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Reactions of di-2-pyridyl sulfide with the palladium(II) and platinum(II) diene or methoxydiene complexes. Dynamic behaviour of the cationic compounds. Crystal structure of Pd(di-2-pyridyl sulfide)Cl_2

Giuseppe Tresoldi*, Enrico Rotondo, Pasquale Piraino
Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, I-98166 Messina (Italy)

Maurizio Lanfranchi and Antonio Tiripicchio
Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze 78, I-43100 Parma (Italy)

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Abstract

The complexes [M(dps)Cl_2] (M = Pd^{II} (**1**); Pt^{II} (**2**)) and the labile compounds [M(MeOdiene)(dps)Cl] (M = Pd^{II}, MeOdiene = $CH_3OC_8H_{12}$ (**3**) or $CH_3OC_{10}H_{12}$ (**4**); M = Pt^{II}, MeOdiene = $CH_3OC_8H_{12}$ (**5**) or $CH_3OC_{10}H_{12}$ (**6**)) have been synthesized by reaction of dps (dps = di-2-pyridyl sulfide) with [M(diene)Cl_2] (diene = cycloocta-1,5-diene or dicyclopentadiene) and the appropriate chloro-bridged methoxydiene complexes, respectively. The last reactions required drastic conditions. Also the reactions of dps with the solvento species [M(diene)(acetone)$_2$]X_2 and [M(MeOdiene)(acetone)$_2$]X (X = BF_4, PF_6, ClO_4) have been studied and the compounds [M(MeOdiene)(dps)]X (M = Pd^{II}, MeOdiene = $CH_3OC_8H_{12}$ (**7**) or $CH_3OC_{10}H_{12}$ (**8**); M = Pt^{II}, MeOdiene = $CH_3OC_8H_{12}$ (**9**) or $CH_3OC_{10}H_{12}$ (**10**)) were prepared. The structure of **1** has been determined by X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions $a = 9.933(4)$, $b = 14.802(5)$, $c = 8.465(3)$ Å, $\beta = 101.94(2)$°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 2163 observed reflections to R and R' values of 0.0277 and 0.0348, respectively. In the square planar coordination around the Pd atom the dps molecule acts as a chelate ligand through the two pyridinic N atoms and adopts a N,N-inside conformation. The six-membered chelate ring shows a boat conformation with the Pd and S atoms out of the plane through the other four atoms on the same side. Although dissociation in the usual solvents prevents full characterization of **3**–**6** IR spectra suggest that the dps acts as monodentate ligand. The ^1H NMR spectra, at variable temperature, and ^{13}C NMR spectra of **7**–**10** show that the cationic complexes in solution undergo at least two dynamic processes; a ligand site exchange and a boat to boat inversion of the chelate dps ring. The ligand site exchange is fast, in the NMR time scale, at room temperature for palladium complexes and at higher temperature for the platinum complexes and makes equivalent the pyridine rings of dps. This process is interpreted in terms of formation of stereochemically non-rigid five-coordinate intermediates. The boat to boat inversion is fast at room temperature at least for platinum complexes. At low temperature the latter process is absent or occurs at markedly reduced rate for palladium complexes while the slow ligand site exchange results in equilibria between two conformers.

Introduction

In recent years the chemistry of alkyl palladium complexes containing flexible nitrogen donor bidentate ligands has received considerable attention [1]. New and more convenient synthetic routes to $Pd^{II}Me_2$ and $Pd^{II}MeX$ (X = Cl, Br, I) complexes of nitrogen donor ligands [1–3] allow the potential of these complexes for catalytic activity [4] and for development of palladium(IV) chemistry [3, 5] to be studied.

As a continuation of our investigation of the coordination chemistry of flexible bipyridine-like ligands [6] we studied the reactions of diene and methoxydiene complexes of palladium(II) and platinum(II) with dps. This molecule adopts in solution, by rotation around the two S–C bonds, three planar and several twisted conformations [7] and each conformer may act as a ligand towards transition-metal substrates determining different stoicheiometries and stereochemistries of the reaction products. During our recent work [6] on chemistry of systems derived from reaction of [Rh(cod)Cl]$_2$ with dps we have studied the equilibria involving

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*Author to whom correspondence should be addressed.

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the starting materials, the binuclear species $[\{Rh(cod)Cl\}_2(\mu\text{-dps})]$ and the ionic species $[Rh(cod)(dps)]^+$, $[Rh(cod)Cl_2]^-$ and Cl^-. In the binuclear and cationic species dps adopts N-inside, N-outside and N,N-inside conformation, respectively. In this paper we report the syntheses and characterization of dps palladium(II) and platinum(II) complexes and the dynamic behaviour of the cationic complexes containing also the MeOdiene moiety. The principal aim of this study is a further investigation of the coordination chemistry of dps and similar flexible ligands [8, 9] as well as the dynamic processes arising from the presence of such ligands [1, 6].

Results and discussion

Reactions of dps with diene and methoxydiene complexes

As shown in Scheme 1 $[M(dps)Cl_2]$ and $[M(MeOdiene)(dps)Cl]$ were prepared by reactions of dps (di-2-pyridyl sulfide) with the complexes $[M(diene)Cl_2]$ (diene = cycloocta-1,5-diene and dicyclopentadiene) and $[M(MeOdiene)Cl]_2$ (MeOdiene = $CH_3OC_8H_{12}$, $CH_3OC_{10}H_{12}$).

$$M(LL')Cl_2 + dps \longrightarrow M(dps)Cl_2 + LL'$$

$$[M(MeOdiene)Cl]_2 + dps \longrightarrow [M(MeOdiene)(dps)Cl]$$

Scheme 1. $M = Pd^{II}$, LL' = cycloocta-1,5-diene (cod), dicyclopentadiene (dcp) or $L = L' = C_6H_5CN$ (**1**); $M = Pt^{II}$, LL' = cod, dcp or $L = L' = Me_2SO$ (**2**); $M = Pd^{II}$, MeOdiene = $CH_3OC_8H_{12}$ (**3**); $M = Pd^{II}$, MeOdiene = $CH_3OC_{10}H_{12}$ (**4**); $M = Pt^{II}$, MeOdiene = $CH_3OC_8H_{12}$ (**5**); $M = Pt^{II}$, MeOdiene = $CH_3OC_{10}H_{12}$ (**6**).

The first reaction, in dichloromethane solution, gave slowly red–orange or yellow crystals of **1** and **2** respectively when the appropriate palladium or platinum diene complexes were used. **1** and **2** can also be obtained more rapidly as yellow solids by reaction of dps with $[Pd(C_6H_5CN)_2Cl_2]$ and $[Pt(Me_2SO)_2Cl_2]$, respectively.

The preparation of the labile complexes $[M(MeOdiene)(dps)Cl]$ is difficult. The reported synthetic routes to pyridine or bipyridine methoxydiene palladium and platinum complexes involve bridge splitting reactions on chloro-bridged methoxydiene dimers by nitrogen donor ligands generally at low temperature [10]. After several unsuccessful experiments in chlorinated solvents at low temperature we synthesized **3**–**6** by dissolution of the appropriate methoxydiene complexes in net dps.

Compounds **1** and **2** are slightly soluble in chloroform and dichloromethane and stable for several months in the solid state and for some weeks in solution. In accordance with the coordination of both pyridine N atoms [6, 11] the IR spectra show a strong band at *c*. 1584 cm^{-1}, assigned to the pyridine-ring stretching, significantly shifted to higher frequencies from its position in the free-ligand spectrum (1572 cm^{-1}). Two very strong bands at *c*. 775 and 765 cm^{-1}, characteristic of the out-of-plane CH deformation, suggest the puckered structure of the chelate ring and two in the range 355–325 cm^{-1} indicate the presence of the terminal *cis* chlorine atoms. The ^1H NMR spectra of **1** and **2** appear as a single ABMX system [6, 7, 12] consistent with the presence of two equivalent pyridine rings. Furthermore the shifts of the H^6 pyridine proton resonances (*c*. 0.65 ppm) and other pyridine signals (*c*. 0.3 ppm), downfield from free ligand values, indicate the N,N′-chelation of the dps ligand.

Description of the structure of the complex [Pd(dps)Cl₂] (1)

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. The Pd atom exhibits an almost ideal square planar geometry involving two Cl atoms (Pd–Cl(1) = 2.286(1) and Pd–Cl(2) = 2.296(1) Å), the two pyridinic N atoms of the dps molecule acting as a chelating ligand (Pd–N(1) = 2.034(3) and Pd–N(2) = 2.028(3) Å). In fact the bond angles are very close to 90° and the displacements of the Pd, Cl(1), Cl(2), N(1) and N(2) atoms from the mean plane passing through them are negligible, namely −0.004(1), 0.008(1), −0.001(1), −0.008(3) and 0.053(3) Å. 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 (88.6°). The six-membered chelate PdN(1)C(1)SC(6)N(2) ring is in a boat conformation; the mean plane passing through N(1)C(1)C(6)N(2) atoms leaves the Pd and S atoms 0.950(1) and 0.821(1) Å out of the plane on the same side and the dihedral angle between the two PdN(1)C(1)S and PdN(2)C(6)S moieties is 64.8(1)°.

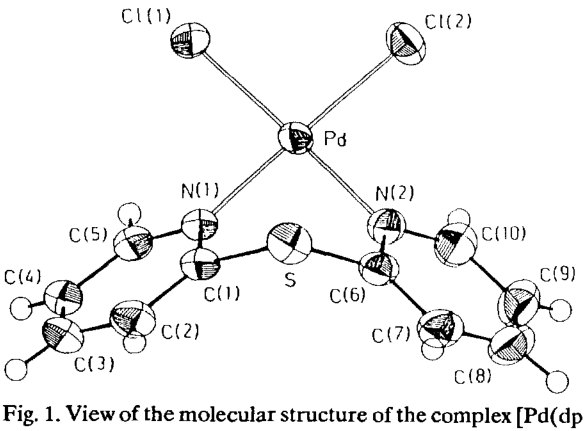


Fig. 1. View of the molecular structure of the complex $[Pd(dps)Cl_2]$ (**1**) with the atomic numbering scheme.

TABLE 1. Important interatomic distances (Å) and angles (°) for complex **1**

Pd–Cl(1)	2.286(1)	C(3)–C(4)	1.364(6)
Pd–Cl(2)	2.296(1)	C(4)–C(5)	1.371(5)
Pd–N(1)	2.034(3)	N(1)–C(5)	1.342(4)
Pd–N(2)	2.028(3)	N(2)–C(6)	1.344(5)
N(1)–C(1)	1.341(4)	N(2)–C(10)	1.341(5)
S–C(1)	1.772(3)	C(6)–C(7)	1.372(5)
S–C(6)	1.778(3)	C(7)–C(8)	1.368(6)
C(1)–C(2)	1.375(5)	C(8)–C(9)	1.345(7)
C(2)–C(3)	1.386(5)	C(9)–C(10)	1.384(5)
Cl(1)–Pd–Cl(2)	91.5(1)	C(3)–C(4)–C(5)	119.2(3)
Cl(1)–Pd–N(1)	89.9(1)	C(4)–C(5)–N(1)	122.3(3)
Cl(2)–Pd–N(2)	90.1(1)	S–C(6)–C(7)	119.0(3)
N(1)–Pd–N(2)	88.6(1)	S–C(6)–N(2)	118.9(2)
C(1)–N(1)–C(5)	118.3(3)	N(2)–C(6)–C(7)	122.0(3)
Pd–N(1)–C(1)	120.6(2)	C(6)–N(2)–C(10)	118.5(3)
Pd–N(1)–C(5)	121.0(2)	Pd–N(2)–C(6)	120.6(2)
C(1)–S–C(6)	99.6(2)	Pd–N(2)–C(10)	120.9(2)
N(1)–C(1)–C(2)	122.1(3)	C(6)–C(7)–C(8)	118.9(3)
S–C(1)–N(1)	119.0(2)	C(7)–C(8)–C(9)	119.6(4)
S–C(1)–C(2)	118.9(3)	C(8)–C(9)–C(10)	119.9(4)
C(1)–C(2)–C(3)	118.7(3)	N(2)–C(10)–C(9)	121.1(3)
C(2)–C(3)–C(4)	119.2(3)		

The structural parameters in the dps molecule are quite regular. In particular the C–S bonds, 1.772(3) and 1.778(3) Å, are in good agreement with those expected for C(sp^2)–S bonds, *c.* 1.77 Å and with those found in the monoprotonated dps (1.75(2) Å), showing an almost planar N,N-inside conformation, in the crystal structure of $[dps]_2[UO_2Cl_4]$ [13]. It should be noted that in $dpsH^+$ the value of the CSC angle, 108(1)°, is very close to the tetrahedral one, while in **1** the value of this angle, 99.6(2)°, is much narrower probably because of the necessities of chelation and the N...N distance, 2.63 Å, is shorter than in **1**, 2.836(4) Å, because it is probably involved in an intramolecular hydrogen bond.

To the best of our knowledge **1** is the first complex of dps structurally characterized. The structures of some palladium complexes with comparable flexible ligands, having pyridyl or pyrazolyl groups, are known [14, 15], in which the chelation ring exhibits a boat conformation. In $[Pd(dpk \cdot H_2O)Cl_2]$ [15b] ($dpk \cdot H_2O$ = dihydroxy-di-2-pyridylmethane) the Pd–Cl, 2.296(3) and 2.301(3) Å, the Pd–N, 2.014(6) and 2.032(6) Å, bond distances and the N–Pd–N bite angle, 87.1(2)°, are quite similar, while the py–C–py angle, 107.0(6)°, does not seem be influenced by chelation. Also in $[PdCl_2\{(CH_3)_2C(pz)_2\}]$, in which the pyrazolyl groups substitute the pyridyl rings, the Pd–Cl, 2.297(1) and 2.282(1) Å, the Pd–N, 2.018(3) and 2.030(3) Å, bond distances and the N–Pd–N bite angle, 87.8(1)°, are quite comparable to the values found in **1**, and the N–C–N angle is still close to the tetrahedral value, 106.4(2)° [14].

Characterization of methoxydiene derivatives

Compounds **3**–**6** are stable in the solid state for several months but in solution decompose rapidly into the starting materials. They analyze as [M(MeOdiene)(dps)Cl] and in the IR spectra the ring bands of the coordinated ligand are generally doubled, one band being nearly coincident with the corresponding one of the free ligand (Table 2). These results are interpreted in terms of the presence of both coordinated and uncoordinated pyridine residues on the same ligand molecule [16]. Furthermore broad bands in the ranges 1100–1083 and 315–290 cm^{-1} indicate the presence of the CH_3O group [10] and chlorine atom (*trans* carbon-metal σ bond), respectively. The fast dissociation in all solvents even at low temperature prevented ^1H NMR measurements of **3**–**6** and on the basis of the available data we suggest that in these labile 1:1 adducts dps acts as a monodentate ligand [8].

Reactions of dps with solvento species

As shown in Scheme 2 the reactions of the solvento species $[M(MeOdiene)(acetone)_2]X$ (X = BF_4, PF_6, ClO_4) with dps gave the complexes [M(MeOdiene)(dps)]X.

$$1/2[M(MeOdiene)Cl]_2 + AgX + dps \longrightarrow [M(MeOdiene)(dps)]X$$

Scheme 2. M = Pd^{II}, MeOdiene = $CH_3OC_8H_{12}$ (**7**); **M = Pd^{II}**, MeOdiene = $CH_3OC_{10}H_{12}$ (**8**); M = Pt^{II}, MeOdiene = $CH_3OC_8H_{12}$ (**9**); M = Pt^{II}, MeOdiene = $CH_3OC_{10}H_{12}$ (**10**).

The reactions proceed smoothly at room temperature and complexes **7**–**10** are obtained in high yields when an excess of dps is used whereas the formation of complexes $[M(diene)(dps)]X_2$ from $[M(diene)(acetone)_2]X_2$ is accompanied by decomposition which leads to unsatisfactory analytical results.

Compounds **7**–**10** are soluble in acetone and methanol and moderately soluble in chloroform and dichloromethane, stable in the solid state for several weeks and in solution for several hours.

The IR spectra of compounds **7**–**10** show the bands characteristic of the dps ligand and O–CH_3 group (Table 2). The solution structures are assigned on the basis of conductivity measurements, UV, ^1H and ^{13}C NMR spectra [10].

Conductivity measurements in acetone or methanol solution indicate they are univalent electrolytes. However in solvent of lower dielectric constant the Λ_M values decrease considerably with increasing concentration, e.g. the molar conductivity of **8** in CH_2Cl_2 drops from 69 to 60 and to 40 S cm^2 mol^{-1} when the concentration is increased from 10^{-4} to 2×10^{-4} and to 10^{-3} mol dm^{-3}. Such concentration influence results from extensive ion-pairing in chlorinated solvents

TABLE 2. Analytical[a] and characteristic IR data[b]

Compounds	Analysis (%)					IR (cm^{-1})	
	C	H	N	S	Cl	$\nu(OCH_3)$	Selected dps bands
$[Pd(dps)Cl_2]$ (**1**)	32.90	2.30	7.65	8.80	19.50		1582s, 778vs, 765vs, 354vs[c],
	(32.86)	(2.21)	(7.67)	(8.77)	(19.40)		328vs[c]
$[Pt(dps)Cl_2]$ (**2**)	26.50	1.80	6.15	7.10	15.70		1586s, 775vs, 765vs, 339vs[c],
	(26.44)	(1.78)	(6.17)	(7.06)	(15.61)		326vs[c]
[Pd(MeOcod)(dps)Cl] (**3**)	44.90	5.10	3.75	4.25	9.50	1085br	1584vs, 1573s[d], 1556m, 776vs,
	(44.82)	(5.10)	(3.73)	(4.27)	(9.45)		768vs[d], 315br[c]
[Pd(MeOdcp)(dps)Cl] (**4**)	51.15	4.70	5.75	6.55	7.15	1096vs	1585s, 1571s[d], 1558s, 779s,
	(51.13)	(4.70)	(5.68)	(6.50)	(7.19)	1081vs	770s[d], 762s, 295s[c]
[Pt(MeOcod)(dps)Cl] (**5**)	40.70	4.10	5.05	5.70	6.30	1088vs	1586vs, 1572s[d], 1559s, 772br,
	(40.90)	(4.15)	(5.02)	(5.75)	(6.35)	1079s	303s[c]
[Pt(MeOdcp)(dps)Cl] (**6**)	43.40	4.05	4.85	5.60	6.10	1100m	1605s, 1572vs[d], 1560s, 770ms[d],
	(43.34)	(3.98)	(4.81)	(5.51)	(6.09)	1083ms	753s, 748s, 290br[c]
$[Pd(MeOcod)(dps)]BF_4$ (**7**)	43.90	4.35	5.40	6.15		1083s[e]	1583s, 788vs, 774s
	(43.83)	(4.45)	(5.38)	(6.16)		1061s[e]	
$[Pd(MeOdcp)(dps)]BF_4$ (**8**)	46.40	4.25	5.15	5.90		1084s[e]	1584s, 791vs, 773vs
	(46.31)	(4.26)	(5.14)	(5.89)		1062s[e]	
$[Pt(MeOcod)(dps)]BF_4$ (**9**)	37.40	3.85	4.50	5.30		1096m[e]	1583s, 780vs, 775vs
	(37.45)	(3.80)	(4.60)	(5.26)		1078ms[e]	
						1058s[e]	
$[Pt(MeOdcp)(dps)]BF_4$ (**10**)	39.90	3.65	4.50	5.10		1095vs[e]	1588s, 781vs, 771vs
	(39.82)	(3.66)	(4.42)	(5.06)		1088vs[e]	
						1079vs[e]	

[a] Required values are given in parentheses. [b] Nujol mulls. [c] ν(M–Cl). [d] Assigned to free dps. [e] Hexafluorophosphate salt.

[17–19] but the formation of non-conducting species with BF_4 anion may also contribute [17, 19].

The electronic spectra in methanol of all the cationic complexes obey the Lambert–Beer law in the range 10^{-4}–10^{-5} mol dm^{-3} whereas slight deviations for **7** and **8** are observed in CH_2Cl_2 (see 'Experimental').

The downfield shifts of proton (Table 3) and carbon (Table 4) pyridine resonances relative to the corresponding signals of free ligand indicate the N,N′-chelation of the dps ligand. A comparison with the ^1H NMR of compound **1** shows that the H^3, H^4 and H^5 pyridine resonances are shifted downfield in the compounds **7** and **8**. A parallel trend is observed when the averaged values of H^3, H^4 and H^5 signals of the non-equivalent pyridine ring of **9** and **10** are compared with those of **2**.

In our opinion these shifts indicate essentially the increased transfer of electron density from the ligand to the metal in cationic compounds [6].

Dynamic behaviour in solution

The broadening and coalescence of the signals of pyridine protons, at variable temperature, suggest that complexes **7–10** undergo dynamic processes in solution.

In spite of the asymmetric nature of the MeOdiene moiety, the ^1H NMR spectra in the pyridine region of compounds **7** and **8**, at room temperature, are consistent with a single ABMX system (Fig. 2(a)) and the ^{13}C NMR spectra show only four signals for C^3, C^4, C^5 and C^6 pyridine carbons (Fig. 3(a)). In contrast when platinum is present in the chelate ring (**9** and **10**) the ^1H NMR (Fig. 2(b)) and ^{13}C NMR (Fig. 3(b)) show unambiguously that the two pyridine rings are no longer equivalent. The resonances at 8.68 (**9**) and 8.65 (**10**) ppm in the ^1H NMR and 152.0 (**9**) and 151.4 (**10**) ppm in the ^{13}C NMR are assigned to H^6 protons and C^6 carbons *cis* to the platinum–olefin η^2-bond. In our opinion the particularly high field shift of the H^6 proton resonances, compared with that of **2** (9.30 ppm), is the result of combined electronic and magnetic effects.In fact the *trans* influence of the carbon σ bonded and the *cis* position of the C=C double bond work in concert.

When the temperature is raised the pyridine proton signals of the platinum compounds **9** and **10** coalesce at *c.* 330 K and are consistent with two equivalent pyridine rings at higher temperature.

These data appear to result essentially from two processes; a ligand site exchange (*cis–trans* isomerization) [20] and a boat to boat inversion of a six-membered metallocycle [1, 21].

Since no dissociation is detected in the UV spectra of **7–10** an associative mechanism may be involved to explain the lower energy ligand site exchange for the palladium complexes. Association of the solvent or, in solvent of low dielectric constant, the counteranion may

TABLE 3. Selected ^{1}H NMR data[a]

Compound	Solvent	T (K)	MeOdiene protons[b]				dps protons[c]			
			$-OCH_3$	–CHOMe	HC=		H^6	H^4	H^3	H^5
1	$CDCl_3$	310					9.17	7.87	7.81	7.43
2	$CDCl_3$	310					9.30	7.82	7.73	7.40
7	$CDCl_3$	310	3.18	3.65	6.31	5.31	8.74	7.92	7.86	7.56
	$CDCl_3$	220	3.14[d]	3.39[d]	6.43[d]	5.20[d]	8.76[f]	8.02[f, h]		7.67[i]
			3.35[e]	3.92[e]	5.94[e]	5.70[e]	8.58[g]	7.86[g, h]		
	$(CD_3)_2CO$	310	3.10	3.60	6.42	5.54	8.83	8.20	8.11	7.72
	$(CD_3)_2CO$	220	3.02[d]	3.47[d]	6.46[d]	5.40[d]	9.08[f]	8.27[f]	8.20[f]	7.80[f]
			3.25[e]	3.87[e]	6.17[e]	5.80[e]	8.70[g]	8.16[g]	8.07[g]	7.66[g]
8[k]	$CDCl_3$	310	2.90	3.77	7.15	5.70	8.79	7.95	7.85	7.60
	$CDCl_3$	220	2.60[d]	3.58[d]	7.23[d]	5.55[d]	8.85[f]	8.05[f]	7.99[f]	7.67[i]
			3.50[e]	4.11[e]	6.68[e]	6.01[e]	8.57[g]	7.92[g]	7.87[g]	
	$(CD_3)_2CO$	310	2.80	3.74	7.24	5.86	8.84	8.16	8.11	7.73
	$(CD_3)_2CO$	220	2.72[d]	3.68[d]	7.22[d]	5.78[d]	8.86[f]	8.13[f, h]		7.67[i]
			3.25[e]	4.12[e]	6.78[e]	6.24[e]	8.76[g]	8.07[g, h]		
9	$(CD_3)_2CO$	310	3.00	3.75	5.64(96)		8.90[f](36.5)	8.32[f]	8.25[f]	7.92[f]
					4.75(72)		8.68[g]	8.17[g]	8.09[g]	7.70[g]
	$(CD_3)_2CO$	220	2.96	3.72	5.63(96)		8.96[f]	8.30[f, h]		7.92[f]
					4.73(73)		8.72[g]	8.22[g]	8.16[g]	7.72[g]
	$(CD_3)_2SO$	350	2.90	3.45	5.42(84)		8.75	8.08	8.00	7.65
					4.82(80)					
10	$(CD_3)_2CO$	310	2.70	3.53	6.32(100)		9.00[f]	8.28[f, h]		7.95[f]
					5.28(78)		8.65[g]	8.23[g, h]		7.75[g]
	$(CD_3)_2CO$-$CD_3C_6D_6$[l]	385	2.71	3.48	5.95(102)		8.47	7.66[g]		7.30
					4.95(80)					

[a] Recorded at 80 MHz; chemical shift in ppm and J(Pt–H) (Hz) in parentheses; $SiMe_4$ as internal standard. [b] The methyl protons are observed as singlet; the olefinic protons and the proton on the methoxyl bearing carbon are observed as broad signals. [c] The protons of free (ref. 6) and coordinated dps give rise to ABMX spectra in which the proton resonances appear as multiplet. [d] Signals of the dominant isomer. [e] Signals of the minor isomer. [f] Pyridine protons *cis* metal–carbon σ-bond. [g] Pyridine protons *cis* metal–olefin η^2-bond. [h] Broad signals of H^3 and H^4 pyridine protons. [i] Broad signals of H^5 pyridine protons. [k] The bridge CH_2 protons of dicyclopentadiene give rise to AB system with chemical shifts 1.16 and 1.6 ppm and $J = 10.2$ Hz in $CDCl_3$ at 310 K. [l] 1:1 ratio.

TABLE 4. Selected ^{13}C NMR data[a]

Compounds	cod carbons				dps carbons			
	olefinic	–CH–OMe	$-OCH_3$	$-CH_2$	C^6	C^4	C^3	C^5
dps					150.9	138.1	126.6	122.8
7	111.4	82.7	56.3	34.8	152.9	141.8	131.6	127.2
	106.3			33.5				
				31.1				
				27.1				
8	115.3	83.6	55.2	60.7[b] 58.9[b]	153.5	141.8	131.6	127.3
	114.5			56.1[b] 43.4[b]				
				40.2[b]				
				36.7 31.9				
9	94.4	79.6	61.0	36.4	153.4	142.6	132.4	128.0
	90.4			34.3	152.0	141.8	131.2	128.0
				32.3				
				27.9				
10	100.5	85.1	57.3	55.7[b] 55.8[b]	152.9	141.7	131.6	127.7
	95.8			42.1[b] 40.0[b]	151.4	140.9	130.4	127.2
				39.0[b]				
				36.7 33.0				

[a] Recorded at 75.56 MHz and 310 K in $(CD_3)_2CO$; chemical shift in ppm; $SiMe_4$ internal standard. [b] CH signals.

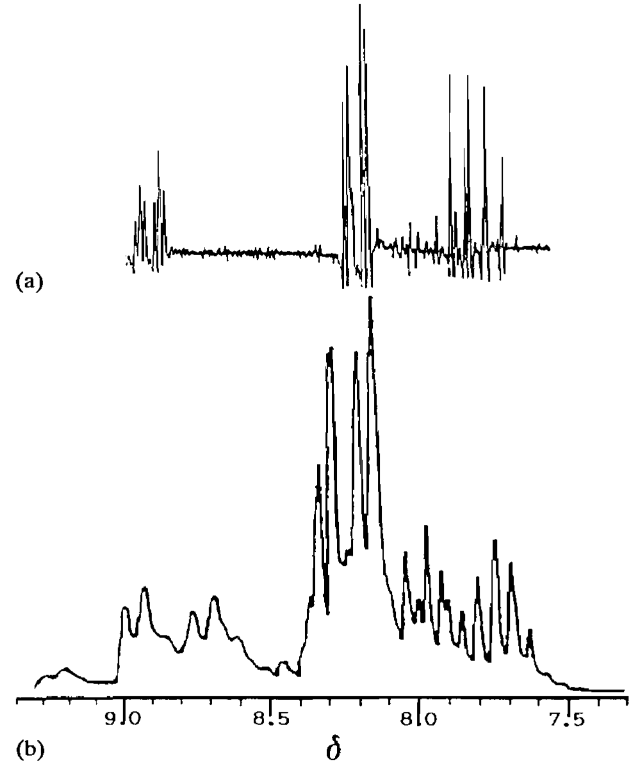


Fig. 2. ^{1}H NMR spectra (pyridine region) in acetone, at 310 K, of $[Pd(CH_3OC_8H_{12})(dps)]BF_4$ (a) and $[Pt(CH_3OC_8H_{12})(dps)]BF_4$ (b).

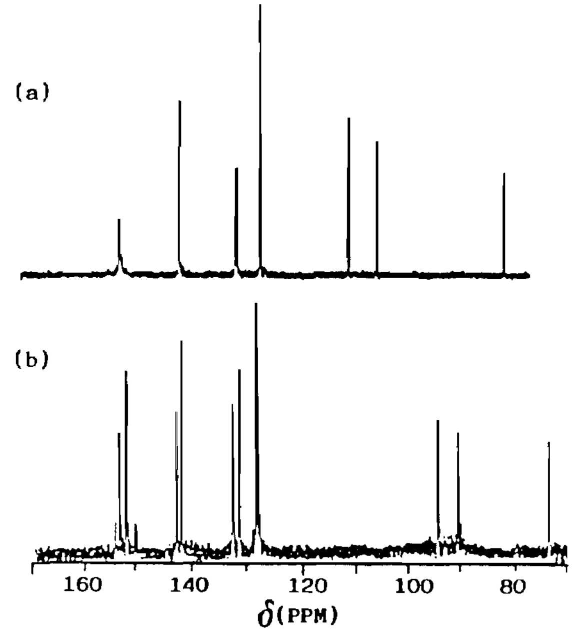
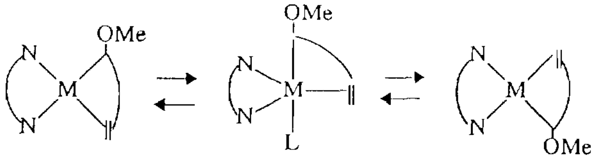


Fig. 3. ^{13}C NMR spectra (range 60–170 ppm) in acetone, at 310 K, of $[Pd(CH_3OC_8H_{12})(dps)]BF_4$ (a) and $[Pt(CH_3OC_8H_{12})(dps)]BF_4$ (b).

give stereochemically non-rigid five-coordinate intermediates [22] which, as depicted in Scheme 3, undergo Berry pseudorotation [17, 19, 20, 23].



Scheme 3. $M=Pd^{II}$ or Pt^{II}, L = solvent or counteranion.

The downfield shifts of H^{6} pyridine resonances in compounds **7** and **8**, relatively to the free ligand, are small (0.2 and 0.25 ppm, respectively) in comparison with that found in complex **1** (0.63 ppm). The same trend is observed when the averged H^{6} resonances of **9** and **10** are compared with that of **2**.

The H^{6} pyridine proton signals are also affected by the nature of the central metal, the solvent and, in $CDCl_3$, by the temperature. Upfield shifts are observed on going from Pd to Pt, from acetone to $CDCl_3$ and in $CDCl_3$ from room to low temperature (Table 3). In our opinion these shifts indicate the increasing of C=C shielding effects on H^{6} protons [6] and the formation of non-conducting species [17] (by association of anion) which decreases the transfer of electron density from the ligand to the metal.

Also the fast exchange between coordinated and free ligand observed at room temperature upon addition of dps to palladium complexes can be accommodated in the association process. This exchange requires the breaking of at least one of the Pd–N bonds probably through a short-lived intermediate in which both the entering and leaving dps ligands are σ-N monodentate to the palladium center [6, 17, 19], although uncommon σ-N coordination of bipyridine like ligands is not unknown [8].

The rate of the ligand site exchange for **7** and **8** is fast at room temperature but at 220 K is considerably depressed and the proton signals of two non-equivalent pyridine rings appear in the ^{1}H NMR spectrum. At this temperature the proton signals of olefinic, $-OCH_3$ and –CHOMe groups indicate the presence of two conformers characterized by the same set of pyridine protons which in turn arise from two non-equivalent pyridine rings. Thus at room temperature (Fig. 4(a)), the ^{1}H NMR spectrum of $[Pd(CH_3OC_{10}H_{12})dps]BF_4$ shows signals arising from equivalent pyridine rings as an ABMX system. The olefinic protons appear at 7.15 and 5.70 ppm while protons of – CHOMe and $-OCH_3$ groups appear at 3.77 and 2.90 ppm, respectively. At 269 K (Fig. 4(b)) the signals coalesce and at 220 K (Fig. 4(c)) the signals of olefinic protons (7.23, 6.68, 6.01 and 5.55 ppm) and of $-OCH_3$ (2.60 and 3.50 ppm) and – CHOMe (3.58 and 4.11 ppm) groups indicate the presence of the above cited isomers (5:2 ratio).

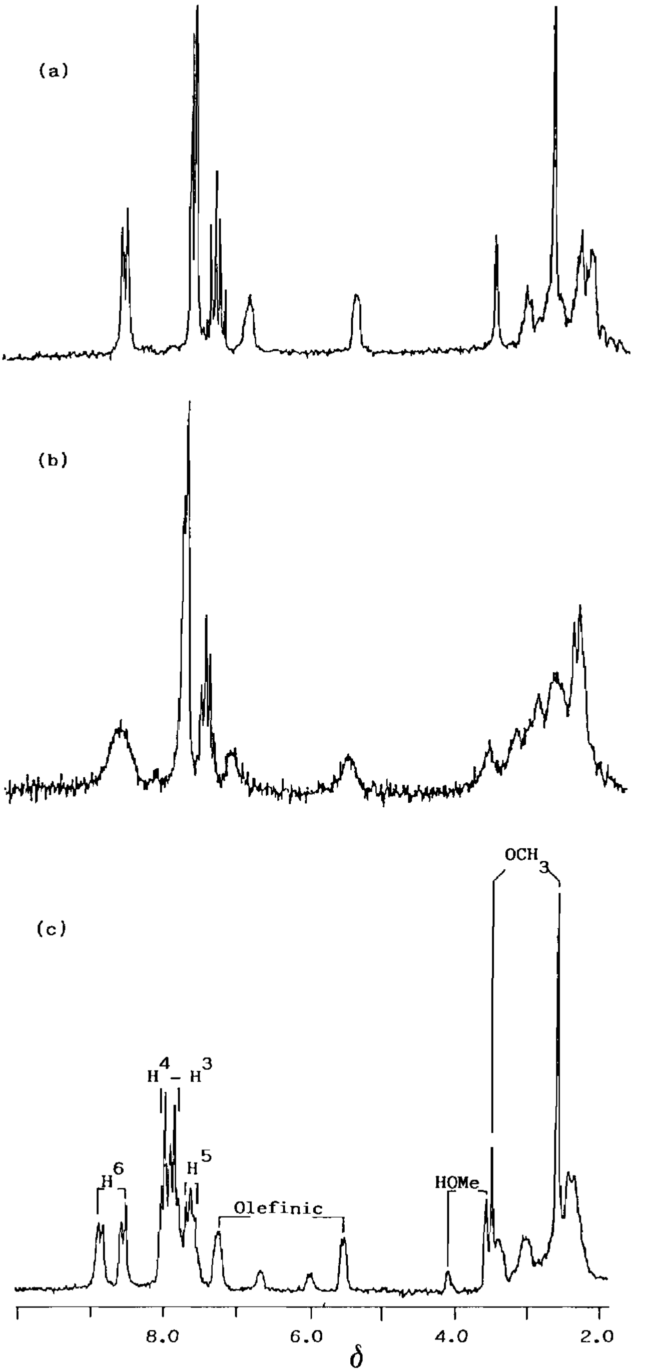


Fig. 4. ^1H NMR spectra in $CDCl_3$ of $[Pd(CH_3OC_{10}H_{12})(dps)]BF_4$ (the signals of the solvent are suppressed for clarity) at: (a) 310 K, (b) 269 K, (c) 220 K.

We were unable to find a coalescence temperature of an independent boat to boat inversion. On the other hand investigation of molecular models indicate that this process is sterically hindered owing to an unfavourable interaction between the H^6 pyridine proton and the hydrogen on the carbon σ bonded to the palladium atom, in the planar intermediate transition state of the boat to boat inversion. On this basis we suggest that the boat to boat inversion is absent or occurs at a markedly reduced rate at 220 K for palladium complexes (**7** and **8**) while the slow ligand site exchange results in equilibria between the boat isomers A and B (Fig. 5).

It is worth noting that the equivalence of the two pyridine rings at room temperature and the presence of the isomers A and B when the temperature is lowered from the fast to the slow exchange limit appear to rule out any dissociative mechanism for *cis–trans* isomerization, involving either breaking of one of the Pd–N bonds or complete dissociation of dps.

Inspection of molecular models suggests that A is the predominant isomer and that the proton signals of $-OCH_3$, $-CHOMe$ and one HC= group experience shielding from the ring current of the *cis* pyridine ring.

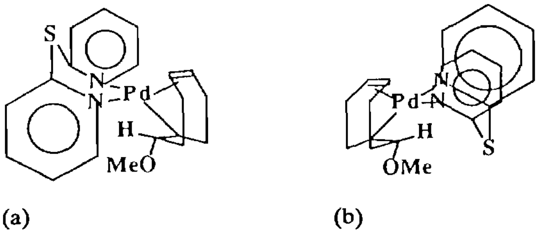
For the platinum compounds **9** and **10** we suggest that the ligand site exchange is slow at room temperature. Thus at 310 K the pyridine protons signals indicate the presence of two non-equivalent pyridine rings (Fig. 2(b)) and at 200 K broaden (probably the coalescence of the boat to boat inversion occurs at lower temperature).

The last observation and the absence of isomers in the slow exchange region suggest that boat to boat inversion is fast at room temperature at least for platinum complexes.

The presence of Pt–olefinic proton coupling constants even in a high-temperature-limiting-spectrum rules out any dissociative mechanism involving breaking of the Pt–olefinic carbons bond.

The Pt–H^6 coupling constants are generally masked by line broadening but at room temperature, in acetone, no exchange between free and coordinated ligand is observed upon addition of dps to platinum complexes. The last observation would rule out a breaking of the Pt–N bond [6, 17].

On the other hand when the ^1H NMR spectra of **9** are recorded in DMSO, which generally promotes the dissociative mechanism [20], a lower coalescence temperature and a fast exchange between free and coordinate ligand are observed.



(a) (b)

Fig. 5. Boat isomers of **7**.

Experimental

The compounds $[Pd(C_6H_5CN)_2Cl_2]$ [24], $[Pt\{(CH_3)_2SO\}_2Cl_2]$ [25], $[Pd(1,5\text{-}C_8H_{12})Cl_2]$ [26], $[Pd(C_{10}H_{12})Cl_2]$ [10c], $[Pt(1,5\text{-}C_8H_{12})Cl_2]$ [26], $[Pt(C_{10}H_{12})Cl_2]$ [26], $[Pd(CH_3OC_8H_{12})Cl]_2$ [27], $[Pd(CH_3OC_{10}H_{12})Cl]_2$ [28], $[Pt(CH_3OC_8H_{12})Cl]_2$ [27], $[Pt(CH_3OC_{10}H_{12})Cl]_2$ [27] and di-2-pyridyl sulfide [7] were prepared by published methods. All other reagents and solvents were used as supplied. Elemental analyses were carried by the Microanalytical Laboratory of Organic Chemistry Institute of Milan and by the Analytische Laboratorien Malissa and Reuter, Elbach, FRG. Conductivity measurements were done on a conductivity meter CDM 3 Radiometer Copenhagen. IR spectra were recorded on Perkin-Elmer 783 and FT-IR 1720 X machines, in nujol mulls, using CsI plates; electronic absorption spectra on a Perkin-Elmer Lambda 5 spectrophotometer; ^1H and ^{13}C NMR spectra on a Bruker Sy 80 and Gemini 300 Varian spectrometers.

Analytical and characteristic IR data are given in Table 2. ^1H and ^{13}C NMR data are given in Tables 3 and 4, respectively.

Preparation

[Pd(dps)Cl₂] (1) and [Pt(dps)Cl₂] (2)

A dichloromethane solution (10 cm^3) of dps (225 mg, 1.2 mmol) was added to a solution (30 cm^3) of $Pd(diene)Cl_2$ or $Pt(diene)Cl_2$ complex (1 mmol) in the same solvent. Red–orange crystals of **1** or yellow crystals of **2** were formed after 2–4 days. The crystals were washed with diethyl ether and dried on P_4O_{10}. Yields **1**: 328 mg, 90%; **2**: 386 mg, 85%. Complexes **1** and **2** were obtained rapidly as yellow solids by reaction of dps with $[Pd(C_6H_5CN)_2Cl_2]$ or $[Pt\{(CH_3)_2SO\}_2Cl_2]$ in C_6H_6 and CH_2Cl_2, respectively.

[Pd(MeOcod)(dps)Cl] (3), [Pd(MeOdcp)(dps)Cl] (4), [Pt(MeOcod)(dps)Cl] (5) and [Pd(MeOdcp)(dps)Cl] (6)

0.5 mmol of chloro-bridged methoxydiene was added to 5 cm^3 of dps. The mixture was stirred with gentle heating (30–40 °C) for *c*. 5 h to achieve complete dissolution of the dimer. The resulting solution was allowed to stand at −15 °C overnight. The solid mixture obtained was washed with diethyl ether until the washing liquids were colorless. The pale-yellow product was dried on P_4O_{10}. Yields **3**: 96 mg, 41%; **4**: 123 mg, 50%; **5**: 98 mg, 35%; **6**: 116 mg, 40%.

[Pd(MeOcod)(dps)]BF₄ (7), [Pd(MeOdcp)(dps)]BF₄ (8), [Pt(MeOcod)(dps)]BF₄ (9) and [Pt(MeOdcp)(dps)]BF₄ (10)

To a stirred acetone solution (10 cm^3) of the 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*. 70 cm^3) of dps (376 mg, 2 mmol). The white or pale yellow precipitate obtained was collected, washed with diethyl ether and dried *in vacuo* on P_4O_{10}. Yields **7**: 416 mg, 80%; **8**: 462 mg, 85%; **9**; 426 mg, 70%; **10**: 443 mg, 70%. Molar conductivities, at 20 °C, of 5×10^{-4} mol dm^{-3} acetone solutions: 156 (**7**), 150 (**8**), 145 (**9**), 140 (**10**) S cm^2 mol^{-1}; of 10^{-3} and 10^{-4} mol^{-1} dm^{-3} methanol solutions: 86 and 100 (**7**), 85 and 98 (**8**), 70 and 85 (**9**); 68 and 80 (**10**) S cm^2 mol^{-1}, respectively; of 10^{-3} and 10^{-4} dichloromethane solutions: 39 and 70 (**7**), 38 and 69 (**8**), 30 and 47 (**9**), 28 and 46 (**10**) S cm^2 mol^{-1}, respectively. UV absorption λ_{max} (nm) (MeOH) (ϵ(dm^{-3} mol^{-1} cm^{-1})) **7**: 280 (8500), **8**: 284 (7900), **9**: 280 (5600), **10**: 282 (5500).

Perchlorate and hexafluorophosphate salts of complexes **7–10** were prepared similarly.

Crystal structure determination of the complex [Pd(dps)Cl₂] (1)

A crystal of approximate dimensions 0.18 × 0.23 × 0.30 mm was used for the X-ray analysis.

Crystal data. $C_{10}H_8Cl_2N_2PdS$, $M=365.55$, monoclinic, space group $P2_1/n$, $a=9.933(4)$, $b=14.802(5)$, $c=8.465(3)$ Å, $\beta=101.94(2)°$, $U=1217.7(8)$ Å^3 (by least-squares refinement from the θ values of 30 accurately measured reflections with θ in the range 13.3–17.9°, $\lambda=0.71073$ Å), $Z=4$, $D_c=1.994$ g cm^{-3}, $F(000)=712$, μ(Mo Kα) = 20.84 cm^{-1}.

Data were collected at room temperature on a Philips PW 1100 single-crystal diffractometer using the graphite monochromated Mo Kα radiation and the $\theta/2\theta$ scan mode. All reflections with θ in the range 3–27 ° were measured; of 2669 independent reflections, 2163, having $I>2\sigma(I)$, were considered observed and used in the analysis. The individual profiles were analyzed according to Lehmann and Larsen [29]. The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during data collection. No correction for absorption effects was applied.

The structure was solved by Patterson and Fourier methods, and refined by full-matrix least-squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all non-hydrogen atoms. All the hydrogen atoms were clearly located in the final ΔF map and refined isotropically. A weighting scheme $w=[\sigma^2(F_o)+gF_o^2]^{-1}$ was used in the last cycles of refinement; at convergence the g value was 0.0013. Final R and R' values were 0.0277 and 0.0348. The SHELX-76 and SHELXS-86 systems of computer programs were used [30]. Atomic scattering factors, cor-

TABLE 5. Fractional atomic coordinates ($\times 10^4$ and $\times 10^5$ for Pd) with e.s.d.s in parentheses for the non-hydrogen atoms of complex **1**

Atom	*x/a*	*y/b*	*z/c*
Pd	34642(2)	10702(1)	6297(3)
Cl(1)	3006(1)	−140(1)	−1073(1)
Cl(2)	3570(1)	2022(1)	−1482(1)
S	1637(1)	1487(1)	3309(1)
N(1)	3381(3)	252(2)	2538(3)
N(2)	3800(3)	2130(2)	2181(3)
C(1)	2568(3)	458(2)	3568(4)
C(2)	2409(4)	−113(3)	4797(4)
C(3)	3134(4)	−919(3)	4991(4)
C(4)	4000(4)	−1115(2)	3981(4)
C(5)	4112(3)	−517(2)	2778(4)
C(6)	3012(3)	2252(2)	3276(4)
C(7)	3197(4)	2972(2)	4320(4)
C(8)	4209(4)	3585(3)	4235(5)
C(9)	5020(4)	3462(3)	3162(5)
C(10)	4813(4)	2723(3)	2138(4)

rected for anomalous dispersion, were taken from ref. 31. Final atomic coordinates for the non-hydrogen atoms are given in Table 5. All calculations were carried out on the CRAY X-MP/48 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

Supplementary material

Additional data available from the authors comprise H-atom coordinates and thermal parameters.

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