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Triazine-Based Polyfluorinated Triquaternary Liquid Salts: Synthesis, Characterization, and Application as Solvents in Rhodium(I)-Catalyzed Hydroformylation of 1-Octene

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Silylation of *N*-(2-hydroxyethyl)imidazole, $HOCH_2CH_2Im$ (**1**), with hexamethyldisilazane gave *N*-(2-trimethylsilyloxyethyl)imidazole, $Me_3SiOCH_2CH_2Im$ (**2**), which underwent quaternization reactions with the alkyl halides and gave three new *N*-(trimethylsilyloxyethyl) imidazolium halides, $Me_3SiOCH_2CH_2Im^+RX^-$, where Im^+ = imidazolium and R/X = Me/I (**3**), CH_2CH_2F/Br (**4**), and $CH_2CH_2CF_3$/I (**5**). The ethyl ether, **6**, formed from **1** and ethyl bromide was quaternized with $CF_3CH_2CH_2I$ to obtain **7**, followed by anion exchange with $LiN(SO_2CF_3)_2$ to obtain **8**. The metathesis reactions of **3**−**5** with cyanuric fluoride in acetonitrile at 25 °C gave tris[2-(*N'*-alkylimidazolium)ethoxy] triazine trihalides, $N_3C_3(OCH_2CH_2Im^+RX^-)_3$, where R/X = Me/I (**9**), CH_2CH_2F/Br (**10**), and $CH_2CH_2CF_3$/I (**11**). Two neutral trimeric compounds, $N_3C_3(OCH_2CH_2Im)_3$ (**12**) and $N_3C_3(OCH_2CH_2NMe_2)_3$ (**14**), were prepared from reactions of cyanuric fluoride and $Me_3SiOCH_2CH_2NMe_2$ (**13**), or **2**, respectively. The quaternization of **12** with MeI gave tris[oxoethyl(trimethyl)ammonium]triazine, $N_3C_3(OCH_2CH_2N^+Me_3I^-)_3$ (**14**). Subsequent exchange of the halides in **9**−**11** and **15** with the weakly coordinating anions of $AgOSO_2CF_3$, $LiN(SO_2CF_3)_2$, $AgNO_3$, or $AgClO_4$ resulted in new triquaternary salts, **16**−**23**, that were characterized by NMR, elemental analyses, and, for some of the compounds, mass spectroscopy. Physical (melting point and density) and thermal properties of **9**−**23** determined with a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA) are reported. In Rh(I)-catalyzed hydroformylation of 1-octene, with Ph_2P(NMPBTA) (**26**) [NMPBTA = *N*-methylpyridinium bis(trifluoromethanesulfonyl)amide] as ligand, the turnover frequency (TOF), conversion, isomer selectivity (n/i), and recyclability were compared when triquaternary salts **17** and **20** or monoquaternary **8** were used as solvents in the biphasic hydroformylation process. A change of **26**/Rh(I) ratio from 4 to 20 resulted in a significant increase of n/i selectivity with **17** or **20**, but was marginal with **8** as solvent.

Introduction

Ionic liquids usually consist of an organic ammonium, phosphonium, pyridinium, imidazolium, or cholinium cation and a fluorinated inorganic anion.[1] The effects of the different cation−anion combinations and structural features on physical properties of ionic liquids have been studied extensively.[2] Generally, ionic liquids melt below 100 °C and exist as stable liquids over a wide temperature range, making them potentially useful as stable polar solvents for organic transformations in industrial processes.[3] They have been investigated for many other applications, such as liquid crystals,[4] heat of transfer fluids useful for thermal storage,[5] CO_2- and H_2S-capture,[5] and as Brønsted acids,[6] lubricants,[7] and electrolytes.[8] Imidazole-bazed ionic liquids have higher thermal stability than the ammonium and pyridinium

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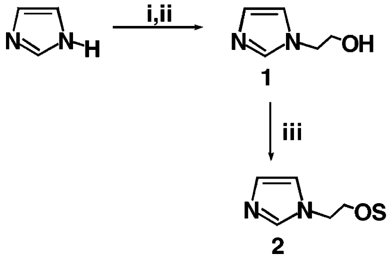
analogues, because the charge is delocalized on the imidazolium cation.[8a] Useful knowledge from the study of dendrimers[9] suggests that repeating a functionality in a unimolecule has advantages in catalysis and as conductors, etc.[10,11] Our experience with dendrimers[12] has led us to investigate the same possible advantages in polyquaternary ionic liquids, which could have higher densities and viscosities than the simple monoquaternary salts that have been of interest so far.

This work focuses on syntheses of tris(oxoethylimidazolium) and tris[oxoethyl(trimethyl)ammonium] ionic liquids built on the triazine ring (**16**−**23**), via the reactions of 1-trimethylsilyl-2-(*N*′-oxoethylimidazolium) halides, **4** and **5**, with cyanuric fluoride and complete quaternization of tris[2-(*N*,*N*-dimethylammino)ethoxy]-triazine (**14**) by methyl iodide. The physical and thermal properties of **3**−**23** were studied in this work. In Rh(I)-catalyzed hydroformylation of 1-alkenes, an efficient process would achieve high yields, excellent control of isomer produced, good catalyst/product separation, and recyclability of the catalyst.[13] Recently, some efforts were directed at research to obtain catalytic leach-free systems.[14−18] Some ionic liquids have been evaluated as solvents for $Rh(acac)(CO)_2$ in the hydroformylation of alkenes.

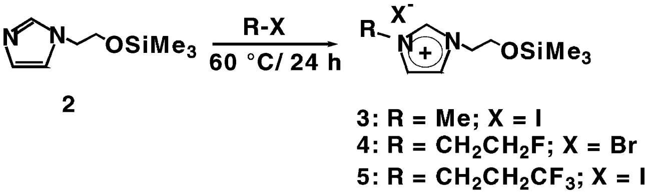
We now report our work on the triquaternary ionic liquids and a new ionic pyridinium phosphine ligand, Ph_2P(NMPBTA) (**26**) [NMPBTA = *N*-methylpyridinium bis(trifluoromethanesulfonyl)amide], that immobilized the $Rh(acac)(CO)_2$/pyridinium phosphine catalyst system in the hydroformylation process. We have compared systems involving the triquaternary salts, **17** and **20**, and their monoquaternary salt, **8**, as solvents in the hydroformylation of 1-octene.

Scheme 1[a]



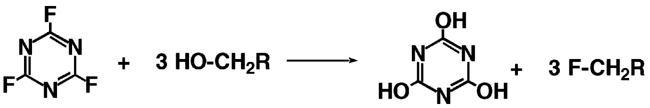
[a] (i) NaH/DMF; (ii) $ClCH_2CH_2OH$/DMF/90 °C/24 h; (iii) $(Me_3Si)_2NH$/80 °C/12 h.

Scheme 2



Results and Discussion

Cyanuric fluoride is a dehydroxy fluorinating agent.[19] Hence, in the steps leading to our target compounds it was necessary to form the reactive trimethylsilyl derivative of $HOCH_2CH_2Im$ (**1**, Im = imidazolyl)[20] from the reaction of **1** and hexamethyldisilazane (Scheme 1).



1-Trimethylsilyl-2-(*N*-imidazolium)ethanol Halides, 3−**5.** Compound **2** was stable in air, with the basic nitrogen atom available for quaternization reactions, and like *N*-trimethylsilylimidazole (Me_3Si-Im),[21] readily underwent metathesis substitution reactions in the presence of fluoride ion. The synthesis of triazine-based triquaternary immidazolium salts was possible after quaternization of **2** with the respective alkyl halide had been achieved. Stirring stoichiometric quantities of $Me_3SiOCH_2CH_2Im$ (**2**) and the respective haloalkane at 60 °C for 24 h gave quaternary ionic compounds in quantitative yields: $[Me_3SiOCH_2CH_2Im^+Me]I^-$ (**3**), $[Me_3SiOCH_2CH_2Im^+CH_2\ CH_2CF_3]I^-$ (**4**), and $[Me_3SiOCH_2CH_2Im^+CH_2CH_2F]Br^-$ (**5**) (Scheme 2).

Crude **3**−**5** were very viscous liquids. Excess alkyl halide was removed in vacuo. After standing for ∼1−2 weeks, **3** and **4** solidified as air-stable, light brown solids. Surprisingly, compound **5** was isolated as a brown-red viscous liquid (d_{25} = 1.55 g cm^{-3}). All three were characterized by IR, NMR, and MS spectroscopy. Multinuclear (^{1}H, ^{13}C, and ^{29}Si) NMR spectroscopy was used to monitor the quaternization reactions of **2**. The position of the ^{29}Si NMR signal at about δ +20 ppm in the spectrum of **2** did not change in those of **3**−**5**. The ^{1}H and ^{13}C signals for the CH_2's in **2** and in the respective alkyl halides experienced significant downfield shifts in the spectra of **3**−**5** (see Experimental

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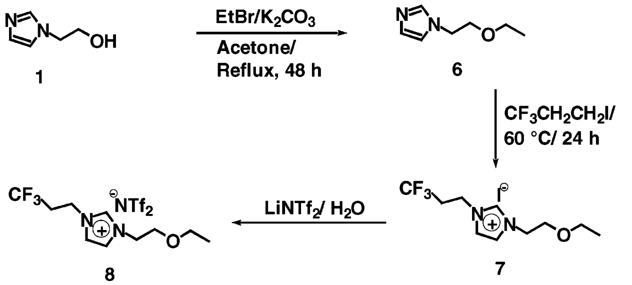
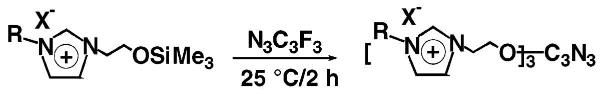
Scheme 3



Scheme 4



3: R = Me; X = I
4: R = CH_2CH_2F; X = Br
5: R = $CH_2CH_2CF_3$; X = I

9: R = Me; X = I
10: R = CH_2CH_2F; X = Br
11: R = $CH_2CH_2CF_3$; X = I

Section). Their MS spectra showed the (M − halide)$^+$ signals as base peaks, at *m*/*z* (intensity (%)) = 199 (100) for **3**, 282 (100) for **4**, and 231 (100) for **5**.

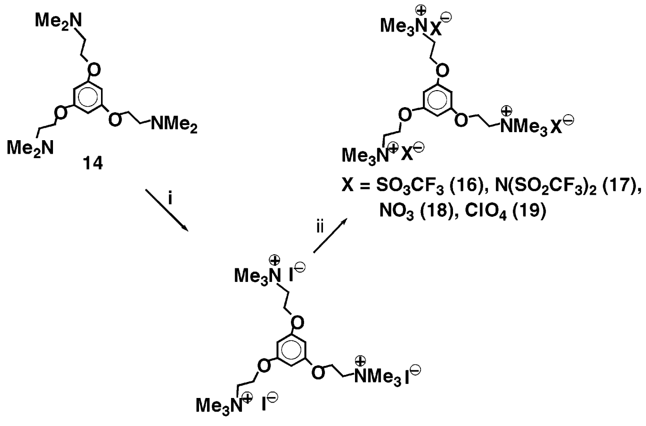
Metathesis reactions of $Ag(OSO_2CF_3)$ [AgOTf] with **3**−**5** occurred without accompanying desilylation. However, with $NaBF_4$, KPF_6, and $LiN(SO_2CF_3)_2$ [$LiNTf_2$] the expected halide exchange occurred, but was accompanied by unexpected desilylation that produced the corresponding alcohols. Resilylation of the alcohols was achieved by warming with hexamethyldisilazane.

Compound **7**, an ethyl ether analogue of **5**, was synthesized in two steps (Scheme 3). Anion exchange with $LiN(SO_2CF_3)_2$ gave 2-oxobutyl-3′,3′,3′-trifluoropropyl imidazolium bis(trifluoromethanesulfonyl)amide, **8**, which was less reactive than **5** and was used as a solvent in catalytic studies described later in this work.

Tris(oxoethylimmidazolium)-, 9−11, and Tris(oxoethylammonium) trihalide, 14. The trimethylsilyl groups in **3**−**5** were introduced to protect the hydroxyl functionality from participating in any side reactions other than quaternization. The synthetic utility of **3**−**5** was demonstrated in their reactions with cyanuric fluoride ($N_3C_3F_3$) that gave **9**−**11**, respectively (Scheme 4). The composition of **9** was confirmed by FAB(+) MS. The signal (intensity) for (M − I)$^+$ ion was seen at 710 (66%). The infrared spectrum showed bands for coordinated water, νH_2O, at 3467 cm^{-1}, and elemental analysis confirmed that **9** was isolated as a dihydrate. Compound **9** is a light yellow solid that melted at 109 °C. Compounds **10** and **11** were synthesized in the same manner as **9**, and all three were characterized by multinuclear NMR spectroscopy and elemental analyses. Pure, bright yellow solid **10** was crystallized from the initial light brown crude oil by using a mixture of acetonitrile/methanol. Compounds **10** and **11** did not show any expected or reliable systematic fragmentation ions when studied with EI, FAB(+), electrospray, and MALDI mass spectroscopy.

Compounds **9**−**11** were very hygroscopic, and although **9** was isolated as a dihydrate, vacuum evaporation at 40 °C produced anhydrous **10** and **11**, based on their elemental analyses. The doublet of triplets signal of cyanuric fluoride in their ^{13}C NMR spectra centered at δ 172 ppm had shifted to singlets at δ 162 (**10**), 172.6 (**9**), and 174.3 (**11**) ppm. The transformations in Scheme 4 were also monitored by ^{19}F NMR spectroscopy. In ^{19}F NMR spectra, the C−F signal at δ ∼ −33 ppm in the spectrum of cyanuric fluoride disappeared in the spectra of **10** and **11**. The signal for $CH_2CH_2CF_3$ in **10** was observed at δ −63.4 ppm (t, $^3J_{H-F}$ = 23 Hz) [cf. δ −67 ppm (t) for $ICH_2CH_2CF_3$, and −65.1 for **5**], and that for CH_2CH_2F in **8**, at δ −220.8 (tt, $^2J_{H-F}$ = 28 Hz, $^3J_{H-F}$ = 20 Hz).

Scheme 5[a]



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[a] (i) MeI/EtOH/reflux, 4 h; (ii) $Ag(OSO_2CF_3)/H_2O$; $LiN(SO_2CF_3)_2/H_2O$; $AgNO_3/H_2O$ or $AgClO_4/H_2O$.

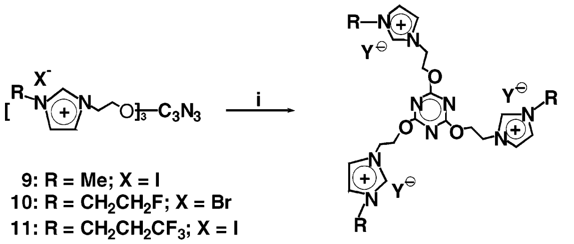
The second route explored for the synthesis of **9**−**11** involved the divergent approach in which the light yellow solid tris[(*N*-imidazolyl)ethoxy]triazine (**12**) was synthesized from the reaction of **2** and cyanuric fluoride. Compound **12**, insoluble in most organic solvents and in water, was recrystallized from warm methanol. Attempted quaternization reactions of **12** with MeI, $BrCH_2CH_2F$, or $ICH_2CH_2CF_3$ did not proceed under solvent-free conditions up to 100 °C, for 4 days, without decomposition. Since **12** is soluble in methanol, unsuccessful attempts were made to quaternize it in this solvent.

However, tris[oxoethyl(trimethyl)ammonium] salts analogous to **12** were accessible by the divergent synthetic approach. To this end, **14** was at first prepared from the reaction of 2-(*N*,*N*-dimethylamino)ethoxy trimethylsilane, $Me_2NCH_2CH_2OSiMe_3$ (**13**), and cyanuric fluoride at room temperature. Subsequent reaction of **14** and methyl iodide in ethanol at reflux gave **15** as a white solid, mp 105 °C, essentially quantitatively (Scheme 5).

Ionic Liquids. A number of colorless, light yellow or light brown ionic liquids, **16**−**23**, were obtained by anion exchange in metathesis reactions of **9**−**11** and **15** with AgOTf, $LiNTf_2$, $AgNO_3$, or $AgClO_4$ (Schemes 5 and 6).

The amide salts, **17**, **21**, and **23**, were hydrophobic and easily obtained as anhydrous compounds by vacuum evaporation. The triflates, **16**, **20**, and **22**, were water-soluble and despite prolonged heating at 40 °C in vacuo were obtained as hydrated products. The tris[oxoethyl(trimethyl)ammonium]trinitrate, **18**, and the triperchlorate, **19**, were solids. Both **18** and **19** were soluble only in water and DMSO. IR spectra and elemental analysis confirmed that that they were isolated as hydrates.

Scheme 6[a]



9: R = Me; X = I
10: R = CH_2CH_2F; X = Br
11: R = $CH_2CH_2CF_3$; X = I

R/Y = Me/OTf (20); Me/NTf_2 (21);
$CH_2CH_2CF_3$/OTf (22);
CH_2CH_2F/NTf_2 (23)

[a] (i) $Na(OSO_2CF_3)/H_2O$ or $LiN(SO_2CF_3)_2/H_2O$.

Table 1. Physical and Thermal Properties of *N*-Alkylimidazolium Salts 3−5 and 8−11

			thermal properties			
	physical properties		DSC			
compound	state	d_{25}[a]	T_g[b]	T_m[c]	T_d[d]	TGA[e]
3	solid			69	183	95
4	solid			126	210	98
5	liquid	1.55	−41	133	240	96
8	liquid	1.52	−39	128	228	97
9	solid		−38	198, 255	279	97
10	solid		−7	175	185	98
11	solid			113	280	99

[a] Density (g cm^{-3}) at 25 °C. [b] Glass transition temperature. [c] Phase transition temperature. [d] Onset of decomposition (°C). [e] Percent of original mass corresponding to the onset of decomposition temperature in the DSC column.

There was minimal or no change in the chemical shift of signals in the ^{1}H and ^{13}C NMR spectra of **16**−**23**, when compared with those of the respective precursor among **9**−**11** and **15**. However, ^{19}F NMR spectroscopy helped estimate the progress of the anion exchange process in the transformation of **10** and **11** to **22** and **23**, respectively. The relative areas of the resonance bands from the fluorine atoms in the anion, NTf_2 = $N(SO_2CF_3)_2$, in **22** and **23** were readily compared with those of fluorine atoms of the polyfluoroalkyl substituent on the organic cation.

Physical and Thermal Properties of 3−5, 8−13, 15, and 16−23. The physical properties of **3**−**5** and **8**−**11** are summarized in Table 1. Thermally induced phase transitions determined by differential scanning calorimety (DSC) thermograms of **3**−**5** showed glass transitions at about −40 °C, an endotherm at a position close to manually determined melting points, and the onset of decomposition at about 200 °C. The oxidative stability was evaluated by thermogravimetric analysis (TGA). Each of the three trimethylsilyl compounds, **3**−**5**, began to lose significant mass shortly above its melting point.

The capillary-determined melting points of **9**−**11** were considerably higher than for their precursors, **3**−**5**, respectively (Table 1 and Scheme 3). The TGA spectrum of **9** showed that less than 6% mass loss had occurred at 200 °C. However, in the DSC thermogram an exothermic phase transition occurred between 198 and 255 °C that resulted from a structural rearrangement and not from decomposition. The decomposition onset temperatures in the DSC spectra of **9**−**11** occurred between 185 and 300 °C.

Table 2. Physical and Thermal Properties of the Amines and Ammonium Salts 12, 14, and 15

			thermal properties			
	physical properties		DSC			
compound	state	d_{25}[a]	T_g[b]	T_m[c]	T_d[d]	TGA[e]
12	liquid	1.22	−44		170	98
14	white solid			111, 118, 121	180	98
15	white solid			102, 168	180	96

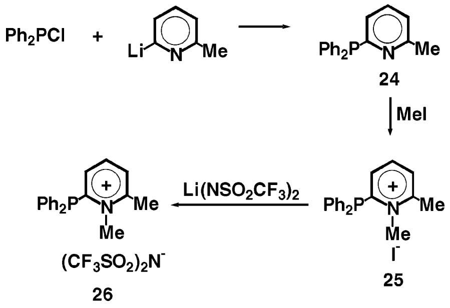
[a] Density (g cm^{-3}) at 25 °C. [b] Glass transition temperature. [c] Phase transition temperature. [d] Onset of decomposition (°C). [e] Percent of original mass corresponding to the onset of decomposition temperature in the DSC column.

Table 3. Physical and Thermal Properties of the Polyquaternary Salts 16−23

			thermal properties			
	physical properties		DSC			
compound	state	d_{25}[a]	T_g[b]	T_m[c]	T_d[d]	TGA[e]
16	liquid	1.88	15	124, 251	290	94
17	liquid	1.69	−35	65	305	99
18	solid		154		178	95
19	solid		49, 85	154, 159	163	98
20	liquid	1.69		132	276	96
21	liquid	1.74	−39	291	340	97
22	solid	1.76		125	236	98
23	liquid	1.72	−35	165	300	99

[a] Density (g cm^{-3}) at 25 °C. [b] Glass transition temperature. [c] Phase transition temperature. [d] Onset of decomposition (°C). [e] Percent of original mass corresponding to the onset of decomposition temperature in the DSC column.

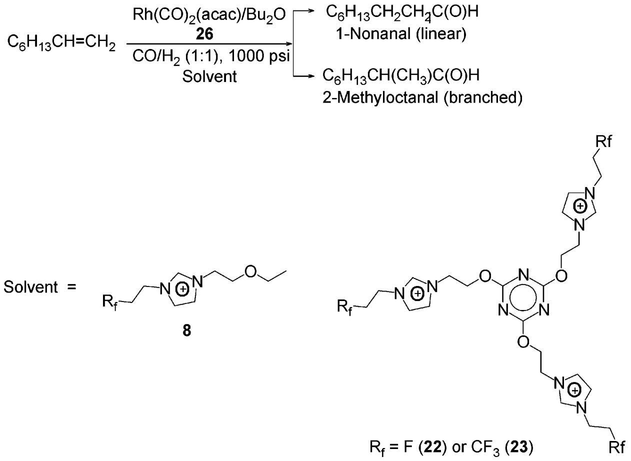
Scheme 7



Tris[oxoethyl(trimethyl)ammonium] triiodide, **15**, was obtained as a white powder. It was not hygroscopic, but had a significantly higher melting point than **14** (see Experimental Section). The manually determined melting points are close to the observed endotherms in the DSC spectra of **14** and **15** (Table 2). The TGA spectra showed that less than a 2% loss of mass of **14** or **15** occurred at 150 °C. However, the compounds began to decompose immediately above their melting points.

The densities of **16**, **17**, and **20**−**23** at between 1.69 and 1.88 g cm^{-3} (Table 3) were higher than those of **5** and **12**, the only liquid precursors. On the basis of the onset of decomposition and TGA data in Tables 2 and 3, the tris[oxoethyl(trimethyl)ammonium] salts, **16**−**19**, were more stable to oxidative thermal decomposition than their iodide precursor, **15**. This pattern was less pronounced in the results with tris(oxoethylimidazolium) analogues when the thermal data in Tables 1 and 3 were compared for the transformations of **9** to **20** and **21**, **10** to **22**, and **11** to **23** (Scheme 7). Phase transitions were common among the ammonium salts, **15**−**19**, at between 100 and 265 °C. The DSC spectrum of tris[oxoethyl(trimethyl)ammonium] triiodide, **15**, did not

Scheme 8



show a glass transition, but the triquaternary triamides, **16**, **17**, **21**, and **23**, showed T_g's at between 15 and 85 °C.

Rh(I)-Catalyzed Hydroformylation of 1-Octene in the Ionic Liquids. Many ionic liquids have been evaluated as solvents or ligands in the hydroformylation of 1-alkenes.[14−18] They are polar, dissolve rhodium(I) catalysts, and are immiscible with aprotic solvents that can dissolve the alkenes. Hydroformylation in bisphasic systems has been a useful method to permit efficient product−catalyst separation at the end of the reaction. The role of the phosphine ligand in Rh(I)-catalyzed hydroformylation of terminal alkenes is significant and is the focus of a number of recent publications.[16−18] If the phosphine ligand is soluble or miscible with the aqueous or organic phase containing the 1-alkene, the Rh(I) catalyst may slowly leach into that phase,[17] eventually preventing good product−catalyst separation, although, at least, about a dozen ligands are known to immobilize Rh in ionic liquids, including a few ionic phosphines.[14−18] To address this difficulty, we prepared a new pyridinium phosphine, **26** (Scheme 7), as ligand for Rh(acac)(CO)$_2$-catalyzed hydroformylation of 1-octene (Scheme 8). The two triquaternary triamides liquid salts, **22** and **23**, or monoquaternary **8**, were utilized as solvents. The choice of the amide anion in **26** was made in order to preclude any possible anion exchange between solvent and ligand.[14] Compound **26** was soluble in organic solvents such as dichloromethane, acetone, and acetonitrile and in the warm mixture of 1-nonanal and 2-methyloctanal but not in 1-octene, ethyl, or butyl ether. According to one previous review, a phosphine pyridinium tetrafluoroborate was used to immobilize Rh during the hydroformylation of various olefins.[1a]

The quaternary liquid amide salts utilized in this work were anhydrous and hydrophobic. This made them attractive solvents for the hydroformylation studies. Although the solubilities of 1-octene in **8**, **22**, and **23** were not determined, it was assumed that the values would be on the order of 2.5 mol % at 25 °C reported for [BMIM][PF$_6$], rather than the reported 10^{-4} mol % in water at the same temperature.[1a,22] With low solubilities of H$_2$/CO and 1-octene in ionic liquids the use of high pressure (~1000 psi) in the hydroformylation reactions was necessary (Scheme 8).

Table 4. Hydroformylation of 1-Octene in Rh(I)/(P, in 26)−Ionic Liquid Biphasic System[a]

ionic liquid	P/Rh	time (h)	TOF[b] (h^{-1})	conversion[c] (%)	n/i[d]
		i. First Run			
8[e]	4	2	85	15[g,h]	1.2
8[f]	4	4	136	26[g,h]	1.3
8[f]	20	4	35	28[g,h]	4
22	4	5	207	59[g,h]	1.7
22	20	5	42	60[g,h]	18
23	20	5	27	32[g,h]	19
		ii. Second Run			
8[e]	4	4	66	12[g]	1.9
8[f]	4	4	112	20[g]	1.3
8[f]	20	4	29	22[g]	3.8
22	4	6	188	45[g]	1.7
22	20	6	32	48[g]	16
23	20	5	26	28[g]	15
		iii. Third Run			
8[e]	4	4	74	36[g]	1.4
8[f]	4	4	110	20[g]	1.2
8[f]	20	4	27	18[g]	3.5
22	4	5	190	40[g]	1.7
22	20	5	38	45[g]	14
23	20	6	20	34[g]	15

[a] Reaction conditions: 40 mL of Bu$_2$O, 90 mmol of 1-octene, 0.083 mmol of Rh(acac)(CO)$_2$, 0.322 mmol (or 1.610 mmol) of **26**, ~1.3 mmol of ionic liquid (=1 molar equiv), 80 °C, 1000 psi (1:1, H$_2$/CO = syngas). [b] The average turnover frequency defined as moles of aldehyde formed per mole of rhodium per hour. [c] The conversion of 1-octene at the time stated. [d] Mole ratio of 1-nonanal/2-methyloctanal. [e] 1.3 mmol of **8**. [f] 3.9 mmol of **8**. [g] Isolated by distillation. [h] Conversion determined by GC−MS.

The objectives of the catalytic studies included the comparison of TOFs (turnover frequency) and isomeric ratio of the aldehydes formed during the hydroformylation, with **22**, **23**, or **8** as solvent. During initial experiments, when Syngas (1:1 H$_2$/CO) was used at 1000 psi pressure in the biphasic setup (~1.3 mmol **8**, **22** or **23** as solvent, 132 mmol of 1-octene in dibutyl ether, 0.083 mmol of Rh(acac)(CO)$_2$, and 0.322 mmol of **26**), with stirring at 80 °C, quantitative conversion of 1-octene to the two aldehyde isomers was achieved over 19 h (**8**) or ~14 h (**22** or **23**). When the volume of solvent (**8**) was tripled (3.9 mmol), hydroformylation of 1-octene was complete in 15 h. These reactions were repeated employing shorter reaction times to determine the TOF and to evaluate recyclability in two repeat runs using the same catalyst system in which the Rh(I)/phosphine ratio was 1:4 or 1:20. The data for the TOF, number of moles turnover per mol Rh(I), overall percent yield over the period of experiment, and the ratio of isomeric aldehydes produced (n/i) are summarized in Table 4.

New ν(CO) stretching bands at 1726 and 1722 cm^{-1} in the IR spectra of the crude products were assigned to 1-nonanal and 2-methyloctanal, respectively. The ^{13}C NMR spectra of the isolated products of the hydroformylation reactions showed that the two isomers were the only aldehydes formed. On the basis of GC, there was no evidence that hydrogenation or isomerization of 1-octene had occurred. No deposits of metallic rhodium were found on the reactor walls after the reactions. The extent of leaching of Rh or Rh−P complex into the organic phase containing the aldehydes, at ppm or ppb levels,[23] was not established for these catalytic systems.

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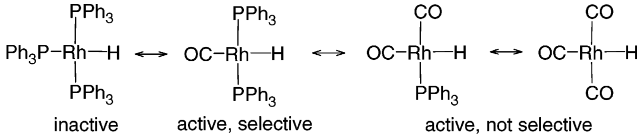
(23) Sandee, A. J.; van der Veen, L. A.; Reek, J. N. H.; Kamer, P. C. J.; Lutz, M.; Spek, A. L.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **1999**, *38* (21), 3231−3233.

Scheme 9. Rh−PPh_3 Dissociation Equilibrium Showing Active Compositions in the Catalytic Cycle[24]



Clean separation of aldehydes from the catalyst was possible by decantation. The crude product was analyzed by GC−MS and separated from butyl ether (internal standard) by distillation (Table 4). The Rh(I) catalyst was successfully immobilized, and each catalyst system was reused in two subsequent recycling experiments. In the recycling experiments, the TOFs, conversion, and n/i ratio were reproduced to within 95% of the first run. The apparent steady drop in catalysts activity, selectivity, and conversion percentages on second and third recycle runs can be due to well-known Rh-induced phosphine ligand cleavage reactions, and an illustration of the Rh−PPh_3 catalytic system is shown in Scheme 9.[24] However, the trend in the TOF, described in the next paragraph, suggests that Rh leaching is responsible, since the kinetics followed the typical negative order with respect to ligand concentration. The extent of catalyst leaching was determined by ICP to be between 0.40 and 26.5 ppm.

While studying the effect of phosphine ligand **26**, the results for **8** and **22** show that changing the P/Rh ratio from 4 to 20 had little effect on the TOFs and conversions, but had a dramatic influence on the isomer selectivity (Table 4). When **8** was used as solvent, the n/i ratio increased from 1.2−1.9 (P/Rh = 4) to 3.5−4 (P/Rh = 20). For **22**, the increase was from 1.7 to ∼16. This was observed also in the experiments that used recycled catalyst systems. With **23** as solvent, the TOFs and conversions were lower than those for **22**, but the values were either the same or higher than found for **8**. However, with P/Rh = 20, the n/i isomer selectivity was also very high at 15−19 (Table 4). The results for **23**, along with those of **22**, suggest that there was a significant difference in the catalytic activity between the monoquaternary liquid salt, **8**, and the triquaternary salts, **22** and **23**, when the P/Rh ratio was as high as 20, with the latter being more effective. Regioselectivity of Rh(I) catalysts is strongly related to the concentration of the phosphine ligand, up to a certain point.[24]

Conclusions

We have prepared and characterized a number of new structurally different trimethylsilylated and tris(oxoethylimidazolium) and tris(oxoethylammonium) ionic salts, including polyfluorinated ones. Their reactivity and physical and thermal stabilities were investigated, and the densities of the polyfluorinated triquaternary salts on the triazine frame were shown to lie between 1.69 and 1.88 g cm^{-3}. The structural advantage of the triquaternized species over the monoquaternary analogue was compared as solvents in the Rh(I)-catalyzed hydroformylation of 1-octene. In those experiments, the TOFs were between 66 and 212 h^{-1}. A new pyridinium phosphine ligand was prepared and used to successfully immobilize the Rh(I) catalyst, which enabled clean separation of product by decantation. A change in the P/Rh ratio from 4 to 20 did not affect the turnover frequencies and conversions. When a triquaternary liquid salt, **22** or **23**, was the solvent, the P/Rh ratio of 20 resulted in significant increase in selectivity with preference for 1-nonanal. In the recycling experiments, the TOFs, conversion, and n/i ratio were reproduced within 95% of the first run. The rhodium leaching, between 0.40 and 26.5 ppm, is likely to be responsible for the reduced conversions in recycling experiments.

Experimental Section

General Considerations. Tetrahydrofuran (THF) and diethyl ether were dried with sodium and distilled over a purple solution of benzophenone. The other chemicals used were obtained commercially from Aldrich, Acros, Lancaster, or Synquest. A standard Schlenk line system was used for handling the air- and moisture-sensitive reactions under nitrogen conditions. Infrared spectra were recorded on a Bio-Rad FTS 3000 Excalibur series infrared spectrometer as neat liquids between KBr plates. ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were obtained on a Bruker AMX spectrometer (200, 300, or 500 MHz) at 200, 50, 188, and 59 MHz, respectively, by using $CDCl_3$ as locking solvent except where otherwise indicated. Chemical shifts are reported relative to Me_4Si or $CFCl_3$. Routine mass spectra were obtained with a Shimadzu Q5050 spectrometer (EI-mode), JEOL JMS-AX505HA mass spectrometer connected to a Hewlett-Packard HP 6890 series GC system (FAB), or Micromass Inc. (electrospray) mass spectrometer. Differential scanning calorimetry (DSC) measurements were performed using a TA Instrument TA10 differential scanning calorimeter equipped with an auto-cool accessory and calibrated using indium. The following procedure was used in experiments for each sample: cooling from 40 °C to −80 °C and heating to 400 or 550 °C at 10 °C/min. Transition temperatures, T_m, were taken as peak maxima. Onset of decomposition was taken as when the abnormal section of the plot began. Thermogravimetric analysis (TGA) measurements were made using a TA Instrument TA50. Samples were heated at 10 °C/min from room temperature to 500 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL/min). Elemental analyses were performed by the Desert Analytics Laboratory, Tucson, AZ, and the SIOC, Shanghai, China. A mini-benchtop reactor Model No. 4560 (Parr Instrument Company, Moline, IL), was used for the catalytic studies. A Perkin-Elmer ICP-AES Optima 3000 spectrometer was employed for rhodium determination.

Syntheses. 2-Imidazolylethanol, [$HOCH_2CH_2Im$ (Im = imidazolyl)] (1). Into a 500 mL two-necked round-bottomed flask fitted with a sidearm and a two-way stopcock and maintained under N_2-atmosphere was placed a magnetic stir-bar and sodium hydride (3.38, 11.3 mmol) in 150 mL of dry dimethylformamide (DMF). Approximately 7.67 g (11.3 mmol) of imidazole in 25 mL of DMF was added slowly to the stirring solution. The mixture was warmed to 90 °C for 1 h and then cooled. Chloroethanol (9.10 mL, 11.3 mmol) in 25 mL of DMF was added slowly to the reaction mixture, which was heated at 90 °C for 24 h. After cooling to 25 °C, the mixture was filtered, and the filtrate was evaporated under reduced pressure to yield crude **1**. NMR (^1H and ^{13}C) evidence showed that the product was >98% **1**. It was not purified further. It solidified (brown wax) on long standing at room temperature.

Analytical data for 1: IR: 3241 cm^{-1} ν(OH). NMR: ^1H, δ 3.79 (t, 2H, NCH_2), 3.98 (t, 2H, CH_2O), 6.54 (br, 1H, O*H*), 6.84 (s, 1H, Im-*H*), 6.90 (s, 1H, Im-*H*), 7.34 (s, 1H, Im-*H*); ^{13}C, δ

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(25) Burke, J. In *Solubility Parameters: Theory and Application*, http://palimpsest.stanford.edu/byauth/burke/solpar/solpar2.html, 1987.

50.0, 61.2, 119.5, 128.3, 137.3 ppm. GC−MS (EI) (*m*/*z*, species, intensity (%)): 112, M$^+$, 65.

1-Trimethylsilyl-2-oxoethylimidazolyl, [$\mathrm{Me_3SiOCH_2CH_2\text{-}Im}$] (2). Into a 50 mL one-necked round-bottomed flask was placed **1** (4.48 g, 40 mmol) and hexamethyldisilazane (3.60 g, 22.4 mmol). The flask was connected to a bubbler. The mixture was warmed to 80 °C for 12 h. On cooling, the excess hexamethyldisilazane and hexamethyldisiloxane were removed by rotary evaporation at 90 °C. Pure, colorless **2** was obtained by distillation at reduced pressure.

Analytical data for 2: Bp: 97 °C/0.7 mm. NMR: ^{1}H, δ −0.28 (s, 9H, Me_3Si), 3.46 (t, 2H, NCH_2), 3.68 (t, 2H, CH_2O), 6.63 (s, 1H, Im-*H*), 6.65 (s, 1H, Im-*H*), 7.16 (s, 1H, Im-*H*); ^{13}C, δ −1.1, 49.1, 61.9, 119.2, 128.6, 137.3; ^{29}Si, δ +19.6 ppm. GC−MS (EI) (*m*/*z*, species, intensity (%)): 184, M$^+$, 74.

1-Trimethylsilyl-2-(oxoethyl-*N*-methylimidazolium) Iodide [$\mathrm{Me_3SiOCH_2CH_2ImMe^+I^-}$, where $\mathrm{ImMe^+}$ = *N*-methyl imidazolium] (3). Compound **2** (5.52 g, 30 mmol), methyl iodide (7.1 g, 50 mmol), and a magnetic stir-bar were placed in a 50 mL 1 in. o.d. Pyrex glass tube. The contents were cooled to −195 °C, and the tube was sealed under vacuum. After allowing the mixture to warm slowly to 25 °C, the mixture was stirred at 60 °C in an oil bath for 48 h. The initial colorless mixture gradually changed to a light brown, more viscous liquid. After cooling and carefully opening the tube, the volatile materials were removed under vacuum, leaving **3** in essentially quantitative yield. MS and NMR evidence showed that **3** was the only product. This product crystallized (brown crystals) when allowed to slowly cool to room temperature.

Analytical data for 3: Mp: 68 °C. NMR: ^{1}H, δ 0.11 (s, 9H, Me_3Si), 3.88 (t, 2H, NCH_2), 4.03 (s, 3H, N*Me*), 4.43 (t, 2H, CH_2O), 7.40 (s, 1H, Im-*H*), 7.45 (s, 1H, Im-*H*), 9.78 (s, 1H, Im-*H*); ^{13}C, δ 0.8, 36.4, 52.7, 60.4; ^{29}Si, δ +25.2 ppm. Electrospray-MS (*m*/*z*, species, intensity (%)): 199, (M$^+$ − I), 100.

1-Trimethylsilyl-2-(oxoethyl-*N*-fluoroethylimidazolium) Bromide, [$\mathrm{Me_3SiOCH_2CH_2ImCH_2CH_2F^+Br^-}$] [$\mathrm{ImCH_2CH_2F^+}$ = *N*-(2′-fluoroethyl)imidazolium] (4): hygroscopic, light brown solid. Mp: 78 °C. Compound **4** was formed during the reaction of **2** (1.47 g, 8.0 mmol) and 1-bromo-2-fluoroethane, $\mathrm{BrCH_2CH_2F}$ (1.27 g, 10.0 mmol), following the procedure described for **3**. Occasionally, the desilylated product, 2-(*N*-fluoroethylimidazolium)ethanol bromide, $\mathrm{HOCH_2CH_2\text{-}ImF^+Br^-}$, formed. The crude product was then warmed with hexamethyldisilazane to reconvert to **4**. Thus, **4** was obtained quantitatively. NMR: ^{1}H, δ 0.04 (s, 9H, Me_3Si), 3.92 (t, 2H, NCH_2CH$_2$O), 4.46 (t, 2H, NCH_2CH$_2$CF$_3$), 4.81 (t, 2H, CH_2O), 4.90 (m, 2H, CH$_2$F), 7.49 (s, 2H, Im-*H*), 8.92 (s, 1H, Im-*H*); ^{13}C, δ 0.8, 50.4 (d, J = 28.Hz), 52.6, 60.6, 82.5 (d, J = 172 Hz), 123.6, 137.3; ^{19}F, δ −220.8 (m); ^{29}Si, δ +19.3 ppm. Electrospray-MS (*m*/*z*, species, intensity (%)): 232, (M$^+$ − Br), 100.

1-Trimethylsilyl-2-(oxoethyl-*N*-3′,3′,3′-trifluoropropylimidazolium) Iodide, [$\mathrm{Me_3SiOCH_2CH_2ImCH_2CH_2CF_3{}^+I^-}$] [$\mathrm{ImCH_2CH_2CF_3}$ = *N*-(3′,3′,3′,-trifluoropropyl)imidazolium cation ring] (5). Using the same procedure as for **3**, compound **5** was formed quantitatively from **2** (1.47 g, 8.0 mmol) and 3,3,3-trifluoropropyl iodide, $\mathrm{ICH_2CH_2CF_3}$ (2.24 g, 10.0 mmol), as a dark brown viscous liquid. NMR: ^{1}H, δ 0.09 (s, 9H, Me_3-Si), 2.96 (m, 2H, CH$_2$CF$_3$), 3.96 (t, 2H, NCH_2CH$_2$O), 4.47 (t, 2H, NCH_2CH$_2$CF$_3$), 4.76 (t, 2H, CH_2O), 7.52 (s, 1H, Im-*H*), 7.57 (s, 1H, Im-*H*), 9.84 (s, 1H, Im-*H*); ^{13}C, δ 0.7, 34.9 (q, J = 30 Hz), 43.9, 52.7, 60.8, 122.3, 123.3, 137.2; ^{19}F, δ, −65.1 (t, J = 15 Hz); ^{29}Si, δ +18.1 ppm. Electrospray-MS (*m*/*z*, species, intensity (%)): 281, (M$^+$ − I), 100.

Compounds 6−8. 2-Oxobutyl-3′,3′,3′-trfluoropropyl Imidazolium Bis(trifluoromethyl ulfonyl)amide, [$\mathrm{CF_3\text{-}CH_2CH_2Im^+CH_2CH_2OCH_2CH_3\ N(SO_2CF_3)_2{}^-}$] (8). In a two-necked 100 mL flask connected with a two-way stopcock were placed **1** (2.24 g, 20 mmol), 30 mL of acetone, 4.36 g (40 mmol) of ethyl bromide, and 2.76 g (20 mmol) of anhydrous potassium carbonate, under nitrogen atmosphere. The mixture was stirred at 65 °C for 48 h. After workup in the Williamson synthesis, which involved filtration and aqueous/organic washing of the crude mixture followed by fractional distillation of the organic phase,[23] pure $\mathrm{ImCH_2CH_2OCH_2CH_3}$ (**6**) was isolated as a colorless liquid.

The reaction of compound **6** (3.5 g, 25 mmol) and 6.16 g (27.5 mmol) of 3,3,3-trifluoropropyl iodide at 60 °C for 24 h gave the quaternary iodide salt, **7**. Subsequently, aqueous solutions of **7** and lithium bis(trifluoromethylsulfonyl)amide gave hydrophobic **8** in a quantitative conversion.

Analytical data for 6: colorless liquid. Bp: 98 °C/0.8 mm. NMR (CDCl$_3$): ^{1}H, δ 1.14 (t, 3H, CH_3CH$_2$O), 3.46 (t, 2H, NCH_2), 3.57 (q, 2H, CH_2O), 6.62 (s, 1H, Im-H), 6.65 (s, 1H, Im-H), 7.16 (s, 1H, Im-H); ^{13}C, δ 15.4, 49.1, 61.7, 118.9, 128.8, 137.4 ppm. GC−MS (EI) (*m*/*z*, species, intensity (%)); 140, M$^+$, 62.

Analytical data for 7: yellow solid. Mp: 110 °C. NMR (acetone-d_6): ^{1}H, δ 1.16 (t, 3H, CH_3CH$_2$O), 3.26 (m, 2H, CF$_3$CH_2), 3.62 (q, 2H, CH$_3$CH_2O), 4.60 (t, 2H, CH_2N), 4.64 (t, 2H, CH_2N), 4.84 (t, 2H, CH_2O), 7.94 (s, 1H, imid-*H*), 7.99 (s, 1H, imid-*H*), 9.28 (s, 1H, imid-*H*); ^{13}C, δ 15.4, 34.4 (q, $^2J_{\mathrm{C-F}}$ = 30 Hz), 43.7, 53.1, 60.8, 67.3, 68.4, 69.8, 120.4 (q), 122.8, 124.0, 137.5; ^{19}F, δ −63.4 ppm (t, 3F, CF$_3$). Electrospray MS (*m*/*z*, species, intensity (%)); 364, M$^+$ − I, 100.

Analytical data for 8: light yellow liquid. NMR (acetone-d_6): ^{1}H, δ 1.14 (t, 3H, CH_3CH$_2$O), 3.22 (m, 2H, CF$_3$CH_2), 3.59 (q, 2H, CH$_3$CH_2O), 4.57 (t, 2H, CH_2N), 4.62 (t, 2H, CH_2N), 4.80 (t, 2H, CH_2O), 7.91 (s, 1H, imid-*H*), 7.96 (s, 1H, imid-*H*), 9.24 (s, 1H, imid-*H*); ^{13}C, δ 15.2, 34.3 (q, $^2J_{\mathrm{C-F}}$ = 30 Hz), 43.9, 53.3, 60.7, 67.0, 68.6, 69.6, 120.1 (q), 123.1, 124.4, 137.9; ^{19}F, δ −63.7 (t, 3F, CF$_3$), −79.9 (s, 6F, N(SO$_2$CF$_3$)$_2$) ppm. Anal. Calcd for $\mathrm{C_{10}H_{16}N_3O_5S_2F_9}$: C, 27.86; H, 3.12. Found: C, 27.31; H, 3.16.

Tris[2-(oxoethyl-*N*-methylimidazolium)]triazine Triiodide Dihydrate, $\mathrm{N_3C_3(OCH_2CH_2ImMe^+I^-)_3{\cdot}2H_2O}$ (9). Into a 50 mL one-necked round-bottomed flask was placed **3** (1.63 g, 5.02 mmol), 15 mL of acetonitrile, and a magnetic stir-bar. It was closed with a rubber septum. After stirring the solution for 2 min at 25 °C, 0.22 g (1.65 mmol) of cyanuric fluoride was added slowly from a syringe. After stirring for 10 min, crude **6** started to separate as an insoluble viscous liquid. Stirring was continued for 3 h. The acetonitrile was then decanted. Two 15 mL portions of boiling acetonitrile were used to wash the crude **6** left in the flask. Any volatile materials in the flask were removed under reduced pressure to give a light yellow solid, **6**, in 97% yield.

Analytical data for 9: light yellow solid. Mp: 109 °C. IR: 3446 cm^{-1} ν(H$_2$O). NMR: ^{1}H, δ 3.88 (s, 9H, N*Me*), 4.64 (t, 6H, CH_2N), 4.72 (t, 6H, CH_2O), 7.74 (s, 3H, imid-*H*), 7.83 (s, 3H, imid-*H*), 9.24 (s, 3H, imid-*H*); ^{13}C, δ 36.6, 48.3, 66.6, 123.2, 124.2, 137.5 172.6 ppm. MS (*m*/*z*, species, intensity (%)): 710, (M$^+$ − I), 66, 582, (M$^+$ − 2I), 33, 488, [(M − I) − CH$_2$ImI]$^+$, 60, 109, (MeImCH═CH$_2$)$^+$, 100, 83, (MeImH)$^+$, 32. Anal. Calcd for $\mathrm{C_{21}H_{34}N_9O_5I_3}$: C, 28.88; H, 3.92. Found: C, 29.04; H, 3.91.

Tris[2-(oxoethyl-*N*-2′-fluoroethylimidazolium)]triazine Tribromide, $\mathrm{N_3C_3(OCH_2CH_2ImCH_2CH_2F^+Br^-)_3}$ (10). Compound **10** was synthesized from **4** (1.57 g, 5.00 mmol) and 0.22 g (1.65 mmol) of cyanuric fluoride, following the procedure described for **9**. The light brown solid **10** was very hygroscopic.

Analytical data for 10: yield 55%. NMR: ^{1}H, δ 4.55 (t, 6H, CH_2O), 4.62 (t, 12H, NCH_2), 4.82 (dt, J = 45 Hz, 6H, CH_2F), 7.85 (s, 6H, imid-*H*), (s, 3H, imid-*H*), 9.29 (s, 3H, imid-*H*); ^{13}C, δ 48.3, 49.8 (d, J = 5 Hz), 66.5, 82.1 (d, J = 168 Hz), 123.2, 123.5, 137.8 161.4; ^{19}F, δ −218.5 ppm. Anal. Calcd for $\mathrm{C_{24}H_{33}Br_3F_3N_9O_3}$: C, 37.38; H, 4.20. Found: C, 37.43; H, 4.54.

Tris[2-(oxoethyl-*N*-3′,3′,3′-trifluoropropylimidazolium)]triazine Triiodide $\mathrm{N_3C_3(OCH_2CH_2ImCH_2CH_2CF_3{}^+I^-)_3}$ (11). Compound **11** was synthesized from **5** (2.04, 5 mmol) and 0.22 g (1.65 mmol) of cyanuric fluoride, following the procedure described for **9**. The solid product separated out of acetonitrile and was filtered. Methanol (5 mL) was added to the filtrate in order to precipitate more **11**. The combined solid **11** was dried under vacuum.

Analytical data for 11: yield 92%, yellow solid. Mp: 168 °C. NMR: ^{1}H, δ 3.00 (m, 6H, C*H*$_2$CF$_3$), 4.50 (t, 6H, NC*H*$_2$CF$_3$), 4.62 (t, 6H, NC*H*$_2$CH$_2$O), 4.75 (t, 6H, C*H*$_2$O), 7.82 (s, 3H, imid-*H*), 7.89 (s, 3H, imid-*H*), 9.25 (s, 3H, imid-*H*); ^{13}C, δ 34.3 (q, $^2J_{\mathrm{C-F}}$ = 29 Hz), 43.9, 49.1, 67.8, 123.7, 124.3, 126.5 ($^1J_{\mathrm{C-F}}$ = 277 Hz), 137.6 163.1; ^{19}F, δ −63.4 ppm. Anal. Calcd for $C_{27}H_{33}N_9O_3I_3F_9$: C, 29.94; H, 3.07. Found: C, 29.51; H, 3.04.

Tris[(oxoethyl-2-imidazolyl)]triazine, $N_3C_3(OCH_2CH_2\text{-}Im)_3$ (12). Into a 50 mL one-necked flask were placed **2** (1.84 g, 10 mmol), 15 mL of acetonitrile, and a magnetic stir-bar. It was stoppered with a rubber septum. After stirring at 25 °C for 5 min, 0.45 g (3.3 mmol) of cyanuric fluoride was added slowly from a syringe. A bright yellow solid formed instantly with each drop of cyanuric fluoride. It was filtered and recrystallized from hot methanol to give pure **12**.

Analytical data for 12: Mp: 105 °C. NMR: ^{1}H, δ 4.49 (t, 6H, NC*H*$_2$), 4.64 (t, 6H, C*H*$_2$O), 7.18 (s, 1H, Im-*H*), 7.34 (s, 1H, Im-*H*), 8.33 (s, 1H, Im-*H*); ^{13}C, δ 47.8, 66.6, 120.8, 122.0, 135.6, 172.2 ppm. GC−MS (*m*/*z*, species, intensity (%)): 411, M$^+$, 30.

1-Trimethylsilyl-2-(*N*,*N*-dimethylamino)ethanol, [$Me_3SiOCH_2CH_2NMe_2$] (13). Compound **13** was obtained from the reaction of 2-*N*,*N*-dimethylaminoethanol (8.9 g, 100 mmol) and hexamethyldisilazane (2.5 g, 15.5 mmol) according to the procedure described for **2** and purified by fractional distillation. Bp: 57 °C/1.0 mm, colorless liquid. NMR: ^{1}H, δ 0.07 (s, 9H, *Me*$_3$Si), 2.21 (s, 6H, N*Me*$_2$), 2.39 (t, 2H, NC*H*$_2$), 3.62 (t, 2H, C*H*$_2$O); ^{13}C, δ −1.1, 47.4, 60.1; ^{29}Si, δ +19.6 ppm. GC−MS (*m*/*z*, species, intensity (%)): 161, M$^+$, 60.

Tris[2-(*N*,*N*-dimethylamino)ethoxy]triazine, $N_3C_3(OCH_2CH_2NMe_2)_3$ (14). Into a 50 mL one-necked flask were placed **13** (6.4 g, 40 mmol), 15 mL of acetonitrile, and a magnetic stir-bar. It was closed with a rubber septum. After stirring at 25 °C for 5 min, 1.8 g (13.33 mmol) of cyanuric fluoride was added slowly from a syringe. A light yellow viscous liquid formed instantly with each drop of cyanuric fluoride. The volatile contents of the flask were evaporated on the rotevaporator at 90 °C, to yield **14**. NMR evidence showed that **14** was not contaminated with **13** or $HOCH_2CH_2NMe_2$. Mp: 98 °C. NMR: ^{1}H, δ 2.17 (s, 18H, N*Me*$_2$), 2.58 (t, 6H, C*H*$_2$N), 4.34 (t, 6H, C*H*$_2$O); ^{13}C δ, 45.7, 57.5, 66.0, 173.0 ppm. MS (*m*/*z*, species, intensity (%)): 342, M$^+$, 58.

Tris[2-(oxoethyl(trimethylammonium)ethoxy]triazine Triiodide Trihydrate, $N_3C_3(OCH_2CH_2N^+Me_3I^-)_3\cdot 3H_2O$ (15). Compound **15** was prepared from 3.42 g (10.0 mmol) of **14** and 7.0 g (49.65 mmol) of methyl iodide, at 60 °C for 24 h. Purification was achieved by vacuum evaporation of the volatile contents of the flask. NMR spectroscopy indicated that complete quaternization of the dimethylamine substituents was achieved. Mp: 179 °C. IR: 3412m^{-1} ν(H$_2$O). NMR: ^{1}H, δ 3.16 (s, 27H, N$^+$*Me*$_3$), 3.82 (t, 6H, N*Me*$_2$), 4.84 (t, 6H, C*H*$_2$O); ^{13}C, δ 54.0, 62.3, 64.5, 171.9 ppm. MS [*m*/*z*, species, intensity (%)]: 641, (M$^+$ − I), 87. Anal. Calcd for $C_{18}H_{45}O_6I_3$: C, 27.71; H, 5.88. Found: C, 27.14; H, 5.01.

General Procedure for Anion Exchange Reactions of 9−11 and 15 in the Preparation of Quaternary Liquids 16, 17, and 20−21 and Solids 18 and 19. The quaternary salts, **16**−**23**, were obtained by anion exchange in the metathesis reactions of stoichiometric amounts of **9**−**11** and **15** with AgOTf, LiNTf$_2$, AgNO$_3$, or AgClO$_4$. This involved stirring the mixture in aqueous solution at 25−40 °C for 1 h.

Compounds **17**, **21**, and **23** were hydrophobic. For their workup, the aqueous solution was decanted, and the crude product washed twice with 20 mL of water. The product was taken up in 10 mL of acetone and dried by vacuum evaporation. The triflates, **16**, **20**, and **22**, were water-soluble. For them, the reaction mixture was filtered and vacuum evaporated at 40 °C. The liquid product was usually left for any residual MI or MBr (M = Li or Ag) to settle at the base of the glass container. The sediments settled rapidly under centrifugation. The liquid ionic triflates were carefully decanted or taken out with a dropping Pasteur pipet, but were all obtained as hydrated products. The tris[oxoethyl(trimethyl)ammonium] trinitrate, **18**, and the triperchlorate **19** were obtained on evaporation of the filtrate from the reactions of aqueous solutions of **15** with AgNO$_3$ and AgClO$_4$, respectively.

Tris[2-(*N*,*N*,*N*-trimethylammonium)ethoxy]triazine Tris(trifluoromethanesulfonate), $N_3C_3[OCH_2CH_2NMe_3{}^+(OSO_2CF_3)^-]_3\cdot 2H_2O$ (16): colorless liquid. IR: 3443 cm^{-1} ν(H$_2$O). NMR: ^{1}H, δ, 3.41 (s, 27H, *Me*$_3$N), 4.11 (t, 6H, C*H*$_2$N), 5.11 (t, 6H, C*H*$_2$O); ^{13}C, δ, 54.3, 63.6, 65.2, 172.5; ^{19}F, δ, −78.9 ppm (s, 9F, OSO$_2$C*F*$_3$). Anal. Calcd for $C_{21}H_{43}N_6O_{14}S_3F_9$: C, 28.97; H, 4.94. Found: C, 28.56; H, 4.79.

Tris[2-(*N*,*N*,*N*-trimethylammonium)ethoxy]triazine tris[bis(trifluoromethanesulfonyl)amide], $N_3C_3[OCH_2CH_2NMe_3{}^+N(SO_2CF_3)_2{}^-]_3$ (17): colorless liquid. NMR: ^{1}H, δ 3.51 (s, 27H, *Me*$_3$N), 4.15 (t, 6H, C*H*$_2$N), 5.10 (t, 6H, C*H*$_2$O); ^{13}C, δ 54.6, 62.8, 65.5, 173.4; ^{19}F, δ −79.8 ppm [s, 18F, N(SO$_2$C*F*$_3$)$_2$]. Anal. Calcd for $C_{24}H_{39}N_9O_{15}S_6F_{18}$: C, 23.47; H, 3.20. Found: C, 23.76; H, 3.28.

Tris[2-(*N*,*N*,*N*-trimethylammonium)ethoxy]triazine Trinitrate], $N_3C_3[OCH_2CH_2NMe_3{}^+(NO_3)_2{}^-]_3\cdot 6H_2O$ (18): purple solid. Mp: 212 °C (dec). IR: 3456 cm^{-1} ν(H$_2$O). NMR: ^{1}H, δ 3.18 (s, 27H, *Me*$_3$N), 3.82 (t, 6H, C*H*$_2$N), 4.84 (t, 6H, C*H*$_2$O); ^{13}C, δ 54.7, 63.2, 65.3, 172.6 ppm. Anal. Calcd for $C_{18}H_{51}N_9O_{18}$: C, 31.69; H, 7.48. Found: C, 31.27; H, 6.57.

Tris[2-(*N*,*N*,*N*-trimethylammonium)ethoxy]triazine Tris(perchlorate), $N_3C_3[OCH_2CH_2NMe_3{}^+(ClO_4)^-]_3\cdot 3H_2O$ (19): white solid. Mp: 151 °C. IR: 3432 cm^{-1} ν(H$_2$O). NMR: ^{1}H, δ 3.22 (s, 27H, *Me*$_3$N), 3.85 (t, 6H, C*H*$_2$N), 4.89 (t, 6H, C*H*$_2$O); ^{13}C, δ 54.8, 63.1, 65.5, 172.8 ppm. Anal. Calcd for $C_{18}H_{45}N_6O_{18}Cl_3$: C, 28.50; H, 6.20. Found: C, 28.20; H, 5.60.

Tris[2-(oxoethyl-*N*-methylimidazolium)]triazine Tris(trifluoromethanesulfonate), $N_3C_3[OCH_2CH_2ImMe^+(OSO_2CF_3)^-]_3\cdot 6H_2O$ (20): brown liquid. IR: 3459 cm^{-1} ν(H$_2$O). NMR: ^{1}H, δ 4.10 (s, 9H, Im*Me*), 4.86 (t, 6H, C*H*$_2$N), 5.00 (t, 6H, C*H*$_2$O), 7.70 (s, 3H, imid-*H*), 7.86 (s, 3H, imid-*H*), 9.13 (s, 3H, imid-*H*); ^{13}C, δ 36.6, 49.2, 67.9, 124.0, 124.7, 138.3, 172.8; ^{19}F, δ −78.9 ppm (s, 9F, OSO$_2$C*F*$_3$). Anal. Calcd for $C_{24}H_{42}N_9O_{18}S_3F_9$: C, 28.46; H, 4.05. Found: C, 27.95; H, 3.79.

Tris[2-(oxoethyl-*N*-methylimidazolium)]triazine Tris[bis(trifluoromethane-sulfonyl)amide], $N_3C_3[OCH_2CH_2ImMe^+N(SO_2CF_3)_2{}^-]_3$ (21): brown liquid. NMR: ^{1}H, δ 4.10 (s, 9H, Im*Me*), 4.87 (t, 6H, C*H*$_2$N), 4.91 (t, 6H, C*H*$_2$O), 7.77 (s, 3H, imid-*H*), 7.82 (s, 3H, imid-*H*), 9.11 (s, 3H, imid-*H*); ^{13}C, δ 36.7, 49.4, 67.0, 124.0, 125.0, 138.0, 173.6; ^{19}F, δ −79.9 ppm [s, 18F, N(SO$_2$C*F*$_3$)$_2$]. Anal. Calcd for $C_{27}H_{30}N_{12}O_{15}S_6F_{18}$: C, 25.00; H, 2.33. Found: C, 25.47; H, 2.37.

Tris[2-(oxoethyl-*N*-3′,3′,3′-trifluoropropylimidazolium)]triazine Tris(trifluoromethanesulfonate) $N_3C_3[OCH_2CH_2ImCH_2CH_2CF_3{}^+(OSO_2CF_3)^-]_3\cdot 6H_2O$ (22). brown liquid. IR: 3427 cm^{-1} ν(H$_2$O). NMR: ^{1}H, δ 2.42 (m, 6H, C*H*$_2$CF$_3$), 3.34 (t, 6H, NC*H*$_2$CF$_3$), 3.83 (t, 6H, NC*H*$_2$CH$_2$O), 4.09 (t, 6H, C*H*$_2$O), 7.13 (s, 3H, imid-*H*), 7.22 (s, 3H, imid-*H*), 8.60 (s, 3H, imid-*H*); ^{13}C, δ 34.1 (q, $^2J_{\mathrm{C-F}}$ = 29 Hz), 43.4, 52.8, 60.5, 122.9, 123.8, 126.0 ($^1J_{\mathrm{C-F}}$ = 277 Hz), 137.0, 163.1; ^{19}F, δ −66.5 (s, 9F, CH$_2$CH$_2$C*F*$_3$), −78.8 ppm (s, 9F, OSO$_2$C*F*$_3$). Anal. Calcd for $C_{30}H_{45}N_9O_{18}S_3F_{18}\cdot 6H_2O$: C, 28.62; H, 3.58. Found: C, 28.43; H, 3.59.

Tris[2-(oxoethyl-*N*-2′-fluoroethylimidazolium)]triazine Tris[bis(trifluoromethanesulfonyl)amide], $N_3C_3[OCH_2CH_2ImCH_2CH_2F^+N(SO_2CF_3)_2{}^-]_3$ (23): brown liquid. NMR: ^{1}H, δ 4.88−4.98 unresolved overlap of (dt, 6H, CH$_2$C*H*$_2$F), (dt, 6H, C*H*2CH$_2$F), (t, 6H, NC*H*$_2$CH$_2$O) and (t, 6H, C*H*$_2$O), 7.87 (s, 3H, imid-*H*), 7.92 (s, 3H, imid-*H*), 9.23 (s, 3H, imid-*H*); ^{13}C, δ 49.6, 51.1 (d, $^3J_{\mathrm{C-F}}$ = 20 Hz), 66.8, 82.4 (d, $^2J_{\mathrm{C-F}}$ = 168 Hz), 124.1, 124.3, 138.0, 173.6; ^{19}F, δ −79.9 [s, 18F, N(SO$_2$C*F*$_3$)$_2$]; −224.3 ppm (septet, 3F, CH$_2$CH$_2$C*F*$_3$). Anal. Calcd for $C_{30}H_{33}N_{12}O_{15}S_6F_{21}$: C, 26.87; H, 2.39. Found: C, 26.90; H, 2.54.

Compounds 24−26. 2-Methyl-5-diphenylphosphine-*N*-methylpyridinium Bis(trifluoromethanesulfonyl)amide,

Ph_2P(NMPBTA) [NMPBTA = *N*-methylpyridinium bis(trifluoromethanesulfonyl)amide] (26). This compound was prepared in three steps outlined in Scheme 7 of the text. A description of the three steps is given below.

In a 100 mL two-necked flask connected with a two-way stopcock and maintained under inert atmosphere was placed 3.44 g (20 mmol) of 2-methyl-5-bromopyridine in 25 mL of diethyl ether. It was cooled to −78 °C, where *n*-butyllithium (12.5 mL, 20 mmol) was added slowly to the stirring solution. After 1 h, 4.41 g (20.0 mmol) of diphenylphosphine chloride was added. After stirring for another 30 min, the mixture was allowed to warm gradually to room temperature. The crude mixture was filtered off, and the filtrate was fractionally distilled to obtain 2-methyl-5-diphenylphosphine pyridine (**24**). This compound was insoluble in diethyl ether, but dissolved readily in acetonitrile, dichloromethane, and chloroform.

Compound **24** (2.77 g, 10.0 mmol) and 4.23 g (30.0 mmol) of methyl iodide were placed in a 100 mL one-necked flask and stirred at 60 °C for 6 h. The orange starting phosphine changed to a green viscous liquid, 2-methyl-5-diphenylphosphinepyridinium iodide (**25**). Purification was achieved by vacuum evaporation.

Stirring aqueous solutions of **25** (2.09 g, 5.0 mmol) and 1.6 g (5.56 mmol) of lithium bis(trifluoromethanesulfonyl)amide at 40 °C for 1 h gave hydrophobic 2-methyl-5-diphenylphosphinepyridinium bis(trifluoromethanesulfonyl)amide (**26**).

Analytical data for 24: orange liquid, 94% yield. Bp: 180 °C/1 mm. NMR ($CDCl_3$): ^{1}H, δ 2.34 (s, 3H, *Me*-Pyr), 7.38−8.60 (m, 13H, aromatic-*H*); ^{13}C, δ 19.2 (J_{P-C} = 2 Hz), 129.4 (J_{P-C} = 23 Hz), 134.8 (J_{P-C} = 20 Hz); ^{31}P, δ −5.00 (s) [cf. δ 81.9 ppm in Ph_2PCl]; GC ret. time = 16.5 min; MS [*m*/*z*, ion, intensity(%)], 276, $(M - H)^+$, 100; 199, $(M - Ph)^+$, 25.

Analytical data for 25: green viscous liquid. NMR ($CDCl_3$): ^{1}H, δ 2.44 (d, J_{P-H} = 7 Hz, 3H, *Me*-Pyr), 3.06 (d, J_{P-H} = 14 Hz, 3H, *Me*-N$^+$), 7.63−8.70 (m, 13H, aromatic-*H*); ^{13}C, δ 19.2 (J_{P-C} = 2 Hz), 24.3 (J_{P-C} = 51 Hz), 129.4 (J_{P-C} = 23 Hz), 134.8 (J_{P-C} = 20 Hz), 153.9 (J_{P-C} = 20 Hz); ^{31}P, δ 17.8 (s).

Analytical data for 26: liquid, d_{25}, 1.73 g cm^{-3}. NMR ($CDCl_3$): ^{1}H, δ 2.50 (s, 3H, *Me*-Pyr), 2.78 (d, J_{P-H} = 14 Hz, 3H, *Me*-N$^+$), 7.65−8.76 (m, 13H, aromatic-*H*); ^{13}C, δ 19.7 (J_{P-C} = 2 Hz), 24.6 (J_{P-C} = 51 Hz), 131.4 (J_{P-C} = 13 Hz), 133.9 (J_{P-C} = 11 Hz); 153.9 (J_{P-C} = 20 Hz); ^{31}P, δ 17.0 (s); ^{19}F, δ −78.8 ppm. Anal. Calcd for $C_{21}H_{19}N_2PO_4S_2F_6$: C, 44.06; H, 3.35. Found: C, 42.82; H, 3.61. DSC: T_g, −15 °C; T_m, 136 °C; onset of decomposition, 224 °C. Corresponding mass of the original in TGA at 224 °C, 99%.

Catalytic Experiments. The hydroformylation reactions were conducted in a Parr stainless steel autoclave mini-benchtop reactor equipped with a mechanical stirrer, pressure gage, thermocouple, gas inlet and release valves, and liquid sampling valve. The ionic catalyst system was first made up by introducing into a Schlenk vessel 2.05 mg (0.0775 mmol) of Rh(acac)$(CO)_2$, ~1.3 mmol of ionic liquid, and 0.184 g (0.322 mmol) or 0.92 g (1.61 mmol) of **26**, the phosphine co-ligand. The mixture was warmed gently at 50 °C with shaking until the system became a homogeneous liquid, which was transferred into the reactor while gently warming the flask. A mixture of 15 g (131.58 mmol) of 1-octene and 10 mL of butyl ether (internal standard for GC determinations) was placed in the stainless steel reactor. The reactor was then pressurized with CO/H_2 (1:1) to 1000 psi, heated to 80 °C, and stirred at 1000 rpm. After 5−6 h, the reactor was cooled to room temperature and degassed. The reaction mixture was biphasic, and the mixture was separated by decantation of the upper organic phase. In some cases, the yields were determined by fractional distillation. Catalytic activity and the n/i selectivity were determined by GC−MS, using di-*n*-butyl ether as internal standard. The reactions were run three times for each of the catalytic systems. Compounds **8**, **22**, and **23** were used as ionic liquids in separate experiments.

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