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Synthetic Methods for Preparing Ionic Liquids Containing Hypophosphite and Carbon-Extended Dicyanamide Anions

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The ability to design small molecules to perform specific tasks is critical to advance fields that range from pharmaceuticals and therapeutics[1,2] to materials science.[3] In addition to molecular compounds, ionic liquids (ILs, salts that melt below 100 °C) represent a specific class of compounds that often demonstrate low volatility and broad applicability to the aforementioned fields.[4,5] The emergence of ionic liquids specifically designed for particular roles[6] has demonstrated that these molten salts can be employed over a wide range of applications, which include solvents,[7] electrolytes,[8] pharmaceuticals and therapeutics,[9] and hydrogen-storage materials.[10]

A hypergolic chemical reaction is defined as the spontaneous combustion reaction between a fuel and an oxidizer.[11,12] During our efforts to prepare new classes of ionic liquids for hypergolic fuel studies, we have developed new synthetic methods for the preparation of ionic liquids. We became interested in studying the physical properties and hypergolic reactivity of ionic liquids containing anions **4**–**6** (Figure 1). Common hypergolic fuels are hydrazine based and are volatile, toxic substances.[12] Hypergolic ionic liquids are considered to be potential surrogates for hydrazine-based fuels in aerospace propulsion applications.[13] Ionic liquids that serve as benchmark fuels often contain the dicyanamide (DCA, **1**), nitrocyanamide (NCA, **2**), or the dicyanoborohydride (DCB, **3**) anions, in which the latter has produced ignition-delay (ID) times below 10 ms when paired with various organic cations (Figure 1).[14] The synthesis and characterization of ionic liquids containing anions **4**, **5**, and **6** have been scarce. In addition, the hypergolic properties of ionic liquids containing these anions have not been reported. Our choice for studying anion **4** was due to its ability to act as a strong reducing reagent. Anions **5** and **6** were studied to prepare carbon-extended derivatives of the DCA anion.

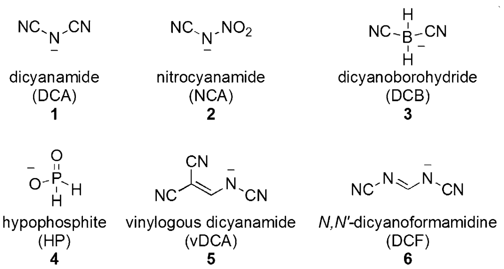
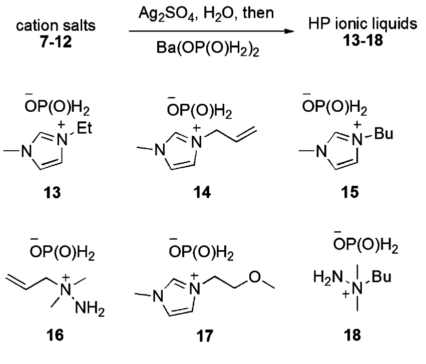


Figure 1. Anions studied in hypergolic ionic-liquid applications.

Initial attempts to use a Brønsted acid/base metathesis reaction between an imidazolium hydroxide and phosphinic acid were unsuccessful. This required the development of an alternative metathesis protocol. The conventional method used to prepare ionic liquids involving the formation of a silver salt of the anion was also attempted. However, these conditions are not applicable to the hypophosphite anion, because the sodium salt readily reduces silver nitrate to silver metal.[15] It was necessary to develop a new and efficient methodology to prepare hypophosphite-containing ionic liquids.[16] To utilize the efficiency of silver-salt metathesis, an intermediate of chemical orthogonality, a bisammonium sulfate, was incorporated into our general synthetic approach (Scheme 1). These intermediates were prepared by the addition of ammonium halide salts (**7**–**12**) to an aqueous suspension of silver sulfate. Filtration of the reaction mixture into a flask containing barium hypophosphite ($Ba(OP(O)H_2)_2$) provided water-soluble ammonium hypophosphite ionic liquids, as well as barium sulfate as a precip-



Scheme 1. Preparation of hypophosphite ionic liquids.

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itate. During this work, an improved synthesis of barium hypophosphite was developed, which involves the reaction of $BaCO_3$ and in situ generated phosphinic acid. This scalable reaction was used to prepare up to 47 g (74 % yield) of $Ba(OP(O)H_2)_2$, and is less cumbersome than known methods of preparation involving the reaction between white phosphorus and barium hydroxide.[17]

As a result of our intended applications, our substrate scope was limited to the production of room-temperature ionic liquids. The instability of aliphatic ammonium (e.g., pyrrolidinium) hypophosphites limited our substrate scope to study the chemistry of hydrazinium- and imidazolium-based cations. According to the method described in Scheme 1, a series of six HP ionic liquids have been prepared in 63–80 % yield. The 1-butyl-1,1-dimethylhydrazinium HP salt **18** was isolated as a waxy, hygroscopic solid at room temperature, and the other products in the HP series exist as liquids at room temperature. The physical properties of the prepared hypophosphite ionic liquids are shown in Table 1.

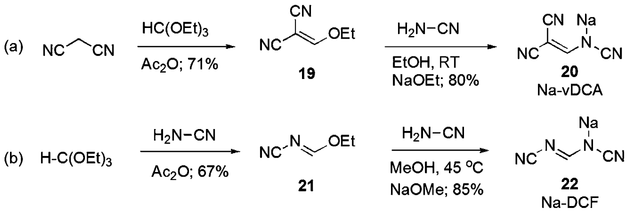
Table 1. Properties of hypophosphite (HP) ionic liquids.[a]

Entry	ILs	T_m [°C]	T_d [°C][b]	η [cP][b]	ρ [g cm^{-3}][b]	ID [ms]
1	**13**	<-80	219	56.2	1.18	203
2	**14**	<-80	200	177.8	1.19	125
3	**15**	<-80	214	154.1[c]	1.11[c]	230
4	**16**	<-80	171	308.9[d]	1.12[d]	NH
5	**17**	<-80	217	251.6	1.25	241
6	**18**	<-80	202	–	1.11[c]	–

[a] IL = ionic liquids prepared; T_m = melting temperature; T_d = decomposition temperature; η = viscosity; ρ = density; ID = ignition delay (average of three measurements by using WFNA as the oxidizer); NH = not hypergolic. [b] Measurements at 25 °C. [c] Measurements at 26 °C. [d] Measurements at 27 °C.

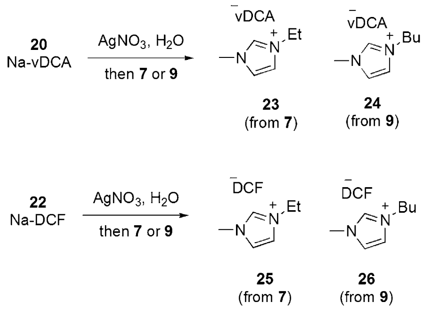
When screened for hypergolic reactivity, the ID times were recorded in triplicate by using white fuming nitric acid (WFNA) as the oxidizer, and the average ID values are reported in Table 1. In general, the ID times for the room-temperature HP ionic liquids are two to six times longer (125–241 ms) compared with those reported for the DCA class with the respective cations. In one case, the 1-allyl-1,1-dimethylhydrazinium hypophosphite ionic liquid **16** was not hypergolic.

Two new classes of anions similar to the DCA anion have also been prepared, as described in Scheme 2. The preparation of the *N*-(2,2-dicyanovinyl)cyanamide sodium salt (Na-vDCA) was accomplished in two steps. The condensation of malononitrile with triethylorthoformate provided the vinyl ethyl ether **19**, which was subsequently treated with sodium cyanamide to give **20** (Scheme 2 a). The preparation of the *N*,*N*′-dicyanoformamidine sodium salt (Na-DCF) was accomplished through the condensation of cyanamide with triethylorthoformate to give ethyl *N*-cyanoformimidate **21**, which underwent an analogous addition/elimination reaction with sodium cyanamide to provide **22** (Scheme 2 b).



Scheme 2. Preparation of vDCA and DCF sodium salts.

The preparation of ionic liquids **23**–**26** containing anions **5** and **6** was accomplished by adding a freshly prepared silver salt of the respective anion to an aqueous solution of the respective cation (**7** or **9**) as shown in Scheme 3. These materials were isolated in 86–90 % yield (see Experimental Section in the Supporting Information).[18]



Scheme 3. Preparation of vDCA and DCF ionic liquids.

The vDCA and DCF anions provided ionic liquids with similar density and viscosity to the DCA benchmarks. The DSC analyses of the DCF- and vDCA-based ionic liquids showed that the decomposition temperatures (T_d) for the DCF class are below those of the vDCA analogues. Both classes were less thermally stable than the DCA benchmark ionic liquids (Table 2). Despite the similarities in physical properties to the DCA ionic liquids, the hypergolic reactivity for ionic liquids **23**–**26** was lower than expected. When using the DCF anion, a hypergolic reaction (ID = 381 ms) was observed when paired with the 1-ethyl-3-methylimidazolium cation **7**, but not with the 1-butyl-3-methylimidazoli-

Table 2. Properties of vDCA and DCF ionic liquids.[a]

Entry	ILs	T_m [°C]	T_d [°C][b]	η [cP][b]	ρ [g cm^{-3}][b]	ID [ms]
1	**23**	<-80	205	69.4	1.12	NH
2	**24**	<-80	193	126.9	1.09	NH
3	**25**	3	197	32.8[c]	1.13[c]	381
4	**26**	<-80	186	80.2	1.08	NH
5	**27**	−21	275	21[d]	1.06	36[e]
6	**28**	n/a	207	42	n/a	43
7	**29**	−90	240	33	1.06	47

[a] IL = ionic liquids; T_m = melting temperature; T_d = decomposition temperature; η = viscosity; ρ = density; n/a = data not available; ID = ignition delay (average of three measurements by using WFNA as the oxidizer); NH = not hypergolic; [b] measurements at 25 °C; [c] measurements at 26 °C; [d] measurement at 20 °C; [e] ID for ionic liquid not previously reported.

um cation **9**. Although the physical properties of the ionic liquids are similar to the analogous DCA ionic liquids, upon the addition of ionic liquids **23** and **24** to WFNA, no hypergolic reaction was observed. For comparison, entries 5–7 in Table 2 outline the physical properties and ID times of known 1-ethyl-[19], 1-allyl-[12] and 1-butyl-3-methylimidazolium[12,20] DCA ionic liquids (**27**–**29**, respectively).

In summary, we have developed new synthetic methods to prepare ionic liquids that contain hypophosphite and carbon-extended dicyanamide anions. Although the prepared ionic liquids containing anions **4**–**6** did not outperform the benchmark hypergolic ionic liquids that contain anions **1**–**3**, their physical and thermodynamic properties are similar.

Experimental Section

Safety precautions: Although we have experienced no difficulties in syntheses and characterization of these materials, proper protective precautions should be used. Manipulations must be carried out in a hood behind a safety shield. Eye protection and gloves must be worn. For the complete experimental details, see the Supporting Information. In addition to full characterization, the heat of formation and specific impulse properties of the ionic liquids have been calculated. All calculated data are provided in the Supporting Information.

General methods: ^1H, ^{13}C, ^{31}P NMR (decoupled) spectra were recorded in [D$_6$]DMSO on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.1, 75.5, and 121.5 MHz, respectively, unless otherwise noted. Chemical shifts were reported relative to the residual solvent peak. Melting and decomposition points for ionic liquids were recorded on a TA Instruments Co., model Q10 differential scanning calorimeter (DSC) from -80 to 400 °C at a scan rate of 5 °C min^{-1} in compressed aluminum pans. Melting and decomposition points for solids were measured by DSC from 40 to 400 °C at a scan rate of 5 °C min^{-1}. IR spectra were recorded as thin films by using a BIORAD model 3000 FTS spectrometer, unless otherwise noted. Densities were measured by using a Micromeritics Accupyc 1330 gas pycnometer. Viscosities were measured with a Grabner MINIVIS II Portable Micro viscometer. Elemental analyses were obtained by using a CE-440 elemental analyzer (EAI Exeter Analytical). Ignition delay (ID) times were measured by using the drop test method, in which 15–20 mg of sample is dropped into excess white-fuming nitric acid (1.0–1.5 mL). The ignition delay times were recorded in triplicate at 500 frames s^{-1} by using an Olympus *i*-Speed camera, and the average ID times are reported.

General synthetic procedures: **1-ethyl-3-methyl-imidazolium hypophosphite, 13**: *General protocol A*: To a suspension of Ag_2SO_4 (2.083 g, 6.681 mmol) in H_2O (4 mL) cooled in an ice bath and protected from light was added a solution of **7** (2.502 g, 13.09 mmol) in H_2O (8 mL). The mixture was stirred while protected from light for 2 h. The solution was then filtered into a flask containing $Ba(H_2PO_2)_2$ (3.676 g, 13.75 mmol), and the solid was rinsed with H_2O (6 mL). The suspension was stirred for 3 h at RT, diluted with absolute EtOH (10 mL), and the volatile materials were removed under reduced pressure. The residue was dissolved in EtOH, stirred with activated carbon, filtered, concentrated under reduced pressure, and dried in vacuo to give **13** (70 % yield; 1.621 g, 9.202 mmol) as a light yellow oil. $T_d = 219$ °C (onset); IR: $\tilde{\nu} = 3385$, 3083, 2984, 2295, 2258, 1661, 1572, 1455, 1195, 1082, 1050, 807 cm^{-1}; ^1H NMR (300.1 MHz, [D$_6$]DMSO): $\delta = 9.29$ (brs, 1 H, CH), 7.80 (s, 1 H, CH), 7.72 (s, 1 H, CH), 7.07 (d, $J = 451.2$ Hz, 2 H, H_2PO_2), 4.20 (q, $J = 7.3$ Hz, 2 H, CH_2), 3.85 (s, 3 H, CH_3), 1.41 ppm (t, $J = 7.3$ Hz, 3 H, CH_3); ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): $\delta = 136.4$, 123.5, 121.9, 44.0, 35.6, 15.0 ppm; ^{31}P NMR (121.5 MHz, [D$_6$]DMSO): $\delta = -5.61$ ppm (s, H_2PO_2); elemental analysis calcd (%) for $C_6H_{13}N_2O_2P + 1 H_2O$ (194.17): C 37.11, H 7.79, N 14.43; found: C 37.44, H 7.63, N 14.15.

1-Ethyl-3-methyl-imidazolium *N*-(2,2-dicyanovinyl)cyanamide, 23: *General protocol B:* To a protected from light solution of **20** (1.320 g, 9.423 mmol) in H_2O (25 mL) at RT, a solution of $AgNO_3$ (1.600 g, 9.419 mmol) in H_2O (15 mL) was added. The resulting suspension was stirred for 1 h, filtered, and rinsed with H_2O. The silver salt was then suspended in a solution of **7** (1.500 g, 7.851 mmol) in H_2O (30 mL). After protected from ambient light mixture was stirred overnight at RT, the mixture was filtered, rinsed with absolute EtOH, and concentrated under reduced pressure. The residue was dissolved in EtOH, stirred with activated carbon, filtered, concentrated, and dried in vacuo to give **23** (87 % yield; 1.555 g, 6.813 mmol) as an amber oil. $T_d = 205$ °C (onset); IR: $\tilde{\nu} = 3472$, 3153, 3111, 2196, 2164, 1549, 1324, 1169 cm^{-1}; ^1H NMR (500 MHz, [D$_6$]DMSO): $\delta = 9.09$ (s, 1 H, CH), 8.08 (brs, 1 H, CH), 7.75 (s, 1 H, CH), 7.67 (s, 1 H, CH), 4.19 (q, $J = 7.3$ Hz, 2 H, CH_2), 3.85 (s, 3 H, CH_3), 1.42 ppm (t, $J = 7.5$ Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 172.5$, 154.5, 136.2, 123.5, 121.9, 120.2, 119.0, 116.2, 44.1, 35.7, 15.0 ppm; elemental analysis calcd (%) for $C_{11}H_{12}N_6$ (228.25): C 57.88, H 5.30, N 36.82; found: C 57.90, H 5.53, N 36.69.

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Keywords: anions · hypergolic fuels · hypophosphite · ionic liquids · synthetic methods

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