

## Pyrazole-based allylpalladium complexes: Supramolecular architecture and liquid crystal behaviour

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Received 29 May 2006; accepted 22 July 2006

Available online 18 August 2006

### Abstract

The co-ordination of non-mesomorphic 3-substituted pyrazoles  $\text{Hpz}^{\text{R}}$  to the  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]^+$  fragment gives rise to four-coordinated complexes  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{Hpz}^{\text{R}})_2]^+$  ( $\text{R} = \text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ ;  $n = 12$  (**I**<sub>12</sub>), 14 (**I**<sub>14</sub>), 16 (**I**<sub>16</sub>), 18 (**I**<sub>18</sub>)), which were isolated with  $\text{BF}_4^-$  as counteranion. The new complexes are proved to have liquid crystal properties exhibiting monotropic or enantiotropic smectic A (SmA) mesophases at low temperatures which range between ca. 40 and 80 °C. The crystal structure of **I**<sub>12</sub> presents a 2D network highly interdigitated, which could be related with the layered structure proposed in the liquid crystalline phase through the X-ray diffraction at variable temperature.

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**Keywords:** Palladium(II) complexes; Pyrazole; Metallomesogen; X-ray structure

For several years, we have been interested in the liquid crystal chemistry of substituted pyrazoles and the related pyrazolylpyridine ligands, as well as their metal complexes. In this context, we have proved that, in contrast to the mesomorphic nature of 3,5-*bis*(4-alkyloxyphenyl)pyrazole ( $\text{Hpz}^{\text{R}2}$ ;  $\text{R} = \text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ ) or 2-[3,5-*bis*(4-alkyloxyphenyl)pyrazol-1-yl]pyridine ( $\text{pz}^{\text{R}2}\text{py}$ ) ligands [1–3], the 3-substituted homologues  $\text{Hpz}^{\text{R}}$  and  $\text{pz}^{\text{R}}\text{py}$  did not exhibit liquid crystal behaviour [4–6]. However, it was interesting to note that all of them were able to induce mesomorphism upon co-ordination to determined palladium(II) fragments [2,3,5–7]. In particular, we have observed that the co-ordination of the mesogenic  $\text{pz}^{\text{R}2}\text{py}$  ligands to  $\text{PdCl}_2$  or  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]^+$  fragments gave rise to metallomesogens [3,7] (Scheme 1). By contrast, the four-coordinated *cis*-dichloropalladium complexes  $[\text{PdCl}_2(\text{pz}^{\text{R}}\text{py})]$  containing the related 3-substituted  $\text{pz}^{\text{R}}\text{py}$  ligands were not mesomorphic, while their co-ordination to the  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]^+$  moi-

ety yielded metallomesogenic derivatives [6] (Scheme 1), this feature suggesting the role of the electron delocalisation in the mesomorphism.

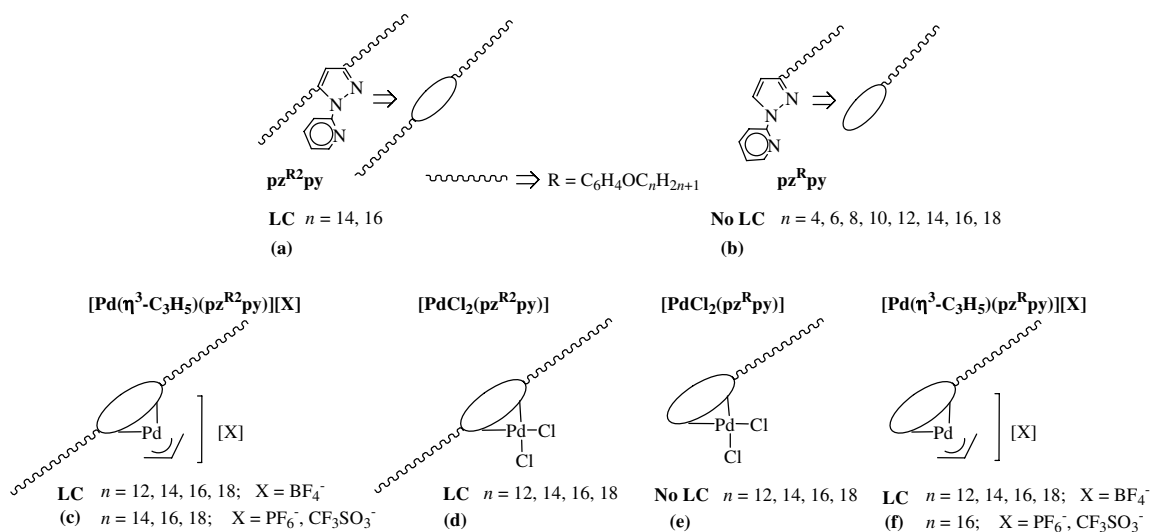
Following these results we decided to prove that the  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]^+$  group can be useful as a candidate to produce metallomesogenic four-co-ordinated compounds by co-ordination to 3-(4-alkyloxyphenyl)pyrazole  $\text{Hpz}^{\text{R}}$  ligands (Scheme 2). We have already determined the mesomorphic properties of the related compounds *t*- $[\text{PdCl}_2(\text{Hpz}^{\text{R}})_2]$  [5].

In this work we describe the synthesis, characterisation and mesomorphic properties of a series of cationic compounds of the type  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{Hpz}^{\text{R}})_2]^+$  ( $\text{R} = \text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ ;  $n = 12$  (**I**<sub>12</sub>), 14 (**I**<sub>14</sub>), 16 (**I**<sub>16</sub>), 18 (**I**<sub>18</sub>)), which were isolated with  $\text{BF}_4^-$  as counteranion.

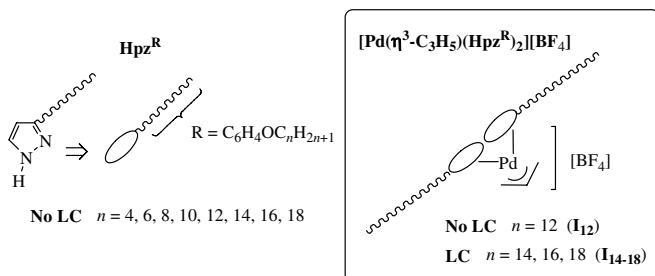
The syntheses of  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{Hpz}^{\text{R}})_2][\text{BF}_4]$  ( $\text{R} = \text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ ;  $n = 12$  (**I**<sub>12</sub>), 14 (**I**<sub>14</sub>), 16 (**I**<sub>16</sub>), 18 (**I**<sub>18</sub>)) [8] were carried out as it has been described for related compounds [6,7]. The spectroscopic (IR and <sup>1</sup>H NMR) and analytical data [9,10] allowed us to establish their identity and they are in agreement with the proposed formulation.

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Scheme 1. Schematic molecular representation and mesomorphic properties of the  $\text{pz}^{\text{R}2}\text{py}$  (a) and  $\text{pz}^{\text{R}}\text{py}$  (b) ligands, and their complexes  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{pz}^{\text{R}2}\text{py})][\text{X}]$  (c),  $[\text{PdCl}_2(\text{pz}^{\text{R}2}\text{py})]$  (d),  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{pz}^{\text{R}}\text{py})][\text{X}]$  (e) and  $[\text{PdCl}_2(\text{pz}^{\text{R}}\text{py})]$  (f) [3,6,7].



Scheme 2. Schematic molecular representation of the complexes  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{Hpz}^{\text{R}})_2][\text{BF}_4]$  (**I**<sub>12–18</sub>) studied in this work.

The  $^1\text{H}$  NMR spectra of **I**<sub>12–18</sub> at room temperature in  $\text{CDCl}_3$  solution show the expected resonances as broad signals attributed to a dynamic behaviour, which was proved by the analysis of their spectra at variable temperatures (from 30 to  $-50^\circ\text{C}$ ) [10]. This behaviour can be explained on the basis of the existence of different isomers related with the relative orientation of the allyl group and the two pyrazoles, which can interchange through a rotation of the allyl group or a tautomeric equilibrium. Many examples in the literature support this proposal [11].

The knowledge of the molecular structure of the mesophases has been a focus of interest in order to understand the liquid crystal behaviour of the compounds. In this context, we think that the X-ray structure of the studied complexes will contribute as a support for the establishment of potential structure/properties relationships. On this basis, we have solved the X-ray single-crystal structure of  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{Hpz}^{\text{ddp}})_2][\text{BF}_4]$  ( $\text{Hpz}^{\text{ddp}} = 3\text{-(4-dodecyloxyphenyl)pyrazole}$ ) (**I**<sub>12</sub>) (Fig. 1), as a representative member of the homologues studied in this work [12]. The crystal structure reveals that the complex is comprised of the  $\text{BF}_4^-$  anion and the cation  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{Hpz}^{\text{ddp}})_2]^+$ , bonded through a strong H-bond (Table 1).

The four-co-ordination around the metal is defined by two nitrogen atoms from two *cis*-pyrazole groups and the two allyl C9 and C11 carbon atoms, in an almost square-planar geometry. It is deduced by the dihedral angle of  $4.7(4)^\circ$  between the planes defined by the Pd, N1 and N3 atoms, and the Pd, C9 and C11 atoms. The Pd atom deviates  $0.044(1)\text{ \AA}$  of the co-ordination plane defined by the N1, N3, C9 and C11 atoms. The Pd–N distances of ca.  $2.08\text{ \AA}$  are similar to those found in related complexes [2,5,6,13–17]. The allyl group shows Pd–C distances of

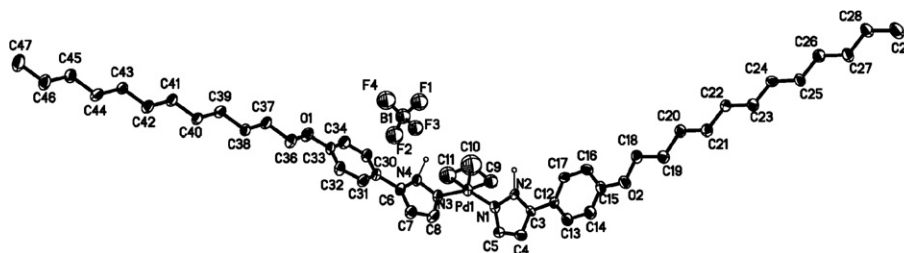


Fig. 1. Perspective ORTEP plot of  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{Hpz}^{\text{ddp}})_2][\text{BF}_4]$  (**I**<sub>12</sub>). Hydrogen atoms, except H2 and H4, have been omitted for clarity. The thermal ellipsoids are at 30% probability level. Selected bond lengths (Å) and angles ( $^\circ$ ): Pd1–N1 2.085(8), Pd1–N3 2.079(8), Pd1–C9 2.10(1), Pd1–C10 2.10(2), Pd1–C11 2.09(1), C9–C10 1.381(5), C10–C11 1.374(5), N1–Pd1–N3 92.9(3), N1–Pd1–C9 99.1(4), N1–Pd1–C10 132.3(4), N1–Pd1–C11 166.6(5), N3–Pd1–C9 167.9(4), N3–Pd1–C10 131.1(4), N3–Pd1–C11 99.7(5), C9–Pd1–C10 38.4(2), C9–Pd1–C11 68.2(5), C10–Pd1–C11 38.3(2), C9–C10–C11 117(2).

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