AB pattern 12.8 Hz AsCH ₂); 5.58 (s, CH, dmpz); 7.20–7.33 (m, Ph)		
			H 4.9 (4.6) N 6.3 (6.5)			

^a v(M-Cl).

^b 1562 cm⁻¹ (ν C=O).

^c Decomposition occurs.

afforded a binuclear methylpalladium complex [Pd₂-Me₂(μ -Cl)₂(BzAsMe₂)₂]. The IR spectrum displayed a band at 245 cm⁻¹ attributable to bridging Pd–Cl stretchings. The ¹H NMR spectrum showed a singlet at 0.54 ppm due to Pd–Me protons.

Treatment of $[Pd_2Cl_2(\mu-OAc)_2(BZAsMe_2)_2]$ with 2 equiv. of 3,5-dimethylpyrazole gave $[Pd_2Cl_2(\mu-dmpz)_2-(BzAsMe_2)_2]$. The corresponding methylpalladium complexes $[Pd_2Me_2(\mu-N^{\wedge}N)_2(BZAsMe_2)_2]$ are obtained by the reaction of $[Pd_2Me_2(\mu-Cl)_2(BZAsMe_2)_2]$ with pyra-

Table 2 ¹⁹⁵Pt{¹H} NMR spectral data in CDCl₃

Complex	δ^{-195} Pt in ppm
$[PtCl_2(BzAsMe_2)_2]$ $[PtBr_2(BzAsMe_2)_2]$	$-4320 \\ -4359$
$[PtI_2(BzAsMe_2)_2]$ $[Pt_2Cl_2(\mu-Cl)_2(BzAsMe_2)_2]$	-5496 -3015

zole or 3,5-dimethylpyrazole in the presence of methanolic sodium hydroxide. The ¹H and ¹³C NMR spectra displayed only one C⁴–H proton/carbon resonance indicative of a *sym–trans* configuration [26,28]. The two arsine ligands are anisochronous as two sets of AsMe₂ and an AB pattern for CH₂As protons are observed. Similarly ¹³C NMR spectra showed two singlets for AsMe₂ carbons.

3.2. Crystal structures of $[MX_2(BzAsMe_2)_2]$ (M = Pt or Pd; X = Cl, Br or I)

The molecular structures of all six compounds have been obtained by single crystal X-ray diffraction with the results summarised in Table 4. The two chloro complexes were found to crystallise in the monoclinic $P2_1$ space group whereas the structures of all other derivatives were solved in $P2_1/c$. Looking at the crystal structures three groups can be defined regarding their intermolecular interactions. The three structures with X = I; M = Pd or Pt and X = Br; M = Pd exhibit shortest $H \cdot \cdot \cdot X$ contacts of 3.22, 3.21 and 3.56 Å, respectively. The corresponding protons are the m-H atoms on the benzyl group. The angles $C-H\cdots X$ around 145° are reasonable for a H bridge, however, the long distances exclude a substantial interaction [29]. The derivative with M = Pt and X = Br shows the same interaction with X···H contacts of 3.004 Å (C–H···Br = 155°), here an additional interaction between Br and one proton of the methyl groups is observed. At 3.033 Å these $X \cdots H$ contacts are slightly longer than the former but the angle of 171.3° is better suitable for a H bridge [29]. Finally, in the two chloro derivatives there are no interactions of the Cl atoms with the m-H atoms of the phenyl ring but appreciable contacts to the methyl groups of the BzAsMe₂ ligand. The Cl···H distances are 2.79 (Pt) or 2.76 Å (Pd), respectively, and the angles are 140.5 and 142.3°, respectively. Due to the short distances and the appropriate angles the latter can be considered to be H bridges of appreciable strength [29].

The main difference in the molecular structures of the examined compounds is the *cis* configuration of the chloro derivatives that contrasts to the exclusive trans configuration of the others (Figs. 1 and 2). This result is unambiguous since it agrees with the observation by NMR spectroscopy in fluid solution (vide supra). In the trans derivatives, the two benzyl groups in the arsine ligands are oriented towards each other in a staggered fashion. In the two cis derivatives, the substituents on the two arsine ligands are in an eclipsed orientation with the benzyl substituents on the same positions. To minimise the steric interaction one of the two benzyl groups is located above the metal centre with the phenyl ring like a shield to the metal. The other phenyl group is tilted in the same direction giving rise to an asymmetry in the molecule. Viewed from the chlorine atoms the phenyl groups are tilted in an anti-clockwise fashion in all molecules of both structures. Since the structures were solved in the non-centrosymmetric space group $P2_1$ we found only one of the two possible enantiomers. The two cis forms show a very small deviation from the ideal planar geometry surrounding the central atoms with 4.0 (Pt) or 4.9° (Pd) dihedral angles between the planes As-M-As and Cl-M-Cl. For the trans isomers, the planes do not deviate significantly from planarity. The bond lengths between the metal M and the halogens decrease as expected along the series $I \gg Br > Cl$. The M-As distances decrease along the same series, however the difference between the palladium and platinum complexes for X = Br or I are rather small. These findings agree well with the expected *trans* influence in such square planar molecules. For the trans forms the arsine ligands face each other in trans position, therefore the M-As distances are the same, only slightly influenced by the marginal cis influence. In the cis forms the arsine face the much weaker chlorine ligands in trans position, therefore their distance to the metal center is much shorter. At the same time, the stronger trans influence exerted by the arsine ligands renders the M-Cl bonds longer than expected from the decreasing size of the X atoms in the series I > Br > Cl. The Pt-As distances are all longer than the one observed in $[PtMe{S_2P(OPr^i)_2}(AsPh_3)] (Pt-As = 2.3293(6) Å) [30].$ The coordination around each arsine ligand is distorted

Table 3

Long-wavelength absorption maxima for complexes [MX₂(BzAsMe₂)₂] (M = Pt or Pd; X = I, Br, or Cl) in CH₂Cl₂

	Pd, I	Pd, Br	Pd, Cl	Pt, I	Pt, Br	Pt, Cl
$\frac{\lambda_2 \text{ in nm} (\varepsilon \text{ in } M^{-1} \text{ cm}^{-1})}{\lambda_1 \text{ in nm} (\varepsilon \text{ in } M^{-1} \text{ cm}^{-1})}$	307 (26010)	286sh	293	288 (6900)	250sh	272
	420 (8240)	369	346	344 (6090)	300	298

Table 4 Crystal data and refinement details for $[MX_2(BzAsMe_2)_2]$ (M = Pt or Pd; X = I, Br, or Cl)

	I-Pt	Br-Pt	Cl-Pt	I–Pd	Br-Pd	Cl-Pd
Formula weight	841.12	747.14	658.22	752.43	658.45	569.53
Space group	$P2_1/c$	$P2_1/c$	P2 ₁	$P2_1/c$	$P2_1/c$	P2 ₁
Unit cell						
a (Å)	11.696	11.524	9.9999	11.656	11.585	10.0244
b (Å)	8.3728	8.1287	10.4762	8.3174	8.1456	10.5075
c (Å)	12.056	11.874	10.1981	12.008	11.891	10.2246
β (°)	104.817	106.39	99.373	104.76	106.395	99.314
Volume (Å ³⁾	1141.4	1067.1	1054.1	1125.8	1076.5	1062.8
$\delta_{\rm calc} ({\rm mg}\;{\rm m}^{-3})$	2.447	2.325	2.074	2.220	2.031	1.780
Absolute coefficient	11.727	13.394	10.022	6.481	7.622	4.211
(mm^{-1})						
F(000)	768	696	624	704	632	560
Crystal size (mm)	$0.3\times0.3\times0.2$	$0.3\times0.2\times0.1$	0.3 imes 0.2 imes 0.2	0.3 imes 0.3 imes 0.2	$0.3\times0.3\times0.1$	0.2 imes 0.2 imes 0.1
Colour	orange	yellow	colourless	deep red	red	yellow
θ Range (°)	3.00-30.00	3.08-28.01	2.02 - 28.00	1.81 - 30.00	3.07-29.00	2.06-30.00
Limiting indices	-1 < h < 16,	-7 < h < 15,	0 < h < 13,	-16 < h < 15,	-8 < h < 15,	-7 < h < 14,
-	-1 < k < 11,	-6 < k < 10,	0 < k < 13,	0 < k < 11,	-3 < k < 11,	-14 < k < 14,
	-16 < <i>l</i> < 16	-15 < l < 15	-13 < l < 13	0 < <i>l</i> < 16	-15 < <i>l</i> < 16	-14 < l < 14
Reflections collected	3642	2332	2818	3284	3268	3413
Independent (R_{int})	2900 (0.0509)	2219 (0.0293)	2675 (0.0516)	3284 (0.0389)	2593 (0.0402)	3083 (0.0788)
Data/restraints/	2900/0/105	2219/0/106	2675/1/210	3284/0/106	2593/0/105	3083/1/207
parameters						
Final R indices	$R_1 = 0.0376,$	$R_1 = 0.0305,$	$R_1 = 0.0378,$	$R_1 = 0.0581,$	$R_1 = 0.0367,$	$R_1 = 0.0412,$
	$wR_2 = 0.0868$	$wR_2 = 0.0760$	$wR_2 = 0.0807$	$wR_2 = 0.1593$	$wR_2 = 0.0855$	$wR_2 = 0.1013$
R indices (all data)	$R_1 = 0.0514,$	$R_1 = 0.0375,$	$R_1 = 0.0518,$	$R_1 = 0.0668,$	$R_1 = 0.0508,$	$R_1 = 0.0492,$
	$wR_2 = 0.0931$	$wR_2 = 0.0794$	$wR_2 = 0.0861$	$wR_2 = 0.1593$	$wR_2 = 0.0912$	$wR_2 = 0.1064$
Goodness-of-fit on F^2	1.053	1.150	1.028	1.165	1.038	1.032
Largest difference peak and hole (e $Å^{-3}$)	1.788 and -1.818	1.232 and -0.926	1.600 and -1.194	2.482 and -2.962	0.797 and -1.322	1.869 and -1.570

Empirical formulae: $C_{18}H_{26}As_2X_2M$; measurement temperature: 173(2) K; wavelength 0.71073 Å; absorption correction: empirical by ψ -scans, only for [PdI₂(BzAsMe₂)₂] empirical correction using xABS2 [33]; refinement method: full-matrix least-squares on F^2 .



Fig. 1. Molecular structures of trans-[PtI₂(BzAsMe₂)₂] (left) and cis-[PtCl₂(BzAsMe₂)₂] (right) with atom numbering. Shown were the thermal ellipsoids at a 50% probability level.



Fig. 2. Molecular structures of *trans*-[PdBr₂(BzAsMe₂)₂] (top) and *cis*-[PdCl₂(BzAsMe₂)₂] (bottom) with atom numbering. Shown were the thermal ellipsoids at a 50% probability level.

tetrahedral since the C(1)-As-M angles are opened compared to the ideal tetrahedral angle to values of around 113° while the H₃C-As-CH₃ angles have been compressed to values in the range $100.8-102.0^{\circ}$ for the trans conformers. For the cis forms the first deviation is smaller but the latter is larger when compared to the trans isomers. From the M-X and M-As distances for X = Br or Cl it seems that the palladium atom is bigger than the platinum atom. This was also found in recent structural work on amido complexes of Pt, Pd and Ni [31] and on a series of heterocubane compounds $[Cp_3Mo_3S_4M(PPh_3)]$ with M = Pt or Pd [32]. This effect is explained by the classical 'lanthanide contraction' and also by relativistic effects. However, in our series for X = I the distances show the reverse trend. We assume that this is due to the fact that the ionic radii increase much more on going from Br (196 pm) to I (220 pm) than from Cl (184 pm) to Br which might compensate for the reduced size of platinum (Table 5).

4. Conclusions

The presented series of palladium and platinum complexes containing the benzyldimethylarsine ligands has revealed some interesting aspects concerning their structures and reactivity. Starting from the simple chloro complexes [MCl₂(BzAsMe₂)₂] a wealth of new

compounds has been created. However, in none of the examined compounds did the benzylarsine ligand undergo cyclometallation as is often observed for the analogous phosphines or amines. This is not totally unexpected since an increasing reluctance towards cyclometallation has been observed when going from the amines to the phosphines. In many cases it is not even possible to prevent that reaction, for the amines it is promoted by interaction between the o-H on the phenyl substituent and the metal center whereas an activation by bases is required in case of the phosphines. The present arsine systems terminates the series in that sense: we could not observe any metallation reactivity, not even for the reactive palladium systems. Strong support also comes from the fact that we do not have any evidence for a metal-H interaction, neither from NMR spectroscopy in solution nor from X-ray structure analyses of the complexes $[MX_2(BzAsMe_2)_2]$ in the solid state. The structure analysis has revealed some weak $H \cdots X$ interactions for the two *cis* configured complexes with X = Cl. However, the interaction occurs between Cl and one methyl substituent of the arsine ligand. A similar interaction was found in the bromo platinum complex although the latter has a trans configuration like the three residual derivatives (X = I with M = Pt orPd and X = Br with M = Pd). It is remarkable that these strictly dichotomous configurations, *cis* for X = Cl and *trans* for X = Br or I, are also found by NMR spectro-

Table 5 Selected bond lengths (Å) and angles (°) for $[MX_2(BzAsMe_2)_2]$

	M = Pt	M = Pd	M = Pt	M = Pd	M = Pt	M = Pd
	X = I	X = I	$\mathbf{X} = \mathbf{B}\mathbf{r}$	X = Br	X = CI	X = CI
Bond lengths						
M-X(1)	2.6169(6)	2.5981(6)	2.4384(7)	2.4417(6)	2.340(3)	2.370(2)
M-X(2)					2.355(3)	2.359(2)
M-As(1)	2.4118(8)	2.4080(7)	2.3898(8)	2.4048(6)	2.3371(14)	2.3524(9)
M-As(2)					2.3343(13)	2.3586(9)
As-C(1)	1.981(7)	1.976(7)	1.969(6)	1.970(4)	1.937(14)	1.977(9)
As-C(11)					1.984(13)	1.959(7)
As-C(8)	1.940(6)	1.939(7)	1.929(6)	1.935(4)	1.935(14)	1.923(7)
As-C(18)					1.925(14)	1.940(9)
As-C(9)	1.948(7)	1.929(7)	1.927(6)	1.935(4)	1.918(14)	1.925(10)
As-C(19)					1.932(14)	1.950(9)
Bond angles						
$X(1) - M - X(1A)^{a}$	180.000(8)	180.000(19)	180.00(3)	180.000(10)	90.05(12)	92.43(7)
$As(1)-M-As(1A)^{a}$	180.000(8)	180.000(19)	180.00(3)	180.000(10)	100.74(5)	99.19(3)
X(1)-M-As(1)	92.42(2)	92.43(2)	92.76(2)	92.794(19)	173.15(10)	174.03(7)
X(2)-M-As(2)					174.84(9)	176.59(6)
X(1)-M-As(1A) ^a	87.58(2)	87.57(2)	87.24(2)	87.206(19)	84.39(9)	84.28(6)
X(2)-M-As(1)					84.88(10)	84.16(5)
M-As(1)-C(1)	113.1(2)	113.49(17)	112.82(17)	112.65(12)	107.7(4)	107.6(2)
M-As(2)-C(11)					109.9(4)	110.0(3)
H ₃ C-As-CH ₃	101.4(4)	100.8(3)	101.7(3)	102.0(2)	100.9(7)	101.7(4)
H ₃ C-As-CH ₃					102.3(7)	99.7(4)

^a For *cis* configuration X(1)-M-X(2), As(1)-M-As(2) and X(1)-M-As(2) are given.

scopy in solution indicating an unusually strong structural selectivity.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 193965 (M = Pt, X = I), 193966 (M = Pt, X = Br), 193967 (M = Pt, X = CI), 193968 (M = Pd, X = I), 193969 (M = Pd, X = Br), and 193970 (M = Pd, X = CI). 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).

5.1. Further supplementary material

Six figures illustrating the crystal structures (unit cell and intermolecular interaction) and full structural data of all six complexes (30 tables) are available from the author on request.

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