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Liquid Crystals of *N*,*N′*-Dialkylimidazolium Salts Comprising Palladium(II) and Copper(II) Ions

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Metal-containing ionic liquid crystals of *N*,*N′*-dialkylimidazolium salts of Pd^{II} and Cu^{II} ($[(C_nH_{2n+1})_2\text{-im}][MCl_4]$, $n = 8$, 10, 12, 14, 16, and 18 for $M = \text{Pd}^{\text{II}}$ and $n = 10$, 12, 14, 16, and 18 for $M = \text{Cu}^{\text{II}}$) were prepared. Crystal structures of two compounds, $[(C_{12}H_{25})_2\text{-im}]_2[PdCl_4]$ and $[(C_{12}H_{25})_2\text{-im}]_2[CuCl_4]\cdot H_2O$, have been characterized by single crystal X-ray diffraction. The cations of these two compounds adopt a U-shaped conformation and are packed in a highly interdigitated bilayer fashion. The square planar $PdCl_4^{2-}$ and distorted tetrahedral $CuCl_4^{2-}$ are sandwiched between the cationic bilayers individually. Both series of compounds exhibit a wide temperature range of SmA mesophase. Thermal decompositions are observed near the clearing tempertures. For the Pd^{II} series, decomposition generates palladium dicarbene and carbene-imidazole complexes. Ionic liquid crystals with different combinations of $[(C_{18}H_{37})_2\text{-im}]_2[PdCl_4]$, $[(C_{18}H_{37})_2\text{-im}]_2[CuCl_4]\cdot H_2O$, and $[(C_{18}H_{37})_2\text{-im}]Cl\cdot H_2O$ are good candidates for $\text{Pd}^{\text{II}}/\text{Cu}^{\text{II}}$ catalyzed reactions carried out under partially ordered environments of ionic liquids.

Introduction

Ionic liquids (ILs) are ionic compounds which have relatively low melting points. Recently, interest in ILs has grown rapidly.[1−7] In addition to being environmentally benign solvents, ILs possess interesting properties such as tunable acidity, polarity, amphiphilicity, coordinating ability, and miscibility with various compounds. Therefore, ILs have also been applied to remove metal-ion pollutants,[8] alter product selectivity,[9] enhance reaction rates,[10] etc. Commonly used ILs are *N*-alkyl-substituted ammonium, imidazolium, phosphonium, and pyridinium salts. Of these ILs, imidazolium salts are the most popular one employed in catalytic reactions. This is especially true when metal−carbene complexes are the catalysts. The reason is that imidazolium salts are excellent carbene precursors, so metal−carbene complexes can be generated in situ.[11]

Ionic liquid crystals (ILCs)[12−15] are ionic compounds possessing liquid crystalline properties. ILCs are also amphiphiles in general. Amphiphilic ILCs can be considered as a special class of ILs.[12,16−24] The partially ordered property possessed by liquid crystals is thus an added value for ILCs as reaction media. The importance

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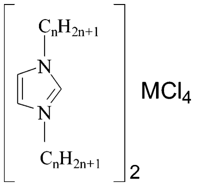
Scheme 1. Schematic representation of $[(C_nH_{2n+1})_2\text{-im}[_2[MCl_4]$, where $[(C_nH_{2n+1})_2\text{-im}]$ represents the *N*,*N′*-dialkyl imidazolium cation with alkyl = C_nH_{2n+1}; *n* = 8, 10, 12, 14, 16, 18 for M = Pd, and *n* = 10, 12, 14, 16, 18 for M = Cu.



of amphiphilic compounds has also been realized in the preparation of mesoporous materials,[25] nanomaterials[26] and layered solids,[27] to name a few. By incorporating metal ions to ILCs, ionic metallomesogens can be formed.[14,28] The presence of metal ions in ILCs provides many additional properties such as color, geometry, and magnetism. These properties cannot be achieved easily by conventional ILCs. Whereas reports on the metal-containing ILCs are relatively rare,[17,22a] examples of their crystal data are even rarer. Recently, several crystal structures of metal-containing ILCs based on pyridinium salts have appeared.[17b,17c] These salts display lamellar structures composing of organic−inorganic hybrid layers. However, reports on the corresponding imidazolium ILCs are lacking. Furthermore, the recent interests of using Pd^{II} salts in ILs of imidazolium salts as catalytic systems[1,29] prompt us to report the results of liquid crystals of *N*,*N*-dialkylimidazolium salts with $PdCl_4^{2-}$ and $CuCl_4^{2-}$ anions intercalated in the layered structure.

Results and Discussion

Synthesis. Metal complexes with general formula of $[(C_nH_{2n+1})_2\text{-im}]_2[MCl_4]$ (Scheme 1, $(C_nH_{2n+1})_2\text{-im}$ = *N*,*N′*-dialkyl imidazolium cations with alkyl chains of C_nH_{2n+1}; $n = 8, 10, 12, 14, 16, 18$ for M = Pd^{II} and $n = 10, 12, 14, 16, 18$ for M = Cu^{II}), were prepared by reacting palladium(II) chloride or copper(II) chloride with imidazolium chlorides in acetonitrile under refluxing conditions. The $PdCl_4^{2-}$ salts are light-brown microcrystalline products and $CuCl_4^{2-}$ salts are yellow-orange. The solubility of these compounds in polar organic solvents decreases with increasing chain length. ^1H NMR spectra of these Pd^{II} complexes are very similar to those of imidazolium halides. There is only a slight difference in the chemical shifts. Cu^{II} salts exhibit very broad ^1H NMR spectra due to the paramagnetic property of the metal ion. Similar to the vast majority of Cu^{II} compounds, the powder esr spectrum of the Cu^{II} salt of $n = 16$ exhibits an isotropic g value of 2.169 at room temperature. At 100 °C in the mesophase a similar signal at $g = 2.166$ was observed. The small difference between the two states indicates a similarity between the two environments. Magnetic fluids, which usually consist of magnetic nanoparticles suspended in liquids, are an interesting recent research subject.[30] The paramagnetic property possessed by liquid crystalline materials may be relevant to this issue.

Crystal Structure. Although structures of 1-alkyl-3-methyl imidazolium tetrachlorometalates, where alkyl is ethyl and butyl, have been reported,[29a,31] the crystal structures of $[(C_{12}H_{25})_2\text{-im}]_2[PdCl_4]$ and $[(C_{12}H_{25})_2\text{-im}]_2[CuCl_4]\cdot H_2O$ are the first example of metal-containing ILCs based on 1,3-dialkylimidazolium salts. The light brown crystals of $[(C_{12}H_{25})_2\text{-im}]_2[PdCl_4]$ were obtained by slow evaporation from THF/*n*-hexane at room temperature. The crystal structure and crystal packing of this compound are given in Figure 1, panels a and b, respectively. Selected bond distances and angles are given in the figure caption. The molecular cation is composed of two long hydrocarbon chains and an imidazolium head core. The two-alkyl chains in the cation run perpendicular to the imidazolium core plane in a same orientation to give a U-shaped conformation, which is similar to that found in the *N*,*N′*-dialkylbenzimidazolium bromide.[32] The imidazolium cations are packed in a head-to-head fashion. The flat imidazole ring heads align parallel to the neighboring flat heads but face those of an opposing layer. The alkyl chains of the cations are highly interdigitated. The metal-containing anion, $PdCl_4^{2-}$, has a regular square-planar geometry around the Pd^{II} center. These anions are sandwiched between the imidazolium rings with the square planes tilted 72.4° from the layer plane. This packing gives a bilayer structure with alternating hydrophobic alkyl chain layer and hydrophilic ionic layer. The hydrocarbon tails form the hydrophobic layer, while the imidazolium rings together with the $PdCl_4^{2-}$ anions form the ionic layer. The repeating layer distance calculated between the Pd^{II} layers is 20.1 Å. Substantial amounts of H-bonds are formed between the chlorides of the $PdCl_4^{2-}$ and the protons from the ring C−H and $N{-}CH_2$ (Figure 1c). It appears that the positive charge on the imidazolium ring induces partial positive charge on the ring C−H and the $N{-}CH_2$ protons. The distances

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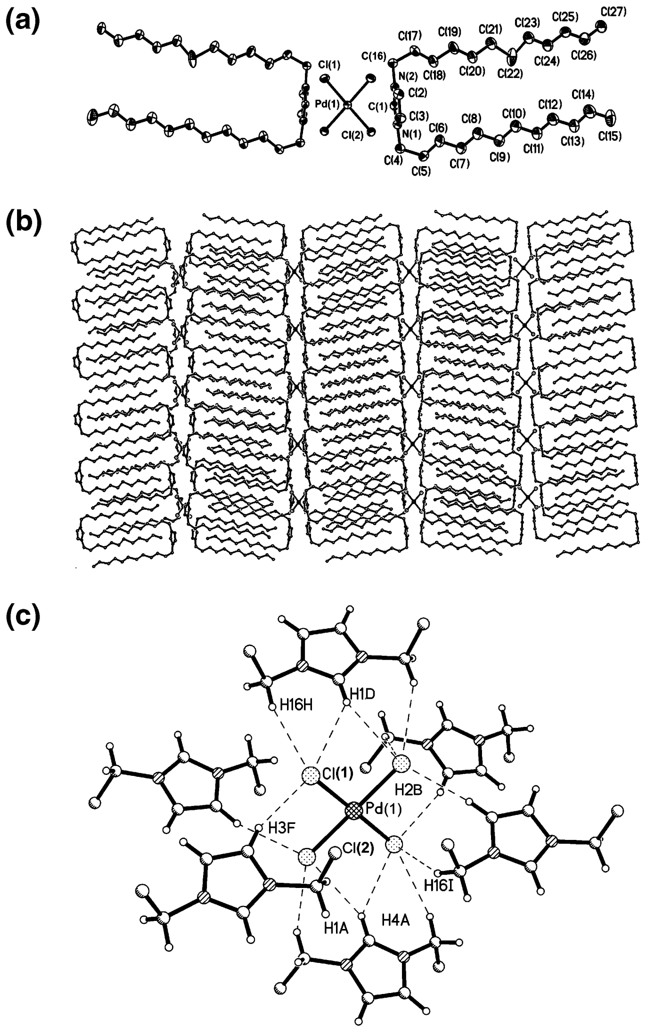

Figure 1. (a) ORTEP drawing of $[(C_{12}H_{25})_2\text{-im}][PdCl_4]$ (30% thermal ellipsolids) with partial atomic numberings, hydrogens omitted for clarity; selected distances [Å] and angles [°]: Pd(1)−Cl(1) 2.2980(17), Pd(1)−Cl(2) 2.3094(16), C(1)−N(1) 1.326(8), C(1)−N(2) 1.326(7); Cl(1)−Pd(1)−Cl(2) 179.48(7). (b) Zigzag crystal packing of $[(C_{12}H_{25})_2\text{-im}][PdCl_4]$, viewed along the *a*-axis. (c) Hydrogen bonds between the cations and $[PdCl_4]^{2-}$. Cl(1)···H1D 2.848, Cl(1)··· H16H 2.661, Cl(1)···H3F 2.680, Cl(2)···H2B 2.711, Cl(2)···H16I 2.784, Cl(2)···H4A 2.874, Cl(2)···H1A 2.842.

of these H···Cl H-bonding interactions are in the range from 2.7 to 2.9 Å, and are within the sum of the van der Waals radii (2.95 Å) of H and Cl. These H-bonds are important in the stabilization of ionic layer.

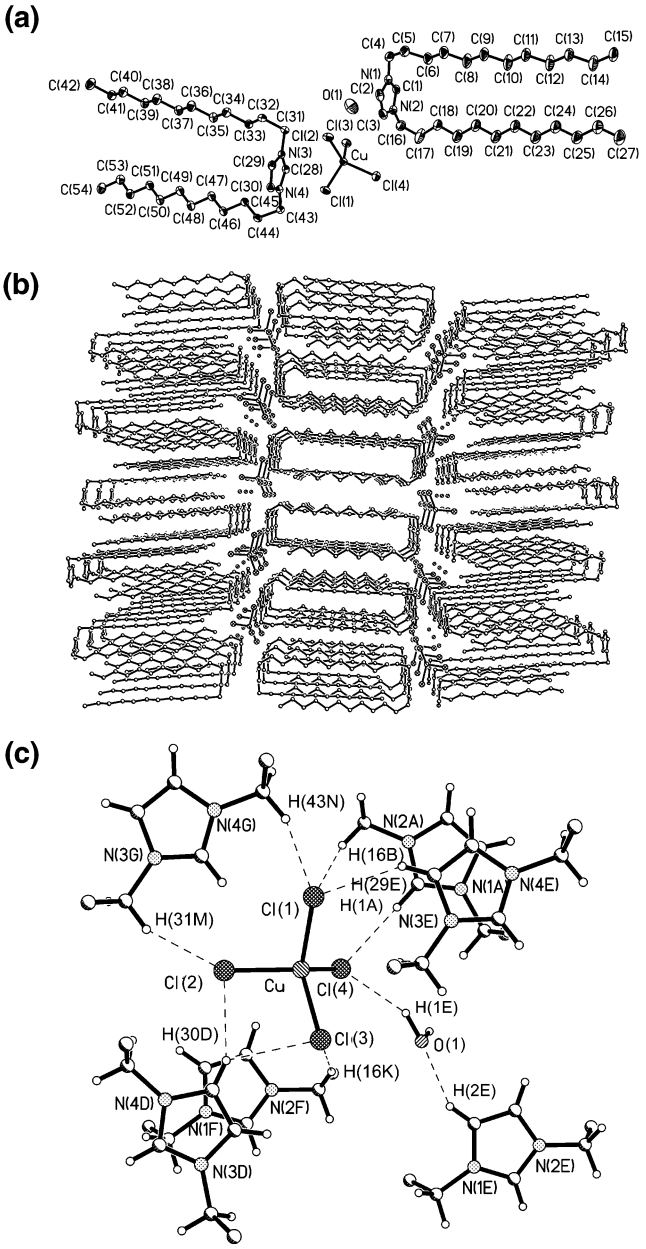

Figure 2. (a) ORTEP drawing of $[(C_{12}H_{25})_2\text{-im}]_2[CuCl_4]\cdot H2O$ (50% thermal ellipsolids) with partial atomic numberings, hydrogens omitted for clarity; selected distances [Å] and angles [°]: Cu−Cl(1) 2.2383(8), Cu−Cl(2) 2.2814(8), Cu−Cl(3) 2.2271(8), Cu−Cl(4) 2.2583(9); Cl(1)−Cu−Cl(3) 137.81(3), Cl(1)−Cu−Cl(4) 98.02(3), Cl(1)−Cu−Cl(2) 97.44(3), Cl(3)−Cu−Cl(4) 97.16(3), Cl(3)−Cu−Cl(2) 100.87(3), Cl(4)−Cu−Cl(2) 132.23(4). (b) Crystal packing of $[(C_{12}H_{25})_2\text{-im}][CuCl_4]\cdot H2O$. (c) Hydrogen bonds between the cations, $[CuCl_4]^{2-}$, and water. Cl(1)···H(29E) 2.837, Cl(1)···H(16B) 2.859, Cl(1)···H(43N) 2.707, Cl(4)···H(1AA) 2.568, Cl(4)···O(1) 2.307, Cl(3)···H(16K) 2.851, Cl(3)···H(30D) 2.807, Cl(2)···H(30D) 2.662, Cl(2)···H(31M) 2.732, O(1)···H(2AE) 2.307.

Yellow crystals of the Cu^{II} salt, $[(C_{12}H_{25})_2\text{-im}]_2[CuCl_4]\cdot H_2O$, were grown from THF/ether with a few drops of water. The crystal structure of this salt with the atomic numbering scheme is depicted in Figure 2a. Selected bond distances and angles are given in the figure cation. The space group of the Cu^{II} compound is identical to that of the Pd^{II} salt. However, an unusual long axis (83.36 Å), two times longer than the Pd^{II} compound, is observed. The bond lengths, bond angles, and the conformation of the cation are similar to those of the Pd^{II} salt. The $CuCl_4^{2-}$ anion adopts a distorted tetrahedral geometry. The angles around the Cu^{II} center are Cl(1)−Cu−Cl(3) 137.81(3)°, Cl(3)−Cu−Cl(2) 100.87(3)°, Cl(4)−Cu−Cl(2) 132.23(4)°, Cl(1)−Cu−Cl(4) 98.02(3)°, Cl(1)−Cu−Cl(2) 97.44(3)°, and Cl(3)−Cu−Cl(4) 97.16(3)°. The packing diagram of this compound is shown in Figure 2b. There are two alternating layers with distances of 19.94 and 21.39 Å in the crystal packing. This is caused by the unevenly sandwiched $CuCl_4^{2-}$ between imidazolium rings of two unequal thicknesses of the hydrophobic layers. Like the structure of the Pd^{II} compound, extended H-bonds between the $CuCl_4^{2-}$ chlorides and the ring C−H, N−CH$_2$, and water O−H protons are observed (Figure 2c). The number of H-bonds is slightly less for the Cu^{II} than for the Pd^{II} compound.

Table 1. Phase-Transition Temperatures of $[(C_nH_{2n+1})_2Cl\text{-im}]_2[PdCl_4]$ by DSC at Rate of 10 °C min^{-1} (ΔH in kJ mol^{-1})

$n = 8$	$\mathrm{Cr} \xrightarrow{56.5(59.0)} \mathrm{SmA} \xrightarrow{133.6(4.1)} I^{d}$
$n = 10$	$\mathrm{Cr} \xrightarrow{70.0(63.6)} \mathrm{SmA} \xrightarrow{190.7(3.2)} I^{d}$
$n = 12$	$\mathrm{Cr} \xrightarrow{84.7(94.4)} \mathrm{SmA} \xrightarrow{210.5(6.3)} I^{d}$
$n = 14$	$\mathrm{Cr} \xrightarrow{91.5(136.9)} \mathrm{SmA} \xrightarrow{212.3(5.8)} I^{d}$
$n = 16$	$\mathrm{Cr} \xrightarrow{94.9(156.9)} \mathrm{SmA} \xrightarrow{214.6(6.0)} I^{d}$
$n = 18$	$\mathrm{Cr} \xrightarrow{93.7,101.0(169.4)} \mathrm{SmA} \xrightarrow{214.2(4.6)} I^{d}$

[a] Abbreviations: Cr, crystal; SmA, smectic A mesophase; *I*, isotropic; *d*, partial decompose.

Table 2. Phase-Transition Temperatures of $[(C_nH_{2n+1})_2Cl\text{-im}]_2[CuCl_4]\cdot H_2O$ by DSC at a Rate of 10 °C min^{-1} (ΔH in kJ mol^{-1})

$n = 10$	$\mathrm{Cr} \xrightarrow{43.5(96.5)} \mathrm{SmA} \xrightarrow{130.0^{a}} I^{d}$
$n = 12$	$\mathrm{Cr} \xrightarrow{56.1(100.1)} \mathrm{SmA} \xrightarrow{155.3^{a}} I^{d}$
$n = 14$	$\mathrm{Cr} \xrightarrow{68.8(108.4)} \mathrm{SmA} \xrightarrow{177.6^{a}} I^{d}$
$n = 16$	$\mathrm{r} \xrightarrow{73.2(158.7)} \mathrm{SmA} \xrightarrow{185.4^{a}} I^{d}$
$n = 18$	$\mathrm{r} \xrightarrow{83.4(176.9)} \mathrm{SmA} \xrightarrow{188.8^{a}} I^{d}$

[a] Observed from POM. [b] Abbreviations used: Cr, crystal; SmA, smectic A mesophase; *I*, isotropic; *d*, partial decomposed.

Formation of H-bonds between imidazolium cation and tetrachlorometalate(II) has also been observed and predicted.[31b] In that report, protons from imidazolium C^2, C^4, and C^5 positions are proton donors, and chlorides from tetrachlorometalate(II) are proton acceptors. In our work, $PdCl_4^{2-}$ and $CuCl_4^{2-}$ are indeed capable of forming H-bonds with imidazolium cations. An additional $N{-}CH_2$ proton donor, however, is observed.

Thermal Behavior. The mesomorphic properties of these compounds were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and powder X-ray diffraction (XRD). All the Pd^{II} and Cu^{II} compounds reported in this work exhibit liquid crystalline behavior.

DSC thermograms of both the Pd^{II} and Cu^{II} compounds are irreversible after the first heating cycle because of thermal decomposition. We will take the Pd^{II} compound of $n = 18$ as an example. The first heating cycle exhibits three endothermic transitions at 93.7, 101.0, and 214.2 °C. The first two transitions are two unresolved peaks with a total ΔH value of 169.4 kJ/mol, and the third transition peak has a ΔH value of 4.6 kJ/mol. The first peak corresponds to the transition of a crystal phase to another crystal phase and cannot be observed optically. The second peak corresponds to the transition of crystal phase to mesophase. The mesophase was examined by optical observation. A typical fan-shape texture with the presence of homeotropic domains was observed when the sample was not subjected to a mechanical stress. Results from DSC and POM therefore suggest the presence of SmA mesophase. The third peak, having a relatively small ΔH value, corresponds to the transition of mesophase to isotropic liquid. This process can also be observed optically. The subsequent cooling and heating processes do not give reproducible results; presumably thermal decomposition occurs during the first heating cycle. All the other members of this series of compounds also exhibit thermal decomposition behavior. Therefore, in Table 1, phase transition temperatures of $[(C_nH_{2n+1})_2\text{-im}]_2[PdCl_4]$ are reported from the first heating cycle of DSC thermogram. In general, melting temperatures of these Pd^{II} compounds increase slightly upon increasing the alkyl chain length. The variation of clearing temperatures with increasing chain length has two different trends. Upon increasing the chain length from $n = 8$ to 10 then 12 there is a substantial increment in the clearing temperature, but very little or no variation with $n = 14$, 16, and 18. The phase-transition temperatures of these symmetrically substituted *N,N′*-dialkylimidazolium tetrachloropalladate(II) salts are compared with those of the corresponding 1-alkyl-3-methylimidazolium tetrachloropalladate(II) salts. The former compounds have lower melting temperatures but higher clearing temperatures than the latter compounds of thr same alkyl chain lengths. The system studied in this work therefore has a wider temperature range of mesophase than the unsymmetrical 1-alkyl-3-methyl imidazolium system. The symmetrically substituted imidazolium tetrachloropalladate(II) salts also have lower melting but higher clearing temperatures than those of N-alkylpyridinium tetrachloropalladate(II) salts. Among these three series of $PdCl_4^{2-}$ salts of ILCs, 1-methyl-3-alkylimidazolium salts are the least thermally stable compounds, whereas the pyridinium salts are the most thermally stable compounds.

For the Cu^{II} compounds of $n = 10$, 12, 14, 16, and 18, thermal decompositions are so severe that the phase transitions from mesophase to isotropic liquid are not observable for the compounds of $n = 10$ and 12 by DSC, but are observable by POM. In Table 2, the phase-transition temperatures of the Cu^{II} compounds are reported from the results of DSC (crystal to mesophase) and POM (mesophase to isotropic). Phase-transition temperatures of this Cu^{II} series also depend on the alkyl chain length. Upon increasing the chain length, both the melting and clearing temperatures of the Cu^{II} compounds increase gradually. In general, the phase-transition temperatures for the Cu^{II} salts are lower than those of the corresponding Pd^{II} salts.

To understand the thermal decomposition process, the Pd^{II} compounds were examined by thermogravimetric analysis (TGA). TGA thermogram of the Pd^{II} compound of $n = 18$ taken at a rate of 10 °C/min shows that decomposition begins at ~200 °C, which is near the temperature of clearing to the isotropic liquid. The Pd^{II} compound of $n = 16$ and lower homologues have a similar TGA thermogram. TGA thermogram of $n = 16$ taken at a constant temperature of 180 °C for a duration of ~3 h shows a weight loss of 2.69%, corresponding to the loss of HCl. The loss of HCl may indicate the formation of $Pd^{II}{-}$carbene complex. The decomposition process was also followed by ^1H and ^{13}C NMR spectroscopies. The Pd^{II} compound of $n = 16$ was first heated neat at 180 °C for 2 h. ^1H and ^{13}C NMR spectra of this thermally decomposed sample (^{13}C NMR spectrum is given in Figure 3b) show that the peaks assignable to the original Pd^{II} compound ($n = 16$) decrease, and a new

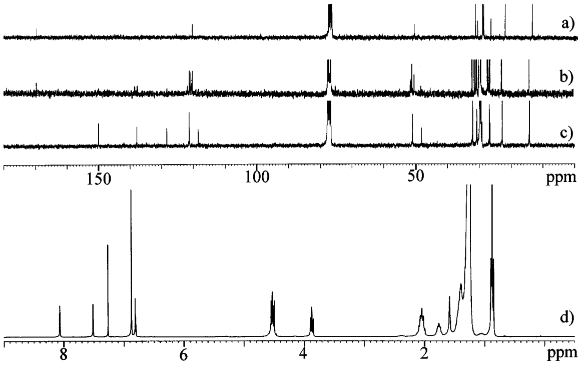

Figure 3. ^{13}C NMR spectra of (a) pure *trans*-[Pd(($C_{16}H_{33})_2$-imy)$_2Cl_2$]; (b) the sample obtained by heating [($C_{16}H_{33})_2$-im]$_2$-[$PdCl_4$] at 180 °C for 2 h; (c) the sample obtained by heating [($C_{16}H_{33})_2$-im]$_2$[$PdCl_4$] at 200 °C 4 h. (d) ^1H NMR spectrum of the sample obtained as for (c).

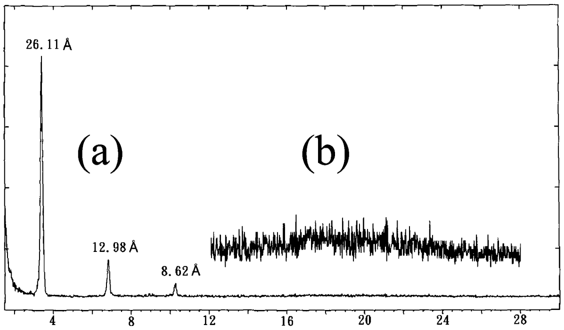

Figure 4. (a) XRD diffractogram for the compound of [($C_{12}H_{25})_2$-im][$PdCl_4$] at 100 °C in the mesophase; (b) with partial enlargement for the halo at 2 Å ≅ 20°.

major species having spectral patterns identical to that of the dicarbene species *trans*-[Pd(($C_{16}H_{33})_2$-imy)$_2Cl_2$][11b] (($C_{16}H_{33})_2$-imy = 1,3-dihexadecanylimidazol-2-ylidene) appears (Figure 3a). This dicarbene complex has been reported in our earlier work.[11b] The Pd^{II} compound of $n = 16$ was also heated at 200 °C for 4 h. A major species different from the dicarbene complex was observed. ^{13}C/^1H NMR spectra (Figure 3c and d) suggest the formation of [Pd($C_{16}H_{33})_2$-imy)($C_{16}H_{33}$-im)Cl_2]. An identical compound was obtained when equal molar [Pd($C_{16}H_{33})_2$-imy)$_2Cl_2$] and [Pd(($C_{16}H_{33}$-im)$_2Cl_2$] were heated neat at 150 °C for 1 h. The formation of Pd^{II}−dicarbene and Pd^{II}−carbene-imidzole compounds is different from that observed for the catalytic system of $PdCl_2$/[BMIM]·BF_4 (BMIM = 1-*n*-butyl-3-methyl imidazolium),[1,29a] and that using imidazolium salts with bulky substituents.[1,29b,29c] Recently, a palladium− carbene−imidazole complex has been synthesized and used as an efficient catalyst for sonogashira cross-coupling reactions.[33] Because salts of *N*,*N′*-dialkylimidazolium chloride or bromide are stable up to 250 °C, formation of *N*-alkylimidazole observed in our system must be catalyzed by the Pd^{II} ion, most likely through the formation of Pd ^{II}−carbene bond.

Structural Characterization of Liquid Crystalline Phase. The mesomorphic structures of these compounds were further studied by XRD. The Pd^{II} series of $n = 12$ (Figure 4) in the mesophase (110 °C) exhibits three sharp peaks of equal spacing at the lower angle region and a faint diffused scattering at ~2 Å = 20°. These sharp peaks suggest a well-defined lamellar structure corresponding with a repeating layer distance of 26.1 Å. The faint halo indicates liquidlike alkyl chains with an averaged domain of ~4.5 Å. The results from XRD are therefore consistent with a mesophase of SmA suggested from the study of POM. The mesomorphic layer distance of 26.1 Å is 6.0 Å longer than the 20.1 Å observed in the crystalline state. This large increase in the layer distance from crystalline phase to smectic phase suggests a structural change from a highly interdigitated bilayer stacking to a partially or none interdigitated bilayer structure. Other compounds in the Pd^{II} and Cu^{II} series have a similar structural transformation from crystalline phase to mesophase. This structural transformation appears to be general for the *N*,*N′*-disubstituted imidazolium salts of equal chain length studied in our laboratory. This mesomorphic structure, however, is different from that observed for 1-alkyl-3-methylimidazolium tetrahalopalladate (II) salts,[22a] in which a fully interdigitated bilayer structure has been suggested. To compare the crystal and liquid crystal structures of the Pd^{II} and Cu^{II} series of $n = 12$, 14, 16, and 18, plots of layer spacings at crystal and liquid crystal phases against carbon chain numbers *n* give straight lines, suggesting that these compounds have similar crystal and mesomorphic structures.

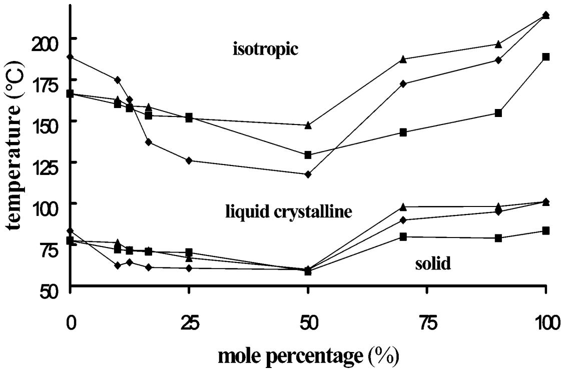

Figure 5. Variation of phase-transition temperatures on the mole percentage of mixtures: (▲) **A/(A+C)**; (■)**B/(B+C)**; (♦)-**A/(A+B)**; where **A** is [($C_{18})_2$-im]$_2$[$PdCl_4$], **B** is [($C_{18})_2$-im]$_2$-[$CuCl_4$]·H_2O, and **C** is [($C_{18})_2$-im]Cl·H_2O.

Mixed ILCs. Many chemical transformations are known to be catalyzed by Pd^{II} and Cu^{II} metal ions. To evaluate the properties of using Pd^{II}/Cu^{II} salts as a catalytic system in ILCs of *N*,*N′*-dialkylimidazolium chlorides,we examined the mesomorphic behaviors of four combinations of different mixtures: **I**, [($C_{18}H_{37})_2$-im]$_2$[$PdCl_4$]/[($C_{18}H_{37})_2$-im]Cl·H_2O; **II** [($C_{18}H_{37})_2$-im]$_2$-[$CuCl_4$]·H_2O/[($C_{18}H_{37})_2$-im]Cl·H_2O; **III** [($C_{18}H_{37})_2$-im]$_2$-[$PdCl_4$]/[($C_{18}H_{37})_2$-im]$_2$[$CuCl_4$]·H_2O; and **IV** [($C_{18}H_{37})_2$-im]$_2$[$PdCl_4$]/[($C_{18}H_{37})_2$-im]$_2$[$CuCl_4$]·H_2O/[($C_{18}H_{37})_2$-im]Cl·H_2O.

In the first combination, samples with different ratios of [($C_{18}H_{37})_2$-im]$_2$[$PdCl_4$] and [($C_{18}H_{37})_2$-im]Cl·H_2O were prepared by first dissolving the two components in CH_2Cl_2, then removing the solvent under vacuum after sonication. Each mixture thus contains an identical imidazolium cation of [($C_{18}H_{37})_2$-im]$^+$ but mixed anions of [$PdCl_4$]$^{2-}$ and Cl^-. Phase-transition temperatures for the first combination are given in Figure 5 (▲). When the mole percentages of the $PdCl_4^{2-}$ salt are greater than 50, the mixtures have melting and clearing temperatures lower than the pure $PdCl_4^{2-}$ salt but higher than the Cl^- salt in general. If components of the

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(33) Batey, R. A.; Shen, M.; Lough, A. J. *Org. Lett.* **2002**, *4*, 1411.

$PdCl_4^{2-}$ salt are less than 50%, the mixtures have melting and clearing temperatures lower than the pure Cl^- and $PdCl_4^{2-}$ salts. The data also show that the decrement on the temperatures of clearing is larger than that of the temperatures of melting. This result indicates that the mixed anions have a greater influence on the clearing process than on the melting. It follows that the clearing process involves mainly the collapse of the ionic layers. The different anions in the ionic layer cause a less symmetrical environment which may facilitate the collapse of the layer on the clearing process. As a consequence, the mixtures have a slightly smaller temperature range of mesophase than those of pure compounds. In mesophase, these mixtures display typical fan texture with homeotropic domains. This observation suggests a SmA phase as was observed for the pure compounds. We also noticed that no biphasic behavior was observed under POM. Finally, no decomposition was observed for the mixtures up to the clearing temperatures.

The mixtures in the second combination have a similar mesomorphic behavior (Figure 5, ■) as compared to the first combination. In the third combination, the larger $CuCl_4^{2-}/PdCl_4^{2-}$ ratio has a pronounced effect on the lowering of melting and clearing temperatures (Figure 5, ◆). Thus, adding a small amount of $PdCl_4^{2-}$ into the ionic layer of $CuCl_4^{2-}$ appears to have a greater influence on the processes of phase transitions than those of the mixtures of opposite ratio. For the fourth combination, only a mixture with a molar ratio of 1:1:8 was examined. Upon cooling, the phase transition from isotropic liquid to mesophase occurs at 137.2 °C and the transition from mesophase to crystal occurs at 50.9 °C. This combination demonstrates the possibility of providing an ordered solvent system for chemical transformations involving catalytic systems of Pd^{II}/Cu^{II} in the ionic liquid crystals of *N*,*N′*-disubstituted imidazolium salts.

ILCs formed by mixing imidazolium and pyridinium salts of PF_6^- have been reported.[22c] The mixtures in that report thus contain PF_6^- salt of different cations. Among those few ratios reported, the melting and clearing temperatures are found to be between those of the pure pyridinium and imidazolium salts. Furthermore, the changes in the melting temperatures are in general larger than those of clearing temperatures. It thus results in a larger mesophase range, which is different from ours. This implies that the mixed cations control the melting process, whereas the mixed anions control the clearing process.

Conclusion

In this work we have prepared two series of metal-containing ionic liquid crystals composed of *N*,*N′*-dialkylimidazolium salts of $PdCl_4^{2-}$ and $CuCl_4^{2-}$. Both series of compounds in the solid state have a well defined lamellar structure in the solid and liquid crystal phases. The metal ions are intercalated between the hydrophobic bilayers composed of U-shaped imidazolium cations with highly interdigitated alkyl chains. These mesogenic compounds have a relatively wide range of mesophase (∼100 °C). However, thermal decomposition occurs before the clearing temperatures. Two decomposition products, a Pd^{II}-dicarbene and a Pd^{II}-carbene−imidazole complex, were identified. Mixtures with different combinations of the $PdCl_4^{2-}$, $CuCl_4^{2-}$, and Cl^- salts also display liquid crystalline properties. Results of these combinations suggest the possibility of providing a partially ordered solvent system for chemical transformations using Pd^{II} and/or Cu^{II} as catalysts.

Experimental Section

General Procedures. All the solvents used were reagent grade and were used as received. Imidazole was purchased from R. D. H. Alkyl halides were obtained from TCI. $PdCl_2$ was obtained from Balance Precious Metal Co. $CuCl_2$ was obtained from Kokusan chemical works and was dried before use. *N*,*N′*-disubstituted imidazolium halides were prepared by the known method.[34] The ^1H NMR spectra were recorded on a Bruker AC-F300 spectrometer in $CDCl_3$. Elemental microanalyses were performed by the Taiwan Instrumentation Center. Optical characterization was performed by using covered microscope slides on an Olympus BH-2 polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 90 central processor. Phase transition temperatures were determined by differential scanning calorimetry at a scan rate of 10 °C/min using a Perkin-Elmer DSC-7 calorimeter calibrated with indium and tin standards in conjunction with a Perkin-Elmer 7700 thermal analysis data station. Powder X-ray diffraction patterns were obtained from an X-ray diffractometer Bruker D-5000 equipped with a temperature controller TTK450.

Crystal data for $[(C_{12}H_{25})_2\text{-im}]_2[PdCl_4]$: $C_{54}H_{106}Cl_4N_4Pd$, $M = 1059.63$, monoclinic, $a = 15.1898(11)$ Å, $b = 10.0913(8)$ Å, $c = 40.111(3)$ Å, $\alpha = 90°$, $\beta = 91.345(2)°$, $\gamma = 90°$, $U = 6146.7(8)$ Å^3, $T = 298$ K, space group $C2/c$, $Z = 4$, $\mu = 0.510$ mm^{-1}, $\sigma_{calcd} = 1.145$ Mg m^{-3}, $1.02 < \theta < 28.28$. Of 18772 reflections measured, 7311 were unique ($R_{int} = 0.0496$) and were used in all calculations. Diffraction data were collected on a Bruker SMART diffractometer equipped with a CCD area detector with graphite- monochromatized Mo*K*α radiation ($\lambda = 0.71073$ Å) in ϕ and ω scan modes. The structure was solved by the heavy atom method and refined (based on F^2 using all independent data) by full matrix least-squares methods (Bruker SHELXTL 97). *R* values are reported for $R1 = 0.0865$ (based on observed data, I > 2ó) and $wR2 = 0.2288$ (based on all data). Nonhydrogen atoms were refined with anisotropic thermal parameters. For H-atoms a riding model was employed.

Crystal Data for $[(C_{12}H_{25})_2\text{-im}]_2[CuCl_4]\cdot H_2O$. $C_{54}H_{108}Cl_4N_4CuO$, $M = 1034.78$, monoclinic, $a = 83.357(3)$ Å, $b = 8.5867(3)$ Å, $c = 16.8486(4)$ Å, $\alpha = 90°$, $\beta = 97.648(1)°$, $\gamma = 90°$, $U = 11957.2(7)$ Å^3, $T = 150$ K, space group $C2/c$, $Z = 8$, $\mu = 0.581$ mm^{-1}, $\sigma_{calcd} = 1.150$ Mg m^{-3}, $1.48 < \theta < 26.37$. Of 29780 reflections measured, 11788 were unique ($R_{int} = 0.0386$) and were used in all calculations. Diffraction data were collected on a Bruker SMART diffractometer equipped with a CCD area detector with graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) in ω scan modes. The structure was solved by the direct method and refined (based on F^2 using all independent data) by full matrix least-squares methods (Bruker SHELXL-93). *R* values are reported for $R1 = 0.0550$ (based on observed data, $I > 2\sigma$) and

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(34) (a) Cannon, W. N.; Powell, C. E.; Jones, R. *G. J. Org. Chem.* **1957**, *22*, 1323. (b) Traylor, T. G.; Magde, D.; Marsters, J.; Jongeward, K.; Wu, G.-Z.; Walda, K. *J. Am. Chem. Soc.* **1993**, *115*, 4808.

*wR*2 = 0.1395 (based on all data). All atoms except H-atom were refined with anisotropic thermal parameters. For H-atoms a riding model was employed except those of water molecules.

Synthesis of $[(C_{18}H_{37})_2\text{-im}]_2[PdCl_4]$. Palladium(II) chloride (320 mg, 1.8 mmol) was allowed to dissolve in 50 mL of acetonitrile at 70 °C. To this solution, $[(C_{18}H_{37})_2\text{-im}]Cl{\cdot}H_2O$ (2000 mg, 3.6 mmol) in 30 mL of acetonitrile was added. The resultant solution was stirred under refluxing conditions for 3 h. The orange precipitant, formed by cooling the solution to room temperature, was filtered and recrystallized from dichloromethane and *n*-hexane. A yield of 90% was obtained. ^{1}H NMR: δ 0.88 (t, $^3J = 7$ Hz, 8H, CH_3), 1.32−1.25 (m, 60H, CH_2), 1.95−1.93 (m, 4H, CH_2), 4.55 (t, $^3J = 7$ Hz, 4H, CH_2), 7.29 (s, 2H, CH), 10.26 (s, 1H, CH). Anal. Calcd. for $C_{78}H_{154}N_4PdCl_4$: C, 67.09; H, 11.12; N, 4.01. Found: C, 67.03; H, 11.12; N, 3.99%.

The following Pd^{II} compounds were prepared by a method similar to that of $[(C_{18}H_{37})_2\text{-im}]_2[PdCl_4]$.

$[(C_{16}H_{33})_2\text{-im}]_2[PdCl_4]$. ^{1}H NMR: δ 0.88 (t, $^3J = 7$ Hz, 6H, CH_3), 1.32−1.24 (m, 52H, CH_2), 1.97−1.93 (m, 4H, CH_2), 4.55 (t, $^3J = 7$ Hz, 4H, CH_2), 7.30 (s, 2H, CH), 10.30 (s, 1H, CH). Anal. Calcd. for $C_{70}H_{138}N_4PdCl_4$: C, 65.47; H, 10.83; N, 4.36. Found: C, 65.20; H, 10.85; N, 4.36%.

$[(C_{14}H_{29})_2\text{-im}]_2[PdCl_4]$. ^{1}H NMR: δ 0.88 (t, $^3J = 7$ Hz, 6H, CH_3), 1.31−1.23 (m, 44H, CH_2), 1.99−1.89 (m, 4H, CH_2), 4.55 (t, $^3J = 7$ Hz, 4H, CH_2), 7.36 (s, 2H, CH), 10.26 (s, 1H, CH). Anal. Calcd. for $C_{62}H_{122}N_4PdCl_4$: C, 63.54; H, 10.49; N, 4.78, Found: C, 63.43; H,10.50; N, 4.77%.

$[(C_{12}H_{25})_2\text{-im}]_2[PdCl_4]$. ^{1}H NMR: δ 0.88 (t, $^3J = 7$ Hz, 6H, CH_3), 1.32−1.17 (m, 36H, CH_2), 2.01−1.93 (m, 4H, CH_2), 4.56 (t, $^3J = 7$ Hz, 4H, CH_2), 7.29 (s, 2H, CH), 10.33 (s, 1H, CH). Anal. Calcd. for $C_{54}H_{106}N_4PdCl_4$: C, 61.21; H, 10.08; N, 5.29. Found: C, 61.07; H, 10.14; N, 5.37%.

$[(C_{10}H_{21})_2\text{-im}]_2[PdCl_4]$. ^{1}H NMR: δ 0.88 (t, $^3J = 7$ Hz, 6H, CH_3), 1.32−1.24 (m, 28H, CH_2), 2.01−1.95 (m, 4H, CH_2), 4.55 (t, $^3J = 7$ Hz, 4H, CH_2), 7.33 (s, 2H, CH), 10.30 (s, 1H, CH). Anal. Calcd. for $C_{46}H_{90}N_4PdCl_4$: C, 58.31; H, 9.57; N, 5.91. Found: C, 57.64; H, 9.53; N, 6.00%.

$[(C_8H_{17})_2\text{-im}]_2[PdCl_4]$. ^{1}H NMR: δ 0.86 (t, $^3J = 7$ Hz, 6H, CH_3), 1.31−1.24 (m, 20H, CH_2), 1.94−1.92 (m, 4H, CH_2), 4.54 (t, $^3J = 7$ Hz, 4H, CH_2), 7.40 (s, 2H, CH), 10.24 (s, 1H, CH). Anal. Calcd. for $C_{38}H_{74}N_4PdCl_4$: C, 54.64; H, 8.93; N, 6.71. Found: C, 54.39; H, 8.91; N, 6.75%.

$[Pd((C_{16}H_{33})_2\text{-imy})(C_{16}H_{33}\text{-im})Cl_2]$. (a). $[(C_{16}H_{33})_2\text{-im}]_2[PdCl_4]$ powder (520 mg, 0.4 mmol) was heated at 200 °C for 4 h. The crude product was purified by CH_2Cl_2/ether. The yield was about 50%.

(b). A mixture of **$[Pd((C_{16}H_{33})_2\text{-imy})_2Cl_2]$** and **$[Pd(C_{16}H_{33}\text{-im})_2Cl_2]$** (molar ratio = 1:1) was heated at 150 °C for 1 h. The yield of the product was over 90%. ^{1}H NMR: δ 0.89 (t, $^3J = 7$ Hz, 6H, CH_3), 1.40−1.19 (m, H, CH_2), 1.79−1.74 (m, 2H, CH_2), 2.10−2.03 (m, 4H, CH_2), 3.88 (t, $^3J = 7$ Hz, 2H, CH_2), 4.54 (t, $^3J = 7$ Hz, 4H, CH_2), 6.82 (s, 1H, CH), 7.52 (s, 1H, CH), 8.08 (s, 1H, CH), 6.89 (s, 2H, CH). ^{13}C NMR($CDCl_3$, 75.5 MHz): 149.85, 137.75, 128.23, 121.18, 118.37, 50.95, 48.08, 31.95−26.56, 22.71, 14.15. FAB/MS: *m*/*z* 951 $(M - Cl)^+$, 517 $((C_{16}H_{33})_2\text{-imy})^+$, 292 $(C_{16}H_{33}\text{-im})^+$. Anal. Calcd. for $C_{54}H_{104}N_4PdCl_2$: C, 65.73; H, 10.62; N, 5.68. Found: C, 65.85; H, 10.68; N, 5.40%.

$[(C_{18}H_{37})_2\text{-im}]_2[CuCl_4]{\cdot}H_2O$. Copper(II) chloride (66 mg, 0.49 mmol) and $[(C_{18}H_{37})_2\text{-im}]Cl{\cdot}H_2O$ (600 mg, 0.98 mmol) were dissolved in 30 and 10 mL of warm acetonitrile, respectively. The $[(C_{18}H_{37})_2\text{-im}]Cl$ solution was slowly added to the $CuCl_2$ solution with stirring. After complete the addition, the solution was refluxed for 3 h. After cooling to room temperature, the resulting yellow precipitate of $[(C_{18}H_{37})_2\text{-im}]_2[CuCl_4]{\cdot}H_2O$ was obtained by filtration. Recrystallization from dichloromethane and *n*-hexane gave a yield of 92%. ^{1}H NMR: δ 0.88 (t, $^3J = 7$ Hz, 3H, CH_3), 1.26 (m, 30H, CH_2), 1.80 (board, 2H, CH_2) 2.60 (board, 2H, CH_2), 5.30 (board, 2H, CH_2), 7.70 (board, 1H, CH). The C^2-H proton was not observed because of the paramagnetic property of the Cu^{II} compound. Anal. Calcd. for $C_{78}H_{156}N_4CuCl_4O$: C, 68.31; H, 11.46; N, 4.09. Found: C, 67.87; H, 11.36; N, 4.20%.

The following Cu^{II} compounds were prepared by a method similar to that of preparing $[(C_{18}H_{37})_2\text{-im}]_2[CuCl_4]{\cdot}H_2O$.

$[(C_{16}H_{33})_2\text{-im}]_2[CuCl_4]{\cdot}H_2O$. ^{1}H NMR: δ 0.88 (t, $^3J = 7$ Hz, 3H, CH_3), 1.26−1.19 (m, 26H, CH_2), 1.80 (board, 2H, CH_2) 2.60 (board, 2H, CH_2), 5.30 (board, 2H, CH_2), 7.60 (board, 1H, CH). Anal. Calcd. for $C_{70}H_{140}N_4CuCl_4O$: C,66.77; H, 11.21; N, 4.45. Found: C, 66.58; H, 11.1;, N, 4.51%.

$[(C_{14}H_{29})_2\text{-im}]_2[CuCl_4]{\cdot}H_2O$. ^{1}H NMR: δ 0.88 (t, $^3J = 7$ Hz, 3H, CH_3), 1.26−1.21 (m, 22H, CH_2), 1.80 (board, 2H, CH_2) 2.60 (board, 2H, CH_2), 5.10 (board, 2H, CH_2), 7.40 (board, 1H, CH). Anal. Calcd. for $C_{62}H_{124}N_4CuCl_4O$: C, 64.92; H, 10.90; N, 4.88. Found: C, 64.92; H, 10.93; N, 4.99%.

$[(C_{12}H_{25})_2\text{-im}]_2[CuCl_4]{\cdot}H_2O$. ^{1}H NMR: δ 0.88 (t, $^3J = 7$ Hz, 3H, CH_3), 1.26−1.19 (m, 18H, CH_2), 1.80 (board, 2H, CH_2) 2.60 (board, 2H, CH_2), 5.30 (board, 2H, CH_2), 7.60 (board, 1H, CH). Anal. Calcd. for $C_{54}H_{108}N_4CuCl_4O$: C, 62.68; H, 10.52; N, 5.41. Found: C, 62.77; H, 10.66; N, 5.43%.

$[(C_{10}H_{21})_2\text{-im}]_2[CuCl_4]{\cdot}H_2O$. ^{1}H NMR: δ 0.88 (t, $^3J = 7$ Hz, 3H, CH_3), 1.28−1.22 (m, 14H, CH_2), 1.80 (board, 2H, CH_2) 2.60 (board, 2H, CH_2), 5.30 (board, 2H, CH_2), 7.60 (board, 1H, CH). Anal. Calcd. for $C_{46}H_{92}N_4CuCl_4O$: C, 59.88; H, 10.05; N, 6.07. Found: C, 60.80; H, 10.12; N, 6.19%. The slightly poor agreement between the calculated and observed values is due to the slight dehydration of the sample.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for $[(C_{12}H_{25})_2\text{-im}]_2[PdCl_4]$ and $[(C_{12}H_{25})_2\text{-im}]_2[CuCl_4]{\cdot}H_2O$ (pdf, 16 pages). An X-ray crystallographic file (CIF).

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