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Versatile ligand behaviour of phenyl 2-pyridyl ketone benzoylhydrazone in palladium(II) complexes

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A series of monometallic palladium(II) complexes with phenyl 2-pyridyl ketone benzoylhydrazone (H_2L) has been synthesized and characterized. The spectroscopic and diffractometric data have revealed a versatile ligand behaviour which mainly depends on the the palladium salt reagent. From the reaction of palladium acetate a cyclopalladated complex, [PdL(MeCN)], was isolated, the exact nature of which has been established by X-ray diffraction. With palladium chloride two complexes, $[Pd(HL)_2]$ and [Pd(HL)Cl], were obtained with the monodeprotonated hydrazone behaving as an N,N-bidentate and N,N,O-terdentate ligand, respectively.

We have recently investigated the catalytic properties of some palladium(II) complexes containing a hydrazonic ligand in the hydrogenation of terminal alkynes and alkenes.[1] In particular the catalytic behaviour of the acetato complex in the hydrogenation of the alkenes and the formation of stable alkynyl-palladium(II) complexes in the hydrogenation of alkynes were evidenced. Other points of interest are the use as catalysts of palladium(II) complexes with a terdentate ligand which, to our knowledge, is rather unusual, the influence of the nature of the palladium salt reagent on the hydrogenation process and the absence of redox processes involving the palladium species, which maintains oxidation state two in the course of the catalytic process.

As an extension of this research program and in order to isolate new palladium(II) complexes with terdentate ligands able to act as reagents or catalysts in organic syntheses,[2–6] as well as to verify the influence of the donor-atom set and the ligand behaviour on the catalytic properties, we have now synthesized and structurally characterized a series of palladium(II) complexes with the phenyl 2-pyridyl ketone benzoylhydrazone (H_2L).

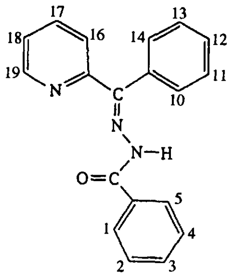
Experimental

Reagents and solvents were standard grade products used without further purification. Phenyl 2-pyridyl ketone and benzoylhydrazine were obtained from Aldrich Chemie.

Elemental analyses (C, H and N) were performed by using a Carlo Erba model EA 1108 apparatus. Determination of palladium was by atomic absorption spectroscopy using a Perkin-Elmer 303-HGA70 instrument. Infrared spectra were recorded with a Nicolet 5PCFT-IR spectrophotometer in the 4000–400 cm^{-1} range by using KBr discs, ^1H NMR spectra on a Brucker 300 FT spectrometer using $SiMe_4$ as internal standard and mass spectra on a Finnigan SSQ 710 spectrometer.

Preparation of phenyl 2-pyridyl ketone benzoylhydrazone (H_2L)

Benzoylhydrazine (1.00 g, 7.34 mmol) was added at room temperature (r.t.) to a methanol (100 cm^3) solution of phenyl 2-pyridyl ketone (1.30 g, 7.30 mmol) containing some drops of glacial acetic acid. The resulting yellow solution was refluxed for 24 h. By slow evaporation of the solvent a crystalline cream product was obtained, filtered off and washed with small portions of diethyl ether (m.p. 142.9–143.7 °C, yield 65%). ^1H NMR ($CDCl_3$, 25 °C): δ 15.11 (s, 1 H, NH), 8.83 [d, 1 H, H^{19}, *J* (*ortho*) 4.41], 7.99 [d, 2 H, $H^{1,5}$, *J* (*ortho*) 7.85], 7.83 [t, 1 H, H^{17}, *J* (*ortho*) 9, *J* (*meta*) 1.5 Hz] and 7.63–7.38 (m, 10 H, 8 H of Ph, 2 H of pyridyl) (Found: C, 75.55; H, 4.80; N, 13.95. Calc. for $C_{19}H_{15}N_3O$: C, 75.75; H, 5.00; N, 13.95%). Mass spectrum (chemical ionization, CI): *m*/*z* 302 ($[M + H]^+$).



H_2L

Reactions of H_2L

With potassium tetrachloropalladate. To a methanol (100 cm^3) solution of H_2L (0.10 g, 0.33 mol) was added dropwise palladium(II) chloride (0.06 g, 0.34 mmol), dissolved in water (35 cm^3) as $K_2[PdCl_4]$. A yellow solid was then isolated and filtered off. Analytical and spectroscopic data were consistent with the formula $[Pd(HL)_2]$. From the solution, by slow evaporation of the solvent, an orange solid of formula [Pd(HL)Cl] was isolated. $[Pd(HL)_2]$: m.p. 250–261 °C (decomp.), yield 54% (Found: C, 65.55; H, 4.10; N, 12.05; Pd, 14.2. Calc. for $C_{38}H_{28}N_6O_2Pd$: C, 64.55, H, 4.00; N, 11.9; Pd, 15.05%). Mass spectrum (FAB): *m*/*z* 708 ($[M + H]^+$). The poor solubility both in $CDCl_3$ and $(CD_3)_2SO$ prevented ^1H NMR spectroscopic analysis. [Pd(HL)Cl]: m.p. 180–210 °C (decomp.), yield 38%. ^1H NMR [$(CD_3)_2SO$, 25 °C]: δ 9.61 (d, 1 H, H^{19}, *J* (*ortho*), 5] 8.21 [t, 1 H, H^{17}, *J* (*ortho*) 7.5], 8.01 [d, 1 H, $H^{1,5}$, *J* (*ortho*) 8], 7.90 (t, 1 H, H^{18}, *J* (*ortho*) 7.5 Hz] and 7.39 (m, 9 H, 8 H of Ph, 1 H of pyridyl) (Found: C, 52.2; H, 3.40; N, 9.70; Pd, 22.75. Calc. for $C_{19}H_{14}ClN_3OPd$: C, 51.6; H, 3.20; N, 9.50; Pd, 24.05%). Mass spectrum (FAB): *m*/*z* 442 ($[M + H]^+$).

With potassium tetraiodopalladate. Palladium(II) iodide (0.12 g, 0.33 mmol), dissolved in acetone–water (10 : 1 v/v, 50 cm^3) as

$K_2[PdI_4]$, was added to H_2L (0.10 g, 0.33 mmol) dissolved in methanol (40 cm^3). The solution was stirred for 3 h at r.t. and then allowed to stand until a brown powder product was filtered off and dried. The analytical data were consistent with the formula $[Pd(H_2L)I_2]\cdot Me_2CO$, m.p. 209–214 °C (decomp.), yield 61%. ^1H NMR [$(CD_3)_2SO$, 25 °C]: δ 14.66 (s, 1 H, NH), 8.97 [d, 1 H, H^{19}, *J* (*ortho*) 4.8], 8.05 (t, 1 H, H^{17}, *J* (*ortho*) 9, *J* (*meta*) 1.6], 7.88 [d, 2 H, $H^{1,5}$, *J* (*ortho*) 6.9 Hz] and 7.66–7.37 (m, 10 H of Ph, 2 H of pyridyl) (Found: C, 44.6; H, 3.55; N, 7.10. Calc. for $C_{22}H_{20}I_2N_3O_2Pd$: C, 44.85; H, 3.10; N, 8.15%). Mass spectrum (FAB): *m*/*z* 661 ($[M + H]^+$) and 533 ($[M + H]^+ - HI$). The determination of the metal by atomic absorption spectroscopy gave a palladium percentage lower than the theoretical value, owing to an incomplete and irregular decomposition of the product, probably due to the presence of the iodide species.

Recrystallization of $[Pd(H_2L)I_2]$ from dimethyl sulfoxide gave orange crystals, the X-ray diffraction analysis of which revealed them to be [Pd(HL)I]. The transformation to the monoiodo-complex can be monitored by the ^1H NMR spectrum of $[Pd(H_2L)I_2]\cdot Me_2CO$ in $(CD_3)_2SO$ solution.

With palladium acetate. Palladium(II) acetate (0.07 g, 0.33 mmol) dissolved in acetonitrile (15 cm^3) was added dropwise to an acetonitrile (45 cm^3) solution of H_2L (0.10 g, 0.33 mmol). The solution was stirred at r.t. for 3 h. A yellow crystalline product was immediately obtained and filtered off. Analytical data were consistent with the formula [PdL(MeCN)], m.p. > 330 °C, yield 58%. ^1H NMR [$(CD_3)_2SO$, 25 °C]: δ 8.91 (d, 1 H, H^{19}), 7.94 [t, 1 H, H^{17}, *J* (*ortho*) 6], 7.36 (m, 9 H, 7 H of Ph, 2 H of pyridyl), 7.11 [t, 1 H, H^{18}, *J* (*ortho*) 7.2], 7.02 [t, 1 H, H^3, *J* (*ortho*) 7.1 Hz] and 2.1 (s, 3 H, MeCN) (Found: C, 56.05; H, 2.85; N, 12.3; Pd, 23.2. Calc. for $C_{21}H_{16}N_4OPd$: C, 56.45; H, 3.60; N, 12.55; Pd, 23.8%).

Reactions of [PdL(MeCN)]

With palladium acetate. The complex [PdL(MeCN)] (0.05 g, 0.11 mmol) was treated with a mixture of acetone (50 cm^3) and dichloromethane (30 cm^3) and the suspension was stirred until complete dissolution. Palladium acetate (0.03 g, 0.11 mmol) dissolved in acetonitrile (10 cm^3) was then added dropwise with stirring at r.t. The red solution was filtered in order to remove the unreacted palladium complex; by slow evaporation of the solvents a red powder product was isolated and filtered off. Analytical data were consistent with the formula $[Pd_2L(MeCO_2)_2]$, m.p. > 320 °C, yield 65% (Found: C, 44.1; H, 3.10; N, 6.95; Pd, 33.9. Calc. for $C_{23}H_{19}N_3O_5Pd_2$: C, 43.85; H, 3.05; N, 6.65; Pd, 33.75%). The poor solubility prevented ^1H NMR spectroscopic analysis.

With acetic acid. A suspension of [PdL(MeCN)] (0.04 g, 0.10 mmol) in toluene (15 cm^3) was refluxed for some minutes; glacial acetic acid (6.30 g, 0.10 mmol) was then added and the clear red solution was refluxed for *ca.* 1 h. The volume was reduced to 15 cm^3 by evaporation under vacuum pressure and the solution treated with hexane (30 cm^3), providing a red-brown solid which was filtered off and dried at 80 °C for *ca.* 2 h, m.p. 280–281 °C decomp., yield 35%. Analytical data were consistent with the formula $[PdL(MeCO_2)]$ (Found: C, 54.15; H, 3.70; N, 9.00; Pd, 22.0. Calc. for $C_{21}H_{17}N_3O_3Pd$: C, 54.0; H, 4.00; N, 8.60; Pd, 22.85%). Owing to the poor solubility both in $CDCl_3$ and $(CD_3)_2SO$ no ^1H NMR analysis could be carried out.

X-Ray crystallography

X-Ray measurements were carried out at room temperature by using a Siemens AED diffractometer and nickel-filtered Cu-Kα radiation for [Pd(HL)Cl] **1** and a Philips PW 1100 diffractometer and monochromatized Mo-Kα radiation for [Pd(HL)I] **2** and [PdL(MeCN)] **3**. Unit-cell dimensions are listed in Table 1 together with a summary of pertinent crystallographic parameters. The intensities were processed with the peak-profile procedure and the data were corrected for Lorentz-polarization factors. A correction for absorption effects was applied after the last isotropic refinement according to the method of Walker and Stuart.[7] For **3** a semiempirical absorption correction was also made using ψ scans of reflections with χ near 90°.

The structures were solved by a combination of direct methods (SIR 92)[8] and Fourier-difference techniques and refined by full-matrix least-squares procedures based on F^2 with all non-hydrogen atoms treated anisotropically. The hydrogen atoms of compounds **1** and **2** were included in the model at their calculated positions and refined riding on their carrier atoms, while those of **3** were all located from Fourier-difference maps and refined isotropically. Calculations were performed on GOULD 6040 and ENCORE 91 computers using the program packages SHELXL 92,[9] ABSORB,[10] PARST[11] and ORTEP.[12] Selected interatomic parameters are listed in Tables 2–4.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/213.

Results and Discussion

Crystal structures

Compounds **1** and **2** are characterized by the presence in the asymmetric unit of two symmetry-independent molecules which do not differ significantly as can be seen from Tables 2 and 3. The ORTEP drawings of one of these molecules (A) are presented in Figs. 1 (**1**) and 2 (**2**) along with the numbering schemes. Both independent molecules of the two compounds contain a palladium atom bound in a square-planar configuration to two nitrogens and an oxygen from HL and the halide. In each case, due to steric effects, the *cis* angles involving the hydrazone donors are markedly acute and the O–Pd–N angle is considerably far from linearity. The co-ordination of HL to palladium produces two planar five-membered chelate rings which are practically coplanar. Apart from one phenyl ring [C(9)–C(14) in molecule A, C(28)–C(33) in B], all the remaining atoms of each ligand lie almost in a plane with atom-to-mean plane distances no longer than 0.21 Å. This plane makes an angle of 63.3(2) (A) and 54.3(2)° (B) in **1** and of 58.6(2) (A) and 60.0(2)° in **2** with the above phenyl ring plane. Up to now, only six square-planar palladium(II) compounds containing the $PdON_2Cl$ co-ordination system, with the two N atoms mutually *cis* positioned, have been characterized by X-ray crystallography[13] and are reported in the Cambridge Structural Database,[14] whereas no compound has been reported containing the $PdON_2I$ system. With a few small exceptions, all bonding parameters found in compound **1** fall in the range in the literature, the values being: Pd–N 1.927–2.100, Pd–O 1.940–2.045, Pd–Cl 2.284–2.333 Å; N–Pd–O 161.9–177.2, N–Pd–Cl 173.9–179.4°. An interesting feature of this structure is an intermetallic Pd(1) ⋯ Pd(2) interaction of 3.447(1) Å, on the basis of which the structure in the solid state could be described as dimeric. By contrast, no Pd ⋯ Pd interaction shorter than 5.0 Å is present in **2**.

The main feature of compound **3** is its cyclopalladated nature, which is illustrated, together with the numbering scheme, in the ORTEP drawing of Fig. 3. The hydrazone molecule behaves as an N_2C terdentate ligand and forms upon co-ordination two chelate rings, one five- (planar to within 0.06

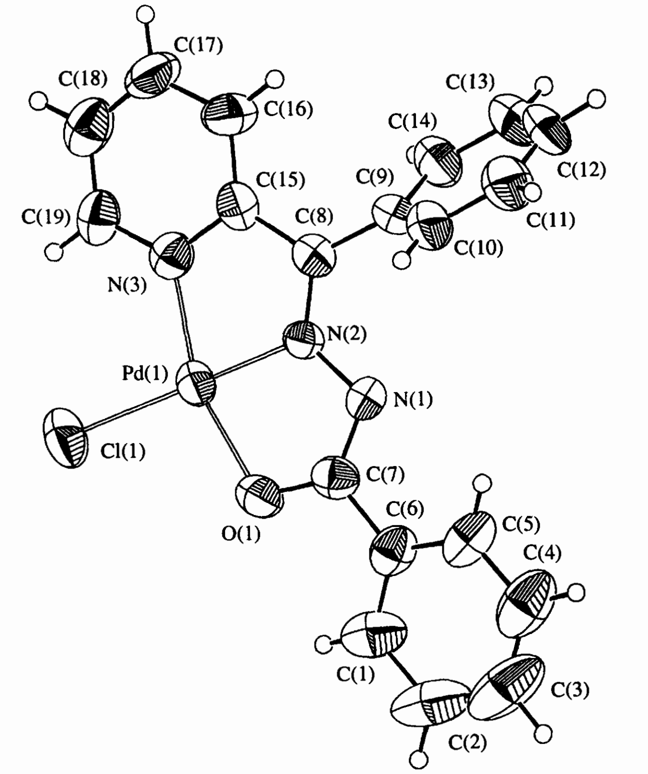


Fig. 1 An ORTEP diagram for [Pd(HL)Cl] **1** (molecule A). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by arbitrarily small spheres

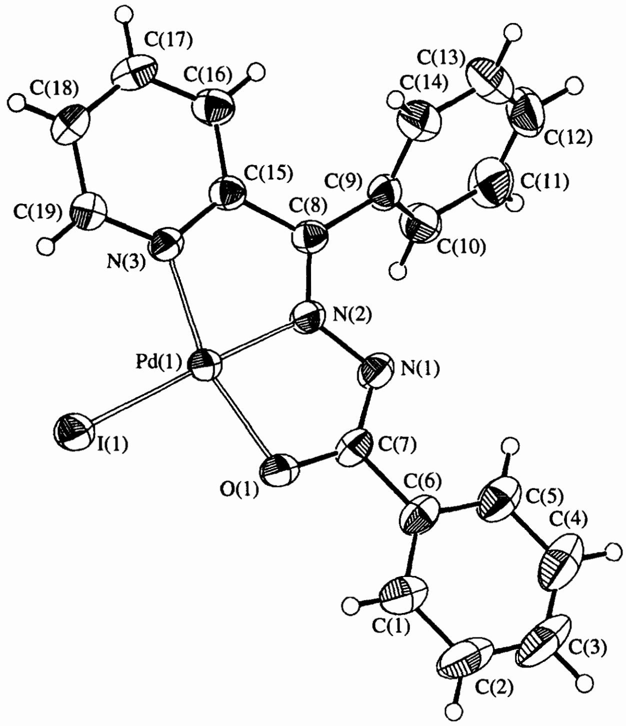


Fig. 2 An ORTEP diagram for [Pd(HL)I] **2** (molecule A). Details as in Fig. 1

Å) and the other six-membered (planar to within 0.13 Å) which are nearly coplanar, the dihedral angle being 5.7(1)°. The nitrogen atom from the acetonitrile ligand completes the square-planar co-ordination sphere. The Pd–N(4)–C(20)–C(21) group is essentially linear with angles of 176.0(5) and 177.9(6)° at N(4) and C(20), respectively. As in **1** and **2**, the hydrazone molecule, except the phenyl ring C(9)–C(14), has an almost planar configuration, with none of the atoms deviating more than 0.26 Å from the best least-squares plane. The phenyl ring is tilted by 83.2(2)° to the rest of the hydrazone moiety. The ligand behaviour of the hydrazone in the three compounds deserves some comment. In spite of always being terdentate, it is monodeprotonated in **1** and **2** and bideprotonated in **3**; moreover, as mentioned above, differences also occur in the nature of the atoms utilized for co-ordination to the palladium atom. Finally, on passing from **1** and **2** to **3** there is a somewhat lengthening of the Pd–N_{py} bond distance (2.003–2.017 *vs.* 2.140 Å). Bond distances and angles in the PdC_3N metallacycle compare favourably with those found in the dianion of N',N'''-(pyridine-2,6-diyldiethylidyne)bis(benzohydrazide),[15] the only structurally characterized cyclopalladated derivative having an adjacent six-membered ring. In particular, in both compounds the Pd–N distance is slightly shorter than the Pd–C one, which agrees fairly well with values quoted for Pd–C(sp^2) bonds, whereas the reverse is observed in other cyclopalladated complexes.[16–18] The molecules in the crystal of **3** are held together by normal van der Waals interactions, the closest approach between atoms of neighbouring molecules being 3.292(8) Å between N(1) and C(18) at $1 - x$, $1 - y$, $2 - z$, whereas the closest intermetallic contact is Pd···Pd ($1 - x$, $1 - y$, $1 - z$) 3.597(2) Å.

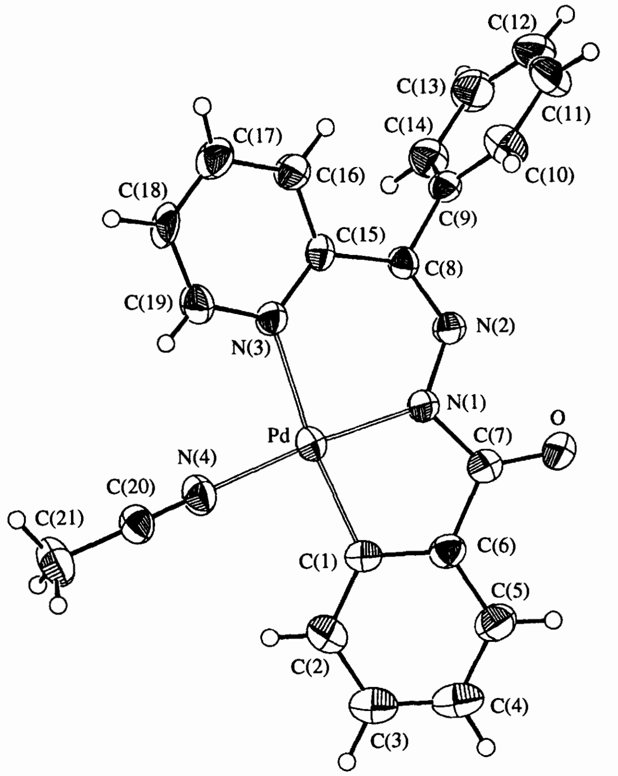


Fig. 3 An ORTEP diagram for [PdL(MeCN)] **3**. Details as in Fig. 1

Infrared spectra

The different ligand behaviour of H_2L in the palladium complexes is well illustrated by comparing the vibrational absorptions in the solid state with those of free H_2L. With the exception of the [Pd(HL)X] (X = Cl, I or $MeCO_2$) complexes, the vibrational spectra of which indicate an analogous co-ordination behaviour of the hydrazone, different spectroscopic patterns are observed for the other complexes related to the different ligand behaviour and the neutral, monodeprotonated and bideprotonated nature of H_2L.

In particular, while the ν(NH) bands are indicative of the neutral or deprotonated nature of the ligand, the ν(CO) bands give an indication about the involvement or the exclusion of the carbonyl oxygen atom in the co-ordination to palladium. In fact

Table 1 Crystal data and summary of intensity data collection and structure refinement for [Pd(HL)Cl] **1**, [Pd(HL)I] **2** and [PdL(MeCN)] **3**

	1	**2**	**3**
Formula	$C_{19}H_{14}ClN_3OPd$	$C_{19}H_{14}IN_3OPd$	$C_{21}H_{16}N_4OPd$
M	442.19	533.64	446.78
Crystal symmetry	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$	$P\bar{1}$
Crystal dimensions/mm	0.10 × 0.11 × 0.46	0.09 × 0.12 × 0.18	0.26 × 0.39 × 0.44
a/Å	20.931(9)	12.798(3)	9.668(5)
b/Å	12.788(5)	15.385(4)	10.955(6)
c/Å	13.212(5)	10.047(3)	8.736(5)
α/°		102.82(1)	97.91(5)
β/°	93.77(5)	97.72(1)	92.75(4)
γ/°		74.42(2)	106.09(5)
U/Å^3	3529(2)	1852.1(9)	876.9(9)
Z	8	4	2
D_c/g cm^{-3}	1.665	1.914	1.692
F(000)	1760	1024	448
λ/Å	1.541 78	0.710 73	0.710 73
μ/cm^{-1}	99.7	26.8	10.8
Scan technique	θ–2θ	θ–2θ	θ–2θ
θ Range/°	2.5–70	3–28	3–30
Reflections measured	7317	8394	5121
Reflections unique used in refinement	6694	8290	4780
Parameters refined	451	451	297
$R1$ [$F_o > 4\sigma(F_o)$]	0.0339	0.0249	0.0363
Reflections observed	3500	5416	3749
$wR2$ (F^2, all data)	0.1063	0.0995	0.1943

Table 2 Bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for [Pd(HL)Cl] **1**

Pd(1)–Cl(1)	2.311(2)	Pd(2)–Cl(2)	2.314(2)
Pd(1)–O(1)	2.033(4)	Pd(2)–O(2)	2.018(4)
Pd(1)–N(2)	1.917(4)	Pd(2)–N(5)	1.919(5)
Pd(1)–N(3)	2.017(5)	Pd(2)–N(6)	2.003(5)
O(1)–C(7)	1.292(8)	O(2)–C(26)	1.288(7)
N(1)–N(2)	1.382(6)	N(4)–N(5)	1.380(7)
N(1)–C(7)	1.330(8)	N(4)–C(26)	1.329(8)
N(2)–C(8)	1.310(7)	N(5)–C(27)	1.299(8)
N(3)–C(15)	1.352(8)	N(6)–C(34)	1.362(9)
N(3)–C(19)	1.354(8)	N(6)–C(38)	1.341(9)
N(2)–Pd(1)–N(3)	80.8(2)	N(5)–Pd(2)–N(6)	80.9(2)
O(1)–Pd(1)–N(3)	160.6(2)	O(2)–Pd(2)–N(6)	161.5(2)
O(1)–Pd(1)–N(2)	79.8(2)	O(2)–Pd(2)–N(5)	80.6(2)
Cl(1)–Pd(1)–N(3)	99.8(2)	Cl(2)–Pd(2)–N(6)	100.2(2)
Cl(1)–Pd(1)–N(2)	177.7(1)	Cl(2)–Pd(2)–N(5)	178.3(2)
Cl(1)–Pd(1)–O(1)	99.6(1)	Cl(2)–Pd(2)–O(2)	98.3(1)
Pd(1)–O(1)–C(7)	108.1(4)	Pd(2)–O(2)–C(26)	107.7(3)
N(2)–N(1)–C(7)	108.2(4)	N(5)–N(4)–C(26)	108.4(4)
Pd(1)–N(2)–N(1)	117.8(3)	Pd(2)–N(5)–N(4)	116.8(3)
N(1)–N(2)–C(8)	123.5(4)	N(4)–N(5)–C(27)	123.9(5)
Pd(1)–N(2)–C(8)	118.6(4)	Pd(2)–N(5)–C(27)	119.2(4)
Pd(1)–N(3)–C(19)	127.1(4)	Pd(2)–N(6)–C(38)	127.8(4)
Pd(1)–N(3)–C(15)	112.9(4)	Pd(2)–N(6)–C(34)	112.3(4)
C(15)–N(3)–C(19)	119.9(5)	C(34)–N(6)–C(38)	119.7(6)
O(1)–C(7)–N(1)	126.0(5)	O(2)–C(26)–N(4)	126.5(6)
N(2)–C(8)–C(15)	113.4(5)	N(5)–C(27)–C(34)	112.4(6)
N(3)–C(15)–C(8)	114.2(5)	N(6)–C(34)–C(27)	114.9(6)

Table 3 Bond distances (Å) and angles (°) with e.s.d.s in parentheses for [Pd(HL)I] **2**

Pd(1)–I(1)	2.602(1)	Pd(2)–I(2)	2.596(1)
Pd(1)–O(1)	2.028(4)	Pd(2)–O(2)	2.016(3)
Pd(1)–N(2)	1.937(4)	Pd(2)–N(5)	1.944(6)
Pd(1)–N(3)	2.015(5)	Pd(2)–N(6)	2.014(4)
O(1)–C(7)	1.307(7)	O(2)–C(26)	1.306(8)
N(1)–N(2)	1.376(8)	N(4)–N(5)	1.379(6)
N(1)–C(7)	1.311(7)	N(4)–C(26)	1.315(8)
N(2)–C(8)	1.294(7)	N(5)–C(27)	1.293(8)
N(3)–C(15)	1.370(7)	N(6)–C(34)	1.377(9)
N(3)–C(19)	1.333(9)	N(6)–C(38)	1.333(7)
N(2)–Pd(1)–N(3)	81.1(2)	N(5)–Pd(2)–N(6)	81.2(2)
O(1)–Pd(1)–N(3)	161.2(2)	O(2)–Pd(2)–N(6)	161.3(2)
O(1)–Pd(1)–N(2)	80.1(2)	O(2)–Pd(2)–N(5)	80.2(2)
I(1)–Pd(1)–N(3)	101.2(1)	I(2)–Pd(2)–N(6)	101.3(2)
I(1)–Pd(1)–N(2)	174.9(1)	I(2)–Pd(2)–N(5)	176.9(2)
I(1)–Pd(1)–O(1)	97.7(1)	I(2)–Pd(2)–O(2)	97.3(1)
Pd(1)–O(1)–C(7)	107.5(4)	Pd(2)–O(2)–C(26)	108.0(3)
N(2)–N(1)–C(7)	109.2(5)	N(5)–N(4)–C(26)	109.3(4)
Pd(1)–N(2)–N(1)	116.8(3)	Pd(2)–N(5)–N(4)	116.3(4)
N(1)–N(2)–C(8)	124.3(5)	N(4)–N(5)–C(27)	124.8(5)
Pd(1)–N(2)–C(8)	118.9(4)	Pd(2)–N(5)–C(27)	118.9(4)
Pd(1)–N(3)–C(19)	128.7(4)	Pd(2)–N(6)–C(38)	128.9(4)
Pd(1)–N(3)–C(15)	111.8(3)	Pd(2)–N(6)–C(34)	111.8(4)
C(15)–N(3)–C(19)	119.5(5)	C(34)–N(6)–C(38)	119.3(5)
O(1)–C(7)–N(1)	126.5(5)	O(2)–C(26)–N(4)	126.1(5)
N(2)–C(8)–C(15)	112.9(5)	N(5)–C(27)–C(34)	112.8(5)
N(3)–C(15)–C(8)	115.2(5)	N(6)–C(34)–C(27)	115.2(2)

the ν(CO) band decreases from 1686 (free H_2L) to 1635 (neutral N,N bidentate), to 1613 (monodeprotonated N,N bidentate) and under 1600 cm^{-1} (monodeprotonated N,N,O terdentate). Other significant vibrational absorptions are ν(C≡N) at 2288 cm^{-1} for [PdL(MeCN)], $\nu_{asym}(CO_2)$ at 1549 cm^{-1} and $\nu_{sym}(CO_2)$ at 1334 cm^{-1} for the bimetallic cyclopalladate complex $[Pd_2L(MeCO_2)_2]$ and $\nu_{asym}(CO_2)$ at 1619 cm^{-1} and $\nu_{sym}(CO_2)$ at 1363 cm^{-1} for the monometallic complex $[Pd(HL)(MeCO_2)]$.[19]

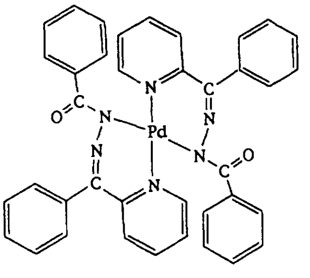
The most interesting feature is the versatility of H_2L in the co-ordination to the palladium atom. From the reaction of H_2L with the palladium salts, palladium(II) complexes have been isolated which differ in stoichiometry and co-ordinating properties of the ligand.

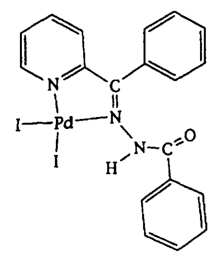
On the basis of the analytical and spectroscopic data, and taking into account the main vibrational absorptions of a large number of metal hydrazone complexes, the structures of which have been previously reported,[1,20–22] a square-planar geometry for $[Pd(HL)_2]$ and $[Pd(H_2L)I_2]\cdot Me_2CO$ can be hypothesized, with an N,N-bidentate behaviour of the ligand involving the hydrazidic nitrogen atoms in the former and the iminic ones in the latter.

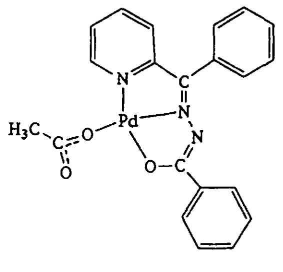
The versatility of the ligand in co-ordination to palladium(II) seems to be promising for its use in homogeneous catalysis, in the context with the ability to introduce appropriate substrates on the metal centre through a modification of the ligand conformation. Cyclometallated compounds, especially palladium(II) derivatives,[23,24] are highly convenient reagents for

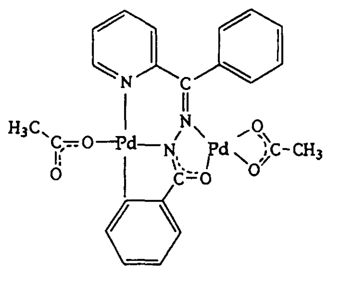
Table 4 Bond distances (Å) and angles (°) with e.s.d.s in parentheses for [PdL(MeCN)] **3**

Pd–N(1)	1.971(5)	N(3)–C(19)	1.332(7)
Pd–N(3)	2.140(4)	N(4)–C(20)	1.133(8)
Pd–N(4)	2.034(5)	O–C(7)	1.220(7)
Pd–C(1)	2.007(5)	C(1)–C(6)	1.396(8)
N(1)–N(2)	1.349(7)	C(6)–C(7)	1.484(9)
N(1)–C(7)	1.394(6)	C(8)–C(15)	1.479(6)
N(2)–C(8)	1.298(6)	C(20)–C(21)	1.450(9)
N(3)–C(15)	1.356(8)		
N(4)–Pd–C(1)	93.0(2)	C(15)–N(3)–C(19)	118.0(4)
N(3)–Pd–C(1)	172.2(2)	Pd–N(4)–C(20)	176.0(5)
N(3)–Pd–N(4)	94.6(2)	Pd–C(1)–C(6)	112.8(4)
N(1)–Pd–C(1)	81.4(2)	Pd–C(1)–C(2)	128.9(4)
N(1)–Pd–N(4)	174.3(2)	C(1)–C(6)–C(7)	117.0(5)
N(1)–Pd–N(3)	90.9(2)	O–C(7)–C(6)	125.1(5)
Pd–N(1)–C(7)	118.1(3)	N(1)–C(7)–C(6)	109.9(5)
Pd–N(1)–N(2)	128.3(3)	N(1)–C(7)–O	125.0(5)
N(2)–N(1)–C(7)	113.5(4)	N(2)–C(8)–C(15)	131.1(5)
N(1)–N(2)–C(8)	123.6(5)	N(3)–C(15)–C(8)	121.9(4)
Pd–N(3)–C(19)	119.8(4)	N(4)–C(20)–C(21)	177.9(6)
Pd–N(3)–C(15)	122.3(3)		

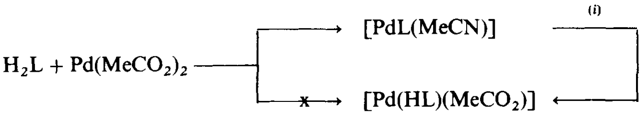








the preparation of various substances. Much work has been reported on the preparation and characterization of mono- and di-nuclear cyclopalladated complexes, the majority of which contain bidentate nitrogen ligands;[25–27] only a few cases of terdentate ligands have been described.[28,29] The very poor solubility of [PdL(MeCN)] in the common solvents prevents its use as reagent in metal–carbon bond insertion processes. Accordingly, the synthesis of more soluble cyclopalladated complexes containing hydrazonic ligands is now in progress in our laboratory. With regard to the reactivity of this class of compounds, of current interest are the dissociation reactions which result in cleavage of the Pd–C bond, involving reduction or protonolysis of the complex by a mineral acid.[30,31] From the protonolysis processes the corresponding organic ligand and palladium metal or palladium(II) salt are usually formed. By contrast, in our case, protonolysis by acetic acid affords the acetato complex [Pd(HL)(MeCO$_2$)], in which the hydrazone is still co-ordinated to the palladium atom as confirmed by its spectroscopic pattern being similar to those of [Pd(HL)X] (X = Cl or I). It is worthy of note that, unlike other palladium(II)–hydrazone acetato-complexes,[1,32] [Pd(HL)-(MeCO$_2$)] is not obtainable by the direct reaction of palladium(II) acetate with the ligand (Scheme 1). In order to obtain a doubly cyclopalladated derivative,[33] [PdL(MeCN)] has been treated with palladium(II) acetate. The reaction gave rise to a monocyclopalladated bimetallic complex, the structure of which is believed to involve one palladium atom maintaining its terdentate donor set and the other one co-ordinating to the iminic nitrogen and the oxygen atom of the hydrazone; two acetate groups complete the square-planar co-ordination geometry around both palladium atoms.



Scheme 1 (*i*) MeCO$_2$H

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References

1 A. Bacchi, M. Carcelli, M. Costa, P. Pelagatti, C. Pelizzi and G. Pelizzi, *Gazz. Chim. Ital.*, 1994, **124**, 429.
2 J.-E. Bäckvall, *Acc. Chem. Res.*, 1983, **16**, 335.
3 J. Tsuji and I. Minami, *Acc. Chem. Res.*, 1987, **20**, 140.
4 W. de Graaf, S. Harder, J. Boersma, G. van Koten and J. A. Kanters, *J. Organomet. Chem.*, 1988, **358**, 545.
5 T. N. Mitchell, *Synthesis*, 1992, 803.
6 D. L. Reger and D. G. Garza, *Organometallics*, 1993, **12**, 554.
7 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
8 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
9 G. M. Sheldrick, SHELXL 92, Program for Structure Refinement, University of Göttingen, 1992.
10 F. Ugozzoli, *Comput. Chem.*, 1987, **11**, 109.
11 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
12 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
13 M. Kurahashi, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2045; H. Elias, E. Hilms and H. Paulus, *Z. Naturforsch., Teil B*, 1982, **37**, 1266; P. Bandyopadhyay, D. Bandyopadhyay, A. Chakravorty, F. A. Cotton, L. R. Falvello and S. Han, *J. Am. Chem. Soc.*, 1983, **105**, 6327; G. Annibale, L. Cattalini, V. Bertolasi, V. Ferretti, G. Gilli and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1989, 1265; R. A. Berthon, S. B. Colbran and D. C. Craig, *Polyhedron*, 1992, **11**, 243; I. Cho, H. Yeo, D. Whong and K. Kim, *Acta Crystallogr., Sect. C*, 1992, **48**, 1488.
14 F. H. Allen and O. Kennard, *Chemical Design Automation News*, 1993, **8**, 1, 31.
15 G. J. Palenik and T. J. Giordano, *J. Chem. Soc., Dalton Trans.*, 1987, 1175.
16 P. W. Clark, S. F. Dyke, G. Smith, C. H. L. Kennard and A. H. White, *Acta Crystallogr., Sect. C*, 1985, **41**, 1742.
17 C. A. O'Mahoney, I. P. Parkin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1989, 1179.
18 P. Espinet, M. Y. Alonso, G. Garcia-Herbosa, J. M. Ramos and Y. Jeannin, *Inorg. Chem.*, 1992, **31**, 2501.
19 N. F. Curtis, *J. Chem. Soc. A*, 1968, 1579.
20 A. Bonardi, C. Merlo, C. Pelizzi, G. Pelizzi, P. Tarasconi and F. Cavatorta, *J. Chem. Soc., Dalton Trans.*, 1991, 1063.
21 M. Carcelli, C. Pelizzi, G. Pelizzi, P. Mazza and F. Zani, *J. Organomet. Chem.*, 1995, **488**, 55.

22 S. Ianelli, P. Mazza, M. Orcesi, C. Pelizzi, G. Pelizzi and F. Zani, *J. Inorg. Biochem.*, 1995, **60**, 89.
23 A. D. Ryabov, *Synthesis*, 1985, 233.
24 M. Pfeffer, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 567.
25 K. Hiraki, Y. Fuchita, H. Nakaya and S. Takatura, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2531.
26 A. D. Ryabov, *J. Organomet. Chem.*, 1984, **268**, 91.
27 F. Maassarani, M. Pfeffer, J. Spencer and E. Wehman, *J. Organomet. Chem.*, 1994, **466**, 265.
28 C. Sinha, D. Bandyopadhyay and A. Chakravorty, *Inorg. Chem.*, 1988, **27**, 1173.
29 S. Chattopadhyay, C. Sinha, P. Basu and A. Chakravorty, *J. Organomet. Chem.*, 1991, **414**, 421.
30 E. L. Weinberg, B. K. Hunter and M. C. Baird, *J. Organomet. Chem.*, 1982, **240**, 95.
31 A. D. Ryabov, V. A. Polyakov and A. K. Yatsimirsky, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1503.
32 A. Bacchi, M. Carcelli, M. Costa, A. Leporati, P. Pelagatti, C. Pelizzi and G. Pelizzi, XIth FECHEM, Parma, 10–15th September 1995.
33 G. B. Caygill, R. M. Hartshorn and P. J. Steel, *J. Organomet. Chem.*, 1990, **382**, 455.

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