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The synthesis and Crystal Structures of di-μ-dichloro-bis{[*N,N*-dimethylaminobenzyl-C^1,*N*]dipalladium(II)} and of the Cocrystals of {chloro-(triphenylphosphino)-bis[*N,N*-dimethylaminobenzyl-C^1,N]palladium(II)} and {*trans*-bis(triphenylphosphino)-chloro-[*N,N*-dimethylaminobenzyl-C]palladium(II)}

Ayfer Mentes[a,*], Raymond D.W. Kemmitt[b], John Fawcett[c], David R. Russell[c]

[a]*Department of Chemistry, Faculty of Arts and Sciences, Zonguldak Karaelmas University, Zonguldak,Turkey*
[b]*Inorganic Research Laboratories Department of Chemistry, The University of Leicester, Leicester, LE1 7RH, UK*
[c]*X-Ray Crystallography Laboratory, Department of Chemistry, The University of Leicester, Leicester, LE1 7RH, UK*

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Abstract

The X-ray crystal structures of cyclopalladated complexes are reported. Reaction of {[Pd(dmba)(μ-Cl)]$_2$}, (**1**), (dmba = $N(CH_3)_2$-$CH_2C_6H_5$) with triphenylphosphine gave crystals containing {chloro–(triphenylphosphino)-bis[*N,N*-dimethylaminobenzyl-C^1,*N*] palladium(II)} (**2a**) and {*trans*-bis(triphenylphosphino)-chloro-[*N,N*-dimethylaminozyl-C]palladium(II)} (**2b**). Complex (**1**) crystallises in the space group *P*2(1)/*c* with $a = 7.849(1)$ Å, $b = 15.635(3)$ Å, $c = 8.352(1)$ Å, $\beta = 109.29°$, and $D_{calc} = 1.895\ g\ cm^{-3}$ for $Z = 2$. Complexes (**2a**) and (**2b**) crystallize together in the space group *P2(1)/n* with $a = 9.964(2)$ Å, $b = 34.228(5)$ Å, $c = 18.127(3)$ Å, $\beta = 91.91$ °, and $D_{calc} = 1.439\ g\ cm^{-3}$.

Keywords: X-ray structure; Cyclopalladated; Palladium(II); *N,N*-dimethylbenzylamine; Triphenylphosphine; Triphenylstibine

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1. Introduction

Benzylamines are prone to cyclometallation by appropriate palladium(II) compounds. The usual products are cyclopalladated dimers of general formula {[Pd(L)(μ-X)]$_2$}, where X = halide or OAc, L = benzylamines [1–5]. Carbon-to-metal σ-bonds also occur with reaction of Pd(II) and differently substituted Schiff bases ligands [6–13].

The insertion of an alkyne in the metal-carbon bond has proved to be attractive for the selective syntheses of both carbo- and heterocycles [8].

The synthesis of polynuclear cyclometallated palladium(II) complexes and their reactivity towards mono- and ditertiary phosphine have been studied [9,13].

Our interest in investigation of carbon-antimony bond fission in reactions of triphenylstibine with palladium(II) complex [14], led us to react dimeric complexes with triphenylstibine and triphenylphosphines. Treatment of the dimeric complex [Pd(dmba)(μ–Cl)]$_2$ (**1**) with triphenylphosphine in a 1:4 molar ratio gives a mixture of cyclometallated mononuclear complex [Pd(dmba)(Cl)(PPh_3)], (**2a**), and the mononuclear complex [Pd(dmba)(Cl)(PPh_3)$_2$], (**2b**), in a typical bridge splitting reaction. Crystals isolated from this mixture proved to be cocrystals of (**2a**) and (**2b**). The reactions of triphenylstibine with dimeric complex (**1**) give cyclometallated complex [Pd(dmba)(Cl)($SbPh_3$)], (**3a**), and [Pd(dmba)(Cl)($SbPh_3$)$_2$], (**3b**).

2. Results and discussion

The compounds described in this paper were characterized by elemental analysis (C, H, N), IR, ^{1}H NMR,

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* Corresponding author. Tel.: +90-372-257-7225 fax: +90-372-2574181.
E-mail address: ayfermentes@yahoo.com (A. Mentes).

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$^{13}C\{^1H\}$-NMR and $^{31}P\{^1H\}$ NMR spectroscopy and by FAB-MS spectroscopy. The IR spectra of (**1**)–(**3**) showed the $\nu(C=C)$ stretching at region 1576–1568 cm^{-1}. The reaction of (**1**) and PPh_3 in dichloromethane in 1:2 molar ratio gave a mononuclear cyclometallated complex $[Pd(dmba)(PPh_3)Cl]$, (**2a**). In the ^1H NMR spectrum of (**2a**), the $-CH_2-N$ resonance was a doublet ($J(PH) = 1.4 >$ Hz), showing coupling to the phosphorus nucleus and the CH_3-N resonance was also a doublet ($J(PH) = 2.4$ Hz), showing coupling to the phosphorus nucleus [4]. In the $^{31}P\{^1H\}$ spectrum the resonance of the coordinated phosphine *trans* to the *N* atom in (**2a**) was a singlet at $\delta = 42.49$. FAB mass spectrum showed peak at $m/z = 537$ for $[Pd(dmba)(PPh_3)Cl]^+$, and 502 for due to loss of chlorine $[Pd(dmba)(PPh_3)]^+$.

The reaction of (**1**) with PPh_3 in dichloromethane in 1:4 molar ratio gave a mixture of mononuclear cyclometallated complex $[Pd(dmba)(PPh_3)Cl]$, (**2a**), and non-cyclometallated complex $[Pd(dmba)(PPh_3)_2Cl]$, (**2b**). Many attempts to chromatographic separation of the reaction mixture on silica gel using variety of solvents were unsuccessful. In the ^1H NMR spectrum of (**2b**), neither the (H6) nor the $-CH_2-N$ protons showed coupling to the ^{31}P-nucleus of the phosphine due to opening of the cyclometallated ring. In the $^{31}P\{^1H\}$ spectrum the resonance of the two *trans* phosphorus atoms was a singlet 27.5 and broad singlet at $\delta = 43.37$ for coordinated phosphine *trans* to the *N* atom [2,5]. FAB mass spectrum showed peak at $m/z = 800$ for $[Pd(dmba)(PPh_3)_2Cl]^+$, 538 for $[Pd(dmba)(PPh_3)_2]^+$.

$^{13}C\{^1H\}$-NMR spectra for (**2a**) and (**2b**) showed resonances at δ149.7, 147.4 (C1, C6) and 136.8 (C2) shifted to higher frequency, confirming metallation of the organic ligand.

The reaction of (**1**) and $SbPh_3$ in dichloromethane gave the mononuclear cyclometallated complex $[Pd(dmba)(SbPh_3)Cl]$, (**3a**). The ^1H NMR spectrum of the complex (**3a**) contained two doublets at 7.03 and 6.68 ppm and two triplets at 6.87 and 6.40 ppm. which can be assigned to aromatic protons of the benzyl group. The aromatic protons of the $SbPh_3$ ligands appeared as a multiplets in the range 7.65–7.35 ppm. Integration of these signals indicated that a sample of (**3a**) has proved the formulation of mononuclear cyclometallated complex $[Pd(dmba)(SbPh_3)Cl]$, (**3a**), carbon-antimony bond fission was not observed. The methyl groups bonded to nitrogen showed a singlet at 2.93 ppm. The $^{13}C\{^1H\}$-NMR spectrum of the complex (**3a**) proved the assignments of these aromatic groups. FAB mass spectrum showed peak at $m/z = 630$ for $[Pd(dmba)(SbPh_3)Cl]^+$ and 594 for $[Pd(dmba)(SbPh_3)]^+$.

The molecular structure of the complex (**1**) is shown in Fig. 1 which also gives the crystallographic numbering scheme. Selected bond distances and angles are given in Table 1. In the complex (**1**) each dmba ligand is bonded to the di-μ-chloro-bridged unit through a nitrogen atom and an aromatic carbon atom, providing two equivalent five-membered N–C–Pd–C-chelate rings. The geometry at the palladium in (**1**) is square planar with the two cyclometallated ligands in a *trans* arrangement with respect to the Pd…Pd axis.

Pd(1)–C(1) bond, [1.961(3) Å] is shorter than the expected value of 2.081 Å based on the sum of the covalent radii of carbon and palladium. This is consistent with those found for related complexes where partial multiple-bond character of the Pd–C was assumed [4,7].

Pd(1)–N(1) bond distance [2.073(3) Å] is in agreement with the value based on the sum of covalent radii for nitrogen and palladium [17] and similar to values reported previously [4,7].

The lengths of the Pd–Cl bonds *trans* to C [2.4658(1) Å], and the Pd–Cl bonds *trans* to *N* [2.327(1) Å], parallel the different *trans* influences exerted by the phenyl carbon and the nitrogen atoms. In the five-membered chelate rings four atoms (Pd1, C1, C6 and C7) are essentially planar [0.0113 Å maximum deviation] with the N1 atom 0.5494 Å out of this plane. The bite angle

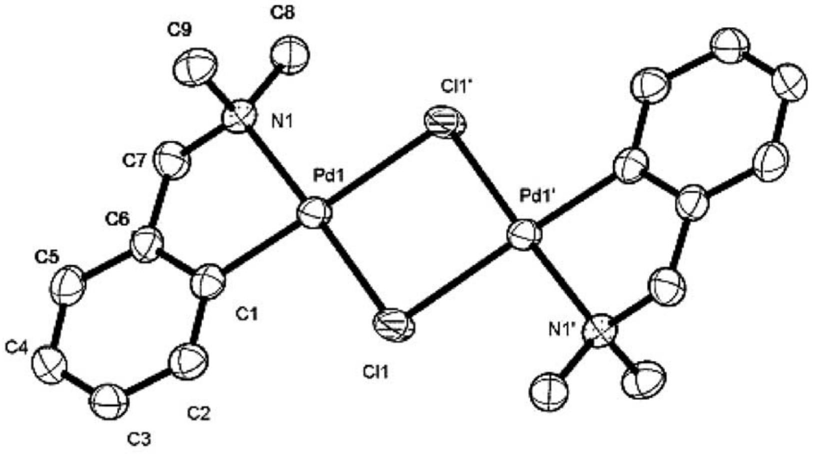


Fig. 1. Molecular structure of (**1**) showing the atom numbering scheme. Displacement parameters are shown at the 50% level. Hydrogen atoms are omitted for clarity. The molecule is located on a centre of symmetry, the primed atoms are generated by symmetry (−x, 1 − y, −z).

Table 1
Selected bond distances (Å) and bond angles (°) with estimated standard deviations in parenthesis for (1) and (2)

	Complexes (**1**)		Complexes (**2**)
Bond distances			
Pd(1)–Cl(1)	2.327(1)	Pd(1)–Cl(1)	2.3808(10)
Pd(1)–C(1)	1.961(3)	Pd(2)–Cl(1a)	2.402(1)
Pd(1)–N(1)	2.073(3)	Pd(1)–N(1)	2.150(3)
C(7)–N(1)	1.502(4)	Pd(1)–P(1)	2.246(1)
N(1)–C(8)	1.475(4)	Pd(2)–P(1a)	2.327(1)
Pd(1)–Cl(1)	2.4658(1)#1	Pd(2)–P(2a)	2.321(1)
		Pd(1)–C(4)	2.012(4)
		Pd(1)–C(4a)	2.009(4)
Bond angles			
C(1)–Pd(1)–N(1)	82.63(13)	Cl(1)–Pd(1)–N(1)	90.96(9)
C(1)–Pd(1)–Cl(1)	94.98(10)	N(1)–Pd(1)–P(1)	175.45(9)
N(1)–Pd(1)–Cl(1)	177.61(8)	C(4)–Pd(1)–N(1)	81.80(13)
N(1)–Pd(1)–Cl(1)#2	96.59(8)	C(4)–Pd(1)–Cl(1)	170.29(11)
		C(4a)–Pd(2)–Cl(1a)	175.25(11)
		P(1a)–Pd(2)–P(2a)	164.23(4)
		C(4a)–Pd(2)–P(1a)	90.37(11)
		C(4a)–Pd(2)–P(2a)	89.58(11)

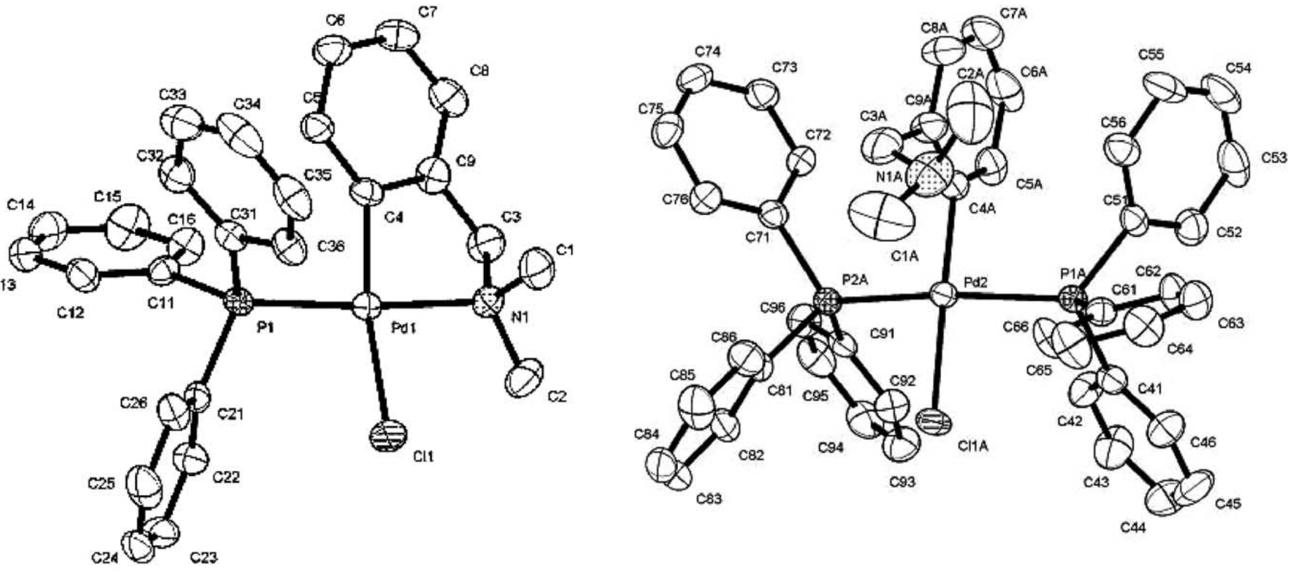
symmetry transformation used to generate equivalent atoms:#1 (− x, 1 − y, 2 − z) #2 (− x, − y + 1, − z).

value [C(1)–Pd(1)–N(1) = 82.63(13)°] is in good agreement with these found in structurally related μ–Cl dimer [7].

The molecular structure of the complex (**2a**), (**2b**) is shown in Fig. 2 which also gives the crystallographic numbering scheme. Selected bond distances and angles are given in Table 1. The geometry at the palladium in (**2a**) is square planar with the chlorine (Cl1) *trans* to the Pd(1)–C(4) bond of the dimethylaminobenzyl ligand and the triphenylphosphine group *trans* to the Pd(2)–N(1) bond. The geometry at the palladium in (**2b**) is square planar with *trans* phosphine donors and substituted phenyl group *trans* to chlorine.

The Pd(1)–P(1), Pd(2)–P(1a), Pd(2)–P(2a) distances (2.246(1), 2.327(1), and 2.321(1) Å, respectively) are similar to those in the palladium(II) phosphine complexes [5,6,10,11].

The Pd(1)–N(1) bond length of 2.150(3) Å is longer than those found in literatures [5,11]. The Pd(1)–C(4) and Pd(1)–C(4a) distances [2.012(4) and 2.009(4) Å, respectively] are also longer than that found in the related complexes but the Pd(1)–Cl(1) distance in (**2a**)



(2a)

(2b)

Fig. 2. Molecular structure of (**2a**), (**2b**) showing the atom numbering scheme. Displacement parameters are shown at the 50% level. Hydrogen atoms are omitted for clarity.

2.3808(10) Å is similar to that found in (1) 2.327(1) Å while Pd(2)–Cl(1a) (**2b**) distance 2.402(1) Å is longer than that found in the related complexes and consistent with the *trans* influence of a phenyl group [10,11].

3. Experimental

3.1. Instruments and reagents

All reactions were performed under a dry, oxygen-free, nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use.

Microanalysis were carried out by Butterworth Laboratories Ltd., 54–56 Waldegrave Rd., Teddington, Middlessex, TW11 8LG and TÜBİTAK Marmara Research Center, Turkey. Melting points were measured on a Reichert hot stage apparatus and are uncorrected. The FAB mass spectrum of the solid complexes were obtained on a Kratos Concept Double Focusing Sector Mass Spectrometer. The ^{1}H NMR spectra were recorded at room temperature in [2H1] chloroform on a BRUKER ARX 250 spectrometer operating at 250.13 MHz with $SiMe_4$ (0.0 ppm) as internal reference, ^{13}C–{^{1}H} NMR spectra were recorded at room temperature in [$^2H_1$]chloroform on a BRUKER ARX 250 spectrometer operating at 62.9 MHz and the ^{31}P–{^{1}H} NMR spectra were recorded in $CDCl_3$ on a BRUKER ARX 250 spectrometer operating at 25.1 MHz unless otherwise stated. The quoted IR spectra were recorded on a Perkin–Elmer 580B spectrophotometer in Nujol mulls between NaCl plates in the range 3000–600 cm^{-1}.

3.2. Synthesis

3.2.1. Preparation of compounds (1)

The synthesis of complex (**1**) has been previously reported [1]. A heterogeneous mixture of *N*,*N*-dimethylbenzylamine, (dmba), (1.35 g, 10 mmol) and palladium(II) dichloride (0.875 g, 5 mmol) in 50 cm^3 of methanol was stirred at room temperature. After 4 h, all of the palladium(II) dichloride had dissolved and was replaced by a yellow-brown crystalline solid of (**1**). The complex was recystallized from boiling benzene/n-hexane to obtain 1.2 g (44% yield based on Pd) of [Pd(dmba)(μ–Cl)]$_2$. M.p. 188–190 °C. (Found; C, 39.5; H, 4.2; *N*, 5.1. $C_{18}H_{24}Cl_2N_2Pd_2$ calc.; C, 39.1; H, 4.3; N, 5.0, %). Fab–Mass: 552 [M$^+$]. ^{1}H NMR (250 MHz, $CDCl_3$) $\delta = 7.10$ (t, 1H, J(HH) = 7 Hz, H^4), 6.89 (t, 1H, J(HH) = 7 Hz, H^5), 6.82 (d, 1H, J(HH) = 7 Hz, H^3, H^6), 3.86 (s, 2H, *CH$_2$*), 2.77 (d, 6H, J(HH) = 5 Hz, N–*CH$_3$*). IR.: 1576 υ(C=C), cm^{-1}.

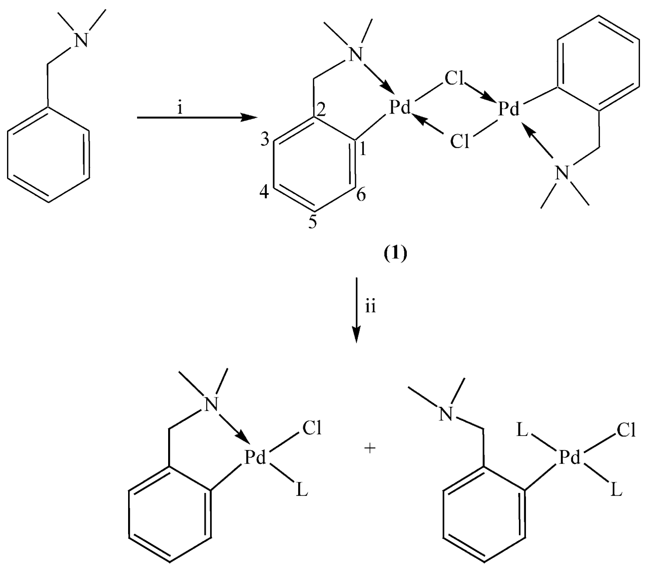
3.2.2. Reaction of (1) with PPh$_3$ and SbPh$_3$

3.2.2.1. Reaction of (1) with PPh$_3$: (2a). A mixture of complex (**1**) (0.1 g, 0.18 mmol) and PPh$_3$ (0.095 g, 0.36 mmol) was refluxed in 10 cm^3 of dichloromethane for 3 h under N$_2$. The solution was cooled to room temperature and diethyl ether was added to precipitate yellow solid of 0.160 g (82% yield based on Pd) of [Pd(dmba)(PPh$_3$)Cl] (**2a**). M.p. 175–178 (dec.) °C. (Found; C, 63.1; H, 5.1; N, 2.3. $C_{27}H_{27}ClNPPd$ calc.; C, 60.2; H, 5.1; N, 2.6, %). Fab–Mass *m/z* : 537 [M]$^+$, 502 [M–Cl]$^+$ (100%.peak). ^{1}H NMR (Bruker–Avance 500 MHz, $CDCl_3$) $\delta = 7.56$–7.52 (m, 6H, P*Ph$_3$*), 7.23–7.06 (m, 9H, P*Ph$_3$*), 6.81 (d, 1H, J(HH) = 6.7 Hz, H^3), 6.63 (t, 1H, J(HH) = 7.2 Hz, H^5), 6.16 (m, 2H, H^4, H^6), 3.88 (d, 2H, J(PH) = 1.4, *CH$_2$*), 2.66 (d, 6H, J(PH) = 2.4, N–*CH$_3$*). ^{13}C{^{1}H}-NMR (Bruker-Avance 125 MHz, $CDCl_3$) $\delta = 138.6$, 137.3 (C1, C6); 136.0 (C2), 124.4, 123.2, 121.8 (C3, C4, C5); P-phenyl: 134.7, 129.9, 128.7, 127.4 (C*o*, C*i*, C*p*, C*m*); 73.2 (*N-CH$_3$*), 50.05 (–CH$_2$–N). ^{31}P–^{1}{H} NMR (Bruker-Avance 202 MHz, $CDCl_3$) $\delta = 42.49$ (s) ppm and small impurities at 23.44 (s) ppm. (28:1 ratio). IR.: 1568 υ(C=C), cm^{-1}.

3.2.2.2. Reaction of (1) with PPh$_3$: (2b). A mixture of complex (**1**) (0.1 g, 0.18 mmol) and an excess of PPh$_3$ (0.190 g, 0.72 mmol) was refluxed in 10 cm^3 of dichloromethane for 3 h under N$_2$. The solution was cooled to room temperature and diethyl ether was added to precipitate yellow solid of 0.225 g of [Pd(dmba)(PPh$_3$)$_2$Cl] (**2b**) and small impurities of [Pd(dmba)(PPh$_3$)Cl] (**2a**). M.p. 183–185 °C. (Found; C, 65.4; H, 5.2; N, 1.9. $C_{45}H_{42}ClNP_2Pd$ calc.; C, 67.5; H, 5.2; N, 1.8, %). Fab-Mass *m/z*: 800 [M]$^+$, 630 [M-2L]$^+$. ^{1}H NMR (300 MHz, CD_2Cl_2) $\delta = 7.71$–7.32 (m, P*Ph$_3$*), 7.00 (d, 1H, J(HH) = 7 Hz, H^3), 6.80 (td, 1H, J(HH) = 7 Hz, H^5), 6.34 (m, 2H, H^4, H^6), 4.07 (s, 2H, *CH$_2$*), 2.80 (s, 6H, N–*CH$_3$*). ^{13}C{^{1}H}–NMR, (62.90 MHz, 298 K, $CDCl_3$,) $\delta = 149.7$, 147.4 (C1, C6), 136.8 (C2), 123.9, 122.8, 121.4 (C3, C4, C5); P-phenyl: 134.0, 130.9, 129.5, 127.2 (C*o*, C*i*, C*p*, C*m*); 72.1 (N–*CH$_3$*), 49.43 (–CH$_2$–N). ^{31}P–^{1}{H} NMR (101.25 MHz, 298 K, CD_2Cl_2) $\delta = 27.5$(s) ppm for (**2b**) and 43.37 (br s) ppm for (**2a**). IR.: 1576 υ(C=C), cm^{-1}.

3.2.2.3. Reaction of (1) with SbPh$_3$: (3a). Complex (**1**) (0.1 g, 0.18 mmol) and SbPh$_3$ (0.130 g, 0.36 mmol) were refluxed in 10 cm^3 of dichloromethane for 5 h under N$_2$. The solution was cooled to room temperature and diethylether was added to precipitate yellow solid of 0.100 g (44% based on Pd) of [Pd(dmba)(SbPh$_3$)Cl], (**3a**). M.p. 159–160 °C. (Found; C, 51.4; H, 4.2; N, 2.0. $C_{27}H_{27}ClNSbPd$ calc.; C, 51.5; H, 4.3; N, 2.2, %). Fab-Mass *m/z*: 630 [M]$^+$, 594 [M–Cl]$^+$. ^{1}H NMR ($CDCl_3$) $\delta = 7.65$–7.35 (m, 15H, Sb*Ph$_3$*), 7.03 (d, 1H, J(HH) = 7 Hz, H^3), 6.87 (t, 1H, J(HH) = 7 Hz, H^4), 6.68 (d, 1H, J(HH) = 8 Hz, H^6), 6.40 (t, 1H, J(HH) = 7 Hz, H^5), 4.10 (s, 2H, *CH$_2$*), 2.93 (s, 6H, N–*CH$_3$*). ^{13}C{^{1}H}-NMR, $\delta = 149.7$, 145.8, 140.6 (C1, C6, C2), 125.8, 124.7, 123.2 (C3, C4, C5); Sb-phenyl: 136.9, 131.3, 130.5, 129.5 (C*o*, C*i*, C*p*, C*m*); 73.8 (N–*CH$_3$*), 51.3 (–CH$_2$–N). IR.: 1568 υ(C=C), cm^{-1}.

3.2.2.4. Reaction of (1) with SbPh$_3$: (3b). Complex (**1**) (0.1 g, 18 mmol) and SbPh$_3$ (0.260 g, 0.72 mmol) were



2a; L = PPh$_3$ **2b**; L= PPh$_3$

3a; L = SbPh$_3$ **3b**; L = SbPh$_3$

Scheme 1. (i) PdCl$_2$ (methanol); (ii) PPh$_3$ or SbPh$_3$ (dichloromethane).

refluxed in 10 cm^3 of dichloromethane for 5 h under N$_2$. The solution was cooled to room temperature and diethylether was added to precipitate yellow solid of 0.300 g (85% based on Pd) of [Pd(dmba)(SbPh$_3$)$_2$Cl], (**3b**). M.p. 138–140 (dec.) °C. (Found; C, 55.9; H, 4.4; N, 1.0. C$_{45}$H$_{42}$ClNSb$_2$Pd calc.; C, 54.9; H, 4.3; N, 1.4, %). Fab-Mass *m/z*: 982 [M]$^+$, 947 [M–Cl]$^+$. ^{1}H NMR (Bruker–Avance 500 MHz, CDCl$_3$) δ = 7.56 − 7.15 (m, 30H, Sb*Ph$_3$*), 6.85 (d, 1H, J(HH) = 7.3 Hz, H^3), 6.70 (t, 1H, J(HH) = 7.3 Hz, H^4), 6.51 (d, 1H, J(HH) = 7.7 Hz, H^6), 6.24 (t, 1H, J(HH) = 7.5 Hz, H^5), 3.92 (s, 2H, *CH$_2$*), 2.76 (s, 6H, N–*CH$_3$*). ^{13}C{^{1}H}-NMR (Bruker-Avance 500 MHz, CDCl$_3$), $\delta = 140.9, 139.6$ (C1, C6), 126.1, 125.0, 123.7, 122.2 (C2, C3, C4, C5); Sb-phenyl: 137.1, 135.9, 133.8, 129.5 (C*o*, C*i*, C*p*, C*m*); 73.5 (N–*CH$_3$*), 50.3 (CH$_2$). IR.: 1576 υ(C=C), cm^{-1}.

3.3. X-ray crystallography

Crystals of (**1**) and (**2a**), (**2b**) suitable for X-ray crystallographic analysis were grown from hot benzene/ n-hexane and dichloromethane/diethyl ether at room temperature, respectively, Scheme 1. The crystal data, a summary of

Table 2
Crystallographic data and parameters of the complexes (**1**) and (**2**)

Compound	(**1**)	(**2**)
Empirical formula	C$_{18}$H$_{24}$Cl$_2$N$_2$Pd$_2$	C$_{72}$H$_{69}$Cl$_2$N$_2$P$_3$Pd$_2$
Formula weight	552.09	1338.90
Temperature	190(2) K	190(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	*P*2$_1$/*c*	*P*2$_1$/*n*
Unit cell dimensions		
a	7.849(1) Å	9.964(2) Å
b	15.635(3) Å	34.228(5) Å
c	8.352(1) Å	18.127(3) Å
α	90°	90°
β	109.29°	91.91°
γ	90°	90°
Volume	967.4(3) Å^3	6179(2) Å^3
Z	2	4
Density (calculated)	1.895 Mg m^{-3}	1.439 Mg m^{-3}
Absorption coefficient	0.2137 mm^{-1}	0.791 mm^{-1}
F(000)	544	2744
Crystal size	0.66 × 0.51 × 0.38 mm	0.74 × 0.68 × 0.52 mm
Theta range for data collection	2.61–24°	2.54-24.0°
Index ranges	$-1 \le h \le 8$, $-1 \le k \le 17$, $-9 \le \ell \le 9$	$-1 \le h \le 11$, $-1 \le k \le 39$, $-20 \le \ell \le 20$
Reflection collected	2023	11986
Independent reflections	1508 [R(int) = 0.0254]	9696 [R(int) = 0.0251]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1508/0/111	9696/0/734
Goodness-of-fit on F^2	1.183	1.070
Final R indices [I > 2sigma(I)]	R1 = 0.0231, wR2 = 0.0614	R1 = 0.0348, wR2 = 0.0731
R indices (all data)	R1 = 0.0237, wR2 = 0.0617	R1 = 0.0501, wR2 = 0.0794
Largest diff. peak and hole	0.307 and −0.597 e Å^{-3}	0.556 and −0.545 e Å^{-3}

Details in common: Siemens P4 diffractometer monochromated Mo–Kα radiation (λ = 0.7107 Å) omega scans, $R1 = \Sigma||Fo-|Fc||/\Sigma|Fo|$, $wR2 = [w(Fo^2-Fc^2)^2/(Fo^2)^2]^{1/2}$, goodness of fit $s = [\Sigma w(Fo^2-Fc^2)^2/(n-p)]^{1/2}$ where n = number of reflections and p = total number of parameters, $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$ where $P = (Fo^2 = Fc^2)/3$.

the data collection and structure refinement parameters are given in Table 2. Crystals were glued on glass fibers. Unit cell dimensions were determined by least squares refinement of optimised setting angles. The data were corrected for Lorentz and polarisation effects, and empirical absorption corrections were applied. The structures were solved by Patterson methods (SHELXTL PC) [15], and refined by full matrix least squares using SHELXL 96 [16]. H atoms were included in calculated positions. The Methyl H atoms had isotropic displacement parameters fixed at 1.5 Ueq of the bonded atom for all other H atoms the value of 1.2 Ueq of the bonded atom was used. All non H atoms were refined with anisotropic displacement parameters.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 221337 and 221338 for compounds (1) and (2), respectively. 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; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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