ORGANOMETALLICS

Thermal Properties and Crystal Structures of Ionic Liquids from Ruthenium Sandwich Complexes with Trialkoxybenzene Ligands: Effects of Substituent Positions and Alkyl Chain Lengths

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Supporting Information

ABSTRACT: A series of ionic liquids containing $[Ru(C_5H_5)-(arene)]^+$, where the arene ligands are $1,2,3-C_6H_3(OC_nH_{2n+1})_3$ and $1,3,5-C_6H_3(OC_nH_{2n+1})_3$ (n = 6, 12, and 18), were synthesized. The counteranions were PF₆ and FSA (bis-(fluorosulfonyl)amide). The melting points of the PF₆ and FSA salts were 33-93 °C and -18-62 °C, respectively. In the PF₆ salts, the melting points of the 1,3,5-derivatives were lower than those of the 1,2,3-derivatives by 28-55 °C, whereas no such tendency was observed in the FSA salts. X-ray crystallography showed the formation of lamellar structures in the PF₆ salts of the 1,2,3-derivatives in the solid state. In these crystals, cation—anion pairs via $C_{Cp}H\cdots F$ H-bond-like



interactions were commonly observed. Several 1,3,5-derivatives showed metastable phases with lower melting points than the stable phases. The salts of the 1,2,3-derivative (n = 2) were also synthesized and characterized.

INTRODUCTION

Ionic liquids are liquid salts with melting points below 100 °C, and they exhibit various characteristic properties such as low volatility, nonflammability, and high ionic conductivity.¹ Most ionic liquids contain organic cations such as imidazolium cations. Recently, metal-containing ionic liquids have received attention because ionic liquids can be diversely functionalized by introducing metal ions.^{2,3} Although many ionic liquids with metal-containing cations have been reported,² fewer ionic liquids with metal-containing cations have been reported.^{3,4} We have synthesized metal-containing ionic liquids from cationic sandwich complexes;⁵ such ionic liquids exhibit intriguing magnetic properties and chemical reactivities.

Understanding the effects of substituents on the thermal properties of ionic liquids is important for designing functional liquids, and many studies, including crystallographic investigations, have been conducted using alkylimidazolium-based and other ionic liquids.⁶ To investigate the effects of substituents in ionic liquids containing organometallic cations, we recently synthesized ionic liquids containing Ru sandwich complexes $[Ru(Cp)(arene)]^+$ (Cp = cyclopentadienyl).⁷ We employed monosubstituted arene ligands with various substituents and investigated the effects of substituent length and polarity on the thermal properties of the ionic liquids.⁷ In the current study, in order explore the potential for the control of physical properties by modification of the substituents, we investigated the effects of the position of the substituents. This article reports the synthesis, thermal properties, and crystal structures of Ru sandwich complexes with 1,2,3- and 1,3,5trialkoxybenzene ligands, represented as [1-Cn][X] and [2Cn][X] (n = 6, 12, and 18), respectively (Figure 1). The salts of the 1,2,3-substituted cation with n = 2 were also synthesized.



Figure 1. Structures of sandwich complexes. (a) [1-Cn][X] and (b) [2-Cn][X].

The counteranions were hexafluorophosphate (PF_6) and bis(fluorosulfonyl)amine (FSA). Designing the constituent cations in such a way that they form solids with higher free energy may help lower the melting points of ionic liquids. Compounds with 1,2,3-trialkylbenzene moieties generally afford lamellar structures and often provide liquid crystals.⁸ In contrast, the substituents in the 1,3,5-derivatives cannot adopt an intramolecular parallel arrangement and are expected to form high-energy conformations owing to packing effects. This

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study aims at investigating whether the use of the latter derivatives is effective in lowering the melting points.

RESULTS AND DISCUSSION

Synthesis and Thermal Properties. The PF₆ salts were synthesized by reacting [Ru(Cp)(NCCH₃)₃][PF₆] with trisubstituted arene ligands (yields ~75%). These salts were solids at room temperature. The FSA salts were synthesized from the PF₆ salts by metathesis using K[FSA] (yields ~70%). [1-C6][FSA], [1-C12][FSA], [2-C6][FSA], and [2-C12][FSA] were colorless liquids, whereas [1-C2][FSA], [1-C18][FSA], and [2-C18][FSA] were white solids at room temperature.

The thermal properties of the salts were investigated by differential scanning calorimetry (DSC). The melting points and relevant parameters of the salts are listed in Table 1. Their

Table 1. Melting Points (T_m) , Melting Enthalpies (ΔH_m) , and Melting Entropies (ΔS_m) of the Salts Synthesized in This Study

	$T_{\rm m}$ (°C)	$(^{\circ}C)^{T_{g}}$	$\Delta H_{\rm m}$ (kJ mol ⁻¹)	$(J mol^{-1} K^{-1})$
PF ₆ salts				
[1-C2][PF ₆]	190.9		32.7	70.3
[1-C6][PF ₆]	70.2		18.9	54.7
[1-C12][PF ₆]	87.9		21.3	59.0
[1-C18][PF ₆]	92.8		66.6	181.5
[2-C6][PF ₆]	42.7	-44	24.9	77.9
[2-C12][PF ₆]	33.1, 29.8 ^a		47.2 ^b	154.1 ^c
[2-C18][PF ₆]	64.1		87.9	258.0
FSA salts				
[1-C2][FSA]	59.8		17.0	50.8
[1-C6][FSA]	25.0	-69	24.4	79.7
[1-C12][FSA]	-17.7		27.1	106.1
[1-C18][FSA]	62.3, 42.0 ^a		89.3 ^b	265.5 ^c
[2-C6][FSA]		-67		
[2-C12][FSA]	13.9, 9.9 ^a		37.6 ^b	130.9 ^c
[2-C18][FSA]	55.9, 43.3 ^a		94.3 ^b	284.1 ^c
^a Melting points	s of metastah	le phases.	^b Melting en	thalpies of stable

"Melting points of metastable phases. "Melting enthalpies of stable phases. "Melting entropies of stable phases.

DSC traces are summarized in Figures S1 and S2 (Supporting Information). The melting points of the salts, except for [2-C6][FSA], were determined; [2-C6][FSA] exhibited only glass transition upon cooling. All of the salts except [1-C2][PF₆] (T_m = 190.9 °C) melted below 100 °C and are regarded as ionic liquids (PF₆ salts: T_m = 33–93 °C, FSA salts: T_m = -18–62 °C).

The melting points are plotted in Figure 2 as a function of the alkyl chain length (n = 6, 12, and 18). Most of the salts exhibited the minimum melting point when n = 12; such chainlength-dependent minima are generally observed in organic compounds with long alkyl chains and also in ionic liquids.^{4d,5d,8} An exception was $[1-Cn][PF_6]$, whose melting point increased with increasing chain length. Notably, the melting points of $[2-Cn][PF_6]$ were lower than those of $[1-Cn][PF_6]$ by 28–55 °C (Figure 2a). This is probably because the 1,3,5-derivatives have high-energy conformations and/or high-energy packing structures. The FSA salts exhibited lower melting points than the PF₆ salts, and the degree of lowering varied significantly depending on the salts (8–106 °C, for n = 6, 12, and 18). The melting-point lowering for n = 2 was even larger than that for the other salts ($[1-C2][PF_6]$: $T_m = 190.9$



Figure 2. Melting points of (a) [1-Cn][X] (O) and (b) [2-Cn][X] (\Box) (stable phases) plotted as a function of the alkyl chain length.

°C, [1-C2][FSA]: $T_{\rm m} = 59.8$ °C). However, in the FSA salts, no clear relationships between the melting points of the 1,2,3and 1,3,5-derivatives were observed. This is probably because the Coulombic interactions significantly varied in the crystals of FSA salts owing to the anisotropic charge distribution and the bent structure of the anion. In contrast, cation—anion arrangements are almost the same in the crystals of [1-Cn][PF₆] (*vide infra*), thus producing comparable Coulombic interactions in all the salts. In this situation, the melting point should reflect the differences in the conformational and/or packing energies.

Another result supporting the high-energy structure of the 1,3,5-derivatives is that the melting point of $[2-C6][PF_6]$ ($T_m = 42.7 \,^{\circ}C$) was lower by 30 $^{\circ}C$ than that expected from the glass-transition temperature ($T_g = -44 \,^{\circ}C$) based on the empirical relationship $T_g/T_m = 2/3$.¹⁰ In contrast, [1-C6][FSA], which also exhibited both T_m and T_g , followed the empirical relationship.

The sums of the entropies of melting and phase transitions in the solid state are shown in Figure 3. Notably, contribution of the solid phase transitions is significant in $[1-Cn][PF_6]$. The values for the salts increased with increasing chain length. The conformational changes in the alkyl chains generally provide an entropy change of ~10.3 J K⁻¹ mol⁻¹ per methylene unit.¹¹ The amounts of increase in the entropies for n = 12-18 were 143.4, 103.9, 160.0, and 153.2 J K⁻¹ mol⁻¹ for $[1-Cn][PF_6]$, $[2-Cn][PF_6]$, [1-Cn][FSA], and [2-Cn][FSA], respectively. These values were smaller than those expected for the contribution of the methylene units (185.4 J K⁻¹ mol⁻¹ = 18 × 10.3 J K⁻¹ mol⁻¹), but this is probably because of the difference in the lattice entropy.

Phase Sequence. The phase sequences of the salts are summarized in Figure 4. [1-C12][PF₆] and [1-C6][FSA] exhibited three and one sharp phase transition, respectively, in the solid state (Table 2). Moreover, very broad peaks were observed in the DSC traces of [1-Cn][PF₆] [n = 6 (~47 °C), 12 (~ -19 °C), and 18 (7 and 41 °C)] (Table 2 and Figure S1, Supporting Information). They are probably related to the motions of the substituents; a similar behavior has been observed in several ferrocenium ionic liquids with long alkyl chains.^{5c} Other salts exhibited no phase transition.

Notably, metastable phases were observed in [2-C12][X] (X = PF₆ and FSA), [1-C18][FSA], and [2-C18][FSA] (Figure 4). The melting points of the metastable phases were lower by 3–20 °C than those of the stable phases (Table 1). In [2-C12][X] (X = PF₆ and FSA), the stable phases were formed upon cooling the melt, whereas the metastable phases were formed



Figure 3. Sum of the phase-transition entropies of (a) $[1-Cn][PF_6]$ (\Box) and $[2-Cn][PF_6]$ (\blacksquare), (b) [1-Cn][FSA] (\Box) and [2-Cn][FSA](\blacksquare). Contribution of the phase transition in the solid state is indicated by hatched lines.

by cold crystallization during the heating process. In [1-C18][FSA] and [2-C18][FSA], the recrystallization mainly produced the crystals of the stable phases, whereas the metastable phases were formed by cooling the melt. Heating of the metastable phases led to double melting (Figures S1 and S2, Supporting Information). These results indicate that the 1,3,5-derivatives afford high-energy metastable packing structures in addition to the stable phases, even though [1-C18][FSA] was an exception. The metastable phases likely originate from the conformational variety of the alkyl substituents in the 1,3,5-positions.

In summary, the thermal measurements have revealed the following: (i) the PF₆ salts of the 1,3,5-derivatives were lowermelting solids than those of 1,2,3-derivatives, (ii) the 1,3,5derivatives exhibited metastable phases, and (iii) a comparison of T_g and T_m showed a high-energy packing structure in at least one of the 1,3,5-derivatives. Overall, these features demonstrate

Table 2. Phase-Transition Data

	phase transitions	$T_{\rm c}$ (°C)	ΔH (kJ mol ⁻¹)	$(J K^{-1} mol^{-1})$			
[1-C6][PF ₆]	а	47 ^b	1.1	3.5			
[1-C12] [PF ₆]	$\mathrm{I} \to \mathrm{II}$	-59.3	5.7	26.6			
	$\mathrm{II} \to \mathrm{III}$	23.7	2.4	0.7			
	$\mathrm{III} \to \mathrm{IV}$	79.2	7.2	20.5			
	а	-19^{b}	3.8	14.9			
[1-C18] [PF ₆]	а	7 ^{<i>a</i>}	4.1	14.7			
	а	41 ^b	17.5	55.7			
[1-C6][FSA]	$\mathrm{I} \to \mathrm{II}$	-37	5.3	22.1			
^{<i>a</i>} Very broad peak. ^{<i>b</i>} Peak-top temperature.							

that the 1,3,5-derivatives form higher-energy solids than the 1,2,3-derivatives. A related phenomenon has been reported in C₆₀ derivatives bearing trialkylbenzene substituents, in which the 1,2,3-derivatives exhibit liquid-crystal phases and the 1,3,5derivatives exhibit lower melting points.¹² Imidazolium salts bearing 1,2,3-trisubstituted benzene moieties with long alkyl substituents also exhibit columnar liquid crystals.^{8b} However, the salts obtained in this study did not exhibit liquid-crystal phases. The liquid-crystal phases were also absent in ferrocenium ionic liquids with anionic 1,2,3-trialkoxybenzene derivatives.¹³ Our previous studies have shown that the ionic liquids obtained from monosubstituted sandwich complexes often exhibit phase transitions in the solid state and that they rarely exhibit metastable phases. 5a,c,7 The ionic liquids synthesized in this study exhibited contrasting features in this regard.

Crystal Structures. The crystal structures of $[1-Cn][PF_6]$ (n = 6, 12, and 18) and [1-C2][X] ($X = PF_6$ and FSA) were determined by X-ray crystallography at 100 K. [1-C2][FSA]belongs to the space group Pn, whereas the other salts belong to the space group $P2_1/c$. In the cations, the Ru–C bond of the carbon atom at the 1-position (~2.28 Å) was the longest among the Ru–C_{arene} bonds (average 2.23 Å), and the Cp and arene rings are canted by 4.5–6.0°. A similar tendency has been observed in other Ru sandwich complexes with electron donating substituents.¹⁴ Two crystallographically independent cations are present in [1-C2][FSA] and $[1-C6][PF_6]$, whereas their structures are almost the same. The Cp rings in the cations in $[1-Cn][PF_6]$ (n = 2, 12, and 18) exhibited 2-fold rotational disorder. The anion in $[1-C18][PF_6]$ exhibited



Figure 4. Phase diagrams of the salts. gl. denotes the glassy phase. Metastable phases are indicated by asterisks.



Figure 5. Packing diagrams of (a) [1-C6][PF₆], (b) [1-C12][PF₆], and (c) [1-C18][PF₆].

rotational disorder, whereas those in the other salts were ordered.

The packing diagrams of $[1-Cn][PF_6]$ (n = 6, 12, and 18) with long alkyl chains are shown in Figure 5. These salts exhibited lamellar structures, in which the ionic cation-anion and alkyl-chain layers were formed. No $\pi - \pi$ interactions were observed between the cations. The alkyl chains in $[1-C6][PF_6]$ were bent and not arranged in a parallel fashion, whereas those in $[1-C12][PF_6]$ and $[1-C18][PF_6]$ were aligned in a parallel fashion, both intra- and intermolecularly. There was no interdigitation between the alkyl chains in $[1-C12][PF_6]$ and [1-C18][PF₆], and therefore, an extended bilayer structure was formed.¹⁵ Several imidazolium salts and other compounds bearing trisubstituted benzene moieties with long alkyl chains (n = 12-14) exhibit similar lamellar structures in the solid state, which lead to either an extended bilayer or interdigitated structure.^{16,17} Similar to the present case, compounds bearing trisubstituted benzene moieties with an intermediate chain length $(n \sim 6)$ are reported to have bent alkyl chains.¹⁸

The packing diagrams of [1-C2][X] (X = PF₆ and FSA) with ethoxy substituents are shown in Figure 6. The cations and anions were packed alternately in these salts, and no lamellar structure was formed. The cations formed dimeric arrangements via $\pi - \pi$ interactions between the benzene rings (interplane distances: 3.26 and 3.21 Å in $[1-C2][PF_6]$ and [1-C2][FSA], respectively).

In all of the salts, the cationic and anionic moieties contacted each other, forming ion-pair-like arrangements. Short intermolecular contacts were observed between the Cp hydrogens and F atoms in the PF₆ salts (CH…F distances: 2.11–2.32 Å). Moreover, short contacts were observed between the arene hydrogens and F atoms (CH…F distances: 2.38–2.46 Å). [1-C2][FSA] exhibited short contacts between the Cp hydrogens and the O atom in the anion (CH…O distance: 2.38 Å). These distances are shorter than the typical van der Waals contact distance by 0.2–0.5 Å. Such C_{Cp} H…X contacts have also been observed in metallocenium ionic liquids and related salts.^{5c,7}

As shown above, the 1,2,3-derivatives ($[1-Cn][PF_6]$, n = 6, 12, and 18) formed lamellar structures. Single crystals of the 1,3,5-derivatives ($[2-Cn][PF_6]$) suitable for X-ray crystallography could not be obtained. However, considering their molecular structure, it seems unlikely that the 1,3,5-derivatives formed lamellar structures. Indeed, a related compound $[Ru(Cp)\{1,3,5-C_6H_3(OC_3H_6CN)_3\}][FSA]$ formed a structure with an alternate cation—anion arrangement.¹⁹ These crystallographic results seem to be consistent with the lower melting points of $[2-Cn][PF_6]$ than $[1-Cn][PF_6]$.

CONCLUSIONS

Ionic liquids were synthesized from Ru sandwich complexes containing trialkoxybenzene ligands, and the effects of substituent positions and alkyl chain length were investigated. In the PF₆ salts, the melting points of the 1,3,5-derivatives were much lower than those of the 1,2,3-derivatives. Several of the 1,3,5-derivatives showed metastable phases with high-energy structures. The thermodynamical feature of the 1,3,5-derivatives is probably related to the molecular structure in which the alkyl



Figure 6. Packing diagrams of (a) $[1-C2][PF_6]$ and (b) [1-C2][FSA]. The dashed lines represent $\pi - \pi$ contacts between the cations.

chains cannot align parallelly within the molecule, probably leading to high-energy structures. However, in the FSA salts no clear correlation was observed between the melting points and the substituent positions. This may be related to the anisotropic molecular shape and charge distribution in the anion, causing variations in the electrostatic interactions in the solid state. The X-ray structures showed that the 1,2,3-derivatives with long alkyl chains formed lamellar structures, in which the alkyl chains are aligned parallel, both intra- and intermolecularly; however, it is unlikely that the 1,3,5-derivatives form such lamellar structures, considering their molecular structures.

In this study, the melting points of ionic liquids could be lowered by changing the substituent positions to form highenergy structures. This concept can be applied to the design of other ionic liquids, and the use of organometallic compounds for ionic liquids should open new avenues in organometallic chemistry. Synthesis of functional ionic liquids from Ru complexes with trisubstituted benzene ligands is underway.

EXPERIMENTAL SECTION

General. $[Ru(Cp)(NCCH_3)_3][PF_6]$,²⁰ 1,2,3-tris(hexyloxy)benzene, 1,2,3-tris(dodecyloxy)benzene, 1,3,5-tris(dodecyloxy)benzene, and 1,3,5-tris(octadecyloxy)benzene²¹⁻²³ were synthesized according to literature methods. ¹H NMR spectra were recorded using a JEOL JNM-ECL-400 spectrometer. Elemental analyses were performed using a PerkinElmer 2400II elemental analyzer. DSC measurements were performed using a TA Q100 differential scanning calorimeter at a scan rate of 10 K min⁻¹.

Synthesis of Ligands. (a) 1,2,3-Tris(ethoxy)benzene: Under a nitrogen atmosphere, pyrogallol (617 mg, 4.87 mmol), potassium carbonate (4.48 g, 32.5 mmol), ethyl iodide (5.6 mL, 70.0 mmol), and tetrabutylammonium chloride (20.0 mg, 0.072 mmol) were dissolved

in acetone (40 mL), and the mixture was heated at 50 $^\circ C$ for 72 h under stirring. The reaction mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, eluent: hexane/dichloromethane (4:1, v/v) and then dichloromethane) and dried under vacuum. The desired compound was isolated as a white solid (0.56 g, 47% yield). ¹H NMR (400 MHz, CDCl₃): δ = 1.36 (t, 3H, CH₃, J = 7.08 Hz), 1.42 (t, 6H, CH₃, J = 6.98 Hz), 4.06 (m, 6H, CH₂), 6.55 (d, 2H, ArH, J = 8.36 Hz), 6.92 (t, 1H, ArH, J = 8.32 Hz). (b) 1,2,3-Tris(octadecyloxy)benzene: Under a nitrogen atmosphere, pyrogallol (0.4 g, 3.17 mmol) and potassium carbonate (3.05 g, 21.8 mmol) were dissolved in DMF (3 mL). Then, 1-bromooctadecane (4.5 mL, 13.1 mmol) was added to the solution, and the mixture was heated at 80 °C for 19 h under stirring. The reaction mixture was added to water and extracted three times with a mixture of ethyl acetate and hexane (1:1, v/v). Purification by column chromatography (silica gel, eluent: hexane/ dichloromethane (4:1, v/v) furnished the desired compound as a white solid (1.32 g, 47% yield). ¹H NMR (400 MHz, $CDCl_3$): $\delta = 0.88$ (t, 9H, CH₃, J = 10.0 Hz), 1.20-1.82 (m, 96H, CH₂), 3.95 (m, 6H, ArOCH₂), 6.54 (d, 2H, ArH, J = 8.0 Hz), 6.90 (t, 1H, ArH, J = 8.0 Hz). (c) 1,3,5-Tris(hexyloxy)benzene: This compound was synthesized as described for 1,2,3-tris(octadecyloxy)benzene using pyrogallol (402 mg, 3.19 mmol), potassium carbonate (2.90 g, 21.0 mmol), and 1-bromohexane (1.6 mL, 11.4 mmol). To facilitate the reaction, 18crown-6 ether (74.3 mg, 0.28 mmol) was added. The desired compound was obtained as a colorless liquid (775 mg, 64% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.90$ (t, 9H, CH₃, J = 6.78 Hz), 1.26– 1.78 (m, 24H, CH₂), 3.90 (t, 6H, ArOCH₂, J = 6.58 Hz), 6.05 (s, 3H, ArH)

Synthesis of $[Ru(Cp){\eta^6-1,2,3-C_6H_3(OC_nH_{2n+1})_3]}[PF_6]$ ([1-Cn]-[PF₆]). (a) $[Ru(Cp){\eta^6-1,2,3-C_6H_3(OC_2H_5)_3}][PF_6]$ ([1-C2][PF₆]): Under a nitrogen atmosphere, [Ru(Cp)(NCCH₃)₃][PF₆] (110 mg, 0.25 mmol) and 1,2,3-tris(ethoxy)benzene (73 mg, 0.35 mmol) were dissolved in acetonitrile (1 mL), and the reaction mixture was heated at 90 °C for 40 h under stirring. After evaporating the solvent, the residue was dissolved in acetone, and diethyl ether was added to precipitate the product. Recrystallization from methanol (-40 °C) afforded the desired compound as a pale yellow solid (95 mg, 73% yield). ¹H NMR (400 MHz, CDCl₃): δ = 1.37 (m, 9H, CH₃), 3.85 (m, 2H, $ArOCH_2$), 4.03 (q, 2H, $ArOCH_2$, J = 5.34 Hz), 4.13 (m, 2H, ArOCH₂), 5.28 (s, 5H, Cp), 5.66 (t, 1H, ArH, J = 6.10 Hz), 5.84 (d, 2H, ArH, J = 5.84 Hz). Anal. Calcd for $C_{17}H_{23}F_6O_3PRu$: C, 39.16; H, 4.45. Found: C, 39.17; H, 4.55. (b) $[Ru(Cp){\eta^{6}-1,2,3-}]$ $C_6H_3(OC_6H_{13})_3$ [PF₆] ([1-C6][PF₆]): Under a nitrogen atmosphere, [Ru(Cp)(NCCH₃)₃][PF₆] (100 mg, 0.39 mmol) and 1,2,3tris(dodecyloxy)benzene (90 mg, 0.584 mmol) were dissolved in acetonitrile (1 mL), and the reaction mixture was heated at 90 °C for 23 h under stirring. After evaporating the solvent, the residue was dissolved in methanol and washed three times with hexane. The product was dissolved in acetonitrile and passed through a short plug of alumina (eluent: acetonitrile). Recrystallization of the product from diethyl ether (-40 °C) followed by vacuum drying provided the desired salt as a colorless solid (118 mg, 76% yield). ¹H NMR (400 MHz, CD₃CN): δ = 0.91 (t, 9H, CH₃, J = 7.00 Hz), 1.32–1.77 (m, 24H, CH₂), 3.75 (m, 2H, ArOCH₂), 3.96 (t, 2H, ArOCH₂, J = 6.32 Hz), 4.08 (m, 2H, ArOCH₂), 5.25 (s, 5H, Cp), 5.65 (t, 1H, ArH, J = 5.90 Hz), 5.84 (d, 2H, ArH, J = 5.88 Hz). Anal. Calcd for C₂₉H₄₇F₆O₃PRu: C, 50.50; H, 6.87. Found: C, 50.64; H, 7.00. (c) $[Ru(Cp){\eta^{6}-1,2,3-C_{6}H_{3}(OC_{12}H_{25})_{3}}][PF_{6}] ([1-C12][PF_{6}]): Under a$ nitrogen atmosphere, [Ru(Cp)(NCCH₃)₃][PF₆] (100 mg, 0.226 mmol) and 1,2,3-tris(dodecyloxy)benzene (200 mg, 0.317 mmol) were dissolved in acetonitrile (1 mL), and the reaction mixture was heated at 90 °C for 19 h under stirring. After evaporating the solvent, the residue was dissolved in acetonitrile and filtered to remove the unreacted ligand. The filtrate was evaporated, and recrystallization of the residue from methanol (-40 °C) afforded the desired compound as a white solid (98 mg, 46% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.88 (t, 9H, CH_{3} , J = 6.60 Hz), 1.27–1.80 (m, 60H, CH_{2}), 3.83 (m, 2H, ArOCH₂), 3.96 (t, 2H, ArOCH₂, J = 6.34 Hz), 4.08 (m, 2H, ArOCH₂), 5.25 (s, 5H, Cp), 5.86 (t, 1H, ArH, J = 4.98 Hz), 5.99 (d,

2H, ArH, J = 6.04 Hz). Anal. Calcd for $C_{47}H_{83}F_6O_3PRu: C, 59.91;$ H, 8.88. Found: C, 59.90; H, 9.01. (d) $[Ru(Cp){\eta^{6}-1,2,3-C_6H_3(OC_{18}H_{37})_3]]PF_6]$ ([1-C18][PF₆]): Under a nitrogen atmosphere, $[Ru(Cp)(NCCH_3)_3][PF_6]$ (100 mg, 0.226 mmol) and 1,2,3-tris(octadecyloxy)benzene (300 mg, 0.340 mmol) were dissolved in acetonitrile (1 mL), and the reaction mixture was heated at 90 °C for 43 h under stirring. Acetonitrile was added to the reaction mixture and heated, and the supernatant was removed by decantation. Recrystallization of the precipitate from methanol (-40 °C) afforded the desired compound as a white solid (216 mg, 80% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.88$ (t, 9H, CH₃, J = 6.82 Hz), 1.26–1.79 (m, 96H, CH₂), 3.82 (m, 2H, ArOCH₂), 3.96 (t, 2H, ArOCH₂, J = 6.34 Hz), 4.09 (m, 2H, ArOCH₂), 5.25 (s, 5H, (Cp)), 5.85 (t, 1H, ArH, J = 6.04 Hz), 6.00 (d, 2H, ArH, J = 5.92 Hz). Anal. Calcd for $C_{63}H_{119}F_6O_3PRu: C, 65.35$; H, 10.04. Found: C, 65.32; H, 10.17.

Synthesis of [Ru(Cp){n⁶-1,2,3-C₆H₃(OC_nH_{2n+1})₃}][FSA] ([1-Cn]-**[FSA]).** (a) $[Ru(Cp){\eta^6-1,2,3-C_6H_3(OC_2H_5)_3}][FSA]$ ([1-C2]-[FSA]): $[Ru(Cp){\eta^{6}-1,2,3-C_{6}H_{3}(OC_{2}H_{5})_{3}}][PF_{6}]$ (30.8 mg, 0.059 mmol) was dissolved in a mixture of water and acetone. An aqueous solution of K[FSA] (25.1 mg, 0.141 mmol) was added to this solution and stirred. After the removal of acetone by evaporation, the resulting suspension was extracted 10 times with dichloromethane. The product was dissolved in a small amount of acetone, and diethyl ether was added. The desired compound precipitated as a white solid (28 mg, 85% yield). ¹H NMR (400 MHz, CD₃CN): δ = 1.37 (m, 9H, CH₃), 3.85 (m, 2H, ArOCH₂), 4.03 (q, 2H, ArOCH₂, J = 7.13 Hz), 4.13 (m, 2H, ArOCH₂), 5.28 (s, 5H, Cp), 5.66 (t, 1H, ArH, J = 5.88 Hz), 5.84 (d, 2H, ArH, J = 5.96 Hz). Anal. Calcd for $C_{17}H_{23}F_2NO_7RuS_2$: C, 36.69; H, 4.17; N, 2.52. Found: C, 36.92; H, 4.37; N, 2.25. (b) $[Ru(Cp){\eta^{6}-1,2,3-C_{6}H_{3}(OC_{6}H_{13})_{3}}][FSA] ([1-C6][FSA]): [Ru(Cp)-{\eta^{6}-1,2,3-C_{6}H_{3}(OC_{6}H_{13})_{3}}][PF_{6}] (36.5 mg, 0.052 mmol) was$ dissolved in a mixture of water and acetone. An aqueous solution of K[FSA] (40.2 mg, 0.23 mmol) was added to this solution and stirred. After the removal of acetone by evaporation, the resulting suspension was extracted 10 times with dichloromethane. The product was dried under vacuum at 80 °C for 15 h to afford a colorless liquid (30 mg, 80% yield). This salt was a liquid after vacuum drying; however, it solidified as a white solid when stored overnight in a refrigerator (6 °C). ¹H NMR (400 MHz, CD₃CN): δ = 0.92 (m, 9H, CH₃), 1.32– 1.79 (m, 24H, CH₂), 3.74 (m, 2H, ArOCH₂), 3.96 (t, 2H, ArOCH₂, J = 6.24 Hz), 4.08 (m, 2H, ArOCH₂), 5.25 (s, 5H, Cp), 5.65 (t, 1H, ArH, J = 6.12 Hz), 5.84 (d, 2H, ArH, J = 6.12 Hz). Anal. Calcd for C29H47F2NO7RuS2: C, 48.05; H, 6.54; N, 1.93. Found: C, 47.73; H, 6.60; N, 1.91. (c) $[Ru(Cp){\eta^{6}-1,2,3-C_{6}H_{3}(OC_{12}H_{25})_{3}}][FSA]$ ([1-C12][FSA]): This compound was synthesized as described for [1-C6]FSA using $[Ru(Cp){\eta^{6}-1,2,3-C_{6}H_{3}(OC_{12}H_{25})_{3}}][PF_{6}]$ (78 mg, 0.082 mmol) and K[FSA] (40 mg, 0.22 mmol). The desired compound was obtained as a colorless liquid (54 mg, 67% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.88 (t, 9H, CH₃, J = 6.56 Hz), 1.27-1.78 (m, 60H, CH₂), 3.83 (m, 2H, ArOCH₂), 3.96 (t, 2H, ArOCH₂, J = 6.32 Hz), 4.10 (m, 2H, ArOCH₂), 5.26 (s, 5H, Cp), 5.86 (t, 1H, ArH, J = 5.92 Hz), 5.99 (d, 2H, ArH, J = 5.96 Hz). Anal. Calcd for C47H83F2NO7RuS2: C, 57.76; H, 8.56; N, 1.43. Found: C, 58.10; H, 8.62; N, 1.45. (d) $[Ru(Cp){\eta^{6}-1,2,3-C_{6}H_{3}(OC_{18}H_{37})_{3}}][FSA]$ ([1-C18][FSA]): This compound was synthesized as described for [1-C6]FSA using $[Ru(Cp){\eta^{6}-1,2,3-C_{6}H_{3}(OC_{18}H_{37})_{3}}][PF_{6}]$ (100 mg, 0.084 mmol) and K[FSA] (39.6 mg, 0.22 mmol). Recrystallization of the product from methanol (-40 °C) furnished the desired compound as a white solid (69.8 mg, 68% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.88 (t, 9H, CH_3 , J = 6.86 Hz), 1.26–1.80 (m, 96H, CH_2), 3.81 (m, 2H, ArOCH₂), 3.97 (t, 2H, ArOCH₂, J = 6.30 Hz), 4.09 (m, 2H, ArOCH₂), 5.26 (s, 5H, Cp), 5.96 (m, 3H, ArH). Anal. Calcd for C₆₃H₁₁₉F₂NO₇RuS₂: C, 63.48; H, 9.75; N, 1.14. Found: C, 63.60; H, 10.00; N, 1.13.

Synthesis of $[Ru(Cp){\eta^6-1,3,5-C_6H_3(OC_nH_{2n+1})_3}][PF_6]$ ([2-Cn]-[PF₆]). (a) $[Ru(Cp){\eta^6-1,3,5-C_6H_3(OC_6H_{13})_3}][PF_6]$ ([2-C6][PF₆]): This compound was synthesized as described for $[1-C6][PF_6]$ using $[Ru(Cp)(NCCH_3)_3][PF_6]$ (149 mg, 0.46 mmol), 1,3,5-tris(hexyloxy)benzene (140 mg, 0.47 mmol), and acetonitrile (1 mL). The product was dissolved in a small amount of ethyl acetate, hexane was added, and the solution was stored at -40 °C. The desired compound precipitated as a white solid (160 mg, 67% yield). ¹H NMR (400 MHz, CD₃CN): $\delta = 0.91(t, 9H, CH_3, J = 6.90 Hz)$, 1.23–1.72 (m, 24H, CH₂), 3.90 (t, 6H, ArOCH₂, J = 6.42 Hz), 5.18 (s, 5H, Cp), 5.99 (s, 3H, ArH). Anal. Calcd for C₂₉H₄₇F₆O₃PRu: C, 50.50; H, 6.87. Found: C, 50.70; H, 6.70. (b) $[Ru(Cp){\eta^{6}-1,3,5-C_{6}H_{3}(OC_{12}H_{25})_{3}}]$ -[PF₆] ([2-C12][PF₆]): This compound was synthesized as described for $[1-C6][PF_6]$ using $[Ru(Cp)(NCCH_3)_3][PF_6]$ (138 mg, 0.32 mmol), 1,3,5-tris(dodecyloxy)benzene (205 mg, 0.32 mmol), and acetonitrile (2 mL). Acetonitrile was added to the crude product, and the solution was washed three times with hexane. After evaporating acetonitrile and drying under vacuum at 80 °C for 15 h, the desired compound was obtained as a pale yellow liquid (148 mg, yield 48%). The liquid crystallized when left at room temperature after cooling to -40 °C. ¹H NMR (400 MHz, CDCl₃): δ = 0.88 (t, 9H, CH₃, J = 6.84 Hz), 1.26-1.75 (m, 60H, CH₂), 3.97 (t, 6H, ArOCH₂, J = 5.82 Hz), 5.20 (s, 5H, Cp), 5.98 (s, 3H, ArH). Anal. Calcd for C₄₇H₈₃F₆O₃PRu: C, 59.91; H, 8.88. Found: C, 59.66; H, 8.95. (c) $[Ru(Cp){\eta^6-1,3,5-}$ $C_{6}H_{3}(OC_{18}H_{37})_{3}][PF_{6}]$ ([2-C18][PF₆]): This compound was synthesized as described for $[1-C6][PF_6]$ using $[Ru(Cp)(NCCH_3)_3]$ -[PF₆] (155 mg, 0.35 mmol), 1,3,5-tris(octadecyloxy)benzene (332 mg, 0.37 mmol), and acetonitrile (1 mL). The product was purified by column chromatography (activated alumina; eluent, toluene and then dichloromethane/THF (1:1, v/v)). Recrystallization from methanol (-40 °C) afforded the desired compound as a white solid (342 mg, 82% yield). ¹H NMR (400 MHz, $CDCl_3$): $\delta = 0.88$ (t, 9H, CH_3 , J =6.84 Hz), 1.25–1.73 (m, 96H, CH₂), 3.97 (t, 6H, ArOCH₂, J = 6.16 Hz), 5.20 (s, 5H, Cp), 5.97 (s, 3H, ArH). Anal. Calcd for C63H119F6O3PRu: C, 65.35; H, 10.04. Found: C, 65.57; H, 10.42.

Synthesis of [Ru(Cp){ η^6 -1,3,5-C₆H₃(OC_nH_{2n+1})₃}][FSA] ([2-Cn]-**[FSÁ]).** (a) $[Ru(Cp){\eta^6-1,3,5-C_6H_3(OC_6H_{13})_3}]$ [FSA] ([2-C6]-[FSA]): This compound was synthesized as described for [1-C6]FSA using $[Ru(Cp){\eta^6-1,3,5-C_6H_3(OC_{18}H_{37})_3}][PF_6]$ (214.0 mg, 0.31 mmol) and K[FSA] (131.1 mg, 0.73 mmol). The desired compound was obtained as a pale yellow liquid (143.1 mg, 64% yield). ¹H NMR (400 MHz, CDCl₃) δ = 0.91 (t, 9H, CH₃, J = 6.88 Hz), 1.30-1.77 (m, 24H, CH₂), 3.94 (t, 6H, ArOCH₂, J = 6.26 Hz), 5.21 (s, 5H, Cp), 5.98 (s, 3H, ArH). Anal. Calcd for C₂₉H₄₇F₂NO₇RuS₂: C, 48.05; H, 6.54; N, 1.93. Found: C, 48.50; H, 6.59 N, 2.01. (b) $[Ru(Cp){\eta^{6}-1,3,5-C_{6}H_{3}(OC_{12}H_{25})_{3}}][FSA]$ ([2-C12][FSA]): This compound was synthesized as described for [1-C6]FSA using $[Ru(Cp){\eta^{6}-1,3,5-C_{6}H_{3}(OC_{12}H_{25})_{3}}][PF_{6}]$ (63.0 mg, 0.067 mmol) and K[FSA] (26.6 mg, 0.15 mmol). The desired compound was obtained as a colorless liquid (41.3 mg, 63% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.88 (t, 9H, CH₃, J = 6.84 Hz), 1.26–1.74 (m, 96H, CH₂), 3.95 (t, 6H, ArOCH₂, J = 6.16 Hz), 5.20 (s, 5H, Cp), 5.98 (s, 3H, ArH). Anal. Calcd for C47H83F2NO7RuS2: C, 57.76; H, 8.56; N, 1.43. Found: C, 58.06; H, 8.76; N, 1.46. (c) $[Ru(Cp){\eta^6-1,3,5-}$ $C_6H_3(OC_{18}H_{37})_3$][FSA] ([2-C18][FSA]): This compound was synthesized as described for [1-C6]FSA using $[Ru(Cp){\eta^6-1,3,5-}]$ $C_6H_3(OC_{18}H_{37})_3$][PF₆] (157 mg, 0.13 mmol) and K[FSA] (98 mg, 0.54 mmol). The product was further purified by gel permeation chromatography (Japan Analytical Industry LC-908, eluent: chloroform) and recrystallized from methanol (-40 °C). The desired compound was obtained as a white solid (116 mg, 72% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.88$ (t, 9H, CH₃, J = 6.84 Hz), 1.26– 1.74 (m, 96H, CH₂), 3.95 (t, 6H, ArOCH₂, J = 6.16 Hz), 5.20 (s, 5H, Cp), 5.98 (s, 3H, ArH). Anal. Calcd for C₆₃H₁₁₉F₂NO₇RuS₂: C, 63.48; H, 9.75; N, 1.14. Found: C, 63.98; H, 10.05; N, 1.15.

X-ray Crystallography. The single crystals of [1-C2][X] (X = PF₆ and FSA) were grown by the slow diffusion of diethyl ether into the concentrated solutions of the salts in acetone. The single crystals of $[1-C6][PF_6]$ and $[1-C12][PF_6]$ were grown by the slow evaporation of methanol solutions. The single crystals of $[1-C18][PF_6]$ were grown by the slow evaporation of ethanol solutions. X-ray diffraction data were collected using a Bruker APEX II Ultra CCD diffractometer using MoK α radiation ($\lambda = 0.71073$ Å). All the calculations were performed using SHELXTL.²⁴ The structures were determined by the direct methods (SHELXS 97). All of the nonhydrogen atoms were refined anisotropically. ORTEP-3 for Windows²⁵ was used to produce the

molecular graphics. The crystallographic parameters are listed in Table S1 (Supporting Information). CCDC-1038528 (for $[1-C2][PF_6]$), -1038529 (for [1-C2][FSA]), -1038530 (for $[1-C6][PF_6]$), -1038531 (for $[1-C12][PF_6]$), and -1038532 (for $[1-C18][PF_6]$) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ASSOCIATED CONTENT

Supporting Information

Crystallographic parameters, DSC charts, Ortep drawings of the molecular structures, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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