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Cyclopalladation of 5-(1-hexyl)-2{[4′-(1-undecyloxy)phenyl]}-pyrimidine. Synthesis and characterization of mononuclear complexes

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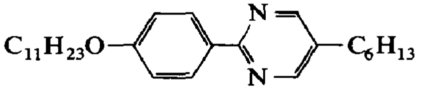
Abstract

The synthesis and characterization of a number of mononuclear cyclopalladated 5-(1-hexyl)-2{[4′-(1-undecyloxy)phenyl]}pyrimidine, HL, derivatives are reported. All these new complexes were obtained by bridge splitting reactions from the dimeric $[Pd(L)Cl]_2$ species.

Introduction

Compounds containing the $\overline{N(sp^2)\text{–}Pd\text{–}C}(sp^2)$ five membered metallacycle, wherein both the carbon and nitrogen atoms are part of aromatic rings are usually obtained from the reaction between palladium (II) salts and heteroaromatic species such as 2-phenylpyridine or structurally related compounds [1,2]. These cyclopalladated derivatives are $[Pd(C,N)(\mu\text{-}X)]_2$ complexes, which readily react with monodentate or polydentate ligands to give neutral or cationic mononuclear compounds [1–4].

We are currently concerned with the preparation of metallomesogens [5], and in this context, the mesogenic 5-(1-hexyl)-2{[4′-(1-undecyloxy)phenyl]}pyrimidine, HL



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(I), has been treated with $[Pd(PhCN)_2Cl_2]$ and we explored the use of the formed dinuclear cyclopalladated complex in reactions leading to the preparation of mononuclear derivatives.

Experimental

Infrared spectra were recorded on a Perkin Elmer 1330 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AW (CW series) 80 spectrometer in $CDCl_3$ solution with Me_4Si as internal standard. Conductivity measurements were carried out on a LKB 5300 B Conductolyser conductivity bridge.

Elemental analysis were performed by the Microanalysis Laboratory of the Dipartimento di Chimica, Università della Calabria, Italy.

The transition temperatures and the textures of the mesophases were observed with a Zeiss Axioskop polarising microscope equipped for photography and with a Linkam CO 600 heating stage. Standard chemicals were used as supplied. $[Pd(PhCN)_2Cl_2]$ was prepared as previously reported [6].

Preparation of $[Pd(L)(\mu\text{-}Cl)]_2$ (1)

In a typical preparation, a suspension of $[Pd(PhCN)_2Cl_2]$ (283.5 mg, 0.74 mmol) and the stoichiometric amount of the **HL** ligand in ethanol (30 ml) was stirred at room temperature (3 h). The resulting pale-yellow solid product was filtered off, washed with petroleum ether, and dried under vacuum. Yield 92%. K → 100 °C (K′) → 177.2 °C (S_A) → 219 °C (I). Anal. Found: C, 58.65, H, 7.57, N, 5.15. $C_{54}H_{82}Cl_2N_4O_2Pd_2$ calcd.: C, 58.80; H, 7.49; N, 5.08%.

Reactions with neutral monodentate ligands

$[Pd(L)(PPh_3)Cl]$ (2). A suspension of triphenylphosphine (10 equivalents) and complex **1**, (40.0 mg, 0.03 mmol) in diethyl ether (10 ml) under nitrogen was stirred for 2 h, to give a pale yellow solution. This was evaporated to dryness and the residue chromatographed on a silica gel column with: diethyl ether–petroleum ether (v/v, 1/1) as eluent. The isolated product was washed with petroleum ether to give a white powder in 49% yield. M.p. 93 °C. Anal. Found: C, 66.14; H, 7.06; N, 3.35. $C_{45}H_{56}ClN_2POPd$ calcd.: C, 66.42; H, 6.93; N, 3.44%.

[Pd(L)(Py)Cl] (3). Complex **1** (60.0 mg, 0.05 mmol) was added to a solution of pyridine (43.0 mg, 5.54 mmol) in acetone. After 24 h stirring the white precipitate was filtered off. The yield was 51%. K → 96 °C (N) → 100 °C (I). Anal. Found: C, 61.52; H, 7.52; N, 6.35. $C_{32}H_{46}ClN_3OPd$ calcd.: C, 60.95; H, 7.35; N, 6.66%.

Reactions with monoanionic chelating ligands

[Pd(L)(8-HOQuin)] (4). To a suspension of complex **1** (100.0 mg, 0.09 mmol) in diethyl ether (5 ml) were added 2.15 ml of an ethanolic solution containing KOH (0.36 mmol) and 8-hydroxyquinoline (52.6 mg, 0.36 mmol). After 18 h the mixture was filtered and the filtrate was evaporated to dryness to leave a yellow solid, which was washed with water, ethanol, and diethyl ether, and dried under vacuum. Yield 63%. M.p. 100 °C. Anal. Found: C, 66.12; H, 7.11; N, 6.17. $C_{36}H_{47}N_3O_2Pd$ calcd.: C, 65.49; H, 7.17; N, 6.36%.

[Pd(L)(AcAc)] (5). An aqueous solution (7 ml) containing $AgNO_3$ (0.36 mmol) and potassium acetylacetonate (0.36 mmol) was added to complex **1** (200.0 mg, 0.18 mmol) and ethanol (8 ml). The suspension was stirred at room temperature for 2 h, then the grey precipitate (salt) was filtered off, to leave a bright yellow solution which was dried over Na_2SO_4 and chromatographed on a silica gel column (eluent:

diethyl ether–petroleum ether (v/v, 1/1)) to give a yellow solid in 90% yield. K → 83 °C (I) → 68 °C (S_A) → 40 °C (K). Anal. Found: C, 61.82; H, 7.80; N, 4.57. $C_{32}H_{48}N_2O_3Pd$ calcd.: C, 62.48; H, 7.86; N, 4.55%.

Complexes **6–8** were all prepared by essentially the same method. Full experimental details are given only for complex **6**.

[Pd(L)(2,2,6,6-Me$_4$-3,5-heptanedionate)] (6). To a suspension of complex **1** (150.0 mg, 0.13 mmol) in ethanol (10 ml) were added three equivalents of potassium 2,2,6,6-tethramethyl-3,5-heptanedionate (90.7 mg, 0.41 mmol). The mixture was shaken for 48 h and the white solid formed was filtered off, washed with water, ethanol, and diethyl ether, and dried in vacuo. Yield: 95%. M.p. 90 °C. Anal. Found: C, 66.57; H, 8.86; N, 3.86. $C_{38}H_{60}N_2O_3Pd$ calcd.: C, 65.27; H, 8.65; N, 4.00%.

[Pd(L)(3-Et-2,4-pentanedionate)] (7). Similarly, complex **1** reacted with potassium 3-ethyl-2,4-pentanedionate (during 4 h) to give a white precipitate in 94% yield. M.p. 89 °C. Anal. Found: C, 64.13; H, 8.33; N, 4.22. $C_{31}H_{52}N_2O_3Pd$ calcd.: C, 63.49; H, 8.14; N, 4.35%.

[Pd(L)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate)] (8). This compound was obtained from complex **1** and potassium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, by the above procedure, in 81% yield. M.p. 72 °C. Anal. Found: C, 53.60; H, 6.02; N, 3.72. $C_{32}H_{42}N_2O_3PdF_6$ calcd.: C, 53.15; H, 5.85; N, 3.87.

Reactions with neutral chelating ligands

[Pd(L)(bipy)]BF$_4$ (9). To a solution of $AgBF_4$ (35.3 mg, 0.18 mmol) in acetonitrile (5 ml) were added 100.0 mg of complex **1** (0.09 mmol); the mixture was stirred for 2 h and filtered to remove the AgCl. The filtrate was evaporated to dryness and the residue added to a suspension of 2,2′-bipyridine (28.3 mg, 0.18 mmol) in ethanol (5 ml). The mixture was shaken overnight and then filtered. A yellow product was obtained after washing with ether and petroleum ether, drying, and recrystallisation from chloroform, with a 76% yield. K → 146.5 °C (N) → 158.1 °C (I). Anal. Found: C, 58.19; H, 6.50; N, 7.28. $C_{37}H_{49}N_4O_2PdBF_4$ calcd.: C, 58.55; H, 6.50; N, 7.38%. IR (KBr disc): $\nu(B\text{–}F) = 1050\ cm^{-1}$. Λ_M (MeCN 10^{-3} mol dm^{-3}) = 123.16 $\Omega^{-1}\ mol^{-1}\ cm^2$.

Using the above method the following compounds **10–14** were prepared.

[Pd(L)(4,4′-Me$_2$-bipy)]BF$_4$ (10). This compound was obtained as a yellow solid by treating complex **1** with 4,4′-dimethyl-2,2′-bipyridine. Yield 76%. M.p. 180.0 °C. Anal. Found: C, 58.70; H, 6.84; N, 6.97. $C_{39}H_{52}N_4OPdBF_4$ calcd.: C, 59.51; H, 6.66; N, 7.12%. IR (KBr disc): $\nu(B\text{–}F) = 1050\ cm^{-1}$. Λ_M (MeCN 10^{-3} mol dm^{-3}) = 122.31 $\Omega^{-1}\ mol^{-1}\ cm^2$.

[Pd(L)(phen)]BF$_4$ (11). This compound was obtained in 90% yield as a yellow solid when 1,10-phenanthroline was used. M.p. 195 °C. Anal. Found: C, 58.91; H, 6.50; N, 7.05. $C_{39}H_{49}N_4OPdBF_4$ calcd.: C, 59.74; H, 6.29; N, 7.15%. IR (KBr disc): $\nu(B\text{–}F) = 1050\ cm^{-1}$. Λ_M (MeCN 10^{-3} moldm^{-3}) = 113.22 $\Omega^{-1}\ mol^{-1}\ cm^2$.

[Pd(L)(2,9-Me$_2$-phen)]BF$_4$ (12). This compound was prepared by treating **1** with 2,9-dimethyl-1,10-phenanthroline. It was obtained as an orange solid, 50% yield, m.p. 170 °C. Anal. Found: C, 59.51; H, 6.53; N, 7.86. $C_{41}H_{53}N_4OPdBF_4$ calcd.: C, 60.71; H, 6.59; N, 6.91%. IR (KBr disc): $\nu(B\text{–}F) = 1050\ cm^{-1}$.

[Pd(L)(5,6-Me$_2$-phen)]BF$_4$ (13). This compound was made from **1** and 5,6-dimethyl-1,10-phenanthroline as a yellow solid, m.p. 215 °C, in 92% yield. Anal.

Found: C, 60.77; H, 6.59; N, 7.03. $C_{41}H_{53}N_4OPdBF_4$ calcd.: C, 60.71; H, 6.59; N, 6.91%. IR (KBr disc): ν(B–F) = 1050 cm^{-1}.

[Pd(L)(4,7-Ph₂-phen)]BF₄ (14). This yellow salt, m.p. 165 °C, was obtained from **1** and 4,7-diphenyl-1,10-phenanthroline in 88% yield. Anal. Found: C, 65.96; H, 6.18; N, 6.05. $C_{51}H_{57}N_4OPdBF_4$ calcd.: C, 65.49; H, 6.14; N, 5.99%. IR (KBr disc): ν(B–F) = 1050 cm^{-1}.

Metathetical anion exchange reactions

[Pd(L)(bipy)]PF₆ (15). A suspension of complex **9** (160.0 mg, 0.21 mmol) and potassium hexafluorophosphate (172.0 mg, 1.05 mmol) in ethanol (10 ml) was stirred at room temperature for 48 h. The yellow precipitate was filtered off, washed with water, ethanol, and diethyl ether, and dried in vacuum. Yield 91%. M.p. 105 °C. Anal. Found: C, 54.90; H, 6.28; N, 6.91. $C_{37}H_{49}N_4OPdPF_6$ calcd.: C, 54.38; H, 6.04; N, 6.86. IR (KBr disc): ν(P–F) = 830 cm^{-1}. Λ_M ($MeNO_2$ 10^{-3} $moldm^{-3}$) = 84.48 Ω^{-1} mol^{-1} cm^2.

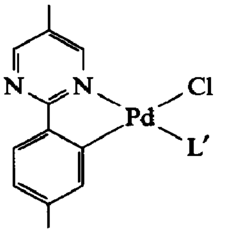
[Pd(L)(bipy)]SbF₆ (16). A solution of complex **9** (150.0 mg, 0.20 mmol) in acetone (10 ml) was added to 5 equivalents of potassium hexafluoroantimonate and the mixture was shaken for 48 h. The precipitate of KCl filtered off, and the solvent evaporated to leave a yellow solid, which was washed with water, ethanol, and diethyl ether, and recrystallised from dichloromethane and diethyl ether. Yield 80%. M.p. 87 °C. Anal. Found: C, 49.46; H, 4.63; N, 6.10. $C_{37}H_{49}N_4OPdSbF_6$ calcd.: C, 48.95; H, 5.44; N, 6.17%. IR (KBr disc): ν(Sb–F) = 650 cm^{-1}. Λ_M ($MeNO_2$ 10^{-3} $moldm^{-3}$) = 77.17 Ω^{-1} mol^{-1} cm^2.

Results and discussion

The **HL** ligand is a solid thermotropic species which exhibits a nematic, *N*, mesophase between 47.7 °C and 59.0 °C. In ethanolic solution, **HL** reacts with $[Pd(PhCN)_2Cl_2]$ to give the pale yellow cyclopalladated complex $[Pd(L)(\mu\text{-}Cl)]_2$, **1**. In the present investigation, **1** was used as the starting material in reactions with either monodentate or chelating ligands.

Reactions with neutral monodentate ligands

Treatment of **1** with the **L′** ligands triphenylphosphine or pyridine gave white precipitates of **2** and **3**, respectively. The products give elemental analyses and spectroscopic data (IR) in agreement with those expected for $[Pd(L)(PPh_3)Cl]$ and [Pd(L)(Py)Cl]. Moreover, the IR spectrum shows a Pd–Cl stretching frequency (**2**: 290, cm^{-1}; **3**: 295 cm^{-1}) corresponding to a chlorine atom *trans* to a Pd–C bond [7]. On the basis of this evidence, the suggested structure for compounds **2** and **3** is that shown in II.

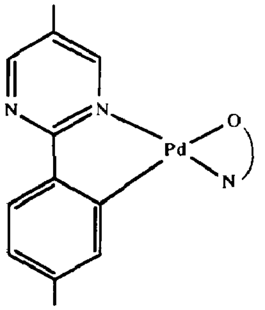


II

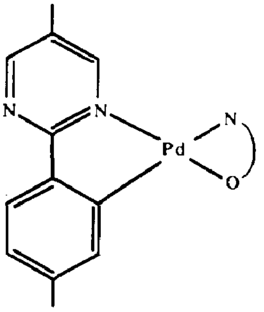
Complex **2** is thermally stable and melts at 93 °C. By contrast, upon heating at about 100 °C, complex **3** loses pyridine and complex **1** is eventually reformed.

Reactions with monoanionic chelating ligands

These reactions involve halogen-bridge cleavage with displacement of the chlorine atoms. Thus, reaction between **1** and the 8-hydroxyquinolinate anion $(\overline{O\ N})$ gives a neutral orange product, which analyses for $[Pd(L)(\overline{O\ N})]$, **4**. A species with the stoichiometry of **4**, could in principle have the either of spectroscopically roughly equivalent structures IIIa and IIIb.



IIIa

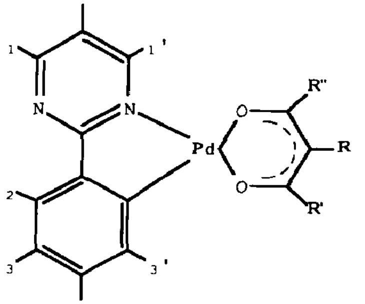


IIIb

However, since an X-ray diffraction study on the similar bis-chelate palladium(II) complex, (8-hydroxyquinolate) [2-(4′-methoxy-phenylazo-N^2)-5-methoxyphenyl]palladium(II), showed it to have a molecular structure of the type IIIb [8], it seems likely that in the present case the Pd–C and Pd–O bonds are again mutually *cis*. Complex **4** melts at 100 °C. Previous reports have described cyclopalladated acetylacetonate compounds prepared from μ-Cl dimers and thallium acetylacetonate [9,10]. We prepared a similar complex, **5**, by reaction of **1** with a mixture containing potassium acetylacetonate and silver nitrate (1 : 1 molar ratio). Complexes **6**–**8** (Fig. 1) were made in the same way.

Products **5**–**8** were characterised by elemental analysis, IR and ^{1}H NMR spectroscopy (Table 1).

Complexes **5**–**8** melt at 83, 90, 89, and 72 °C respectively. When complex **5** is cooled down from the isotropic fluid, a smectic A mesophase, S_A, stable between 68 and 40 °C, appears.



5: R = H; R′ = R″ = Me
6: R = H; R′ = R″ = CMe$_3$
7: R = Et; R′ = R″ = Me
8: R = H; R′ = R″ = CF$_3$

Fig. 1. Complexes **5**–**8**: molecular structure and proton numbering scheme.

Table 1

^{1}H NMR data[a] for the palladated phenylpyrimidine fragment and the $\widehat{O\,O}$ chelating ligand in compounds **5–8**

Compound	H^1	$H^{1'}$	H^2	$H^{3'}$	H^3	R	R′	R″
5	8.54(d)	8.48(d)	7.64(d)	7.08(d)	6.66(dd)	5.35(s,1H)	2.10(s,2H)	2.00(s,3H)
6	8.60(d)	8.50(d)	7.60(d)	7.20(d)	6.66(dd)	5.70(s,1H)	n.a.[b]	n.a.
7	8.50(d)	8.50(d)	7.60(d)	7.10(d)	6.60(dd)	n.a.	n.a.	n.a.
8	8.40(d)	8.20(d)	n.a.	n.a.	n.a.	6.00(s)	–	–

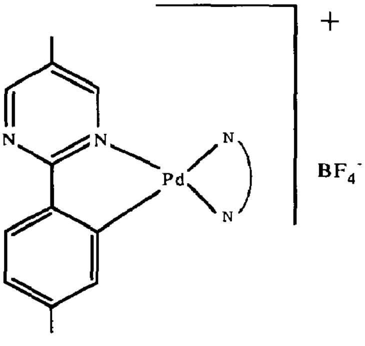
[a] Chemical shifts (δ) are relative to internal Me_4Si. [b] n.a. = not assigned.

Reactions with neutral chelating ligands

The bridge splitting brought about by reaction with neutral nitrogen-containing chelating ligands $\widehat{N\,N}$, involves a two step process. First, in accord with reported procedures [11], **1** was allowed to react in acetonitrile solution with silver tetrafluoroborate. Under such conditions, the silver ion acts as a chlorine scavenger and the solvate species $[Pd(L)(MeCN)_2][BF4]$ forms. Subsequent addition of 2,2′-bipyridine, 1,10-phenantroline or their substituted derivatives, gives the $[Pd(L)(\widehat{N\,N})][BF4]$ complexes **9–14** (Fig. 2), which were characterized by elemental analysis, IR spectroscopy, and conductivity measurements (which showed them to be 1 : 1 electrolytes [12]).

The bipyridine complex **9** exhibits thermotropism, giving a nematic mesophase, N, above 146 °C with a clearing point at 158 °C. In contrast, **10** and the phenanthroline compounds **11–14** simply melt at temperatures ranging between 165 °C (**14**) and 215 °C (**13**).

The interesting mesomorphic properties featured by compound **9** led us to investigate the connection between mesomorphism and nature of the uncoordinated anion. For this purpose the species $[Pd(L)(\widehat{N\,N})][X]$, ($\widehat{N\,N}$ = 2,2′-bipyridine; **15**: $X = PF_6$; **16**: $X = SbF_6$) were prepared by metathetical exchange between **9** and ammonium hexafluorophosfate or potassium hexafluoroantimonate. A similar reaction, carried out on **9** with potassium iodide, gave instead the neutral iodo-bridged complex $[Pd(L)(\mu\text{-}I)]_2$. Both **15** and **16**, as well as **9**, are 1 : 1 electrolytes in acetonitrile but, unlike **9**, neither **15** nor **16** are mesogenic.



$\widehat{N\,N}$ = 2,2'-bypiridine, **9**

4,4'-Me_2-2,2'-bypiridine, **10**

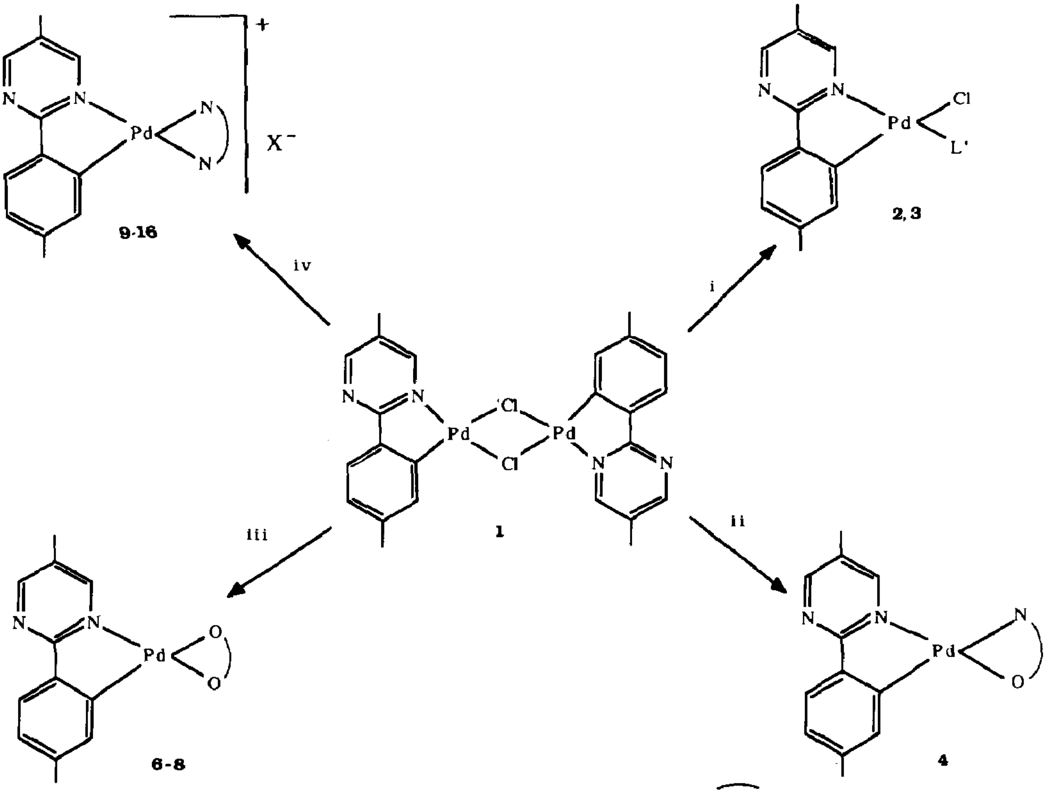
1,10-phenantroline, **11**

2,9-Me_2-1,10-phenantroline, **12**

5,6-Me_2-1,10-phenantroline, **13**

4,7-Ph_2-1,10-phenantroline, **14**

Fig. 2. Structure proposed for the $[Pd(L)(\widehat{N\,N})][BF4]$ salts **9–14**.



Scheme 1. Reaction scheme of complex **1**. i: L' = PPh_3 (**2**), Py (**3**); ii: $\widehat{\mathrm{O\,N}}$ = 8-hydroxyquinolate (**4**); iii $\widehat{\mathrm{O\,O}}$ = various acetylacetonate (**5**–**8**); iv: $\widehat{\mathrm{N\,N}}$ = 2,2'-bipyridine- and 1,0-phenanthroline-like ligands (**9**–**16**).

Conclusions

The μ-Cl dimer **1** reacts under mild conditions, as outlined in Scheme I, to give novel mononuclear complexes which were isolated in good yields. Compound **2** is formed upon treatment of **1** with an excess of PPh_3, whereas under the same conditions, cyclopalladated azobenzene [13] or *N*-phenylbenzaldimine [9] cleave the Pd–N bond.

A new mesogenic species [Pd(L)(2,2'-bipy)][BF4], **9** has been prepared. This complex is a further example of the unique class of thermotropic liquid crystals formed by ionic compounds [14].

Acknowledgement

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