DALTON COMMUNICATION

The first palladium(II) complexes containing arsino(phosphino)-methanes as ligands †

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Treatment of $[PdCl_2(R_2AsCH_2PPr^i_2)]$ (3a,b) with $AgPF_6$ leads, depending on the reaction conditions, either to the formation of $[\{Pd(\mu\text{-}Cl)(\kappa^2As,P\text{-}R_2AsCH_2PPr^i_2)\}_2](PF_6)_2$ (4a,b) or $[Pd(CH_3CN)_2(\kappa^2As,P\text{-}R_2AsCH_2PPr^i_2)](PF_6)_2$ (5a,b); the methyl derivative $[Pd(Me)(Cl)(Bu^t_2AsCH_2PPr^i_2)]$ (7) reacts with $Na[B(Ar_F)_4]$ ($Ar_F = C_6H_3(CF_3)_2$-3,5) to afford the complex $[Pd_2(Me)_2(\mu\text{-}Cl)(\mu\text{-}Bu^t_2AsCH_2PPr^i_2)_2][B(Ar_F)_4]$ (8) of the A-frame type, which was characterized by X-ray structure analysis.

In our quest for new unsymmetrical, possibly hemilabile, chelating systems, we recently reported the synthesis of arsino(phosphino)methanes $R_2AsCH_2PR'_2$,[1] which behave as monodentate as well as bidentate chelating ligands towards rhodium(I) as the metal center.[2] As an extension of these studies, we have now prepared the first palladium(II) complexes with both $Bu^t_2AsCH_2PPr^i_2$ (**2a**) and $Pr^i_2AsCH_2PPr^i_2$ (**2b**) as ligands, which coordinate either in a chelating or bridging mode.

Addition of equimolar amounts of **2a** or **2b** to a solution of *trans*-$[PdCl_2(NCPh)_2]$ (**1**) in CH_2Cl_2 gives the air-stable chelate complexes **3a** and **3b** in, respectively, 75% and 83% yield (Scheme 1).‡ In the ^1H and ^{13}C NMR spectra of **3a,b**, the most typical features are the positions of the signals for the protons and carbon atoms of the bridging CH_2 group,§ which are significantly shifted to lower field compared to the free ligands **2a** and **2b**.[1]

The X-ray crystal structure analysis of **3a** confirms that the coordination geometry around the palladium(II) center is distorted square-planar (Fig. 1).¶ The As–Pd–P bite angle [74.94(3)°] is quite small and comparable to the P–Pd–P bite angle for compounds of the type $[PdX_2(\kappa^2P,P'\text{-}Ph_2PCH_2PPh_2)]$ (X = Cl,[3] I[4]).

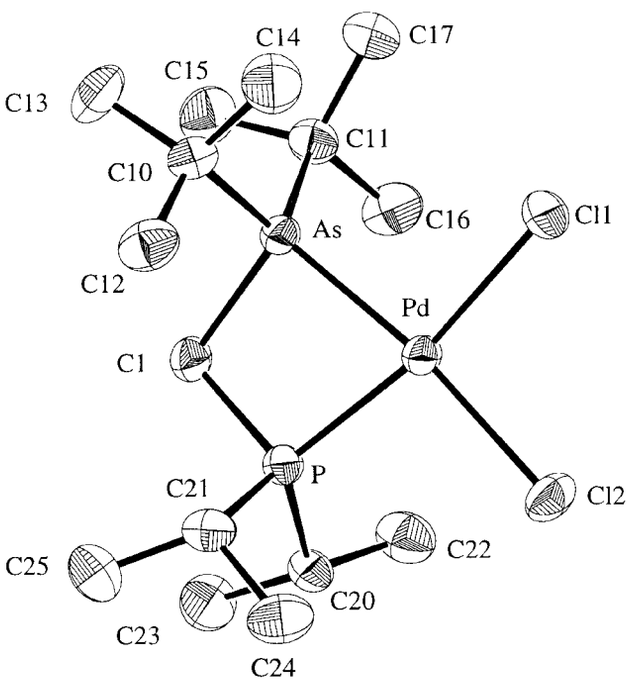
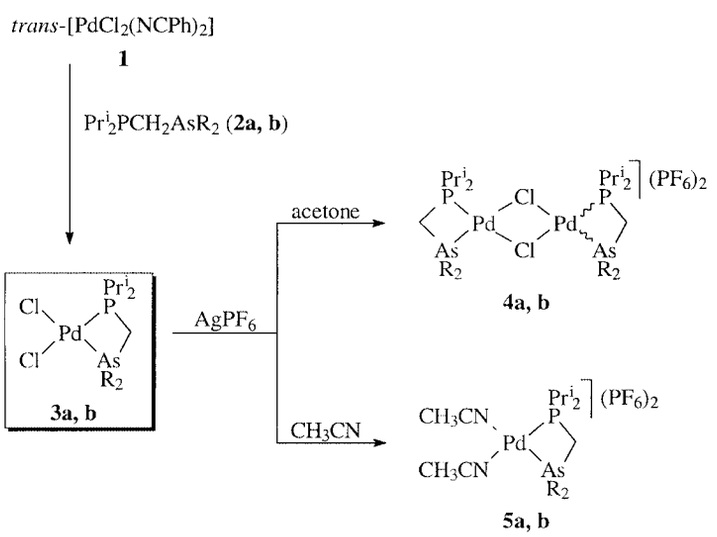


Fig. 1 Molecular structure (ORTEP[9] plot) of compound **3a**. Selected bond distances (Å) and angles (°): Pd–As 2.3526(7), Pd–P 2.2427(13), Pd–Cl1 2.3595(14), Pd–Cl2 2.3657(13), As–C1 1.974(5), P–C1 1.840(5); As–Pd–P 74.94(3), As–C1–P 94.3(2), Cl1–Pd–Cl2 93.66(5), As–Pd–Cl2 170.24(4), P–Pd–Cl1 170.08(5), As–Pd–Cl(1) 95.23(4), P–Pd–Cl2 96.25(5).

† Electronic supplementary information (ESI) available: preparative procedures, yields, melting points and elemental analyses for compounds **3a**,**b**, **4a**,**b**, **5a**,**b**, **7** and **8**. See http://www.rsc.org/suppdata/dt/b0/b001237h/



Scheme 1 **a**: R = Bu^t; **b**: R = Pr^i.

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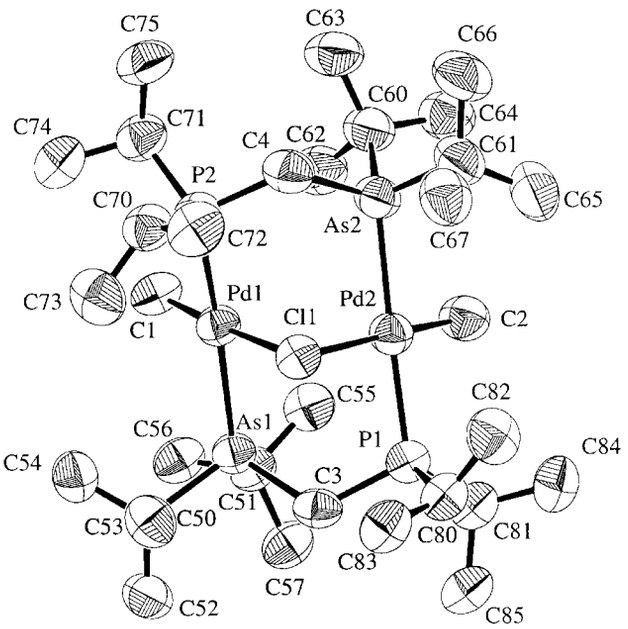
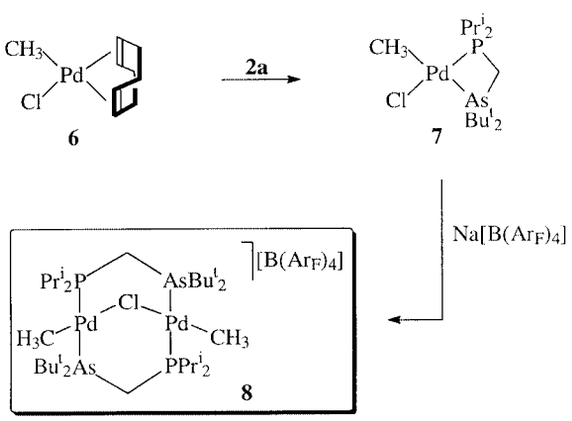


Fig. 2 Molecular structure (ORTEP[9] plot) of compound **8**. Selected bond distances (Å) and angles (°): Pd1–C1 2.052(6), Pd1–As1 2.4823(18), Pd1–P2 2.306(2), Pd1–Cl1 2.459(2), Pd2–C2 2.064(6), Pd2–As2 2.4678(18), Pd2–P1 2.301(2), Pd2–Cl1 2.460(3); As1–C3–P1 119.2(3), As2–C4–P2 118.5(3), C1–Pd1–Cl1 176.3(2), As1–Pd1–P2 173.45(4), As2–Pd2–P1 173.44(4), C2–Pd2–Cl1 176.3(2), Pd1–Cl1–Pd2 77.51(10).

Both chelate complexes **3a**,**b** react with $AgPF_6$ to give, depending on the molar ratio of the substrates, two different types of products. While the addition of one equivalent of $AgPF_6$ to a solution of **3a**,**b** in acetone/CH_2Cl_2 leads to the formation of the chloro-bridged dimers **4a** and **4b**,‡ the reaction of the starting materials **3a**,**b** with two equivalents of the silver salt in acetonitrile affords the mononuclear dicationic compounds **5a** and **5b**, respectively.‡ The new complexes **3a**,**b** thus behave similarly toward $AgPF_6$ as the well-known dppm derivative $[PdCl_2(Ph_2CH_2PPh_2)]$.[5]

In contrast to the reaction of $[Pd(CH_3)(Cl)(\eta^4\text{-}C_8H_{12})]$ (**6**) with **2b**, which leads to a mixture of products, treatment of **6** with one equivalent of **2a** affords cleanly the corresponding chelate complex **7** (Scheme 2).‡ Owing to the NMR spectro-



Scheme 2 $Ar_F = \{C_6H_3(CF_3)_2\text{-}3,5\}$.

scopic data of **7**,§ there is no doubt that only one of the two possible stereoisomers is formed. Since the doublet resonance of the Pd–CH_3 carbon atom at $\delta = 0.9$ shows a rather small P–C coupling of 5.7 Hz,§ we conclude in agreement with data from the literature[6] that the methyl group and the PPr^i_2 unit are in *cis*-disposition.

Quite unexpectedly, the reaction of **7** with $Na[B(Ar_F)_4]$ in diethyl ether leads to the formation of the A-frame type complex **8** in excellent yield.‡ The NMR data of **8** indicate that only the head-to-tail isomer with the phosphorus and the arsenic atoms *trans* to each other is formed.§ This was confirmed by an X-ray crystal structure analysis (Fig. 2).¶ The dinuclear cation consists of two $Pd(CH_3)$ fragments which are bridged by two $Bu^t_2AsCH_2PPr^i_2$ ligands and one chloride. The coordination sphere around the palladium(II) centers is approximately square planar. The Pd–Pd distance of 3.079(4) Å is within the range reported for other structurally related palladium compounds of the A-frame type [2.976(6)–3.190(4) Å].[7]

In summary, the work presented in this paper has shown that the new arsino(phosphino)methanes **2a** and **2b** with bulky substituents at the two donor centers can behave both as chelating and bridging ligands toward palladium(II). Besides neutral and mono- as well as di-nuclear cationic compounds, in which **2a** and **2b** are bonded in a chelating fashion, a di-nuclear complex of the A-frame type could also be generated. We note that prior to our work only a few examples of dimeric rhodium or mixed platinum–rhodium compounds with $Ph_2AsCH_2PPh_2$ as the ligand were described in the literature.[8]

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Notes and references

‡ Preparative procedures including yields, melting points and elemental analyses for **3a**,**b**, **4a**,**b**, **5a**,**b**, **7** and **8** are found in the ESI.

§ Selected data for **3**–**8**, omitting the ^1H and ^{13}C NMR data for the $[B(Ar_F)_4]$ counter ion and the substituents R and R′ at the phosphorus and arsenic atoms: **3a**: NMR (CD_2Cl_2): δ_H (400 MHz) 2.94 [2 H, d, J(PH) 9.7 Hz, PCH_2As]; δ_C (100.6 MHz) 21.4 [d, J(PC) 18.1 Hz, PCH_2As]; δ_P (162.0 MHz) −12.9 (s). **3b**: NMR (CD_2Cl_2): δ_H (400 MHz) 2.88 [2 H, d, J(PH) 9.7 Hz, PCH_2As]; δ_C (100.6 MHz) 21.1 [d, J(PC) 21.0 Hz, PCH_2As]; δ_P (162.0 MHz) −6.1 (s). **4a**: NMR (CD_2Cl_2): δ_H (400 MHz) 3.31 [4 H, d, J(PH) 10.6 Hz, PCH_2As]; δ_C (100.6 MHz) 21.2 [d, J(PC) 24.8 Hz, PCH_2As]; δ_P (162.0 MHz) −12.1 (s, PCH_2As), −144.3 [sept, J(FP) 712.8 Hz, PF_6]. **4b**: NMR (CD_2Cl_2): δ_H (400 MHz) 3.35 [4 H, d, J(PH) 10.2 Hz, PCH_2As]; δ_C (100.6 MHz) 20.2 (m, PCH_2As); δ_P (162.0 MHz) −4.7 (s, PCH_2As), −144.4 [sept, J(FP) 710.6 Hz, PF_6]. **5a**: NMR (CD_3NO_2): δ_H (400 MHz) 3.41 [2 H, d, J(PH) 10.6 Hz, PCH_2As], 2.43 (6 H, s, br, CH_3CN); δ_C (100.6 MHz) 125.3 (m, br, CH_3CN), 19.5 [d, J(PC) 25.4 Hz, PCH_2As], 2.4 (s, br, CH_3CN); δ_P (162.0 MHz) −16.1 (s, PCH_2As), −144.6 [sept, J(FP) 706.3 Hz, PF_6]. **5b**: NMR (CD_3NO_2): δ_H (400 MHz) 3.40 [2 H, d, J(PH) 10.6 Hz, PCH_2As], 2.41 (6 H, s, br, CH_3CN); δ_C (100.6 MHz) 125.4 (s, br, CH_3CN), 18.4 [d, J(PC) 25.8 Hz, PCH_2As], 2.5 (s, br, CH_3CN); δ_P (162.0 MHz) −8.6 (s, PCH_2As), −144.6 [sept, J(FP) 708.4 Hz, PF_6]. **7**: NMR ($CDCl_3$): δ_H (400 MHz) 2.58 [2 H, d, J(PH) 10.0, PCH_2As], 0.73 [3 H, d, J(PH) 0.9 Hz, $PdCH_3$]; δ_C (100.6 MHz) 21.2 [d, J(PC) 18.1, PCH_2As], 0.9 [d, J(PC) 5.7 Hz, $PdCH_3$]; δ_P (162.0 MHz) 22.1 (s). **8**: NMR ($CDCl_3$): δ_H (400 MHz) 2.75 [2 H, m, in $^1H\{^{31}P\}$ d, J(HH) 14.0, PCH_2As], 2.19 [2 H, m, in $^1H\{^{31}P\}$ d, J(HH) 12.5, PCH_2As], 0.93 [6 H, d, J(PH) 4.4 Hz, $PdCH_3$]; δ_C (100.6 MHz) 13.0 [m, in $^{13}C\{^1H, ^{31}P\}$ s, PCH_2As], −6.4 (s, br, $PdCH_3$); δ_F (376.4 MHz) −62.7 (s, CF_3); δ_P (162.0 MHz) 30.6 (s).

¶ Crystal data for complex **3a**: $C_{15}H_{34}AsCl_2PPd$, $M = 497.61$, monoclinic, $P2_1/c$, $a = 18.408(3)$, $b = 8.1421(9)$, $c = 14.335(2)$ Å, $\beta = 109.071(18)°$, $V = 2030.6(5)$ Å^3, $Z = 4$, $\mu = 2.864$ mm^{-1}, $T = 173(2)$ K. 19820 reflections scanned, 3442 unique, 2715 observed ($I > 2\sigma(I)$), 192 parameters, reflex/parameter ratio 17.93; $R1 = 0.0378$, $wR2 = 0.0960$. Crystal data for complex **8**: $C_{64}H_{86}As_2BClF_{24}P_2Pd_2$, $M = 1782.24$, triclinic, $P\bar{1}$, $a = 14.487(9)$, $b = 17.323(11)$, $c = 17.554(12)$ Å, $\alpha = 112.46(8)°$, $\beta = 96.69(8)°$, $\gamma = 101.79(8)°$, $V = 3892(4)$ Å^3, $Z = 2$, $\mu = 1.545$ mm^{-1}, $T = 173(2)$ K. 38138 reflections scanned, 12934 unique, 7671 observed ($I > 2\sigma(I)$), 1028 parameters, reflex/parameter ratio 12.58; $R1 = 0.0404$, $wR2 = 0.0827$. One molecule of CH_2Cl_2 per unit formula was located in the lattice. CCDC reference number 186/1884. See http://www.rsc.org/suppdata/dt/b0/b001237h/ for crystallographic files in .cif format.

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