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Combination of molecular rods and half-discs: transition from lamellar to columnar order in multichain mononuclear *ortho*-palladated metallomesogens

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Novel *ortho*-palladated phenylpyrimidine-1,3-diketonato organyls with successively increasing numbers of alkyl chains were synthesized and investigated by polarizing optical microscopy and X-ray diffraction. A discontinuous transition from a lamellar to a columnar organization is observed, dependent on the number of chains: molecules with four or five chains from smectic phases (SmA, SmC), the related compound with six chains in the molecule is non-mesomorphic, whereas molecules with seven or eight chains form hexagonal columnar mesophases.

1. Introduction

The design of novel molecules close to the calamitic/discotic cross-over point is of real interest in liquid crystal research. Such materials can show especially interesting liquid crystalline phases, such as cubic phases [1], discotic lamellar phases [2] and lamello-columnar [3] phases, as well as potentially biaxial nematic phases [4]. Several different approaches have been tested to obtain such molecules. At first, calamitic molecules were grafted with several alkyl chains at their terminal ends (polycatenar compounds) [5]. Furthermore, the number of chains attached to disc-like molecules was systematically reduced [2, 6], disc-like molecules were stretched into a board-like shape [2, 7], and molecular discs were combined with one or more molecular rods [8, 9]. An alternative way could be the combination of rod-like molecules with laterally attached half-discs to obtain novel mesogens with a shape intermediate between rod-like and disc-like mesogens; see figure 1 (*b*).

As is well known, metal-containing liquid crystals allow the creation of quite unusual molecular geometries that are difficult to achieve with purely organic molecules [10]. In this context, palladium-containing metallomesogens especially attracted our interest, because readily available N-containing rod-like molecules can be *ortho*-palladated to create new mesogenic structures. Several different types of such metallomesogens have been reported in the past. Smectic phases were found for dinuclear halogen-bridged cyclopalladated diarylazines [11], azobenzenes [12], diarylimines [13] and phenylpyrimidines [14], whereas binuclear and tetranuclear multichain diarylimine derivatives with a disc-like molecular shape formed columnar phases [15]. Mononuclear cyclopalladated complexes can be easily obtained from such dinuclear μ-chloro palladium complexes by ligand exchange reactions with various bidentate ligands to give neutral (with 1,3-diketonates) or cationic (with bipyridines) compounds [16]. Also K-shaped mesogenic molecules with smectic phases have recently been obtained in a series of mononuclear *ortho*-palladated complexes incorporating a Schiff's base unit and a 1,3-diketonate ligand [17].

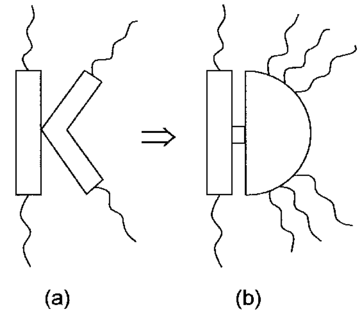

Figure 1. Mesogenic species with (*a*) K-shape and (*b*) rod/half-disc shape.

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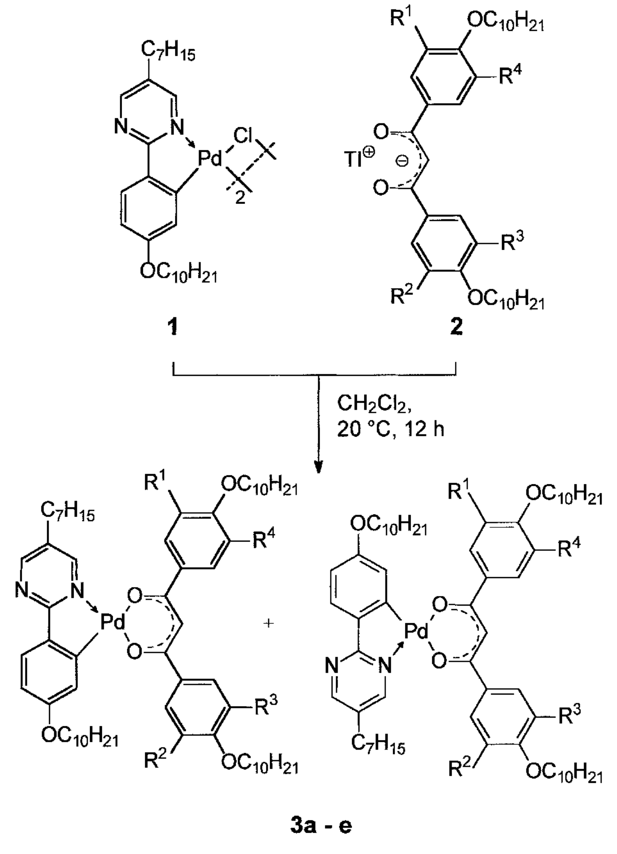
Here, we report a novel concept for controlling the mesophase structure of mononuclear *ortho*-palladated complexes by the combination of a calamitic disubstituted 2-phenylpyrimidine core with a 1,3-diketonate unit having a successively increasing number of alkyl chains, so providing a step by step transition from a K-shaped geometry to a molecular shape combining a calamitic and a half-disc unit (figure 1).

2. Results and discussion

The palladium(II)organyl **1** and the thallium-1,3-diketonates **2** were prepared and characterized according to literature procedures [16, 18]. The preparation of the mononuclear *ortho*-palladated complexes was carried out as described in the scheme, in a similar manner to that published by Serrano and coworkers [17]. Compounds **3b** and **3d** with unsymmetrically substituted 1,3-diphenylpropan-1,3-dionate units, were obtained as mixtures of isomers, differing in the coordination of the diketonate unit with respect to the 2-phenylpyrimidine core. The ratio of these isomers is approximately 1 : 1 as determined by ^{1}H NMR spectroscopy.



Scheme. Synthesis of the mononuclear palladium complexes **3**.

The compounds were first investigated by polarizing optical microscopy using a heating stage. The results are summarized in the table. Compound **3a** with only four chains shows an enantiotropic SmA phase identified by its typical fan-like texture and regions with homeotropic orientation. On further cooling, the transition to a tilted smectic phase (SmC phase) takes place; this could be detected by the formation of a typical schlieren texture in the homeotropically aligned regions of the SmA phase. Enhancing the number of alkyl chains reduces the stability of the SmA phase. Hence, for compound **3b**, only a monotropic SmA phase was found, which on further cooling rapidly crystallizes. Compound **3c** shows no liquid crystalline behaviour; on heating above 115°C, the crystalline solid melts and on cooling no mesophase can be detected down to a temperature of 95°C, when crystallization begins.

However, a further increase in the number of chains gives rise to regeneration of liquid crystalline behaviour. For compounds **3d** and **3e** with seven and eight chains, enantiotropic mesophases were found in the ranges 72–134°C and 79–163°C, respectively. Both mesophases are characterized by textures typical for columnar phases (see figure 2). X-ray scattering investigations confirm the results obtained by microscopy. Three sharp reflections corresponding to a ratio of their positions of $1:\sqrt{3}:2$ were observed in the small angle region (Guinier film camera); this confirms a hexagonal lattice with a lattice parameter $a_{\mathrm{hex}} = 2.84$ nm for **3d** and $a_{\mathrm{hex}} = 2.87$ nm for **3e** ($\mathrm{Col_h}$ phases). Additionally, there are two outer regions of diffuse scattering, one corresponding to 0.45 nm, typical for molten alkyl chains, and a second one corresponding to 0.36 nm, which is assigned to core–core correlations. Therefore, the structure facilitates very close intermesogen contacts of the organometallic centres, and Pd–Pd interaction could be expected in the range of the observed intermesogen spacing ($d^8 - d^8$—closed shell interactions) [19] (see figure 3).

Table. Phase transition temperatures for compounds **3a**–**3e**.

Compound	R^1	R^2	R^3	R^4	T/°C
3a	H	H	H	H	Cr 113 SmC 117 SmA 133 I
3b	$OC_{10}H_{21}$	H	H	H	Cr 117 (SmA 101) I
3c	$OC_{10}H_{21}$	$OC_{10}H_{21}$	H	H	Cr 115 I
3d	$OC_{10}H_{21}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$	H	Cr 72 $\mathrm{Col_h}$ 134 I
3e	$OC_{10}H_{21}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$	Cr 79 $\mathrm{Col_h}$ 163 I

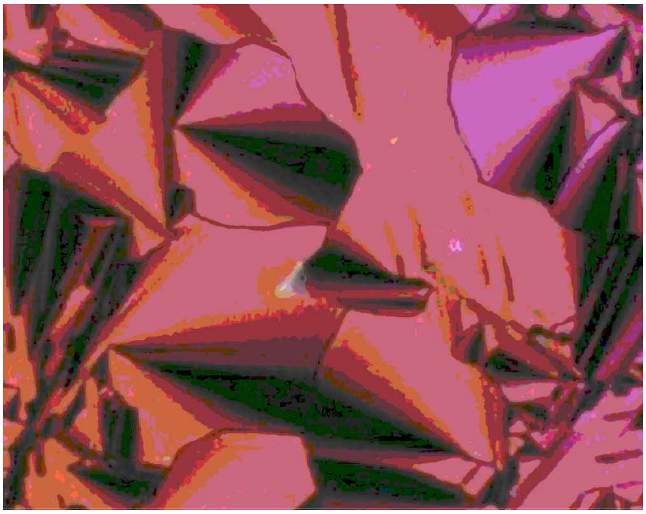


Figure 2. Polarized optical micrograph of the hexagonal columnar phase of **3e** at 95°C.

Taking into account the molecular dimensions obtained from space filling models, as shown in figure 4(*a*), we decided on the model for the observed hexagonal columnar phase shown in figure 4(*b*). The flat central cores of the molecules, caused by the square planar geometry of the Pd(II) atoms, are arranged face to face on top of one another and the Pd atoms may form chains in the centres of the columns. The fluid alkyl chains should efficiently fill the space around these polar core regions. To obtain an optimal space filling an antiparallel arrangement on average of the nearest neighbour half-discs seems favourable [20].

Thus, a discontinuous transition from lamellar to columnar mesophase behaviour takes place, controlled by the number of alkyl chains attached to the 1,3-diketonate unit. To study the transition from lamellar to columnar mesophases in this system in more detail, the contact region between the SmA phase of **3b** and the Col$_h$ phase of **3d** was investigated. The schematic

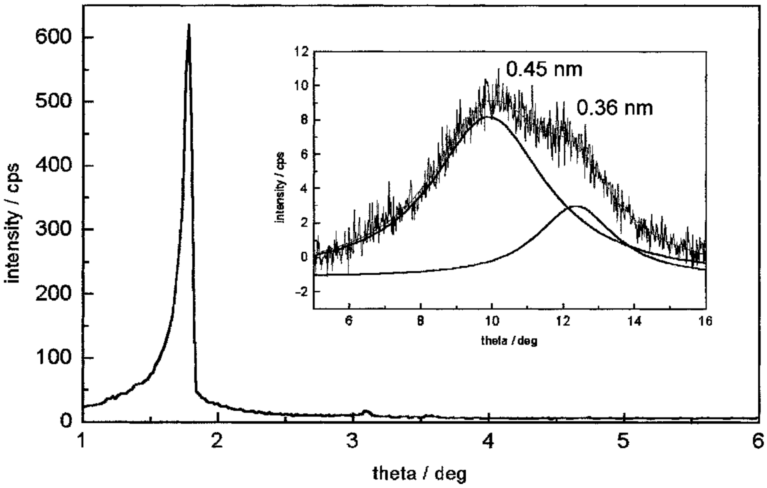


Figure 3. X-ray diffraction pattern of **3e** at 120°C.

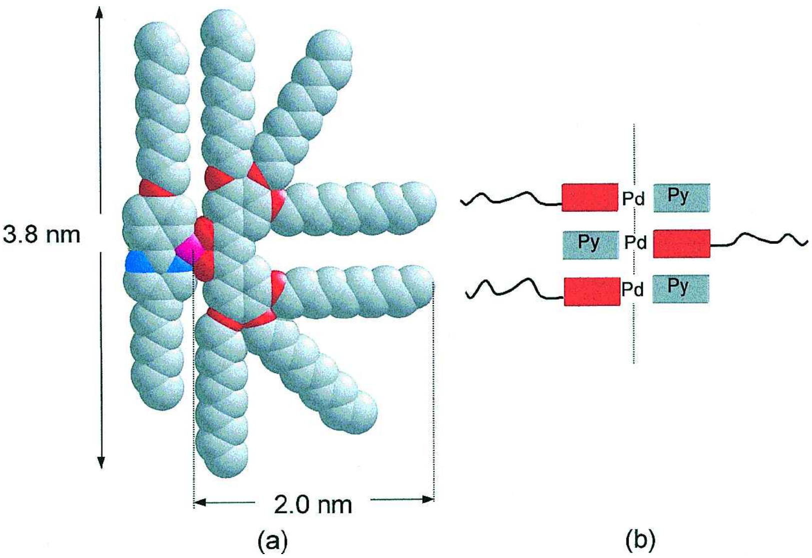


Figure 4. (*a*) Space-filling model of **3e** with all-*trans*-conformation of the alkyl chains (H atoms are not shown) and (*b*) arrangement suggested for the molecules of **3d** and **3e** in the hexagonal columnar mesophases.

phase diagram of this binary system is shown in figure 5. In the contact region, the mesophases of the pure compounds were destabilized and a new strongly birefringent mesophase with a non-specific texture (M) was induced. It could not be homeotropically aligned. Therefore, it could be an intermediate phase, at present unidentified, but not cubic.

3. Conclusions

In summary, it was found that the combination of two molecular sub-units of different shape in mononuclear *ortho*-palladated complexes leads to new liquid crystalline materials with a rich polymorphism and much lower transition temperatures than the related dinuclear chloro bridged organometallic compounds. By increasing the number of flexible alkyl chains, a discontinuous transition from a lamellar to a columnar organization of the molecules is observed, but no cubic phase could be detected as an intermediate phase, as is known to occur for polycatenar compounds [5] and amphiphilic molecules [21]. Moreover, compounds **3d** and **3e** are the first mononuclear *ortho*-palladated phenylpyrimidine-1,3-diketonato organyls that show thermotropic columnar mesophase behaviour.

4. Experimental

The synthesis of compound **3d** is described as a representative example of the experimental procedures.

1: A suspension of 2.05 mmol (860 mg) of 2-(4-decyloxyphenyl)-5-heptylpyrimidine and 2.05 mmol (592 mg) of bis(benzonitrile)-palladium(II) chloride in 80 ml of ethanol was stirred for 4 h at room temperature. The resulting yellow solid was filtered off, washed successively with 50 ml portions of petroleum ether, acetone and ethanol, and crystallized from chloroform/ethanol to give 1.1 g (95% yield) of **1** as a yellow solid. Cr_1 125 Cr_2 156 SmA 218 I(°C). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.58$ (br s, 2H, H-6 Py), 8.52 (br s, 2H, H-4 py), 7.59 (d, $^3J(H,H) = 8.2$ Hz, 2H, H-6′ ph), 6.97 (br s, 2H, H-3′ ph), 6.66 (d, $^3J(H,H) = 8.4$ Hz, 2H, H-5′ ph), 4.01 (t, $^3J(H,H) = 6.2$ Hz, 4H, OCH_2), 2.58 (m, 4H, $arCH_2$), 1.80–1.76 (m, 4H, OCH_2CH_2), 1.62–1.26 (m, 48H, CH_2), 0.87–0.84 (m, 12H, CH_3). Elemental analysis: found (calc. for $C_{54}H_{82}N_4O_2Cl_2Pd_2$): C 58.61 (58.80), H 6.91 (7.49), N 5.11 (5.08)%.

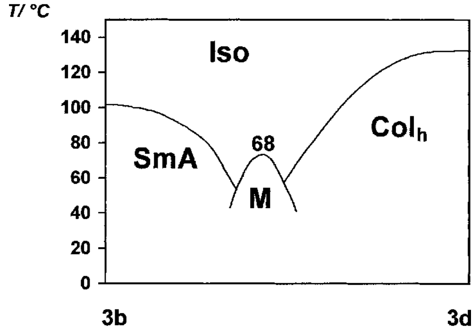


Figure 5. Schematic binary phase diagram of the system **3b**/**3d**; M = birefringent mesophase with unknown structure; crystalline phases are not shown.

2d: 1-(3,4,5-Tridecyloxyphenyl)-3-(3,4-didecyloxyphenyl)propan-1,3-dionato thallium(I) (**2d**) was prepared following a published procedure [18]. Cr 78 (Col 77) I; ref. [18]: Cr 75 (Col 69) I(°C).

3d: To a suspension of 0.073 mmol (80 mg) of **1** in 4 ml of dry CH_2Cl_2, a suspension of 0.145 mmol (175 mg) of **2d** in 4 ml of dry CH_2Cl_2 was added all at once. The resulting mixture was stirred for 18 h at room temperature. After complete reaction (TLC) the mixture was filtered and the solvent removed under reduced pressure. The crude material was purified by column chromatography (silica gel; CH_2Cl_2/ethanol, 10:0.5) and crystallized from an ethanol/ethyl acetate mixture (5:1) to give 173 mg (78% yield) of **3d** as a yellow solid (*cis*:*trans* ~ 1:1). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.78$, 8.76 (2d, $^4J(H,H) = 2.7$, 2.5 Hz, 1H, H-6 py), 8.56 (d, $^4J(H,H) = 2.5$ Hz, 1H, H-4 py), 7.70 (d, $^3J(H,H) = 8.6$ Hz, 1H, H-6′ py*ph*), 7.66–7.56 (m, 1H, ar-H), 7.55–7.53 (m, 1H, ar-H), 7.28, 7.25 (2d, $^4J(H,H) = 2.3$, 2.5 Hz, 1H, H-3′ py*ph*), 7.24, 7.17 (2s, 2H, ar-H), 6.92–6.88 (m, 1H, ar-H), 6.73–6.69 (m, 1H, H-5′ py*ph*), 6.56, 6.55 (2s, 1H, CH), 4.13–4.02 (m, 12H, OCH_2), 2.63–2.57 (m, 2H, $arCH_2$), 2.04–1.74 (m, 12H, OCH_2CH_2), 1.69–1.64 (m, 2H, $arCH_2CH_2$), 1.58–1.21 (m, 92H, CH_2), 0.90–0.86 (m, 21H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 183.2$ (C), 183.1 (C), 182.8 (C), 182.7 (C), 172.1 (C), 161.7 (C), 159.4 (CH), 155.6 (C), 155.5 (CH), 154.0 (C), 153.9 (C), 153.0 (C), 149.9 (C), 142.1 (C), 136.7 (C), 136.4 (C), 135.7 (C), 134.0 (C), 133.8 (C), 132.0 (C), 131.9 (C), 128.4 (CH), 121.8 (CH), 116.9 (CH), 116.6 (CH), 114.6 (CH), 114.0 (CH), 113.6 (CH), 113.1 (CH), 112.8 (CH), 107.7 (CH), 107.3 (CH), 95.9 (CH), 95.8 (CH), 74.6 (CH_2), 70.4 (CH_2), 70.3 (CH_2), 70.1 (CH_2), 68.8 (CH_2), 61.3 (CH_2), 32.8 (CH_2), 32.7 (CH_2), 32.6 (CH_2), 31.6 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 31.2 (CH_2), 30.7 (CH_2), 30.6 (CH_2), 30.59 (CH_2), 30.54 (CH_2), 30.49 (CH_2), 30.45 (CH_2), 30.40 (CH_2), 30.32 (CH_2), 30.30 (CH_2), 30.27 (CH_2), 30.14 (CH_2), 30.0 (CH_2), 29.9 (CH_2), 27.2 (CH_2), 27.14 (CH_2), 27.10 (CH_2), 27.05 (CH_2), 26.9 (CH_2), 23.6 (CH_2), 23.5 (CH_2), 23.4 (CH_2), 15.06 (CH_3), 14.95 (CH_3), 14.90 (CH_3). Elemental analysis: found (calc. for $C_{92}H_{152}N_2O_8Pd$): C 72.78 (72.67), H 10.09 (10.07), N 1.64 (1.84)%.

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References

[1] Göring, P., and Diele, S., 1998, *Handbook of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill (Weinheim: Wiley-VCH), p. 887.

[2] Ohta, K., Yamaguchi, N., and Yamamoto, I., 1998, *J. mater. Chem.*, **8,** 2637.

[3] Lattermann, G., Schmidt, S., Kleppinger, R., and Wendorff, J.-H., 1992, *Adv. Mater.*, **4,** 30; El-Ghayoury, A., Douce, L., Skoulios, A., and Ziessel, R., 1998, *Angew. Chem. int. Ed. Engl.*, **37,** 1255; Ziessel, R., Douce, L., El-Ghayoury, A., Harriman, A., and Skoulios, A., 2000, *Angew. Chem. int. Ed. Engl.*, **39,** 2033.

[4] Chandrasekhar, S., Nair, G. G., Praefcke, K., and Singer, D., 1996, *Mol. Cryst. liq. Cryst.*, **288,** 7; Chandrasekhar, S., Nair, G. G., Rao, D. S. S., Prasad, S. K., Praefcke, K., and Blunk, D., 1998, *Current Science*, **75,** 1042; Sadashiva, B. K., 1998, *Handbook of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill (Weinheim: Wiley-VCH), p. 933.

[5] Nguyen, H.-T., Destrade, C., and Malthete, J., 1998, *Handbook of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill (Weinheim: Wiley-VCH), p. 866.

[6] Ohta, K., Higashi, R., Ikejima, M., Yamamoto, I., and Kobayashi, N., 1998, *J. mater. Chem.*, **8,** 1979.

[7] Norbert, W. D. J. A., Goodby, J. W., Hird, M., and Toyne, K. J., 1997, *Liq. Cryst.*, **22,** 631.

[8] Fletcher, I. D., and Luckhurst, G. R., 1995, *Liq. Cryst.*, **18,** 175; Janietz, D., 1998, *J. mater. Chem.*, **8,** 265.

[9] Budig, H., Diele, S., Göring, P., Paschke, R., Sauer, C., and Tschierske, C., 1995, *J. chem. Soc., Perkin Trans. 2*, 767; Kreuder, W., Ringsdorf, H., Herrmann-Schönherr, O., and Wendorff, J. H., 1987, *Angew. Chem. int. Ed. Engl.*, **26,** 1249.

[10] Serrano, J. L., 1996, *Metallomesogens* (Weinheim: VCH); Donnio, B., and Bruce, D. W., 1999, *Structure and Bonding 95: Liquid Crystals II*, edited by D. M. P. Mingos (Berlin: Springer), p. 193.

[11] Barbera, J., Espinet, P., Lalinde, E., Marcos, M., and Serrano, J. L., 1987, *Liq. Cryst.*, **2,** 833.

[12] Ghedini, M., Longeri, M., and Bartolino, R., 1982, *Mol. Cryst. liq. Cryst.*, **84,** 207; Ghedini, M., Pucci, D., Cesarotti, E., Francescangeli, O., and Bartolino, R., 1994, *Liq. Cryst.*, **16,** 373.

[13] Ros, M. B., Ruiz, N., Serrano, J. L., and Espinet, P., 1991, *Liq. Cryst.*, **9,** 77.

[14] Ghedini, M., Pucci, D., Bartolino, R., and Francescangeli, O., 1993, *Liq. Cryst.*, **13,** 255; Ghedini, M., Pucci, D., de Munno, G., Viterbo, D., Neve, F., and Armentano, S., 1991, *Chem. Mater.*, **3,** 65.

[15] Praefcke, K., Bilgin, B., Usol'tseva, N., Heinrich, B., and Guillon, D., 1995, *J. mater. Chem.*, **5,** 2257; Praefcke, K., Holbrey, J. D., and Usol'tseva, N., 1996, *Mol. Cryst. liq. Cryst.*, **288,** 189; Heinrich, B., Praefcke, K., and Guillon, D., 1997, *J. mater. Chem.*, **7,** 1363.

[16] Ghedini, M., and Pucci, D., 1990, *J. organomet. Chem.*, **395,** 105.

[17] Thompson, N. J., Serrano, J. L., Baena, M. J., and Espinet, P., 1996, *Chem. Eur. J.*, **2,** 214; Thompson, N. J., Iglesias, R., Serrano, J. L., Baena, M. J., and Espinet, P., 1996, *J. mater. Chem.*, **6,** 1741.

[18] Barberà, J., Cativiela, C., Serrano, J. L., and Zurbano, M. M., 1991, *Adv. Mater.*, **3,** 602.

[19] Miller, J. S., and Epstein, A. J., 1976, *Progr. inorg. Chem.*, **20,** 1; Williams, J. M., 1983, *Inorg. Radiochem.*, **26,** 235; Pyykkö, P., 1997, *Chem. Rev.*, **97,** 597.

[20] Zheng, H., Lai, C. K., and Swager, T. M., 1994, *Chem. Mater.*, **6,** 101; Zheng, H., Xu, B., and Swager, T. M., 1996, *Chem. Mater.*, **8,** 907.

[21] Borisch, K., Diele, S., Göring, P., Kresse, H., and Tschierske, C., 1998, *J. mater. Chem.*, **8,** 529.