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PALLADIUM(II) AND PLATINUM(II) DERIVATIVES WITH CHIRAL 2,2'-BIPYRIDINES. X-RAY STRUCTURE OF $C_{18}H_{15}ClN_2Pd$; C- AND N-INTRAMOLECULAR COORDINATION IN A SIX-MEMBERED METALLACYCLE

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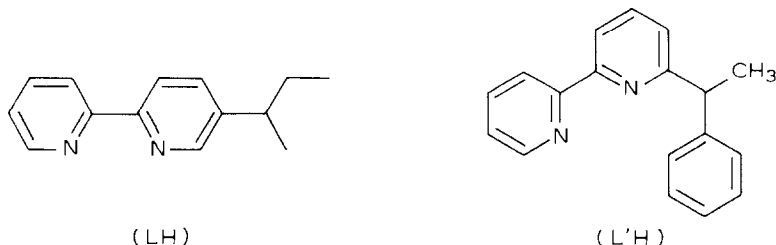
Summary

The reactions of (+)-(S)-5-s-butyl-2,2'-bipyridine (LH) and 6-(1-methylbenzyl)-2,2'-bipyridine (L'H) with $Na_2[PdCl_4]$ and $K_2[PtCl_4]$ give the 1:1 adducts (LH)MCl₂ (M = Pd, **1**; M = Pt, **2**) and the metallated species (L')MCl (M = Pd, **3**; M = Pt, **4**), respectively. In complexes **3** and **4**, the deprotonated bipyridine behaves as a tridentate ligand; there is coordination to the metal through the two nitrogen atoms and the *ortho*-carbon atom of the phenyl ring to give a six-membered metallacycle. The X-ray structure of complex **3** shows that the coordination around the palladium atom is distorted towards tetrahedral from the usual square-planar geometry.

Introduction

Several 2,2'-bipyridines having chiral alkyl substituents on one of the heterocyclic rings, such as LH and L'H, have been recently synthesized [1]. Complexes of 2,2'-bipyridines are known to display a remarkable catalytic activity towards the reduction of olefins and ketones under mild conditions [2]. In addition, quite recently the chiral ligands LH and L'H in the presence of rhodium(I) derivatives have been shown by some of us to be able to promote the asymmetric transfer hydrogenation of acetophenone [3]. It thus seemed of interest to investigate the

reactions of the new ligands with several transition metal ions, and we report here the initial results, involving interactions with palladium(II) and platinum(II) salts.

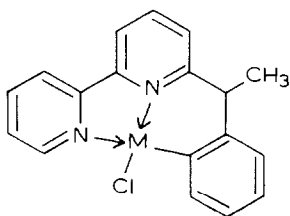


Results and discussion

In an attempt to obtain the 1:1 adducts, both the ligands LH and L'H (racemic) were treated with $\text{Na}_2[\text{PdCl}_4]$ and $\text{K}_2[\text{PtCl}_4]$ according to the procedure described by Morgan for the synthesis of the adducts $(\text{bipy})\text{MCl}_2$ (bipy = 2,2'-bipyridine; M = Pd, Pt), i.e. in aqueous HCl [4]. The reaction with the ligand LH afforded the expected adducts $(\text{LH})\text{PdCl}_2$ (**1**) and $(\text{LH})\text{PtCl}_2$ (**2**) in reasonable yields (65–70%).

The complexes **1** and **2** are non-electrolytes and monomeric in dichloromethane solution: in agreement, the IR spectra show two M–Cl stretching vibrations in the range expected for a *cis*- N_2MCl_2 arrangement (e.g. complex **2**, $\nu(\text{Pt-Cl})$ 335, 325 cm^{-1}). In the ^1H NMR spectrum (CD_2Cl_2 , r.t.) the protons of the alkyl chain are not significantly affected by the coordination to the metal, a slight deshielding effect being observed only for the CH proton bonded to the heterocyclic ring. In contrast, a sharp difference is observed in the aromatic region where two protons are markedly shifted to lower fields: the palladium complex, **1**, exhibits two well separated resonances (1/1), while the platinum derivative, **2**, shows a more complex unresolved pattern, suggesting that a long-range platinum–hydrogen coupling is active. Thus, we ascribe these signals to the 6,6'-protons, even though in some octahedral tris(2,2'-bipyridine) derivatives, the lowest-field resonances have been shown to be due to the 3,3' protons [5].

The reaction with the ligand L'H, under the same conditions, followed a different path and neither with $\text{Na}_2[\text{PdCl}_4]$ nor $\text{K}_2[\text{PtCl}_4]$ were the adducts isolated. The species obtained were identified by elemental analyses and ^1H NMR spectra as neutral monomeric metalated derivatives, $(\text{L}')\text{MCl}$ (**3** and **4**).



(**3**, M = Pd ;
4, M = Pt)

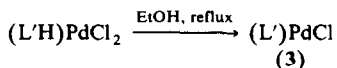
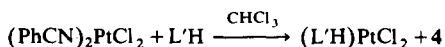
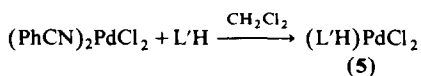
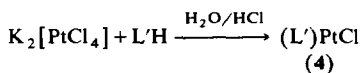
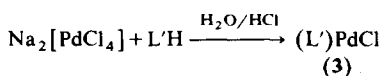
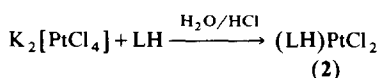
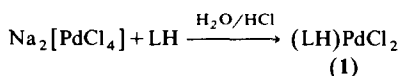
In **3** and **4** the deprotonated bipyridine acts as a tridentate ligand, being coordinated to the metal through the two nitrogen atoms and the *ortho*-carbon atom

of the phenyl substituent; such behaviour has been confirmed, inter alia, by the X-ray structure of complex **3** (vide infra).

The adduct $(L'H)PdCl_2$ (**5**) however, can be obtained by a different route, namely by reaction of the ligand with $(PhCN)_2PdCl_2$ in refluxing dichloromethane. The addition product **5** is likely to be an intermediate in the synthesis of the metalated derivative **3**; conversion, i.e. dehydrochlorination, of **5** to **3** is indeed, readily achieved by refluxing in ethanol.

The corresponding platinum derivative, $(L'H)PtCl_2$, was not isolated in pure form: the reaction between $(PhCN)_2PtCl_2$ and the ligand gives a mixture of **4** and the adduct. The latter was identified by comparison of its 1H NMR spectrum with that of the palladium analogue.

The overall pattern of the reactions of the ligands LH and L'H is summarized in Scheme 1.



SCHEME 1

The 1H NMR spectra of **3** and **4** are quite similar: in the platinum complex **4**, even the signal due to the methyl protons (doublet, $^3J(H, H)$ ca. 7 Hz) is accompanied by satellites (1/4/1) due to the coupling with ^{195}Pt , ($^5J(Pt, H)$ 4.5 Hz); such a long range coupling is rather unusual. A comparison of the spectrum of the free ligand L'H with those of the metalated species **3** and **4** reveals no appreciable downfield shift for the resonance of the CH_3CH proton as a consequence of the incorporation of the benzylic carbon into a six-membered ring. In contrast, a sharp deshielding of the same CH proton is observed in the adduct **5**; a similar effect has been reported previously for some adducts and cyclopalladated derivatives of 2-benzylpyridine [6]. In the complexes **3**, **4** and **5**, once again, one of the aromatic protons resonates at very low field: the observed coupling to ^{195}Pt ($^3J(Pt, H)$ ca. 6 Hz, complex **4**) allows the resonance to be assigned to 6'H with certainty.

It is noteworthy that in our work the metalated species were obtained from tetrachloropalladate(II) and platinate(II) ions, whereas previous studies with aryl-substituted nitrogen bases and aryl-sulfides afforded cyclopalladated complexes by

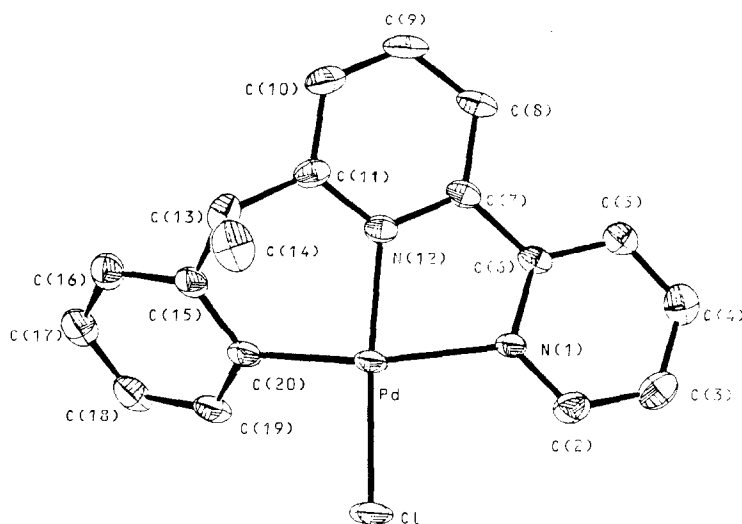


Fig. 1. ORTEP view of complex **3**.

reaction with palladium acetate but not with palladium chloride or the tetrachloropalladate ion [7]. Preliminary results on the reaction of the chiral aryl-substituted 2-(1-methylbenzyl)pyridine with $\text{Na}_2[\text{PdCl}_4]$ as well as with $(\text{PhCN})_2\text{PdCl}_2$, indicate that no metalated species is formed [8], suggesting that with the chloro derivatives metalation occurs easily only when a chelating ligand is employed, i.e. if the resulting molecule contains more than one cycle. In agreement with this, Newkome and coworkers have recently obtained a series of palladium metalated derivatives by reaction of $\text{Li}_2[\text{PdCl}_4]$ with functionalized bidentate nitrogen ligands [9].

Six-membered cyclometalated complexes having nitrogen donor atoms have been reported [6,9,10], but they are rare [11], and there is only one mention on their structures in the solid state [9]. Consequently an X-ray investigation of complex **3** was undertaken. Figure 1 shows the structure of **3** in the solid state. The crystal consists of discrete molecules and there are no unusual intermolecular interactions. Crystal data, relevant bond distances and angles and positional parameters are listed in Tables 3, 4 and 5, respectively.

The coordination geometry around the metal atom is distorted towards a tetrahedral configuration, with a dihedral angle of 16° between planes $\text{N}(1), \text{Pd}, \text{N}(12)$ and $\text{C}(20), \text{Pd}, \text{Cl}$. Such a deviation from the idealized square-planar geometry seems to be essentially due to the limited flexibility of the tridentate substituted bipyridine ligand, which precludes coplanarity for atoms $\text{N}(1), \text{N}(12), \text{C}(20)$ and Pd and also the linearity of the interactions $\text{C}(4) \cdots \text{N}(1)\text{-Pd}$, $\text{C}(9) \cdots \text{N}(12)\text{-Pd}$ and $\text{C}(17) \cdots \text{C}(20)\text{-Pd}$. Some intramolecular overcrowding is also apparent in the $\text{Cl} \cdots \text{H}(19)$ and $\text{Cl} \cdots \text{H}(2)$ contacts (2.76 and 2.86 Å, respectively).

The $\text{Pd}\text{-N}(12)$ bond length, 2.008(4) Å, can be compared with that for the $\text{Pd}\text{-N}$ bond in $(\text{bipy})\text{Pd}(\text{C}_5\text{HF}_6\text{O}_2)$, 2.007 Å [12], while the $\text{Pd}\text{-N}(1)$ bond is ca. 0.11 Å longer, as expected on the basis of the high *trans*-influence of the aryl carbon atom $\text{C}(20)$.

The six-membered metallacycle displays a boat-like conformation, with the Pd and C(13) atoms 0.52 and 0.62 Å, respectively, above the "best" plane of atoms C(11), N(12), C(15) and C(20). The bond distances and angles within the ring are quite normal, and do not appear to be affected by strain effects. Thus it seems that the difficulty of obtaining species having both C- and N-intramolecular coordination in a six-membered cycle is not to be ascribed to an instability of the molecule in the ground state.

The presence on the metal atom of a [5.6]-fused-ring system in **3** and **4** may give rise to unusual reactivity, and this possibility merits investigation. Preliminary results indicate that carbon monoxide inserts into the palladium-carbon bond to give the corresponding acyl derivative, whereas the platinum complex **4** affords species containing a terminal carbonyl ligand [8].

Experimental

The ligands LH and L'H were made as described in refs. 1 and 3, respectively. Analytical and other data are reported in Table 1 and ¹H NMR data in Table 2.

TABLE 1
ANALYTICAL DATA

| Compound | Found (calcd.) (%) | | | | MW ^a |
|------------------------|--------------------|--------|--------|--------|-----------------|
| | C | H | N | Cl | |
| (LH)PdCl ₂ | 43.56 | 4.25 | 7.10 | — | 421 |
| (1) | (43.15) | (4.11) | (7.19) | — | (389.3) |
| (LH)PtCl ₂ | 35.10 | 3.34 | 6.02 | — | — |
| (2) | (35.15) | (3.37) | (5.86) | — | — |
| (L')PdCl | 53.05 | 3.75 | 6.87 | 8.75 | 438 |
| (3) | (53.88) | (3.74) | (6.98) | (8.84) | (400.85) |
| (L')PtCl | 44.07 | 3.19 | 5.88 | 8.07 | 485 |
| (4) | (44.12) | (3.06) | (5.72) | (7.24) | (489.5) |
| (L'H)PdCl ₂ | 49.30 | 3.98 | 5.94 | — | — |
| (5) | (49.38) | (3.66) | (6.40) | — | — |

^a Methylene chloride as solvent; calculated values in parentheses.

TABLE 2
¹H NMR DATA^{a,b}

| Compound | CH ₃ CH ₂ | CH ₃ CH | CH ₂ | CH | Aromatic |
|----------------------------|---------------------------------|---------------------------|-----------------|---------------------------|----------|
| LH | 0.85 t (7.2) | 1.30 d (6.8) | 1.65 m | 2.65 m | 7.2–8.8 |
| (LH)PdCl ₂ (1) | 0.80 t (7.2) | 1.25 d (6.9) | 1.55 m | 2.75 m | 7.4–9.3 |
| (LH)PtCl ₂ (2) | 0.85 t (7.2) | 1.30 d (6.9) | 1.60 m | 2.85 m | 7.5–9.9 |
| L'H | — | 1.80 d (~ 7) | — | 4.35 q (~ 7) | 7.1–8.7 |
| (L')PdCl (3) | — | 1.80 d (~ 7) | — | 4.35 q (~ 7) | 6.8–9.2 |
| (L')PtCl (4) | — | 1.75 d (~ 7) ^c | — | 4.30 q (~ 7) ^d | 6.8–9.5 |
| (L'H)PdCl ₂ (5) | — | 1.75 d (~ 7) | — | 6.25 q (~ 7) | 7.2–9.3 |

^a Chemical shifts, δ (ppm); coupling constants (Hz) in parenthesis. ^b CD₂Cl₂, room temperature. ^c ³J(Pt, H) 4.5 Hz. ^d ⁴J(Pt, H) 4.8 Hz.

Infrared spectra were recorded with Perkin–Elmer 1310 and 983 photometers using Nujol mulls. ^1H NMR were recorded with a Varian CFT-20 and a Bruker instrument operating at 80 MHz.

Synthesis of compounds 1 and 2

Compound 1. To a solution of $\text{Na}_2[\text{PdCl}_4] \cdot 0.33 \text{H}_2\text{O}$ (460.7 mg, 1.54 mmol) in water (80 ml) are added 300 mg (1.65 mmol) of the racemic LH and 5 ml of 2*N* HCl. The mixture is heated on a water bath until the solution is colorless; then cooled and the pale yellow precipitate is filtered off, washed successively with water, ethanol, and diethyl ether, then recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, yield 66%, m.p. (dec.) 275°C

Compound 2. This was made similarly from $\text{K}_2[\text{PtCl}_4]$; orange-yellow, yield 70%, m.p. (dec.) 280°C.

Synthesis of compounds 3 and 4

Compound 3. To a solution of $\text{Na}_2[\text{PdCl}_4] \cdot 0.33 \text{H}_2\text{O}$ (300.2 mg, 1 mmol) in water (50 ml) were added 260 mg (1 mmol) of the racemic L/H and 3.1 ml of 2*N* HCl. The procedure used for compound 1 then gave the yellow product in 73% yield, m.p. 244–246°C.

Compound 4. This was made similarly from $\text{K}_2[\text{PtCl}_4]$; orange-yellow, yield 65%, m.p. 289–290°C.

TABLE 3

CRYSTAL DATA AND DETAILS OF MEASUREMENTS

| | |
|--|---|
| Formula | $\text{C}_{18}\text{H}_{15}\text{ClN}_2\text{Pd}$ |
| Formula weight | 401.2 |
| Crystal system | monoclinic |
| <i>a</i> (Å) | 7.790(5) |
| <i>b</i> (Å) | 19.853(18) |
| <i>c</i> (Å) | 10.033(7) |
| β (°) | 95.43(2) |
| <i>V</i> (Å ³) | 1545 |
| <i>d</i> _{calcd.} (g cm ⁻³) | 1.725 |
| <i>Z</i> | 4 |
| Space group | $P2_1/c$ |
| <i>F</i> (000) | 800 |
| Radiation | Mo- K_α (λ 0.71073 Å) |
| μ (Mo- K_α) | 13.56 |
| Scan range (°) | $3 < \theta < 25$ |
| Scan method | ω |
| Scan interval (°) | $1.4 + 0.35 \tan \theta$ |
| Prescan speed (° min ⁻¹) | 3.3 |
| Prescan acceptance σ (<i>I</i>)/ <i>I</i> | 0.66 |
| Required σ (<i>I</i>)/ <i>I</i> | 0.03 |
| Max. time for data collection (s) | 45 |
| Collected octants | $\pm h, +k, +l$ |
| No. of reflections collected | 2707 |
| observed reflections ($I > 3 \sigma(I)$) | 1963 |
| <i>R</i> , <i>R</i> _w | 0.050, 0.061 |
| Crystal size (mm) | $0.1 \times 0.15 \times 0.25$ |

TABLE 4
SELECTED BOND DISTANCES (Å) AND ANGLES (°) (with e.s.d.'s in parentheses)

| | | | |
|-------------|-----------|-------------------|----------|
| Pd-Cl | 2.295(2) | Cl-Pd-C(20) | 93.7(2) |
| Pd-N(1) | 2.119(4) | Cl-Pd-N(1) | 95.9(1) |
| Pd-N(12) | 2.008(4) | Cl-Pd-N(12) | 173.6(1) |
| Pd-C(20) | 1.980(6) | N(1)-Pd-N(12) | 79.5(2) |
| N(1)-C(2) | 1.318(8) | N(1)-Pd-C(20) | 162.3(2) |
| C(2)-C(3) | 1.371(9) | N(12)-Pd-C(20) | 91.9(2) |
| C(3)-C(4) | 1.366(10) | Pd-N(1)-C(6) | 111.7(4) |
| C(4)-C(5) | 1.361(10) | N(1)-C(6)-C(7) | 115.5(5) |
| C(5)-C(6) | 1.379(8) | C(6)-C(7)-N(12) | 114.7(5) |
| C(6)-C(7) | 1.477(8) | C(7)-N(12)-Pd | 116.0(4) |
| C(7)-C(8) | 1.382(8) | Pd-N(12)-C(11) | 124.7(4) |
| C(8)-C(9) | 1.380(9) | N(12)-C(11)-C(13) | 118.2(5) |
| C(9)-C(10) | 1.344(9) | C(11)-C(13)-C(15) | 111.0(5) |
| C(10)-C(11) | 1.414(8) | C(13)-C(15)-C(20) | 121.7(5) |
| C(11)-N(12) | 1.354(7) | C(15)-C(20)-Pd | 120.6(4) |
| C(11)-C(13) | 1.504(9) | Pd-N(1)-C(2) | 128.3(4) |
| C(13)-C(15) | 1.519(9) | Pd-C(20)-C(19) | 120.2(5) |
| C(15)-C(20) | 1.398(9) | | |
| C(7)-N(12) | 1.372(7) | | |
| C(6)-N(1) | 1.366(7) | | |

Synthesis of compound 5

The ligand L'H (130 mg, 0.5 mmol) is added to a solution of $(\text{PhCN})_2\text{PdCl}_2$ (192 mg, 0.5 mmol) in dichloromethane (50 ml). The mixture is refluxed for 1 h, then

TABLE 5
POSITIONAL PARAMETERS FOR THE NON-HYDROGEN ATOMS (with e.s.d.'s in parentheses)

| Atom | x | y | z |
|-------|------------|------------|------------|
| Pd | 0.17451(6) | 0.08192(3) | 0.24489(4) |
| Cl | 0.2535(3) | 0.0718(1) | 0.4704(2) |
| N(1) | 0.3283(7) | 0.0012(3) | 0.1857(5) |
| N(12) | 0.1331(7) | 0.0893(3) | 0.0447(5) |
| C(2) | 0.4203(9) | -0.0420(4) | 0.2623(7) |
| C(3) | 0.479(1) | -0.1023(4) | 0.2172(9) |
| C(4) | 0.440(1) | -0.1181(4) | 0.0853(9) |
| C(5) | 0.3478(9) | -0.0743(4) | 0.0025(7) |
| C(6) | 0.2899(8) | -0.0149(3) | 0.0537(6) |
| C(7) | 0.1871(8) | 0.0357(3) | -0.0270(6) |
| C(8) | 0.1489(9) | 0.0313(4) | -0.1642(7) |
| C(9) | 0.056(1) | 0.0825(4) | -0.2301(6) |
| C(10) | 0.014(1) | 0.1374(4) | -0.1619(7) |
| C(11) | 0.0530(9) | 0.1417(4) | -0.0216(7) |
| C(13) | 0.020(1) | 0.2043(4) | 0.0566(8) |
| C(14) | 0.191(1) | 0.2404(4) | 0.095(1) |
| C(15) | -0.0824(9) | 0.1882(4) | 0.1742(7) |
| C(16) | -0.238(1) | 0.2217(4) | 0.1831(8) |
| C(17) | -0.3442(9) | 0.2046(5) | 0.2818(8) |
| C(18) | -0.294(1) | 0.1555(5) | 0.3726(8) |
| C(19) | -0.135(1) | 0.1246(4) | 0.3695(7) |
| C(20) | -0.0258(9) | 0.1402(4) | 0.2707(6) |

concentrated to small volume and diethyl ether is added. The precipitate is filtered off and recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ to give the pure peach-coloured product, yield 85%, m.p. 255–256°C.

X-Ray structure of compound 3

Crystal data and other experimental details are summarized in Table 3. The unit cell parameters were determined by least-squares refinement of the setting angle of 25 well centered high- θ reflections. The diffraction intensities were corrected for Lorentz, polarization and absorption. Anomalous dispersion coefficients for atomic scattering factors were taken from ref. 14. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, the minimized function being $\sum w(|F_o| - k|F_c|)^2$. Weights assigned to individual observations were $w = 1/(\sigma(F_o))^2$ where $\sigma(F_o) = |\sigma^2(I) + (0.06I)^2|^{1/2}/2F_o$ Lp. All computations were carried out on a PDP 11/34 computer using the Enraf–Nonius SDP package of crystallographic programs. Lists of thermal parameters and structure factors are available from the authors.

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