Cyclometallated derivatives of platinum(II) derived from 1,4-benzodiazepin-2-ones. Crystal and molecular structure of Pt(L)(HL)Cl (HL = 7-chloro-1,3-dihydro-1-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one, DIAZEPAM), a molecule containing a neutral and a deprotonated 1,4-benzodiazepin-2-one

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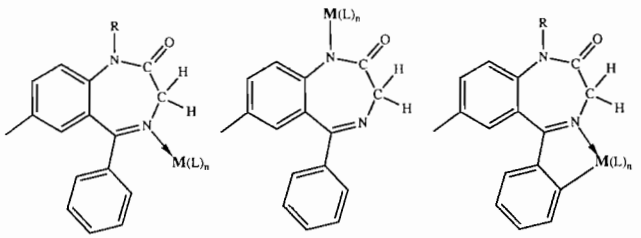
Abstract

The complexes $[Pt(L)Cl]_2$ (**1**), Pt(L)(HL)Cl (**2**), (two conformers, **2a** and **2b**), $Pt(L)(Ph_3P)Cl$ (**3**), $Pt(L)(3,5\text{-}Me_2\text{-}py)Cl$ (**4**) and Pt(L)(CO)Cl (**5**) (HL = 7-chloro-1,3-dihydro-1-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one, DIAZEPAM) have been prepared and characterized by IR, MS and ^1H, ^{13}C, ^{31}P and two-dimensional correlation NMR spectra Complexes **1–5** contain a deprotonated DIAZEPAM coordinated to the metal through the N(4) atom and the *ortho*-carbon of the 5-phenyl substituent. In complex **2**, as shown by a single crystal X-ray structure determination, carried out on conformer **2a**, in addition to the cyclometallated system, a neutral molecule of DIAZEPAM is coordinated through the N(4) atom. The crystals of compound **2a**, $C_{32}H_{25}Cl_3N_4O_2Pt$, are monoclinic, space group $P2_1/n$ with $a = 13.601(3)$, $b = 15.951(5)$, $c = 13.837(3)$ Å, $\beta = 96.38(2)°$, $Z = 4$. The structure was refined to $R = 0.021$ and $R_w = 0\,032$ on the basis of 4922 unique reflections with $I > 3\sigma(I)$. The platinum atom is in a square planar geometry with the carbon atom *trans* to the chloride ligand: Pt–C = 1.983(3), Pt–Cl = 2.402(1), Pt–N = 2.031(3) and 2 009(3) Å.

Key words. Crystal structures; Platinum complexes; Cyclometallated ligand complexes; Hydrido complexes

Introduction

The interaction of 1,4-benzodiazepin-2-ones [1] with metal ions has been the subject of several investigations. Adducts of copper(II) [2], gold(III) [3], gold(I) [4] and palladium(II) [5] ions have been reported: in some of these [2, 3, 5], coordination through the N(4) atom has been established unambiguously by X-ray analysis (Scheme 1(a)). Coordination of deprotonated 1,4-benzodiazepin-2-ones has also been observed: examples include N(1)-bonded molecules arising from N(1)-unsubstituted ligands (Scheme 1(b)), e.g. $Au(L)(Ph_3P)$ [4] (HL = NITRAZEPAM) and metallated derivatives, where a $C(sp^2)$–metal bond is assisted by coordination of a nitrogen atom (N4) (Scheme 1(c)), e.g. Pd(L)-$(Ph_3P)Cl$ [6] (HL = PRAZEPAM, DIAZEPAM, etc.). The activation of the C–H bond of the 5-phenyl substituent is likely to be favoured by the building up of a five-membered C,N ring which is known to have a remarkable stability [7].



Scheme 1.

As a part of an investigation on the reactivity of 1,4-benzodiazepin-2-ones with d^8 metal ions, herein we describe a series of cyclometallated derivatives of platinum(II) derived from DIAZEPAM, **1–5**. The new species have been characterized by an array of spec-

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troscopic techniques (IR, ^{1}H, ^{13}C, ^{31}P NMR and FAB MS spectra). In addition, the X-ray structure of one conformer (**a**) of complex **2**, Pt(L)(HL)Cl (HL = DIAZEPAM) is described in detail. The latter is the first species having both a neutral and a deprotonated 1,4-benzodiazepine bonded to a metal atom.

1:1 and 2:1 platinum(II) adducts $Pt(HL)Cl_2$ and $Pt(HL)_2Cl_2$ of some of these drugs were reported some years ago [8]: the former (HL = DIAZEPAM) were claimed to be dimers with bridging heterocyclic ligands [8a]. In spite of several attempts carried out on various platinum(II) intermediates, under different experimental conditions, we were unable to isolate any simple adduct. Quite recently, 1:1 adducts of platinum with some 1,5-benzodiazepines, (HL'), and BROMAZEPAM have been described, e.g. $Pt(HL')(DMSO)(CH_3)_2$ [9].

A preliminary report of this work has been given [10].

Experimental

Elemental analyses were performed with a Perkin-Elmer elemental analyzer 240B by Mr A. Canu (Dipartimento di Chimica, Università di Sassari) or by Pascher Mikroanalytisches Laboratorium, Remagen, Germany. IR spectra were recorded with Perkin-Elmer 1310 and 983 spectrophotometers. NMR spectra were recorded with a Varian VXR 300 or a Bruker instrument operating at 80 MHz; the 2D experiments were performed on a Varian VXR 300 instrument by means of COSY-90, HETCOR and NOESY programs. Fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on a VG 7070 instrument, with 3-nitrobenzyl alcohol (NBA) as matrix for the FAB spectra.

Synthesis of the metallated derivatives 1 and 2 ($[Pt(L)Cl]_2$ (1), Pt(L)(HL)Cl (2); HL = DIAZEPAM)

(a) From $K_2[PtCl_4]$ (HL/Pt = 1)

A solution of the ligand (284.5 mg, 1 mmol) in ethanol (20 ml) was added to a solution of $K_2[PtCl_4]$ (415 mg, 1 mmol) in water (20 ml). The solution was stirred for 2 weeks at room temperature: the brown precipitate was filtered off, washed with water, ethanol and diethyl ether. The precipitate was dissolved in chloroform and the solution was filtered through Celite. Addition of diethyl ether gave an orange product, which was crystallized from chloroform/diethyl ether. Yield 70%, **2** (mixture of **2a** and **2b** ~ 2:1 (^{1}H NMR criterion)).

The mother solution (ethanol/water) was concentrated to small volume to give a precipitate. The crude was dissolved in dichloromethane. After filtration, the solution was kept several days at room temperature: the red product which formed, insoluble in all common solvents, was collected and washed several times with dichloromethane Yield 20%, **1**.

1, $[Pt(L)Cl]_2$, no dec. up to 290 °C. *Anal.* Found: C, 37.27; H, 2.39; N, 5.86; Pt, 38.8, Cl, 14.0. Calc. for $C_{32}H_{24}Cl_4N_4O_2Pt_2$: C, 37.43; H, 2.34; N, 5.46; Pt, 38.01; Cl, 13.84%. IR (Nujol) (cm^{-1}): 1680vs, 1580s.

2, Pt(L)(HL)Cl, no. dec. up to 290 °C. *Anal.* Found: C, 46.49; H, 3.19; N, 6.81. Calc. for $C_{32}H_{25}Cl_3N_4O_2Pt$: C, 48.09; H, 3.13; N, 7.01%. IR (Nujol) (cm^{-1}): 1690vs, 1589m, 272s.

(b) From $K_2[PtCl_4]$ (HL/Pt = 2)

A solution of the ligand (569 mg, 2 mmol) in ethanol (30 ml) was added to a solution of $K_2[PtCl_4]$ (415 mg, 1 mmol) in water (30 ml). The solution was stirred for 3 weeks at room temperature: the orange–yellow precipitate was filtered off, washed with water, ethanol and diethyl ether. The crude was dissolved in chloroform: addition of diethyl ether to a concentrated solution gave an orange product. Yield 80%, **2** (mixture of **2a** and **2b** ~ 2:1). By concentration to small volume of the mother solution a crude can be recovered· ^{1}H NMR spectra and TLC (silica) give evidence of a mixture of several species.

The mixture of conformers **2a** and **2b** was separated by chromatography on a column of silica gel (benzene/acetone 2/1). Yield 50%, **2a** 33%, **2b** 17%, **2a** no dec. up to 290 °C, **2b** dec. > 250 °C.

(c) From $PtCl_2$ in chloroform (HL/Pt = 2)

A solution of DIAZEPAM (569 mg, 2 mmol) in chloroform (50 ml) was added to a suspension of $PtCl_2$ (266 mg, 1 mmol) in the same solvent. The mixture was stirred and refluxed for 1 week until a reddish suspension was obtained After removal of an insoluble material, the solution was concentrated to small volume and diethyl ether added to give an orange precipitate which was recrystallized from chloroform/diethyl ether. Yield 70%, **2** (mixture of **2a** and **2b**). Pt(L)(LH)Cl, no dec. up to 290 °C. *Anal.* Found. C, 48.08; H, 3.27; N, 7.03; Cl, 12.9; Pt, 24.3. Calc. for $C_{32}H_{25}Cl_3N_4O_2Pt$: C, 48.09; H, 3.13; N, 7.01; Cl, 13.34; Pt, 24.42%. IR (Nujol) (cm^{-1}): 1690vs, 1589m, 272s.

(d) From $PtCl_2$ in benzene (HL/Pt = 2)

A solution of DIAZEPAM (569 mg, 2 mmol) in benzene (50 ml) was added to a suspension of $PtCl_2$ (266 mg, 1 mmol) in the same solvent The mixture was stirred and refluxed for 1 week. A brown material was filtered and extracted with chloroform. The chloroform solution was concentrated to small volume and diethyl ether was added. The precipitate was crystallized from chloroform/diethyl ether. Yield 60%, **2a**. Pt(L)(LH)Cl, m.p. no dec. up to 290 °C *Anal.* Found:

C, 48.13; H, 3.47; N, 6.84. Calc. for $C_{32}H_{25}Cl_3N_4O_2Pt$: C, 48.09; H, 3.13; N, 7.01%.

The mother yellow solution was concentrated to small volume: a yellow precipitate was filtered and crystallized from benzene/diethyl ether (50 mg). TLC gives evidence of a mixture of several products.

Synthesis of compounds 3–5 (Pt(L)(PPh$_3$)Cl (3), Pt(L)(3,5-Me$_2$-py)Cl (4), Pt(L)(CO)Cl (5))

Compound 3

(a) A solution of triphenylphosphine (33.1 mg, 0.13 mmol) in chloroform (10 ml) was added to a solution of compound **2** (101 mg, 0.126 mmol) in the same solvent (20 ml). The mixture was stirred at room temperature for 12 h. The yellow solution was concentrated to small volume and diethyl ether was added: the precipitate was filtered off and crystallized from chloroform/diethyl ether. Yield 79%, **3**. Pt(L)(PPh$_3$)Cl: no dec. up to 290 °C. *Anal.* Found: C, 52.80; H, 3.66; N, 3.76; Cl, 9.16; Pt, 25.2. Calc. for $C_{34}H_{27}Cl_2N_2OPPt$: C, 52.28; H, 3.48; N, 3.61; Cl, 9.15; Pt, 25.13%. IR (Nujol) (cm^{-1}): 1680vs, 1580s, 275.

From the mother solution, DIAZEPAM was recovered almost quantitatively.

(b) To a suspension of compound **1** (77 mg, 0.075 mmol) in chloroform (20 ml) was added triphenylphosphine (39.3 mg, 0.15 mmol) in the same solvent; the mixture was stirred at room temperature until a yellow solution was obtained (~1 h). The solution was concentrated to small volume and diethyl ether was added: the yellow precipitate was filtered off and crystallized from chloroform/diethyl ether. Yield 77%, **3**. Pt(L)(PPh$_3$)Cl, no dec. up to 290 °C. *Anal.* Found: C, 52.02; H, 3.65; N, 3.66. Calc. for $C_{34}H_{27}Cl_2N_2OPPt$: C, 52.28; H, 3.48; N, 3.61%. IR (Nujol) (cm^{-1}): 1680vs, 1580s, 275s. MS spectra: FAB (positive ions) $[M]^{+\cdot}$ 775; EI $[M+H]^+$ 776, base peak, $[M-Cl]$ 740.

Compound 4

To a suspension of compound **1** (40 mg, 0.039 mmol) in dichloromethane (15 ml) were added 8.34 mg (0.078 mmol) of 3,5-Me$_2$-pyridine in the same solvent. The mixture was stirred and refluxed for 4 h. The orange–yellow solution was concentrated to small volume and diethyl ether was added. The orange–yellow precipitate was filtered off and crystallized from dichloromethane/diethyl ether. Yield 81%, **4**. Pt(L)(3,5-Me$_2$-pyridine)Cl, m.p. 287–88 °C. *Anal.* Found: C, 44.31; H, 3.59; N, 6.95. Calc. for $C_{23}H_{20}Cl_2N_3OPt$: C, 44.52; H, 3.23; N, 6.77%. IR (Nujol) (cm^{-1}): 1680vs, 1580s, 275.

Compound 5

(a) Compound **1** (103.9 mg, 0.10 mmol) was suspended in dichloromethane (25 ml) and CO was bubbled at room temperature for 4 h until a yellow solution was obtained. Concentration to small volume and addition of diethyl ether gave a yellow precipitate which was filtered off, and crystallized from dichloromethane/diethyl ether. Yield 68%, **5**.

(b) Into an orange solution of compound **2** (200 mg, 0.25 mmol) in dichloromethane (40 ml) CO was bubbled at room temperature for two days until the solution turned yellow. Concentration to small volume and addition of diethyl ether gave a yellow precipitate which was filtered off and crystallized from dichloromethane diethyl ether. Yield 70%, **5**. Pt(L)(CO)Cl, no dec. up to 290 °C. *Anal.* Found: C, 37.85; H, 2.38; N, 5.28. Calc. for $C_{17}H_{12}Cl_2N_2O_2Pt$: C, 37.64; H, 2.21; N, 5.17%. IR (Nujol) (cm^{-1}): 2079vs, (CH_2Cl_2: 2102); 1680vs, 1580s, 311m. MS (EI): $[M]^+$ 541, $[M-CO]$ 513 (100%).

From the mother liquor, DIAZEPAM was recovered almost quantitatively.

X-ray data collection and structure determination

Crystal data and other experimental details are summarized in Table 1. The diffraction experiment was carried out on a Enraf-Nonius CAD-4 diffractometer at room temperature with Mo Kα radiation ($\lambda = 0.71073$ Å). The diffracted intensities were corrected for Lorentz, polarization and absorption (empirical correction) [11], but not for extinction. Scattering factors and anomalous dispersion corrections for scattering factors of non-hydrogen atoms were taken from ref. 12. The structure was solved by Patterson and Fourier methods and refined

TABLE 1 Crystallographic data

Formula	$C_{32}H_{25}Cl_3N_4O_2Pt$
Formula weight (amu)	799.03
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	13.061(3)
b (Å)	15 951(5)
c (Å)	13 837(3)
β (°)	96.38(2)
U (Å^3)	2983(2)
Z	4
D_{calc} (g cm^{-3})	1 779
μ(Mo Kα) (cm^{-1})	50 58
Min. transmission factor	0.84
Scan mode	ω
ω Scan width (°)	1.0+0 35 tan θ
θ Range (°)	3–27
Octants of reciprocal space explored	$+h, +k, \pm l$
Measured reflections	6732
Unique observed reflections with $I > 3\sigma(I)$	4922
Final R and R_w indices[a]	0.021, 0 032
No. variables	379
e s d [b]	1.270

[a] $R = [\Sigma(F_o - k\|F_c\|)/\Sigma F_o]$; $R_w = [\Sigma w(F_o - k\|F_c\|)^2/\Sigma w F_o^2]^{1/2}$. [b] e s d = $[\Sigma w(F_o - k\|F_c\|)^2/(N_{obs} - N_{var})]^{1/2}$; $w = 1/(\sigma(F_o))^2$, $\sigma(F_o) = [\sigma^2(I) + (0\ 04I)^2]^{1/2}/2F_o$Lp.

by full-matrix least-squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$.

All the calculations were performed on a PDP11/73 computer using the SDP-Plus structure determination package [13].

Anisotropic thermal factors were refined for all the non-hydrogen atoms. Hydrogen atoms were introduced in the model at calculated positions with C–H = 0.95 Å, and not refined.

The final difference Fourier synthesis showed maxima residuals of 0.6 e/Å^3, close to the platinum atom. The atomic coordinates of the structure model are listed in Table 2.

TABLE 2 Fractional atomic coordinates with e.s.d.s

Atom	x	y	z
Pt	0.22742(1)	0.14631(1)	−0.01547(1)
Cl(1)	0.09286(8)	0.07164(7)	−0.10394(8)
Cl(21)	0.1635(1)	0.25891(8)	0.52068(8)
Cl(22)	0.4769(1)	0.1493(1)	−0.51788(9)
O(11)	0.2211(3)	−0.1023(2)	0.1310(2)
O(12)	0.2312(3)	0.4003(2)	−0.1031(2)
N(11)	0.2509(3)	−0.0267(2)	0.2702(3)
N(12)	0.3442(3)	0.3573(2)	−0.2014(3)
N(41)	0.2019(2)	0.1043(2)	0.1163(2)
N(42)	0.2621(2)	0.1955(2)	−0.1428(2)
C(21)	0.2066(3)	−0.0391(3)	0.1773(3)
C(22)	0.2580(4)	0.3480(3)	−0.1587(3)
C(31)	0.1401(3)	0.0314(3)	0.1336(3)
C(32)	0.2016(3)	0.2674(3)	−0.1823(3)
C(51)	0.2458(3)	0.1446(2)	0.1910(3)
C(52)	0.3344(3)	0.1715(3)	−0.1884(3)
C(61)	0.2047(3)	0.1910(3)	0.3529(3)
C(62)	0.4004(4)	0.1703(3)	−0.3483(3)
C(71)	0.1889(4)	0.1752(3)	0.4463(3)
C(72)	0.4364(4)	0.2093(3)	−0.4249(3)
C(81)	0.1944(4)	0.0951(3)	0.4838(3)
C(82)	0.4375(4)	0.2961(3)	−0.4327(3)
C(91)	0.2132(4)	0.0295(3)	0.4248(3)
C(92)	0.4041(4)	0.3427(3)	−0.3580(4)
C(101)	0.2279(3)	0.0426(3)	0.3287(3)
C(102)	0.3704(3)	0.3048(3)	−0.2773(3)
C(111)	0.2251(3)	0.1257(2)	0.2915(3)
C(112)	0.3661(3)	0.2171(3)	−0.2726(3)
C(121)	0.3168(3)	0.2082(2)	0.1678(3)
C(122)	0.3887(3)	0.0924(3)	−0.1596(3)
C(131)	0.3233(3)	0.2164(2)	0.0673(3)
C(132)	0.4902(4)	0.0906(3)	−0.1401(4)
C(141)	0.3921(3)	0.2740(3)	0.0402(3)
C(142)	0.5385(4)	0.0148(4)	−0.1188(4)
C(151)	0.4504(3)	0.3216(3)	0.1091(3)
C(152)	0.4860(5)	−0.0574(4)	−0.1205(4)
C(161)	0.4439(3)	0.3115(3)	0.2058(3)
C(162)	0.3852(5)	−0.0563(3)	−0.1406(4)
C(171)	0.3774(3)	0.2543(3)	0.2366(3)
C(172)	0.3356(4)	0.0177(3)	−0.1594(4)
C(181)	0.3167(4)	−0.0919(3)	0.3171(4)
C(182)	0.4097(5)	0.4309(3)	−0.1727(4)

Results and discussion

Synthesis of compounds 1–5

In a previous paper of ours [5d] it was shown that by reaction of palladium(II) intermediates with 1,4-benzodiazepines, DIAZEPAM included, both 2:1 adducts, *trans*-$Pd(HL)_2Cl_2$, or cyclometallated derivatives $[Pd(L)Cl]_2$ (HL = DIAZEPAM or PRAZEPAM) could be obtained according to reactions (1) or (2), respectively.

$$PdCl_2 \text{ (or } (PhCN)_2PdCl_2) + 2HL \longrightarrow \textit{trans}\text{-}Pd(HL)_2Cl_2 \quad (1)$$

$$2[PdCl_4]^{2-} + 2HL \longrightarrow [Pd(L)Cl]_2 + 2HCl + 4Cl^- \quad (2)$$

The reaction of the corresponding platinum(II) chlorides, $PtCl_2$ and $PtCl_4^{2-}$, with DIAZEPAM, is much more complex and was investigated under various experimental conditions and with different ligand-to-metal molar ratios. The reaction of $K_2[PtCl_4]$ with DIAZEPAM was first tested with a 1:1 molar ratio in ethanol/water solution, i.e. in the conditions claimed to give the 1:1 adduct, $Pt(HL)Cl_2$ [8a]. To avoid decomposition to platinum metal, the reaction was carried out at room temperature: after several weeks under stirring, an unattractive brown precipitate was filtered off and recrystallized from chloroform/diethyl ether to give the orange complex **2**, Pt(L)(HL)Cl (mixture of conformers **2a** and **2b**). From the mother solution, by concentration, a crude was obtained, which consists of a mixture of **2** (**2a** and **2b**) and several other species. In the attempt to separate these species, the crude was dissolved in dichloromethane. From the solution, kept at room temperature, a brilliant-red product, insoluble in all common solvents, separated: complex **1**, $[Pt(L)Cl]_2$. Thus it is likely that in the mother solution a solvato cyclometallated derivative was present, Pt(L)(S)Cl (S = H_2O or EtOH), arising from competition in solution between the ligand HL and a coordinating solvent. In the absence of an excess of the latter, e.g. in CH_2Cl_2, the solvato species evolves to the insoluble, halide-bridged species **1**. In order to drive the reaction toward complex **2**, the ligand-to-metal ratio was raised to 2:1. Once again however it was found that, besides complex **2** (mixture of conformers, yield ~80%), several species are formed. Attempts to obtain adducts reacting DIAZEPAM with $PtCl_2$ (2:1) in chloroform or benzene, were unsuccessful: cyclometallation occurs even in these conditions to give complex **2** as the main product. NMR evidence suggests that the minor components formed under different experimental conditions are various, so that their identity was not pursued.

Complex **2** is obtained in most cases as a mixture of two conformers (**2a** and **2b**): separation can be accomplished by chromatography on silica gel. Almost

pure **2a** is obtained in the reaction of $PtCl_2$ in benzene (see 'Experimental').

Complexes **3–5** Pt(L)(L')Cl (L' = PPh_3 (**3**), 3,5-Me_2-pyridine (**4**), CO (**5**)) were synthesized according to reaction (3) or (4).

$$[Pt(L)Cl]_2 + 2L' \longrightarrow 2Pt(L)(L')Cl \quad (3)$$

$$Pt(L)(HL)Cl + L' \longrightarrow Pt(L)(L')Cl + HL \quad (4)$$

The syntheses are straightforward, the products are easily separated and the yields are fairly good. It is worth noting that even carbon monoxide displaces the neutral benzodiazepine from complex **2** (reaction (4)). Of the two possible geometrical isomers, *trans*-N-Pt-L' and *trans*-C-Pt-L', one only is formed in all the cases.

Characterization of compounds 1–5

Compounds **1–5** were characterized by elemental analyses and an array of spectroscopic techniques.

For complex **1**, characterization in solution was hampered by insolubility in common solvents. Evidence in the FAB-MS spectra (positive ions) of a peak with a significant intensity at *m/z* 1027 allows us to think of complex **1** as a dimeric species. In the chemistry of cyclometallated derivatives of palladium(II) and platinum(II) with nitrogen ligands, dimers of this type, with bridging chlorides, are common [7].

In the IR spectra (Nujol mull), the strong absorptions, assigned in the free ligand to the prevailing contributions of ν(CO) and ν(CN), respectively, are shifted with respect to the free DIAZEPAM (e.g. ν(CN) = 1580 versus 1600 cm^{-1}) [5a]. The disappearance of the absorption at 700 cm^{-1}, assigned in the ligand to an out-of-plane skeletal mode, typical of a mono-substituted phenyl ring [14], can be assumed as diagnostic of cyclometallation. In agreement, the same feature is observed in the spectra of complexes **4** and **5**. In the range 400–200 cm^{-1}, the pattern of the IR spectrum is rather complex, suggesting perhaps the presence of both *syn–syn* and *syn–anti* isomers.

In contrast to complex **1**, the mononuclear complexes **2–5** are soluble, so that full characterization in solution has been possible. The ^1H NMR spectra ($CDCl_3$, r.t.) of complex **2**, as obtained through most of the procedures described above, indicate the presence in solution of two species, **2a** and **2b**, with very similar NMR parameters. Fortunately, the mixture is amenable to separation, so that assignment of the resonances in the ^1H and ^{13}C NMR spectra was possible (see Table 3).

In both species, **2a** and **2b**, two well separate sets of signals, assignable to the protons of the CH_2 groups, give evidence of non-equivalent ligands. The resonances appear as typical AB systems, suggesting that inversion of the heptaatomic ring is slow on the NMR time scale even at room temperature. The same behaviour has been observed previously for the free ligand [15]. By comparison with the spectra of compounds **3–5**, where only a deprotonated DIAZEPAM is present, as well as with those of related palladium species [5a], we feel confident to assign to the cyclometallated ring the AB resonance which displays the larger $\Delta\nu$ value. One arm of the system is strongly shifted to low fields, likely

TABLE 3 ^1H NMR data[a]

Compound	CH_3		CH_2		Aromatics
Pt(L)(LH)Cl					
Conformer **2a**[b]	3.35s	H(A) 6 10 ^3J(Pt–H) = 35	J(A–B) = 12 6	H(B) 3.85 ^3J(Pt–H) = 35 8	8 2–6 2
	3.55s	H(A) 5.54 ^3J(Pt–H) = 35	J(A–B) = 12.7	H(B) 4.29 ^3J(Pt–H) = 60	
Conformer **2b**[c]	3 39s	H(A) 6.07 ^3J(Pt–H) = 33	J(A–B) = 12 6	H(B) 3.80 ^3J(Pt–H) = 34	8 2–6 2
	3 56s	H(A) 5.60 ^3J(Pt–H) = 33	J(A–B) = 12 2	H(B) 4.26 ^3J(Pt–H) = 51	
Pt(L)(PPh_3)Cl[d] (**3**)	3 40s	H(A) 6 41 ^3J(Pt–H) = 23 ^4J(P–H) = 3.2	J(A–B) = 12 4	H(B) 3.80 ^3J(Pt–H) = 25 ^4J(P–H) = 4.1	7.8–6 6
Pt(L)(3,5-Me_2-py)Cl (**4**)	3.39s	H(A) 6 12 ^3J(Pt–H) = 32 2	J(A–B) = 12 4	H(B) 3.92 ^3J(Pt–H) = 35 1	8 6–6 4
Pt(L)(CO)Cl[e] (**5**)	3 40s	H(A) 5 88 ^3J(Pt–H) = 26.9	J(A–B) = 12 7	H(B) 3 67 ^3J(Pt–H) = 30 1	7 7–7.3

[a]Spectra recorded at room temperature, $CDCl_3$, chemical shifts in ppm relative to internal TMS, coupling constants in Hz [b] ^{13}C NMR δ CH_2, 55 48, 64.42, CH_3, 34.90 (overlapping). [c] ^{13}C NMR δ CH_2, 55.54, 64.24, CH_3, 34.91 (overlapping) [d] ^{196}Pt NMR δ −4204.4 (relative to external Na_2PtCl_6); ^{31}P δ 23 26 (relative to external 85% H_3PO_4), J(Pt–P) = 4297 Hz [e] ^{13}C NMR: δ CH_2, 52.21 (J(Pt–C) = 40 Hz), CH_3, 35.00

owing to the deshielding effect of the chlorine atom. The H–H geminal coupling constants are larger than in the free ligand, as observed previously [5a]. The ^3J(Pt–H) values (30–60 Hz) are in the range expected for coupling through three bonds: it is worth noting that a not negligible difference is observed between the values relative to the protons (H_a and H_b) of the CH_2 group in the neutral ligand. As stated above, the ^{1}H and ^{13}C NMR spectra (see Table 3) of compounds **2a** and **2b** are very similar, some resonances being almost coincident and this opens questions as to the difference in the nature of the two species. Of course **2a** and **2b** might be geometrical isomers having N–Pt–N or N–Pt–C *trans* arrangement, respectively. Although a full analysis of the ^{1}H NMR spectrum in the aromatic region has not been made owing to its complexity, we note that: (i) the range of the resonances, δ 8.2–6.2, is the same in **2a** and **2b**; (ii) the resonance of the proton adjacent to the metal–carbon bond, H3′, is almost coincident in **2a** (δ 6.34 ppm, ^3J(Pt–H) = 48–50 Hz) and **2b** (δ 6.36 ppm, ^3J(Pt–H) = 48–50 Hz). A chlorine atom *cis* to the phenyl ring should exert a deshielding effect on this proton. In addition, no significant difference is observed in the IR spectra, even in the region 350–250 cm^{-1} where the stretching modes of the platinum–chlorine vibrations are expected: an absorption at ~270 cm^{-1} in the spectra of **2a** and **2a** + **2b**, is consistent with a Pt–Cl bond *trans* to a ligand with a high *trans* influence such as a phenyl group [16]. On these bases, on the whole, we consider **2a** and **2b** as two molecules having the same coordination sequence around the platinum atom. We propose therefore that **2a** and **2b** are conformers, arising either by different conformations of the heptaatomic rings or by hindered rotation of the neutral ligand around the metal-nitrogen bond. We have not much at present to offer in the way of accounting for the difference between **2a** and **2b** except to point out that. (i) the existence of conformers is peculiar to compound **2**, being not observed for **3–5** where only a cyclometallated benzodiazepine is present; (ii) inspection of molecular models rules out a free rotation of the HL ligand, so that molecules where the neutral ligand is frozen in two limiting spatial arrangements, should be considered. The structure in the solid state of compound **2a** has been solved and will be discussed later. Unfortunately, we were unable to get crystals of **2b**, suitable for an X-ray analysis. Finally, it is worth noting that a very slow conversion of conformer **2a** into **2b** and vice versa occurs in solution, as shown by ^{1}H NMR spectra recorded on samples stored at −10 °C for one month.

For complex **3**, Pt(L)(PPh_3)Cl, as obtained from **1** through a bridge-splitting reaction or from **2** by substitution of the ligand HL, the ^{31}P NMR spectra give clear cut evidence of one species alone in solution. The thermodynamic product is the isomer with a *trans*-N–Pt–P arrangement as shown by the large ^1J(Pt–P) value, 4297 Hz. We have no evidence, even as an intermediate, of the other geometrical isomer which might form under kinetic control. The same isomer was observed previously for the analogous palladium complex [5a]. The ^{1}H NMR spectrum shows that the seven-membered ring of the metallated benzodiazepine is rigid at room temperature: the CH_2 resonance appears as a rather complex system, with platinum satellites. A ^{1}H{^{31}P} spectrum explained the apparent complexity of the resonance as due to a long-range coupling to the ^{31}P nucleus and allowed the full set of the coupling constants, ^1J(H–H), ^4J(P–H) and ^3J(Pt–H), to be estimated.

Complex **4**, Pt(L)(3,5-Me_2-py)Cl, was synthesized mainly with the aim of analysing the aromatic region of the ^{1}H and ^{13}C NMR spectra. To this purpose, several NMR techniques were employed such as 2D ^{1}H–^{1}H (COSY 90), 2D ^{1}H–^{13}C (HETCOR) (Fig. 1) and ^{1}H 2D NOESY spectra. The chemical shifts and coupling constants are reported in Table 4 together with the numbering scheme. The assignment of the resonances in the ^{1}H and ^{13}C spectra was unambiguous, with the exception of those of the quaternary carbon atoms. The latter signals are in the expected number: one of the two resonances observed in the free ligand at low field, δ 169.8 and 168.8 ppm, and attributed to C(2) and C(5), respectively [17], is substantially deshielded in complex **4**, 182.4 ppm. Most likely, it is assignable to C(5), strongly affected by coordination to the metal through N(4). The IR spectrum suggests that complex **4** is the *trans* N–Pt–N isomer. In order to gain conclusive evidence on this point, a ^{1}H 2D NOESY experiment was performed. Analysis of the cross-peaks in the 2D diagram, shows an NOE effect from H(3′) to H(2″) protons, supporting the N–Pt–N geometry.

On bubbling CO at room temperature into a suspension of **1** or a solution of **2** in dichloromethane, complex **5**, Pt(L)(CO)Cl, is obtained. A strong and sharp absorption at 2079 cm^{-1} in the IR spectrum (Nujol) indicates a terminal carbonyl ligand: in contrast to the analogous palladium species [6], complex **5** is stable even in the solid state. In the ^{1}H NMR spectrum a striking difference is observed between **5** and compounds **2–4** for the aromatic region. The resonance of the proton near the metal–carbon bond (H3′ δ 7.54) is strongly deshielded with respect to **2–4**. This agrees with a chlorine *cis* to the phenyl ring suggesting that the isomer having the neutral ligand *trans* to the carbon atom is formed. Thus it seems that the ligands DIAZEPAM, PPh_3 and 3,5-Me_2-pyridine prefer to coordinate *trans* to the N(4) atom and CO *trans* to the phenyl group. It is possible in this case that the difference

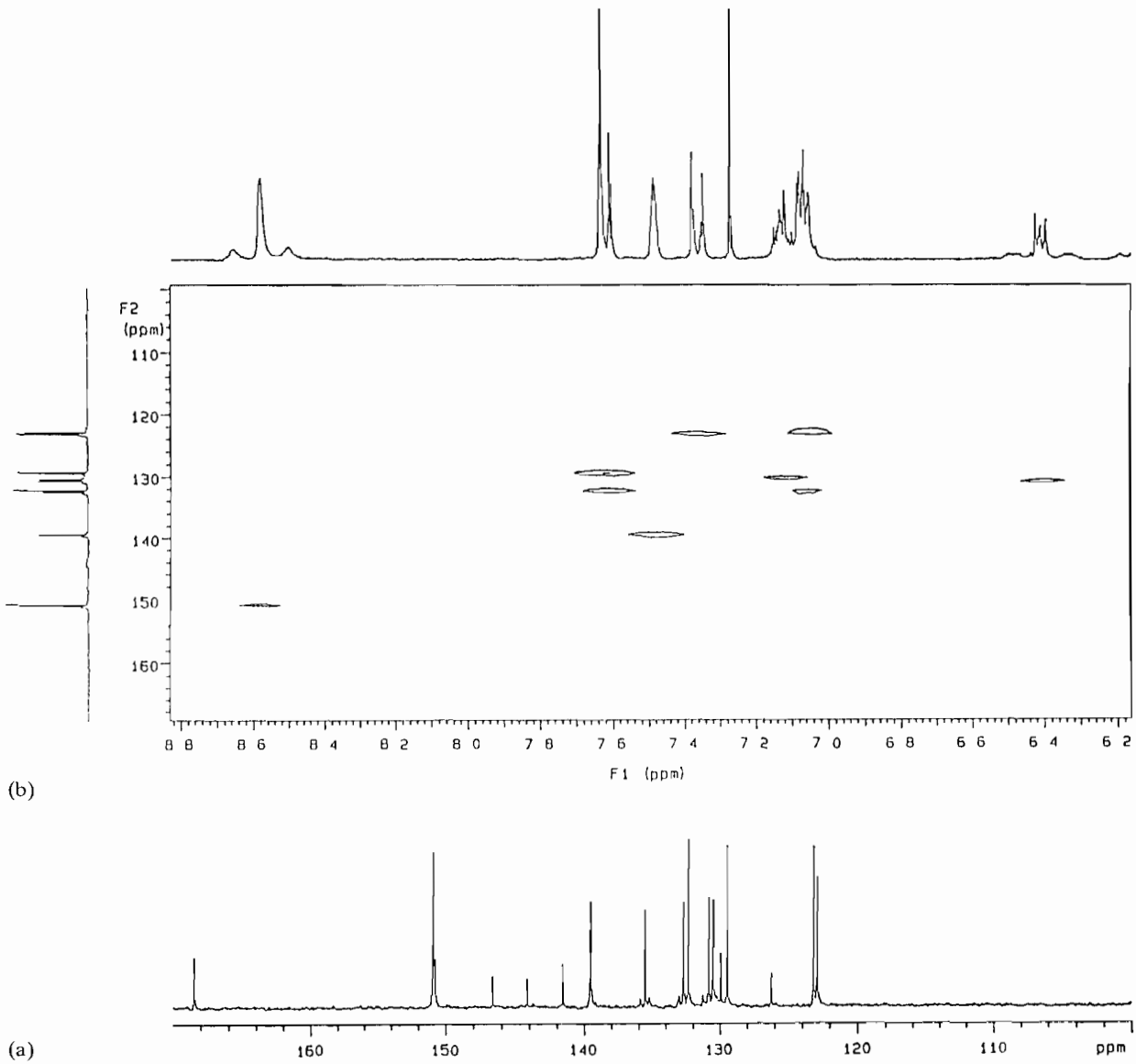


Fig 1. Complex **4**· NMR spectra of the aromatic region (r t., $CDCl_3$, 300 MHz) (a) $^{13}C\{^1H\}$ spectrum, (b) ^{13}C–^1H 2D correlated spectrum.

is due to the minor steric requirements of CO versus the other ligands.

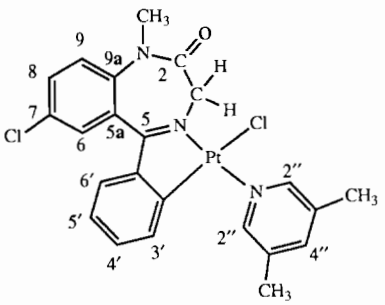
Structure in the solid state of compound **2a**

Crystals of compound **2a** contain discrete molecular units separated by no unusual intermolecular contacts; the shortest intramolecular Pt·· H interactions are Pt–H(31A), 3.038 Å, and Pt–H(32A), 2.891 Å. An ORTEP drawing of **2a** is shown in Fig. 2, together with the atom labelling scheme. Selected bond distances and angles are reported in Table 5. The complex contains two DIAZEPAM molecules coordinated in two different ways. One of them acts as a bidentate anionic ligand through nitrogen N(41) and the phenylic carbon atom C(131), whereas the other one coordinates to the metal in a monodentate fashion through nitrogen N(42). The platinum atom exhibits the expected square planar coordination, only slightly distorted towards tetrahedral, with two *cis* positions occupied by the bidentate cyclometallated benzodiazepine ligand, the chlorine and the N(42) atoms being *trans* to the C(131) and N(41) atoms, respectively. Deviations from the average coordination plane are: Pt 0.058(1), Cl(1) −0.071(1), N(41) 0.056(3), N(42) 0.049(3) and C(131) −0.092(4) Å. The Pt–Cl distance (2.402(1) Å) clearly shows the effect of a lengthening due to the *trans* coordinated carbon atom [18]. The two Pt–N bonds [18b, 19] are slightly but significantly different (2.009(3) versus 2.031(3) Å); it is questionable to state whether such a difference can be due to electronic rather than to

TABLE 4. ^{1}H (aromatic region) and $^{13}C\{^{1}H\}$ NMR data[a] of compounds **4** and **5**

		Compound **4**[b]		Compound **5**[c]	
		δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
^{1}H	H(6)	7 63d [1]		7 71d [1]	J(H–H) = 2 4
	H(8)	7 62d [1]	J(H–H) = 7.6	7.73dd [1]	J(H–H) = 2 4, 8.8
	H(9)	7 36d [1]	J(H–H) = 7.6	7 44d [1]	J(H–H) = 8 8
	H(3′)	6 41m [1]	^{3}J(Pt–H) = 42	7.54dt [1]	J(H–H) = 7 1
	H(4′)	7 06m[d] [1]		7.29m[d] [1]	
	H(5′)	7.05m[d] [1]		7.28m[d] [1]	
	H(6′)	7.12m[d] [1]		7 32m[d] [1]	
	H(2″)	8 58s [2]	^{3}J(Pt–H) = 46		
	H(4″)	7.48s [1]			
^{13}C	CH_3	18.2			
	N-CH_3	34.9		35.0	
	CH_2	55.8	^{2}J(Pt–C) = 45	52.2	^{2}J(Pt–C) = 40
	C(2″)	150 9	^{2}J(Pt–C) n o		
	C(4″)	139.5			
	C(6)	129 4		130 1	
	C(8)	132 4		133 8	
	C(9)	123 2		123 4	
	C(3′)	130 8	^{2}J(Pt–C) = 60	136.5	^{2}J(Pt–C) = 104 6
	C(4′)	132 7	^{3}J(Pt–C) = 54	132 4	^{3}J(Pt–C) = 36
	C(5′)	122.9		125.3	
	C(6′)	130 5	^{3}J(Pt–C) = 40	135 4	^{3}J(Pt–C) = 66
	C(CH$_3$)	135.8	^{3}J(Pt–C) = 50 5		
	C(5)	182.4[e]			
	C(2)	168.5[e]			

[a]Assignments based on COSY and HETCOR spectra, room temperature, $CDCl_3$, chemical shifts in ppm from internal TMS [b]Quaternary carbon atoms (C(9a), C(5a), C(1′), C(2′), C(7)) were not assigned δ 146 6, 144 2, 141 6, 126 3, 129 9. [c]Quaternary carbon atoms (C(2), C(5), C(5a), C(7), C(9a), C(1′), C(2′)) were not assigned δ 125 2, 130 4, 142 3, 142.8, 146 0, 164 5, 167.9, 186.4 [d]Overlapping [e]Assignment may be reversed



4

packing effects. The bond angles at the platinum atom show distortions deriving from the asymmetric environment about the central atom and from the need of preserving normal interligand contacts. The most significant deviation from the ideal geometry with right angles is that generated by the constraints imposed by the chelate ring (N(41)–Pt–C(131) = 80.4(1)°). The latter displays an envelope conformation with the N(41)C(51)C(121)C(131) moiety strictly planar and the platinum atom displaced from the plane by 0.184(1) Å. As observed for other 1,4-benzodiazepine molecules, either coordinated [2, 3, 4, 5a] or not [20], the seven-membered rings display a boat-shaped conformation which can be described by the angles between the central planes N(1j)C(2j)N(4j)C(5j) (j = 1,2) and the bow and stern planes consisting of atoms C(2j)C(3j)N(4j) and N(1j)C(10j)C(11j)C(5j), respectively. The bow and the stern dihedral angles with the central plane are 57.3 and 40.8° for the neutral ligand and 58.5 and 37.0° for the anionic one.

The pattern of bond distances and angles within the neutral DIAZEPAM ligand is essentially the same as that observed in the uncoordinated molecule [20], whereas some significant differences with respect to the free molecule are observed for the anionic ligand. For instance the C(51)–C(121) bond of 1.461(5) Å is

TABLE 5. Selected bond distances (Å), angles (°) and torsion angles (°)

Pt–Cl(1)	2.402(1)	Pt–C(131)	1 983(3)
Pt–N(41)	2.009(3)	Pt–N(42)	2 031(3)
N(41)–C(31)	1.469(4)	N(42)–C(32)	1 481(4)
N(41)–C(51)	1.304(4)	N(42)–C(52)	1 285(5)
C(31)–C(21)	1.525(6)	C(32)–C(22)	1 513(6)
C(21)–O(11)	1 222(5)	C(22)–O(12)	1 217(5)
C(21)–N(11)	1 373(5)	C(22)–N(12)	1.378(6)
N(11)–C(181)	1.474(5)	N(12)–C(182)	1.500(5)
N(11)–C(101)	1 425(5)	N(12)–C(102)	1.420(5)
C(101)–C(111)	1.421(5)	C(102)–C(112)	1.402(5)
C(111)–C(51)	1 481(5)	C(112)–C(52)	1.477(5)
C(111)–C(61)	1 392(5)	C(112)–C(62)	1.407(5)
C(61)–C(71)	1.357(5)	C(62)–C(72)	1.366(6)
C(71)–C(81)	1.377(6)	C(72)–C(82)	1.388(6)
C(71)–Cl(21)	1 744(4)	C(72)–Cl(22)	1.741(4)
C(81)–C(91)	1 368(6)	C(82)–C(92)	1.390(7)
C(91)–C(101)	1 383(5)	C(92)–C(102)	1.391(6)
C(51)–C(121)	1.461(5)	C(52)–C(122)	1.494(5)
C(121)–C(131)	1 409(5)	C(122)–C(132)	1.377(6)
C(131)–C(141)	1 392(5)	C(132)–C(142)	1.393(7)
C(141)–C(151)	1 395(5)	C(142)–C(152)	1 353(8)
C(151)–C(161)	1 360(6)	C(152)–C(162)	1 368(8)
C(161)–C(171)	1.385(6)	C(162)–C(172)	1 371(6)
C(171)–C(121)	1.397(5)	C(172)–C(122)	1.393(6)
N(41)–Pt–N(42)	175.1(1)	Cl(1)–Pt–C(131)	171.6(1)
Cl(1)–Pt–N(41)	95 66(9)	Cl(1)–Pt–N(42)	89.23(8)
N(41)–Pt–C(131)	80.4(1)	N(42)–Pt–C(131)	94.7(1)
C(51)–N(41)–C(31)	118.7(3)	C(52)–N(42)–C(32)	118.2(3)
N(41)–C(31)–C(21)	108 8(3)	N(42)–C(32)–C(22)	109.4(3)
C(31)–C(21)–N(11)	116 4(3)	C(32)–C(22)–N(12)	115 7(3)
C(31)–C(21)–O(11)	121 6(4)	C(32)–C(22)–O(12)	122.6(4)
N(11)–C(21)–O(11)	122.0(4)	N(12)–C(22)–O(12)	121.7(4)
C(21)–N(11)–C(101)	122.8(3)	C(22)–N(12)–C(102)	123 3(3)
C(21)–N(11)–C(181)	119.5(3)	C(22)–N(12)–C(182)	118.7(4)
C(101)–N(11)–C(181)	117 3(3)	C(102)–N(12)–C(182)	117.8(4)
N(11)–C(101)–C(111)	121 1(3)	N(12)–C(102)–C(112)	122.6(3)
C(101)–C(111)–C(51)	122 0(3)	C(102)–C(112)–C(52)	123.1(3)
C(111)–C(51)–N(41)	121 7(3)	C(112)–C(52)–N(42)	123.2(3)
C(111)–C(51)–C(121)	123 2(3)	C(112)–C(52)–C(122)	116.6(3)
N(41)–C(51)–C(121)	115.1(3)	N(42)–C(52)–C(122)	120.2(3)
C(51)–C(121)–C(131)	113.4(3)	C(52)–C(122)–C(132)	121.6(4)
C(51)–C(121)–C(171)	124 7(3)	C(52)–C(122)–C(172)	118.8(4)
Pt–N(41)–C(51)	116 4(2)	Pt–N(42)–C(52)	125.1(2)
Pt–N(41)–C(31)	124 8(2)	Pt–N(42)–C(32)	116.6(2)
C(121)–C(131)–Pt	114 1(2)	C(121)–C(131)–C(141)	116.4(3)
C(131)–C(121)–C(171)	121.8(3)	Pt–C(131)–C(141)	129.4(2)
N(41)–C(51)–C(111)–C(101)	50 3	N(42)–C(52)–C(112)–C(102)	40 4
C(51)–C(111)–C(101)–N(11)	−0 1	C(52)–C(112)–C(102)–N(12)	−0 3
C(111)–C(101)–N(11)–C(21)	−48 4	C(112)–C(102)–N(12)–C(22)	−48 5
C(101)–N(11)–C(21)–C(31)	7 6	C(102)–N(12)–C(22)–C(32)	12 2
N(11)–C(21)–C(31)–N(41)	69 0	N(12)–C(22)–C(32)–N(42)	64 6
C(21)–C(31)–N(41)–C(51)	−68.5	C(22)–C(32)–N(42)–C(52)	−76.5
C(31)–N(41)–C(51)–C(111)	−7.7	C(32)–N(42)–C(52)–C(112)	6 1
O(11)–C(21)–N(11)–C(181)	−1.1	O(12)–C(22)–N(12)–C(182)	4 4
C(51)–C(111)–C(101)–C(91)	176.4	C(52)–C(112)–C(102)–C(92)	177 9
C(61)–C(111)–C(51)–C(121)	49 4	C(62)–C(112)–C(52)–C(122)	33 3
N(41)–C(51)–C(121)–C(131)	1.7	N(42)–C(52)–C(122)–C(132)	−127 8
C(51)–C(121)–C(131)–Pt	4.6	C(121)–C(131)–Pt–N(41)	−6.4
C(131)–Pt–N(41)–C(51)	7.7	Pt–N(41)–C(51)–C(121)	−7.2
C(51)–N(41)–Pt–Cl(1)	−164 8	C(52)–N(42)–Pt–Cl(1)	−103.5

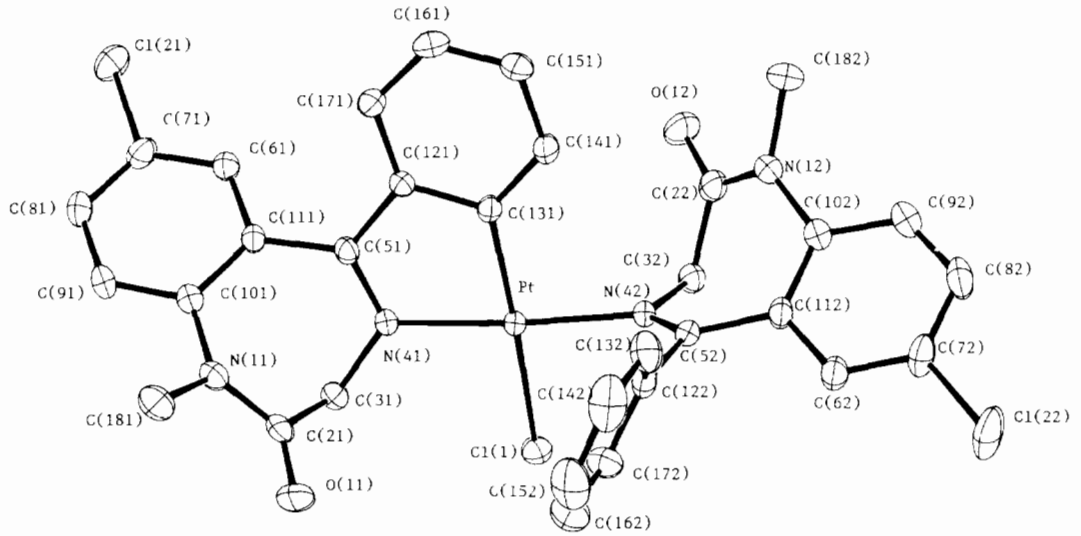


Fig 2. ORTEP drawing of compound **2a** Thermal ellipsoids are drawn at 30% probability

shorter than the corresponding one in the free DIAZEPAM molecule (1.492 Å). The N(41)–C(51)–C(121) and C(51)–C(121)–C(131) angles, 115 1(3) and 113.4(3)°, respectively, are smaller with respect to the ideal value of 120 °, which is nearly observed in the present complex for the monodentate DIAZEPAM ligand (120.2(3) and 121.6(4)°, respectively). Both these effects, as well as other differences involving the angles at the coordinated nitrogen atoms, could be related to the strain imposed by the formation of the five-membered metallacycle upon coordination

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