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Crystal structure of [Pd(η^3-2-propenyl)(dps)][Pd(η^3-2-propenyl)Cl_2]. NMR evidence of binuclear η^3-allyl palladium(II) species with bridging dps

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Abstract

The reactions of di-2-pyridyl sulfide (dps) with (η^3-allyl)palladium chloride dimers gave the ionic compounds [Pd(η^3-allyl)(dps)][Pd(η^3-allyl)Cl_2] (allyl = 2-propenyl (**1**), 2-methyl-2-propenyl (**2**), 2-butenyl (**3**)). The structure of **1** has been determined by X-ray diffraction methods. Crystals are triclinic, space group $P\bar{1}$, with $Z=2$ in a unit cell of dimensions $a=8.840(1)$, $b=8.928(1)$, $c=12.317(2)$ Å, $\alpha=98.82(1)$, $\beta=90.46(1)$, $\gamma=95.46(1)$°. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least-squares on the basis of 3855 observed reflections to R and R_w values of 0.0269 and 0.0339, respectively. Compound **1** consists of discrete complex ion pairs, containing allyl groups coordinated to both the cationic and anionic palladium centres. In the cationic portion the dps acts as a chelate ligand and adopts an N,N inside conformation. The six-membered chelate ring shows a boat conformation. The cation and anion are connected by a short Pd2...Cl2 interaction (3.073(1) Å) which determines pseudo-five-coordination for the cation. At low temperature the ^{1}H NMR spectra in CD_3OD of **1** and **2** confirm the presence of the cation and the anion while in $CDCl_3$ they also indicate the presence of a binuclear species with bridging dps. The ^{1}H NMR spectra, at variable temperature, show that **1**, **2** and **3** in solution undergo dynamic processes. In $CDCl_3$, a lower energy process makes the π-allyl groups equivalent at room temperature, a higher energy process determines the magnetic equivalence of *syn* and *anti* π-allyl protons at high temperature.

Introduction

The chemistry of (π-allyl)palladium and platinum derivatives has been extensively studied with regard to the fluxional behaviour of the allyl moiety involving, in some cases, ionic species [1, 2].

The reactions of (π-allyl)palladium complexes with nucleophiles have found extensive application in organic synthesis [3]. In some of these reactions it has been assumed that the added ligand displaces the anionic ligand and produces cationic organopalladium intermediates which undergo nucleophilic addition [4]. On the other hand cationic (π-allyl)palladium and platinum complexes were prepared with a view of their utilization in organic synthesis [5].

These ionic species were sometimes formulated, as ion pairs with the allyl groups present in both the cation and the anion counterparts on the basis of analytical, conductometric and NMR data [2]. To the best of our knowledge only one example of such ion pairs has been structurally characterized [6].

As a continuation of our investigation on the coordination chemistry of flexible bipyridine like ligands [7], we examined the reactions of di-2-pyridyl sulfide (dps) and $[M(allyl)Cl]_2$ (M = Pt(II), allyl = 2-propenyl; M = Pd(II), allyl = 2-propenyl, 2-methyl-2-propenyl, 2-butenyl) complexes.

The flexible bipyridine like ligands can adopt several coordination modes [8], namely monodentate, bridging or chelated. In the last case some crystal structure determinations showed that the six-membered ring is in the boat configuration [9]. On the other hand NMR studies showed that these ligands favour dynamic processes in solution [10]. Dps and its derivatives adopt in the three state of the matter several twisted N,N inside, N,N outside and N inside, N outside confor-

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mations [11]. The chelated dps adopts the N,N inside conformation [7b] and the N inside, N outside conformation [12]. The latter is also present when it behaves as a bridging ligand [7a].

In this paper the crystal structure of [Pd(η^3-2-propenyl)(dps)][Pd(η^3-2-propenyl)Cl_2] (**1**) and the dynamic behaviour of [Pd(η^3-allyl)(dps)][Pd(η^3-allyl)Cl_2] (allyl = 2-propenyl (**1**); 2-methyl-2-propenyl (**2**), 2-butenyl (**3**)) are reported.

Results and discussion

The compounds [Pd(η^3-allyl)(dps)][Pd(η^3-allyl)Cl_2] were prepared according to eqn. (1)

$$[\mathrm{Pd}(\eta^3\text{-allyl})\mathrm{Cl}]_2 + \mathrm{dps} \longrightarrow [\mathrm{Pd}(\eta^3\text{-allyl(dps)}][\mathrm{Pd}(\eta^3\text{-allyl})\mathrm{Cl}_2] \quad (1)$$

allyl = 2-propenyl (**1**), 2-methyl-2-propenyl (**2**), 2-butenyl (**3**)

The bridge splitting reaction of chloro-bridged palladium allyl dimers by dps gave the compounds **1**, **2** and **3** as yellow solids. The same reaction with [Pt(C_3H_5)Cl]$_4$ did not allow the preparation of any stable allyl compound. All attempts to prepare [M(π-allyl(dps)]Cl using an excess of dps and different solvents were unsuccessful but in the presence of $NaClO_4$ the [M(η^3-allyl(dps)]ClO_4 salts were obtained.

Equation 2 shows an alternative and more convenient route to prepare the [M(η^3-allyl)(dps)]X salts

$$1/2[\mathrm{M}(\eta^3\text{-allyl})\mathrm{Cl}]_2 + \mathrm{AgX} + \mathrm{dps} \longrightarrow [\mathrm{Mn}(\eta^3\text{-allyl})(\mathrm{dps})]\mathrm{X} \quad (2)$$

X = ClO_4^-, PF_6^-, BF_4^-; M = Pd(II); allyl = 2-propenyl (**4**), 2-methyl-2-propenyl (**5**), 2-butenyl (**6**); M = Pt(II); allyl = 2-propenyl (**7**)

Compounds **1**–**7** are stable for several months in the solid state and for several days in solution. The IR spectra show strong bands associated with the dps ligand [7, 12a] at *c*. 1585 and *c*. 780 cm^{-1}. Furthermore two ν(M–Cl) in the IR spectra of **1**–**3** at *c*. 270 and *c*. 253 cm^{-1} suggest the presence of the anions [Pd(η^3-allyl)Cl_2]$^-$ [2].

Conductivity measurements in acetone or methanol solutions indicate that the compounds behave as 1:1 electrolytes (100–120 S cm^2 mol^{-1}) whereas in CH_2Cl_2 the Λ_M values of **1**–**3** are more reduced (7–8 S cm^2 mol^{-1}).

The UV spectra of all complexes in methanol obey the Lambert–Beer law in the range 5×10^{-4}–10^{-5} mol dm^{-3} whereas in CH_2Cl_2 some deviations are observed for complexes **1**–**3**. The conductivity and UV data of compounds **1**–**3** in solvents of lower polarity are consistent with cation anion association and formation of non-conducting species [2b].

Description of the structure of the complex [Pd(η^3-C_3H_5)(dps)][Pd(η^3-C_3H_5)Cl_2]

The X-ray diffraction study showed unequivocally that the solid state structure of [Pd(η^3-C_3H_5)(dps)][Pd(η^3-C_3H_5)Cl_2] consists of discrete ion pairs where the cation and the anion interact through a Cl atom. The structure of **1** is shown in Fig. 1 together with the atomic numbering system; selected bond distances and angles are given in Table 1. In the cationic portion the Pd atom exhibits a square planar geometry involving two C atoms of the π-allyl group and the two pyridine N atoms of the dps molecule acting as a chelating ligand. The Pd(2)–C(11) and Pd(2)–C(13) bond distances (mean 2.108(4) Å) and the C(11)–Pd(2)–C(13) bond angle (69.6(1)°) are similar to those found in the (π-allyl)(tetramethylethylenediamine)-palladium(II) cation (mean 2.15(3) Å and 70.5(8)°) [6] and in other palladium complexes involving π-allyl ligands [13, 14]. The displacement of the central C(12) atom of the π-allyl group from the mean coordination plane (N(1), N(2), C(13), C(11)) is 0.646(4) Å and the distance from the metal atom is 2.108(4) Å. The dihedral angle between the η^3-allyl group and the square planar coordination plane of Pd(2) is 113.9(3)° while the C(11)–C(12)–C(13) bond angle is 119.0(4)°, in good agreement with those found in related compounds [5e, 13, 14]. As a consequence of the *trans* influence of the π-allyl group the Pd(2)–N(1) and Pd(2)–N(2) bond distances (mean 2.106(2) Å) are significantly longer than those found in [Pd(dps)Cl_2] (mean 2.032(3) Å) [7b] and shorter than those found in the (π-allyl)(tetramethylethylenediamine)palladium(II) cation (mean 2.155(15) Å)). Such a difference must be related to the different hybridization of the nitrogen atoms.

In the cationic portion the dps molecule adopts a twisted N,N inside conformation in order to chelate the Pd atom, through the two N atoms, with a very favourable bite angle (88.8(1)°) similar to that reported

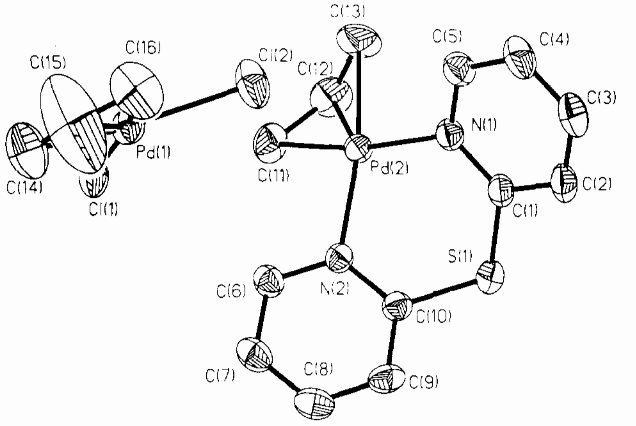


Fig. 1. Structure of the complex [Pd(2-propenyl)(dps)][Pd(2-propenyl)Cl_2] (**1**) with the atomic numbering scheme.

TABLE 1. Bond distances (Å) and angles (°)

Pd(1)–Cl(1)	2.399(1)	C(1)–C(2)	1.391(4)
Pd(1)–Cl(2)	2.383(1)	C(2)–C(3)	1.374(5)
Pd(1)–C(14)	2.101(5)	C(3)–C(4)	1.378(6)
Pd(1)–C(15)	2.065(8)	C(4)–C(5)	1.376(5)
Pd(1)–C(16)	2.102(4)	N(2)–C(6)	1.344(3)
Pd(2)–N(1)	2.108(2)	N(2)–C(10)	1.338(3)
Pd(2)–N(2)	2.104(2)	C(6)–C(7)	1.394(5)
Pd(2)–C(11)	2.109(3)	C(7)–C(8)	1.362(5)
Pd(2)–C(12)	2.108(4)	C(8)–C(9)	1.386(5)
Pd(2)–C(13)	2.107(4)	C(9)–C(10)	1.376(4)
S(1)–C(1)	1.779(3)	C(11)–C(12)	1.394(6)
S(1)–C(10)	1.778(3)	C(12)–C(13)	1.400(6)
N(1)–C(1)	1.329(4)	C(14)–C(15)	1.22(1)
N(1)–C(5)	1.345(4)	C(15)–C(16)	1.26(1)
C(14)–Pd(1)–C(16)	69.1(2)	C(1)–N(1)–C(5)	117.8(3)
S(1)–C(1)–N(1)	118.3(2)	Cl(2)–Pd(1)–C(16)	95.8(2)
N(1)–C(1)–C(2)	123.1(3)	Cl(2)–Pd(1)–C(14)	164.9(2)
S(1)–C(1)–C(2)	118.5(2)	Cl(1)–Pd(1)–C(16)	168.4(2)
C(1)–C(2)–C(3)	118.0(3)	Cl(1)–Pd(1)–C(14)	99.3(1)
C(2)–C(3)–C(4)	119.6(3)	Cl(1)–Pd(1)–Cl(2)	95.8(1)
C(3)–C(4)–C(5)	118.7(3)	C(11)–Pd(2)–C(13)	69.6(1)
N(1)–C(5)–C(4)	122.7(3)	N(2)–Pd(2)–C(13)	170.2(1)
Pd(2)–N(2)–C(10)	120.9(2)	N(2)–Pd(2)–C(11)	100.7(1)
Pd(2)–N(2)–C(6)	120.3(2)	N(1)–Pd(2)–C(13)	100.8(1)
C(6)–N(2)–C(10)	118.8(2)	N(1)–Pd(2)–C(11)	170.4(1)
N(2)–C(6)–C(7)	121.1(3)	N(1)–Pd(2)–N(2)	88.8(1)
C(6)–C(7)–C(8)	119.8(3)	C(1)–S(1)–C(10)	101.2(1)
C(7)–C(8)–C(9)	119.0(3)	Pd(2)–N(1)–C(5)	121.1(2)
C(8)–C(9)–C(10)	118.8(3)	Pd(2)–N(1)–C(1)	121.1(2)
N(2)–C(10)–C(9)	122.6(3)	S(1)–C(10)–N(2)	118.3(2)
S(1)–C(10)–C(9)	119.1(2)	C(11)–C(12)–C(13)	119.0(4)
C(14)–C(15)–C(16)	148.1(8)		

in [Pd(dps)Cl_2] (88.6(1)°). The six-membered chelate ring Pd(2)N(1)C(1)S(1)C(10)N(2) is in a boat conformation; the mean plane passing through the N(1)C(1)C(10)N(2) atoms leaves the Pd(2) and S(1) atoms −0.912(1) and −0.851(1) Å out of the plane on the same side and the dihedral angle between the two Pd(2)N(1)C(1)S(1) and Pd(2)N(2)C(10)S(1) moieties is 63.0(1)°. The structural parameters in the dps ligand of the present compound are quite similar to those reported for the complex [Pd(dps)Cl_2] [7b] whereas some differences are observed for the monoprotonated dps [15]. In fact the C–S bond lengths are 1.779(3) and 1.778(3) Å in good agreement with those expected for C(sp^2)–S bonds and with those found in the monoprotonated dps (1.75(2) Å) and in [Pd(dps)Cl_2] (1.772(3) and 1.778(3) Å). The CSC angle is 101.2(1)°, significantly different from the tetrahedral one and from the value reported in dpsH$^+$ (108(1)°) but comparable with that reported for the [Pd(dps)Cl_2] complex (99.6(2)°). The N...N separation is 2.95 Å quite similar to 2.84 Å in Pd(dps)Cl_2 but longer than 2.63 Å in dpsH$^+$ where an intramolecular hydrogen bond is probably involved.

In the crystal, the cation and anion are connected by the Pd2...Cl2 interaction at 3.07 Å, the cationic centre being pseudo-five-coordinated; in fact the vector Pd–Cl makes an angle of 90° with the coordination plane while the Pd2–Cl2–Pd1 angle is 129°. Both the anionic Pd–Cl bond distances (mean 2.391(1) Å) are comparable to those reported in the corresponding dichloro(π-allyl)palladium anion (mean 2.395(5) Å) whereas the Cl(2)–Pd(1)–Cl(1) bond angle is 95.8(2)°, less than that reported in the cited complex (97.9(2)°); such a small difference may arise from the above mentioned cationic–anionic interaction. The Pd(1)–C(16), Pd(1)–C(15) and Pd(1)–C(14) bond distances (2.102(4), 2.065(8) and 2.101(5) Å, respectively) and the C(16)–Pd(1)–C(14) bond angle (69.1(2)°) do not differ from the values found in the cationic portion of [(π-allyl)(tetramethylethylenediamine)palladium(II)]-[dichloro(π-allyl)palladate(II)]. The bond distances C(14)–C(15) and C(15)–C(16) (1.22(1) and 1.26(1) Å, respectively) and the angle C(14)–C(15)–C(16) (148.1(8)°) of the π-allyl group in the anionic portion are unusual. The very short inter-nuclear distances and the larger bond angle are due probably to the disorder of the central carbon atom as can be seen from the high C(15) thermal parameters. An attempt to resolve this atom in two occupancy site factors was unsuccessful and after anisotropic refinement for C(15) the largest electronic residue was found in its vicinity.

To the best of our knowledge the crystal structure of **1** is the second example of a complex ion pair containing a π-allyl moiety in both cationic and anionic portions.

Solution structure and dynamic behaviour

The NMR spectra show a downfield shift of the pyridine protons and carbons with respect to the free ligand indicating a marked decrease of electron density in the coordinated ligand. The room temperature ^{1}H NMR spectra of compounds **1**–**6**, in $CDCl_3$, are simple, due to the absence of appreciable coupling between *syn* and *anti* protons and the equilibration of the cation and anion allyl groups (for **1**–**3** see below). Thus the characteristic signals of the η^3-allyl moiety, with separate resonances for *syn* and *anti* protons, are observed. The *anti* protons of the CH_2 groups, which appear at higher field than the *syn* protons, show in **1** and **3** the larger coupling constant with a central proton (*c*. 12 Hz). The $CDCl_3$ spectrum of **3** shows the presence of almost pure *syn* isomer, the *anti* isomer being less than 5%. The assignment of the *syn* configuration to the major isomer was confirmed by NOE measurements (positive NOE was observed between the *syn* CH_3 at 1.36 ppm and the central allyl proton). For **7** the allyl resonances are more complicated due to the coupling with the ^{195}Pt isotope and to a *syn*–*anti* coupling of 1.9 Hz.

According to ^{1}H NMR spectra the ^{13}C NMR spectra of compounds **1**–**3** (see Table 2 and 'Experimental')

TABLE 2. Selected ^{1}H and ^{13}C NMR data[a] for **2** and **5**

Compound and species	T (K)	dps									Allyl					
		Proton resonances				Carbon resonances					Proton resonances			Carbon resonances		
		H^6	H^4	H^3	H^5	C^2	C^6	C^4	C^3	C^5	H_{syn}	H_{anti}	CH_3	C-Me	CH_2	CH_3
2	330[b]	8.80(m)	7.98(m)	7.90(m)	7.53(m)						3.90(s)	3.10(s)	2.15(s)			
cation	240[b]	8.95(m)	8.10(m)	8.04(m)	7.59(m)						4.07(s)	3.40(s)	2.22(s)			
anion											3.75(s)	2.79(s)	2.05(s)			
	335	8.70(m)	7.71(m)	7.55(m)	7.39(m)						3.26(br)[c]	3.26(br)[c]	1.90(s)			
	300	8.85(m)	7.75(m)	7.58(m)	7.40(m)	154.1(m)	153.5(s)	138.4(s)	127.8(s)	123.4(s)	3.69(s)	2.86(s)	1.95(s)	131.8(s)	61.1(s)	22.9(s)
binuclear	215	9.25(m)	7.88(m)	7.79(m)	7.52(m)	158.2(s)	156.4(s)	140.3(s)	130.2(s)	126.5(s)	3.88(br)	2.89(br)	2.13(s)	134.4(s)	62.7(s)	24.5(s)
											3.83(br)		2.10(s)	130.0(s)		24.1(s)
cation		8.75(m)	7.84(m)	7.75(m)	7.29(m)	152.2(s)	153.5(s)	140.1(s)	130.2(s)	125.0(s)	3.73(s)	2.86(s)	2.06(s)	129.9(s)	60.9(s)	24.0(s)
anion											3.65(s)	2.72(s)	1.98(s)	125.8(s)	60.1(s)	23.9(s)
5	300[d]	9.04(m)	8.19(m)	8.13(m)	7.66(m)	n.o.	156.4(s)	141.8(s)	131.4(s)	126.4(s)	4.19(s)	3.49(s)	2.30(s)	137.6(s)	62.7(s)	23.3(s)
[Pd(all)(dps)]Cl[e]	215	8.99(m)	7.98(m)	7.89(m)	7.56(m)						3.92(s)	3.28(s)	2.14(s)			

[a] Recorded at 300 and 75.56 MHz, respectively, in $CDCl_3$ unless stated otherwise; chemical shift in ppm and with multiplicity in parentheses; $SiMe_4$ as internal standard. s = singlet, m = multiplet, br = broad and n.o. = not observed. [b] CD_3OD. [c] Broad signal of *syn* and *anti* protons. [d] $(CD_3)_2CO$. [e] **2** + dps in ratio 1:1.

show single resonances in the ranges 58–61 and 18–22 ppm assigned to the CH_2 groups and the CH_3 groups (**2** and **3**), respectively. The resonances of the central CH groups (**1** and **3**) and the terminal CH groups (**3**) are found in the range 112–113 ppm and at *c.* 80 ppm [16].

The variable temperature ^{1}H NMR spectra of **1**–**3** have been studied in CD_3OD and in $CDCl_3$ in the range 335–210 K. Selected data are listed in Table 2 and in 'Experimental'.

We observed three dynamic processes in solution. (i) An allyl equilibration: although the X-ray structure of **1** clearly shows the presence of two different allyl groups the ^{1}H NMR spectra of compounds **1**–**3** show, at room temperature, signals of magnetically equivalent allyl-groups. (ii) A *syn–anti* inversion at high temperature: the signals of the *syn* and *anti* protons of compounds **1**–**3** in $CDCl_3$ coalesce at 330–335 K. (iii) A *cis–trans* isomerization: although the protons and carbons of the two rings of dps are non-equivalent in **3** and **6** due to the asymmetric 2-butenyl group, the ^{1}H and ^{13}C NMR spectra show magnetically equivalent pyridine rings. The last process is too fast to be frozen. Moreover we have already investigated the *cis–trans* isomerization for methoxydiene derivatives [7b].

At low temperature the ^{1}H NMR spectra of compounds **1**–**3** in CD_3OD and $CDCl_3$ show dramatic differences. In CD_3OD in the rangc 260–210 K for **1** and **2** the allyl signals of the cation and the anion are resolved. In $CDCl_3$ in the range 220–210 K proton allyl resonances of three different species are detected while pyridine signals of two different dps are observed.

The assignment of the chemical shifts of the allyl protons in CD_3OD at low temperature was made by comparison of the ^{1}H NMR spectra of **1** and **2** with those of the salts $[Pd(\eta^3\text{-allyl})(dps)]X$ (**4** and **5**) for the cation and $[Pd(\eta^3\text{-allyl})Cl_2][As(C_6H_5)_4]$ [2a, 6] for the anion. All data are in agreement with the assumption that the increased shielding in the anion with respect to the cation, shifts the π-allyl ligand signals to a higher field.

Moreover in CD_3OD, at 330 K the ^{1}H NMR spectra of compounds **1**–**3** show the allyl proton signals of equivalent allyl groups. For **1** and **2** the coalescence temperatures are observed at 310 and 300 K and the $\Delta G^{\neq}$ values were calculated to be 15.2 and 14.6 Kcal, respectively whereas the allyl signals of **3** broaden at the lowest temperature suggesting a faster equilibration process of the allyl groups between the cation and anion.

For compounds **1**–**3** in $CDCl_3$ the coalescence temperature is observed at 240–235 K indicating a faster allyl equilibration in this solvent.

At 215 K in the ^{1}H NMR spectrum of **2** the pyridine proton resonances of two non-equivalent dps ligands are detected, with intensity ratio 1:1 (see Table 2 and Fig. 2(b)). At the same temperature in the ^1H NMR spectrum of **1** and **3** pyridine signals of two non-equivalent dps ligands are observed, with intensity ratio 2:1 (see 'Experimental').

The presence, in $CDCl_3$, of two species containing the dps ligand is consistent with an allyl equilibration through an intermediate **B** [17] in which a dps ligand is bonded to both metal centers as shown in eqn. (3)

$$[Pd(all)(dps)]^+[Pd(all)Cl_2]^- \rightleftharpoons \underset{\mathbf{B}}{[(all)ClPd](\mu\text{-dps})[(all)ClPd]} \quad (3)$$

In the ^1H NMR spectra of compounds **1**–**3** the resonances of the H^6 protons at 9.36, 9.25 and 9.25 ppm are assigned to the bridge dps of **B** while the signals at 8.71, 8.75 and 8.60 ppm are assigned to the cations.

We suggest the Pd(η^3-allyl) unit scrambling is promoted by anion and cation Cl interaction in a tight ion pair. According to this suggestion no appreciable change in line shapes of the allyl and pyridine proton resonances and in coalescence temperature was observed on lowering the concentration of **1**–**3** solution from 5×10^{-2} to 5×10^{-3} mol dm^{-3} whereas these systems are markedly affected by the polarity of the solvent. Moreover the pyridine and allyl proton signals of the cations in the low temperature spectra of **1**–**3** in $CDCl_3$ resonate at lower frequencies of *c*. 0.4 ppm than in the corresponding compounds **4**–**6** probably due to partial or complete bonding of the coordinating anion to the metal of the cation through a chloride. Analogous interaction was evinced by the X-ray structure of **1**.

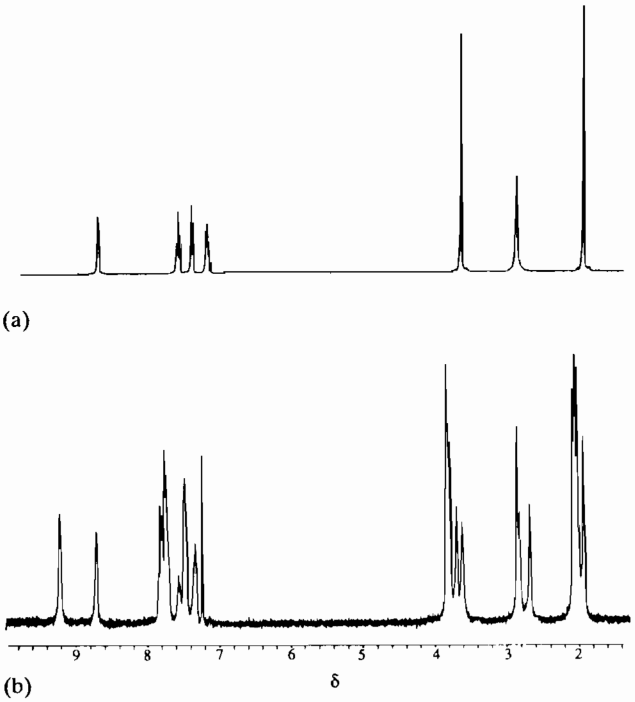


Fig. 2. ^1H NMR spectra of **2** in $CDCl_3$ at: (a) 310 K, (b) 215 K.

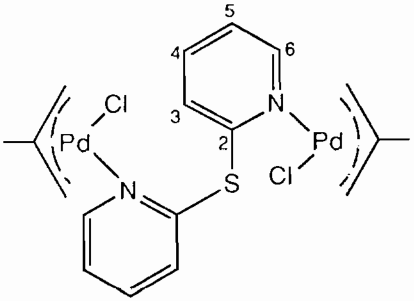
The features of the low temperature spectra of **1** and **2**, in the allyl region, are consistent with the presence of the **B** species.

In the ^1H NMR spectrum of **1**, at 215 K, although a signal is observed for *anti* protons of **B** at 2.86 ppm ($J_{anti}=11.8$ Hz), two signals at 4.09 ($J_{syn}=6.8$ Hz) and 3.94 ($J_{syn}=6.3$ Hz) ppm are resolved for the *syn* protons. This result is consistent with the presence of allyl protons *trans* to the N and the Cl atoms, respectively.

In the ^1H NMR of **2** (Fig. 2) the singlet at room temperature of the *syn* protons (3.69 ppm) is resolved at 215 K in rather broad signals at 3.88 and 3.83 ppm and two singlets at 3.73 and 3.65 ppm, and the singlet of the *anti* protons (2.86 ppm) in the signals at 2.89, 2.86 and 2.72 ppm. The methyl signal (1.95 ppm) is splitt into four resonances at 2.13, 2.10, 2.06 and 1.98 ppm. We assigned the resonances at 3.73, 2.86 and 2.06 and those at 3.65, 2.72 and 1.98 ppm to the cation and anion, respectively, while the resonances at 3.88, 3.83, 2.89, 2.13 and 2.10 were assigned to the allyl groups of species **B**. The intensity ratio between the allyl signals of **B** and those of the cation or anion (2:1) confirms the presence of an approximately equimolar mixture of binuclear and ionic species.

The CH_2 carbon signal of **B** (62.7 ppm) is not resolved in the ^{13}C NMR spectrum of **2** at low temperature whereas the CH_2 resonances of the cation and anion are observed at 60.9 and 60.1 ppm and the pyridine carbon signals of the cation and the binuclear species are resolved (Fig. 3(b)). In accordance with the ^1H NMR spectrum four methyl carbon resonances are observed in the ^{13}C NMR spectrum of **2**. The signals at 24.5 and 24.1 ppm are assigned to **B** and those at 24.0 and 23.9 ppm to the cation and anion, respectively. Moreover four signals are observed for the allyl central carbons.

Although only a X-ray determination could elucidate the structure of the binuclear species **B**, inspection of molecular models suggest that the dps ligand adopts in the binuclear species at twisted N inside, N outside conformation with equivalent pyridine rings. In this



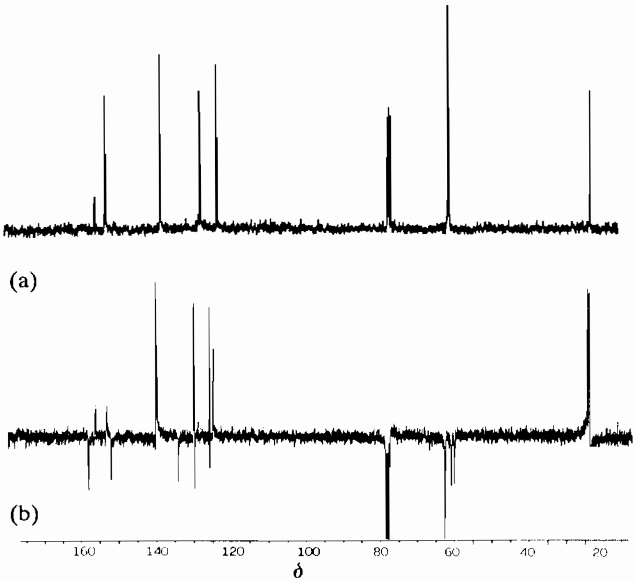


Fig. 3. ^{13}C NMR spectra of **2** in $CDCl_3$ at: (a) 310 K, (b) 215 K (j-modulated spin-echo pulse sequence).

configuration the terminal carbons of the two allyl groups *trans* to the Cl atoms (or the N atoms) are equivalent; the central carbons and the methyl groups lie out of the coordination planes (e.g. the dihedral angle between the allyl and the coordination planes in **1** is 113.9°) on the same or the opposite side. The disorder of the allyl central carbon atom in the Pd(2-propenyl)Cl_2^- anion of **1** suggests that the two allyl groups may occupy in the binuclear species, at low temperature, two discrete orientations within the coordination spheres of both the metal centers [18] and give rise to two conformers with equivalent pyridine and terminal allyl protons and carbons but non-equivalent methyl and central carbons.

The addition of dps to a chloroform solution of compounds **1–3** shifts the equilibrium depicted in eqn. (4) to the right. In fact at low temperature the pyridine and allyl proton signals of the binuclear species disappear while at room temperature the pyridine proton signals shift to lower frequencies (e.g. the H^6 proton signal of **1** shifts from 9.03 to 8.84 ppm). When free dps reaches the molar ratio 1:1, a species formulated as [Pd(allyl)(dps)]Cl is predominant. The correspondence between the chemical shifts found for these species and those found for **4–6** is good.

$$\mathbf{B} \rightleftarrows [Pd(all)(dps)]^+[Pd(all)Cl_2]^- \overset{+dps}{\rightleftarrows} 2[Pd(all)(dps)]Cl \qquad (4)$$

When dps is further added to [Pd(allyl)(dps)]Cl the ^{1}H NMR spectra show at room temperature a single set of resonance for the free and the coordinated dps which can be resolved at 260 K into two sets of resonances. These experiment indicate that the dps exchange between [Pd(allyl)(dps)]Cl and the free ligand is frozen at 260 K.

The absence of free dps resonances in the ^{1}H NMR spectra of **1–3** and the slow dps exchange when the ligand is in excess appear to rule out a dissociative mechanism for the allyl equilibration involving dissociation of dps at least in $CDCl_3$. Moreover no dissociation in the UV spectra of compounds **1–3** is observed. The relatively low value (11.5 Kcal for **2**) of $\Delta G^{\neq}$ in the equilibrium between the binuclear and the cationic species (eqn. (3)) could favour the formation of the dps bridge intermediate **B** with respect to the dissociation of the ligand.

The ^{1}H NMR spectra of compounds **1–3** at high temperature in $CDCl_3$ show that the *syn–anti* exchange is operative. In $CDCl_3$ when the temperature is increased the ^{1}H NMR spectra of **1**, **2** and **3** show the *syn* and *anti* proton signals coalesce at 330 ($\Delta G^{\neq} = 15.3$ Kcal), 335 ($\Delta G^{\neq} = 15.6$ Kcal) and 335 ($\Delta G^{\neq} = 15.4$ Kcal) K, respectively. At coalescence temperature the central proton of **1** appears as a quintuplet and that of **3** as a quartet confirming the equivalence of the *syn* and *anti* protons.

Binuclear intermediates with an allyl bridge have been proposed to explain the equilibration of the allyl protons as well as the *syn–anti* exchange [6]. It is worth noting that the two dynamic processes take place in our case separately and that the activation energy for the first process in $CDCl_3$ is about 4 Kcal lower than that of the *syn–anti* exchange. It seems likely that the formation of labile chloro bridge intermediates plays an important role in the *syn–anti* exchange observed for compounds **1–3**. The poor influence of the concentration on the dynamic process and its lack for compounds **4–6** (in which the $[Pd(\eta^3\text{-allyl})Cl_2]^-$ anions are absent) are consistent with this suggestion.

Conclusions

This work clearly shows that the ionic structure of **1** detected in the solid state by X-ray analysis is still present in the low temperature methanolic solution of **1** and **2**. It indicates as well that the interaction between a Cl atom of the anion and the metal center of the cation present in the solid state for **1** is also operative, in $CDCl_3$, for compounds **1–3** in a tight ion pair as can be inferred by the insignificant influence of the concentration on the dynamic processes and the lack of these when the Pd(all)Cl_2^- anion is absent.

The allyl equilibration and the *syn–anti* isomerization may proceed through a chloro bridge intermediate containing a dps ligand as suggested by ^{1}H NMR spectra of **1–3** at low temperature. The flexibility of the dps and the potential of the N,N outside and N inside, N outside conformations to bond two metal centers appear to favour the breaking of one of the Pd–N bonds and the formation of an intermediate (detected at low temperature) with a bridging dps ligand. However at high temperature a metal–allyl bond can break as in [(η^3-2-propenyl)(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)palladium][dichloro(η^3-2-propenyl)palladate(II)].

Experimental

The compounds [Pd(2-propenyl)Cl]$_2$ [19], [Pd(2-methyl-2-propenyl)Cl]$_2$ [20], [Pd(2-butenyl)Cl]$_2$ [20], [Pt(2-propenyl)Cl]$_4$ [21] and di-2-pyridyl sulfide [11b] were prepared by published methods. Elemental analyses were carried out by the Microanalytical Laboratory of Organic Chemistry, Institute of Milan and by Analytische Laboratorien, D-5250 Engelskirchen, Germany. Conductivity measurements were done on a conductivity meter CDM 3 Radiometer, Copenhagen. IR spectra were recorded on Perkin-Elmer 783 and FT-IR 1720X machines, in nujol mulls, using CsI plates. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 5 spectrophotometer and the ^{1}H and ^{13}C NMR spectra on Bruker Sy 80 and Gemini 300 Varian spectrometers.

The values of $\Delta G^{\neq}$ at the coalescence temperature (T_c) were calculated from the chemical shift difference ($\Delta\delta$) in Hz in the absence of exchange using the equation $\Delta G^{\neq}_{T_c}=4.58T_c\ [10.32+\log(T_c\sqrt{2}/\pi\Delta\delta)]$.

Preparation

[Pd(η^3-2-propenyl)(dps)][Pd(η^3-2-propenyl)Cl$_2$] (1)

A benzene solution (2 cm^3) of dps (113 mg, 0.6 mmol) was added to a solution (10 cm^3) of [Pd(η^3-2-propenyl)Cl]$_2$ (183 mg, 0.5 mmol) in the same solvent. Addition of diethyl ether induced the precipitation of yellow crystals of the title product, which were washed with diethyl ether and dried *in vacuo* on P_4O_{10} (164 mg, 90%). *Anal.* Found: C, 34.75; H, 3.35; N, 5.10; S, 5.75; Cl, 12.70. Calc. for $C_{16}H_{18}N_2SPd_2Cl_2$: C, 34.70; H, 3.30; N, 5.05; S, 5.80; Cl, 12.80%. ν_{max} (cm^{-1}) (PdCl): 265s and 251s. Molar conductivities, at 25 °C, of 5×10^{-4} mol dm^{-3} methanol and dichloromethane solutions: 101 and 7 S cm^2 mol^{-1}, respectively. UV absorption λ_{max} (nm) (MeOH) (ϵ (dm^{-3} mol^{-1} cm^{-1})): 283 (9400); δ_H (300 MHz; solvent CDCl$_3$; 300 K; standard SiMe$_4$): 9.03 (2H, m, $2H_{dps-6}$), 7.74 (2H, m, $2H_{dps-4}$), 7.60 (2H, m, $2H_{dps-3}$), 7.34 (2H, m, $2H_{dps-5}$), 5.52 (2H, m, $2H_2$), 4.03 [4H, d, J_{syn}(HH) 6.6, $2H_{1s}2H_{3s}$] and 3.16 [4H, d, J_{anti}(HH) 12.0, $2H_{1a}2H_{3a}$]; (330 K) 8.67 (2H, m, $2H_{dps-6}$), 3.53 [8H, br, $4H_{1s}4H_{3s}$], 5.47 [2H, qn, J(HH) 9.4, $2H_2$]; (215 K) 5.50 (2H, br, $2H_2$), {binuclear 9.36 (2H, m, $2H_{dps-6}$), 7.83 (2H, m, $2H_{dps-4}$), 7.77 (2H, m, $2H_{dps-3}$), 7.40 (2H, m, $2H_{dps-5}$), 4.09 [2H, d, J_{syn}(HH) 6.7, $1H_{1s}1H_{3s}$], 3.94 [2H, d, J_{syn}(HH) 6.4, $1H_{1s}1H_{3s}$] and 2.86 [4H, d, J_{anti}(HH) 11.8, $2H_{1a}2H_{3a}$]} {cation and anion 8.71 (2H, m, $2H_{dps-6}$), 7.70 (2H, m, $2H_{dps-4}$), 7.67 (2H, m, $2H_{dps-3}$), 7.35 (2H, m, $2H_{dps-5}$), 3.80 [4H, br, $2H_{1s}2H_{3s}$], 3.07 [2H, d, J_{anti}(HH) 11.2, $1H_{1a}1H_{3a}$] and 3.01 [2H, br, $1H_{1a}1H_{3a}$]}; (solvent CD$_3$OD; 240 K) {cation: 8.97 (2H, m, $2H_{dps-6}$), 8.11 (2H, m, $2H_{dps-4}$), 8.06 (2H, m, $2H_{dps-3}$), 7.63 (2H, m, $2H_{dps-5}$), 5.00 (2H, br, $2H_2$ cation and anion), 4.26 [2H, d, J_{syn}(HH) 6.3, $1H_{1s}1H_{3s}$] and 3.57 [2H, d, J_{anti}(HH) 11.3, $1H_{1a}1H_{3a}$]} {anion: 3.94 [2H, d, J_{syn}(HH) 6.8, $1H_{1s}1H_{3s}$] and 2.94 [2H, d, J_{anti}(HH) 12.3, $1H_{1a}1H_{3a}$]; δ_C 154.5 (2C, s, $2C_{dps-2}$), 154.0 (2C, s, $2C_{dps-6}$), 138.8 (2C, s, $2C_{dps-4}$), 128.6 (2C, s, $2C_{dps-3}$), 124.0 (2C, s, $2C_{dps-5}$), 113.2 (2C, s, $2C_2$) and 61.8 (4C, s, $2C_12C_3$)}.

[Pd(η^3-2-methyl-2-propenyl)(dps)][Pd(η^3-2-methyl-2-propenyl)Cl$_2$] (2)

2 was prepared similarly (193 mg, 85%). *Anal.* Found: C, 37.25; H, 3.80; N, 4.90; S, 5.50; Cl, 12.25. Calc. for $C_{18}H_{22}N_2SPd_2Cl_2$: C, 37.15; H, 3.80; N, 4.80; S, 5.50; Cl, 12.20%. ν_{max} (cm^{-1}) (PdCl): 275vs and 254sh. Molar conductivities, at 25 °C, of 5×10^{-4} mol dm^{-3} methanol and dichloromethane solutions: 99 and 8 S cm^2 mol^{-1}. UV absorption λ_{max} (nm) (MeOH) (ϵ (dm^{-3} mol^{-1} cm^{-1})): 283 (9500).

[Pd(η^3-2-butenyl)(dps)][Pd(η^3-2-butenyl)Cl$_2$] (3)

3 was synthesized by reaction of [Pd(η^3-2-butenyl)Cl]$_2$ (197 mg, 0.5 mmol) and dps (113 mg, 0.06 mmol) in benzene solution (5 cm^3) for 10 min. Removal of the solvent from the yellow solution under reduced pressure and addition of light petroleum gave a crude product which was worked up with diethyl ether until a yellow solid was formed (170 mg, 75%). *Anal.* Found: C, 37.00; H, 3.90; N, 4.80; S, 5.50; Cl, 12.20. Calc. for $C_{18}H_{22}N_2SPd_2Cl_2$: C, 37.15; H, 3.80; N, 4.80; S, 5.50; Cl, 12.20%. ν_{max} (cm^{-1}) (PdCl): 277vs and 254sh. Molar conductivities, at 25 °C, of 5×10^{-4} mol dm^{-3} methanol and dichloromethane solutions: 98 and 7 S cm^2 mol^{-1}. UV absorption λ_{max} (nm) (MeOH) (ϵ (dm^{-3} mol^{-1} cm^{-1})): 283 (9500); δ_H (300 MHz; solvent CDCl$_3$; 300 K; standard SiMe$_4$) 8.84 (2H, m, $2H_{dps-6}$), 7.72 (2H, m, $2H_{dps-4}$), 7.57 (2H, m, $2H_{dps-3}$), 7.32 (2H, m, $2H_{dps-5}$), 5.34 (2H, m, $2H_2$), 4.00 (2H, m, $2H_{3a}$), 3.88 [2H, d, J_{syn}(HH) 5.6, $2H_{1s}$], 2.93 [2H, d, J_{anti}(HH) 11.4, $2H_{1a}$] and 1.36 [6H, d, J(HH) 6.1, 2CH$_3$]; (335 K) 8.70 (2H, m, $2H_{dps-6}$), 5.25 [2H, q, J(HH) 10.5, $2H_2$], 3.90 (2H, m, $2H_{3a}$), 3.32 [4H, br, $2H_{1s}2H_{1a}$] and 1.25 [6H, d, J(HH) 5.9, 2CH$_3$]; (215 K) 5.35 (4H, br, $4H_2$), {binuclear 9.25 (2H, m, $2H_{dps-6}$), 4.15 (2H, br, $2H_{1s}$) 3.90 (2H, m, $2H_{3a}$), 2.95 [2H, d, J_{anti}(HH) 11.5, $2H_{1a}$] and 1.46 [6H, d, J(HH) 6.1, 2CH$_3$]} {cation: 8.60 (2H, m, 2H$_{dps-6}$), 3.80 (2H, br, 2H$_{3a}$, cation and anion), 2.55 [2H, d, J_{anti}(HH) 11.5, 2H$_{1a}$, cation and anion] 1.20 [3H, d, J(HH) 6.1, 1CH$_3$]} and 1.10 [3H, d, J(HH) 6.4, 1CH$_3$, anion]; δ_C 156.0 (2C, s, 2C$_{dps-2}$), 152.3 (2C, s, 2C$_{dps-6}$), 139.1 (2C, s, 2C$_{dps-4}$), 127.5 (2C, s, 2C$_{dps-3}$), 123.2 (2C, s, 2C$_{dps-5}$), 112.3 (2C, s, 2C$_2$), 79.8 (2C, s, 2C$_3$), 57.6 (2C, s, 2C$_1$) and 17.9 (2C, s, 2CH$_3$).

[Pd(η^3-2-propenyl)(dps)]BF$_4$ (4), [Pd(η^3-2-methyl-2-propenyl)(dps)]BF$_4$ (5), [Pd(η^3-2-butenyl)(dps)]BF$_4$ (6) and [Pt(η^3-2-propenyl)(dps)]BF$_4$ (7)

To a stirred acetone solution (20 cm^3) of appropriate chloro-bridged complex (0.5 mmol) was added solid AgBF$_4$ (195 mg, 1 mmol). AgCl was separated by filtration and the resulting solution of the solvent species added with stirring to a diethyl ether solution (*c.* 100 cm^3) of dps (282 mg, 3 mmol). The white precipitate obtained was collected, washed with diethyl ether and dried *in vacuo* on P$_4$O$_{10}$. Complex **4**: yield 190 mg, 90%. *Anal.* Found: C, 36.90; H, 3.20; N, 6.60; S, 7.60. Calc. for C$_{13}$H$_{13}$N$_2$SPdBF$_4$: C, 36.95; H, 3.10; N, 6.65; S, 7.60%. Molar conductivities, at 25 °C, of 5×10^{-4} mol dm^{-3} methanol solutions: 122 S cm^2 mol^{-1}. UV absorption λ_{max} (nm) (MeOH) (ϵ (dm^{-3} mol^{-1} cm^{-1})): 283 (8400); δ_H (300 MHz; solvent (CD$_3$)$_2$CO; 300 K; standard SiMe$_4$). 8.99 (2H, m, 2H$_{dps-6}$), 8.17 (2H, m, 2H$_{dps-4}$), 8.12 (2H, m, 2H$_{dps-3}$), 7.66 (2H, m, 2H$_{dps-5}$), 6.13 (2H, m, 2H$_2$), 4.40 [4H, d, J_{syn} 6.9, 2H$_{1s}$2H$_{3s}$] and 3.63 [4H, d, J_{anti} 12.3, 2H$_{1a}$2H$_{3a}$]; δ_C 155.8 (2C, s, 2C$_{dps-6}$), 141.6 (2C, s, 2C$_{dps-4}$), 130.8 (2C, s, 2C$_{dps-3}$), 126.0 (2C, s, 2C$_{dps-5}$), 120.0 (1C, s, 1C$_2$) and 63.8 (4C, s, 2C$_1$2C$_3$).

Complex **5**: yield 175 mg, 80%. *Anal.* Found: C, 38.50; H, 3.50; N, 6.30; S, 7.40. Calc. for C$_{14}$H$_{15}$N$_2$SPdBF$_4$: C, 38.50; H, 3.45; N, 6.40; S, 7.35%. Molar conductivities, at 25 °C, of 5×10^{-4} mol dm^{-3} methanol solutions: 123 S cm^2 mol^{-1}. UV λ_{max} (nm) (MeOH) (ϵ (dm^{-3} mol^{-1} cm^{-1}): 283 (8970).

Complex **6**: yield 164 mg, 75%. *Anal.* Found: C, 38.50; H, 3.55; N, 6.35; S, 7.40. Calc. for C$_{14}$H$_{15}$N$_2$SPdBF$_4$: C, 38.50; H, 3.45; N, 6.40; S, 7.35%. Molar conductivities, at 25 °C, of 5×10^{-4} mol dm^{-3} methanol solutions: 120 S cm^2 mol^{-1}. λ_{max} (nm) (MeOH) (ϵ (dm^{-3} mol^{-1} cm^{-1})): 284 (8900); δ_H (300 MHz; (solvent CDCl$_3$; 300 K; standard SiMe$_4$) 8.81 (2H, m, 2H$_{dps-6}$), 7.98 (2H, m, 2H$_{dps-4}$), 7.93 (2H, m, 2H$_{dps-3}$), 7.56 (2H, m, 2H$_{dps-5}$), 5.72 (2H, m, 2H$_2$), 4.31 (2H, m, 2H$_{3a}$), 4.05 [2H, d, J_{syn}7.0, 2H$_{1s}$], 3.33 [2H, d, J_{anti} 11.6, 2H$_{1a}$] and 1.38 [6H, d, J(HH) 6.2, 2CH$_3$]; δ_C 152.0 (2C, s, 2C$_{dps-6}$), 141.1 (2C, s, 2C$_{dps-4}$), 130.9 (2C, s, 2C$_{dps-3}$), 126.5 (2C, s, 2C$_{dps-5}$), 119.9 (1C, s, 1C$_2$), 80.1 (2C, s, 2C$_3$), 60.4 (2C, s, 2C$_1$) and 18.2 (2C, s, 2CH$_3$).

Complex **7**: yield 179 mg, 70%. *Anal.* Found: C, 30.60; H, 2.70; N, 5.60; S, 6.30. Calc. for C$_{13}$H$_{13}$N$_2$SPtBF$_4$: C, 30.55; H, 2.55; N, 5.50; S, 6.25%. Molar conductivities, at 25 °C, of 5×10^{-4} mol dm^{-3} methanol solutions: 105 S cm^2 mol^{-1}. UV absorption λ_{max} (nm) (MeOH) (ϵ (dm^{-3} mol^{-1} cm^{-1})): 283 (7400); δ_H (300 MHz; solvent (CD$_3$)$_2$CO; 300 K; standard SiMe$_4$). 9.27 (2H, m, J_{Pt-H} 39, 2H$_{dps-6}$), 8.30 (2H, m, 2H$_{dps-4}$), 8.23 (2H, m, 2H$_{dps-3}$), 7.74 (2H, m, 2H$_{dps-5}$), 5.25 (2H, m, 2H$_2$), 4.19 [4H, dt, J_{syn} 6.9, $J_{syn-anti}$ 1.9, J_{Pt-H} 25, 2H$_{1s}$2H$_{3s}$] and 3.12 [4H, dt, J_{anti} 12.3, J_{Pt-H} 72, 2H$_{1a}$2H$_{3a}$]; δ_C 146.9 (2C, s, 2C$_{dps-6}$), 142.4 (2C, s, 2C$_{dps-4}$), 131.5 (2C, s, 2C$_{dps-3}$), 127.2 (2C, s, 2C$_{dps-5}$), 110.1 (1C, s, J_{Pt-C} 80, 1C$_2$) and 46.8 (4C, s, J_{Pt-C} 238, 2C$_1$2C$_3$).

Perchlorate and hexafluorophosphate salts of complexes **4**, **5**, **6** and **7** were prepared similarly

X-ray data collection and structure refinement

Suitable crystals of **1** were obtained by slow evaporation of solvent from a benzene–diethyl ether solution and sealed in Lindemann capillaries.

Crystal data

C$_{16}$H$_{18}$N$_2$SCl$_2$Pd$_2$, $M=554.1$, triclinic ($P\bar{1}$), $a=8.840(1)$, $b=8.928(1)$, $c=12.317(2)$ Å, $\alpha=98.82(1)$, $\beta=90.46(1)$, $\gamma=95.46(1)$°, $V=956.0(2)$ Å^3, (by least-squares refinement of 30 strong reflections in the range $15<2\theta<30$° automatically centred reflections, $\lambda=0.71073$ Å), $Z=2$, $D_c=1.89$ Mg m^{-3}, $F(000)=520$. Crystal dimensions $0.16\times0.22\times0.11$ mm, μ(Mo Kα) = 2.24 cm^{-1}.

Data collection and processing

Siemens R3m/v four-circle diffractometer, ω–2θ mode with ω scan range 1.50° plus Kα-separation, ω scan speed variable; 2.5 to 15.00°/min in ω, graphite-monochromated Mo Kα radiation; 4533 reflections measured ($1.5\leqslant\theta\leqslant27$°, $h\pm k\pm l$), 4208 unique (merging $R=0.011$, absorption correction was made using an empirical method based on ψ scans ($\psi=0$–360° every 10°) for χ values near 90°), giving 3755 with $I>3.0\sigma(I)$.

Structure analysis and refinement

Direct methods (Pd, S and Cl). Full-matrix least-squares refinements, and difference Fourier maps. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added at calculated positions and included in the structure factor calculations with fixed thermal parameter. Weighting scheme $w=1.00/(\sigma^2(F_o)+0.00137F_o^2)$, with $\sigma(F_o)$ from counting statistics. Final residuals R and R_w: 0.0269 and 0.0339, quality-of-fit indicator = 1.15, largest peak = 0.74 e Å^{-3}, largest difference hole 0.77 e Å^{-3}, for 209 refined parameters. Scattering factors for non-hydrogen atoms were taken from ref. 22 and for hydrogen atoms from ref. 23. Anomalous dispersion correction for Pd, S and Cl was taken from ref. 24.

TABLE 3. Fractional atomic coordinates

Atom	x/a	y/b	z/c
Pd(1)	0.08847(3)	0.32865(3)	0.07705(2)
Pd(2)	−0.29909(2)	0.20287(2)	0.34352(2)
S(1)	−0.35342(9)	−0.1366(1)	0.41369(7)
Cl(1)	0.1661(1)	0.4593(1)	0.25663(7)
Cl(2)	−0.1687(1)	0.2638(1)	0.12222(7)
N(1)	−0.4405(3)	0.0183(3)	0.2580(2)
C(1)	−0.4546(3)	−0.1164(3)	0.2921(3)
C(2)	−0.5505(3)	−0.2399(3)	0.2407(3)
C(3)	−0.6333(4)	−0.2210(4)	0.1497(3)
C(4)	−0.6162(4)	−0.0837(5)	0.1109(3)
C(5)	−0.5188(4)	0.0328(4)	0.1667(3)
N(2)	−0.1293(2)	0.0549(2)	0.3520(2)
C(6)	0.0154(3)	0.0981(3)	0.3294(2)
C(7)	0.1297(3)	0.0023(4)	0.3361(3)
C(8)	0.0945(4)	−0.1386(4)	0.3638(3)
C(9)	−0.0556(4)	−0.1846(3)	0.3836(3)
C(10)	−0.1633(3)	−0.0843(3)	0.3781(2)
C(11)	−0.1868(4)	0.4097(3)	0.4238(3)
C(12)	−0.3430(5)	0.4117(4)	0.4372(4)
C(13)	−0.4393(5)	0.3811(4)	0.3440(4)
C(14)	0.2942(6)	0.3599(7)	−0.0045(5)
C(15)	0.202(1)	0.282(2)	−0.0685(7)
C(16)	0.0655(7)	0.2284(8)	−0.0889(3)

All calculations were performed with SHELX76 [25] and PARST [26] set of programs on the VAX 3400 computer at the 'Centro Interdipartimentale di Servizi per la Diffrattometria a Raggi-X dell' Università di Messina'. The final atomic coordinates for non-hydrogen atoms are given in Table 3.

Supplementary material

H-atom coordinates, anisotropic temperature factors, calculated and observed structure factors (Table SI–SIII) are available from the authors on request.

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