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Platinum- and Palladium-Isonitrile Complexes.
A New Family of Organometallic Liquid Crystalline Material

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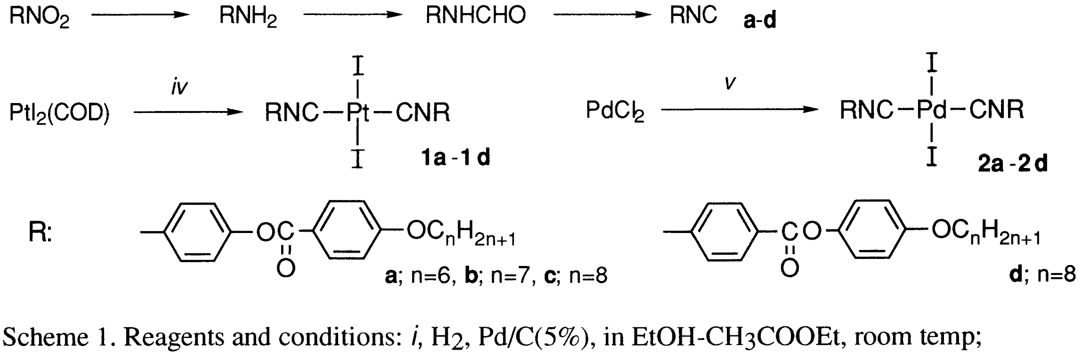
The title complexes having phenylisonitrile derivatives as a ligand show mesomorphic properties in a wide temperature range.

In recent years, there has been an increasing interest in liquid crystals which contain transition metals, metallomesogens, owing to their potentially unique properties (electronic, magnetic, and so on). Though various metallomesogens have already been reported thus far,1) organometallic mesogens bearing a direct bond between metal and carbon are rare. This is because thermally stable organometallic complexes are essentially limited. Most of stable organometallic complexes contain stabilizing ligands such as η^5-cyclopentadienyl, phosphines, carbon monoxide, and isonitriles in a molecule. Previously we have revealed that platinum alkynyls containing phosphine ligands show a high thermal stability and exhibit mesomorphic properties.2) Here we wish to report the first transition metal-isonitrile complexes which form stable mesophases in a wide temperature range.

Isonitriles have an isoelectronic structure with carbon monoxide, and can coordinate to a variety of metals in both low and high oxidation states. Thus, mesogenic isonitriles may make us possible to synthesize new organometallic mesogens incorporated with a variety of transition metals.

The synthetic route to several mesogenic isonitriles(**a**-**d**) and their complexes of platinum(**1**) and palladium(**2**) is shown in Scheme 1. Isonitrile derivatives were prepared from corresponding amines, that is, formylation of the amino group with formic acid and acetic anhydride, followed by dehydration with phosphoryl chloride and diisopropylamine3) gave arylisonitriles in good yields.



Scheme 1. Reagents and conditions: *i*, H_2, Pd/C(5%), in EtOH-CH_3COOEt, room temp; *ii*, $(CH_3CO)_2O$ in HCOOH, 50 °C; *iii*, $POCl_3$, diisopropylamine in CH_2Cl_2 then Na_2CO_3 in H_2O, 0 °C-room temp; *iv*, **a**-**d** in $CHCl_3$, room temp; *v*, **a**-**d**, KI in acetone, room temp.

All of isonitriles shown in the scheme formed a nematic phase in the temperature range of 60-90 °C, though they are somewhat unstable in a free state and a colorless sample of **a-d** became pale green after heating up to the N-I transition temperature.

The platinum complexes **1** were obtained in 70-90% yield by the ligand-exchange reaction of $PtI_2(COD)$ with 2 equiv. of an appropriate isonitrile in chloroform, and the palladium analogues **2** were also prepared in 80-90% yield by the reaction of $PdCl_2$ with 2 equiv. of an isonitrile in the presence of excess (5 equiv.) KI in acetone. Complexes **1** and **2** were identified by elemental and spectral analyses including IR and NMR spectra. A *trans*-configuration of the complex was confirmed by the IR spectra in a solid state as well as in a solution which showed only one absorption around 2200 cm^{-1} due to the stretching frequency of an isocyano group.

All the isonitrile complexes synthesized in the present work formed a stable nematic phase. Identification of mesophases was made on the basis of optical textures in the air. Table 1 summarizes the phase transition temperatures and enthalpy data in an argon atmosphere for complexes **1** and **2**. Both metal complexes showed extremely high thermal stabilities and exhibited mesomorphic properties in a wide temperature range. Since the N-I transition temperatures were very high, palladium complexes **2a-d** transformed into an isotropic phase with some decomposition, while the platinum analogues were still stable at such high temperatures in the air. The isonitrile complexes seem to be form thermally more stable mesophases than their structural isomer, nitrile complexes $(ArCN)_2MCl_2$ which similarly form mesophases at high temperature.[1] With respect to the influence of terminal alkyl groups, complexes with longer alkoxy chains showed lower N-I transition temperatures and for complex **1d** a smectic phase was observed in addition to a nematic phase. The present transition metal-isonitrile complexes may provide a new family of organometallic liquid crystalline materials.

Table 1. Transition[a)] temperatures(°C) and enthalpies[b)](kJ mol^{-1}) for complexes **1** and **2** [c)]

Complex	C		S		N		I	Complex	C		S		N		I
1a	•	173 [40]			•	254 [2.5]	•	**2a**	•	168 [49]			•	267 [2.8]	•
1b	•	161 [44]			•	240 [2.4]	•	**2b**	•	155 [47]			•	252 [3.0]	•
1c	•	163 [49]			•	230 [2.3]	•	**2c**	•	157 [51]			•	241 [2.1]	•
1d	•	194 [60]	•	220 [1.5]	•	261 [2.8]	•	**2d**	•	186 [49]	•	218 [1.3]	•	265 [1.5]	•

a) C: crystal, S: smectic, N: nematic, I: isotropic liquid. b) Values in parentheses.
c) DSC data obtained on 2nd scan for **1** and on 1st scan for **2** in an argon atmosphere.

References
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