Journal of Organometallic Chemistry 712 (2012) 20–28

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Dinuclear *ortho*-metallated palladium(II) azobenzene complexes with acetato and chloro bridges: Influence of polar substituents on the mesomorphic properties

Trirup Dutta Choudhury [a], Yongqiang Shen [b], Nandiraju V.S. Rao [a,*], Noel A. Clark [b]

[a] *Department of Chemistry, Centre for Soft matter, Assam University, Dargakona, Silchar 788 011, Assam, India*
[b] *Department of Physics, Liquid Crystal Materials Research Centre, University of Colorado, Boulder, CO 80309, USA*

ARTICLE INFO

Article history:
Received 12 February 2012
Received in revised form
30 March 2012
Accepted 2 April 2012

Keywords:
Liquid crystal
Metallomesogen
Palladium
Azo compound
Ortho-metallation
Polar compound

ABSTRACT

The synthesis, characterization and mesomorphic properties of a new series of acetate and chloro-bridged dinuclear orthopalladated complexes derived from azobenzene with terminal groups of hexadecyloxy moiety at one end and different polar groups (Me, Cl, F, NO_2, CN) at the other end are described. The mesomorphic properties of both the ligands and complexes were investigated by polarizing optical microscopy and X-ray studies to understand the effect of polar group in the nature of mesophase produced. Among the complexes, all chloro-bridged complexes predominantly exhibited SmA phase. However the rare phenomenon of observing mesomorphism in acetato-bridged palladium (II) complexes due its typical open book shape had been realized in substituted acetato-bridged complexes with fluoro and cyano substituents in the ligands. Nitro and cyano substituted ligands only exhibited monotropic Smectic A phase. Model molecular arrangement based on X-ray studies is presented.

1. Introduction

One of the potential applications of cyclopalladated complexes is ligand transformation using the reactions of Pd–C bond [1–5]. The importance of orthopalladated dinuclear complexes derived from salicylaldimine ligands exhibiting very good catalytic activity, dependent upon the substituent, towards the hydrogenation of nitrobenzene and cyclohexene has been demonstrated recently [5]. Mesogenic behaviour is realised in usually unfavourable acetato/carboxylato bridged ortho-metallated dinuclear Pd(II) complexes of salicylaldiimine ligands with increased peripheral chains/crown ethers, in spite of destabilization due to the non-planarity in such complexes [6–12]. Hence functional properties along with their potential applications due to the perceived advantage of combining properties of transition metal with the coordinating molecules of liquid crystalline compounds promoted basic as well as applied research activity in this area. This research area has been well reviewed recently, with the excellent work appearing regularly [13–20]. The coordination of a metal ion to the mesogenic/non-mesogenic coordinating organic ligands with an increased contribution of aromatic core resulted to yield linear [21–27] and square planar [28–35] complexes exhibiting liquid crystalline behaviour with enhanced thermal stability. One of the predominant class of metallomesogens is the organometallic complexes of “(C, N)Pd” metallacycle viz., orthocyclopalladated imines [36–39], azines [40], and azobenzenes [41–44].

Cyclopalladated compounds have proved to be an active area of research with different examples by several groups [45–55] out of which orthopalladated imine and azobenzene compounds exhibiting large thermal range of mesomorphism have been extensively studied due to their ease of synthesis and thermal stability. Further the nature of the bridging group as well as polarity of the substituent played an important role in the mesomorphic characteristics and photo-physical properties. Hence it not only changes the geometry of the system but also alter the liquid crystalline properties. A comparative study on the azo-based cyclopalladated dimers with various bridging systems (X = Cl, Br, I, N_3, SCN) revealed that all the complexes are planar [52–55] and exist in trans conformation. However the acetato (OAc) bridged complexes exists in a typical “roof-shape” or “open-book shape” and exists in cis:trans mixture. The mesomorphism was observed for chloro, bromo, azido, and oxalato complexes but not for the iodo, thiocyanato, or acetate derivatives [18,47,56]. Further the effect of polar substituent such as H, F, Cl, NO_2, CN, OMe etc. either in para

---

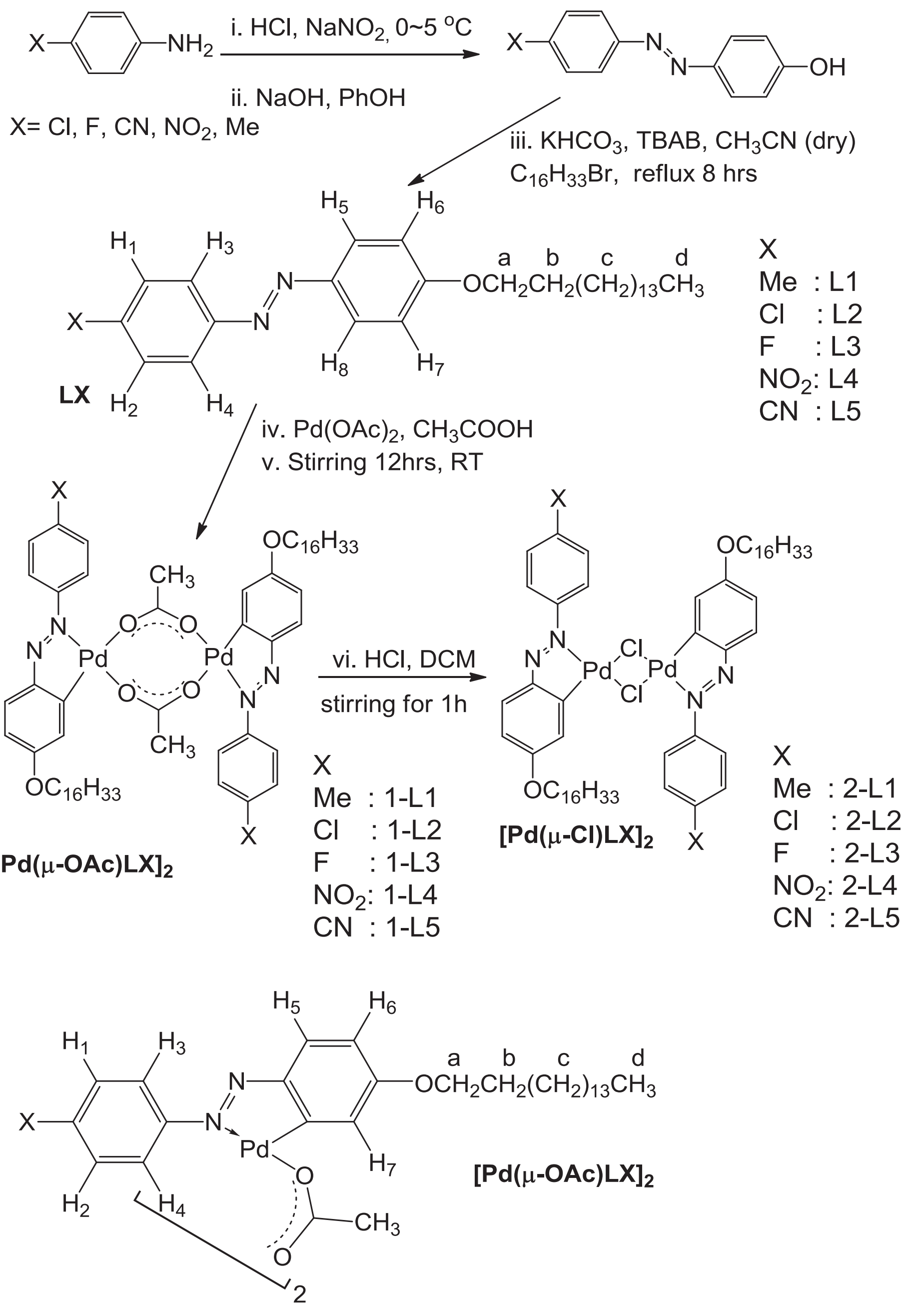
* Corresponding author. Tel.: +91 94355 22541; fax: +91 3842 270806.
E-mail address: nandirajuv@gmail.com (N.V.S. Rao).

0022-328X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2012.04.001

position of the aldehyde ring [57] or aniline ring [58] of chloro-and acetato-bridged complexes, derived from benzylidene imine ligand, had been studied extensively. However no such study was reported on azo cyclopalladated complexes. One of the important reasons is that the azo-based system need sufficiently long chain on both ends to fulfil the structural requirement for liquid crystalline behaviour. Most of the azo-based systems with small aliphatic chain length are non-mesogenic, whereas complexes show mesomorphic behaviour above 200 °C and decomposed on clearing point. However greater mobility of the ring having the polar substituent in *para* position together with the longer distance from the central core may allow a more important participation of the different polar groups in the molecular interactions. As a result, changes in mesogenic behaviour such as nature of mesomorphic phase, mesomorphic phase range, etc., can be expected [59], and except the few contributions from Ghedini et al. [1,40,51,55] on dinuclear cyclopalladated azo compounds with alkyl end chains at both ends of the ligand, there are no other report available in literature with a polar group in the molecule till date to our knowledge. In this article we report the synthesis and liquid crystalline properties of azo compounds with a polar group at one end and long n-hexadecyloxy chain at the other end followed by complexation with palladium acetate to infer the influence of polar end group on mesomorphism of both chloro-and acetate bridged dinuclear azo- palladium complexes.

2. Results and discussion

The chloro, fluoro, cyano, nitro and methyl substituted azo compounds were synthesized as presented in Scheme 1, following



Scheme 1. Synthesis of the dinuclear Pd(II) *ortho*-metallated compounds.