JOC Articles

# Carbon-Centered Strong Bases in Phosphonium Ionic Liquids

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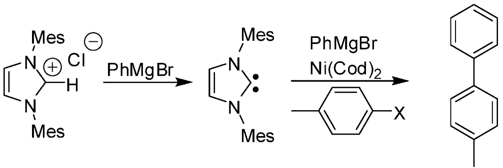

Cod = 1,5-bis-cyclooctadiene
X = F, Cl, Br, I

Phosphonium ionic liquids (PhosILs), most notably tetradecyl(trihexyl)phosphonium decanoate (PhosIL-$C_9H_{19}COO$), are solvents for bases such as Grignard reagents, isocyanides, Wittig reagents (phosphoranes), and *N*-heterocyclic carbenes (NHCs). The stability of the organometallic species in PhosIL solution is anion dependent. Small bases, such as hydroxide, react with the phosphonium ions and promote C−H exchange as suggested by deuterium-labeling studies. A method to dry and purify the ionic liquids is described and this step is important for the successful use of basic reagents in PhosIL. NHCs have been generated in PhosIL, and these persistent solutions catalyze organic transformations such as the benzoin condensation and the Kumada−Corriu cross-coupling reaction. Phosphoranes were generated in PhosIL, and their reactivity with various organic reagents was also tested. Inter-ion contacts involving tetraalkylphosphonium ions have been assessed, and the crystal structure of $[(n\text{-}C_4H_9)_4P][CH_3CO_2{\cdot}CH_3CO_2H]$ has been determined to aid the discussion. Decomposition of organometallic compounds may also proceed through electron-transfer processes that, *inter alia*, may lead to decomposition of the IL, and hence the electrochemistry of some representative phosphonium and imidazolium ions has been studied. A radical derived from the electrochemical reduction of an imidazolium ion has been characterized by electron paramagnetic resonance spectroscopy.

## Introduction

Environmental pressure to reduce waste and reuse materials has prompted studies into "Green Chemistry"[1,2] and several reviews have been written concerning this emerging field.[3−5] One of the biggest industrial concerns is the replacement of volatile organic compounds (VOCs),[6] particularly those that are toxic, such as $CH_2Cl_2$, and those that are highly volatile and flammable, such as ethers. Simply substituting one solvent for another that is more environmentally friendly is often impossible, due to the multifaceted functions of the solvent. Some of these functions include behavior as a heat sink for exothermic processes, as well as promotion of homogenization and the mixing of reactants.[1] Of particular importance to this paper are ethereal solvents, primarily diethyl ether or tetrahydrofuran,

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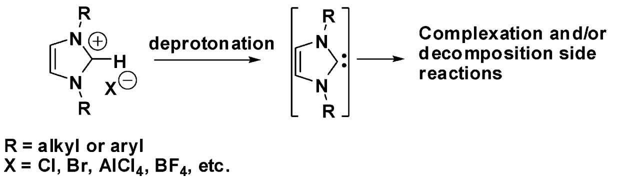
10.1021/jo701289d CCC: $40.75

**SCHEME 1. Deprotonation of an Imidazolium Ion in an ImIL**

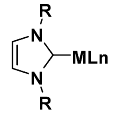


which are commonly used for reactions involving strong bases. At present, few neoteric or novel solvents with advantageous properties have been studied as alternative reaction media for reactions involving electron-rich or highly basic reagents.

The use of ionic liquids (ILs)[7] to replace or reduce VOCs is a move that could have significant positive environmental impact. There would also be safety benefits resulting from the preferential use of ILs over VOCs, largely due to their low or nonflammability with normal use.[5,8] The most extensively studied class of ILs is based on imidazolium cations and this diverse class is generally referred to as imidazolium based ionic liquids (ImILs). These solvents exhibit high thermal stability, low volatility, and variation in cosolvent miscibility.[9] Some processes using these liquids are currently being commercialized. For example, ImILs can serve as useful materials for transporting reactive gases such as $BF_3$ and $PH_3$,[10] which form complexes with the anionic component of the IL.

ILs are inherently two-component systems, namely an anion and a cation. The disparate nature of cations and anions, specifically, intimate sites of high electron deficiency and high electron richness, suggests the ionic liquids may be ideal solvents to enable chemistry that is perhaps not possible in normal molecular solvents. For these two-component mixtures, each constituent of the solvent should ideally be inert. Otherwise, *either* of these components could become concomitantly involved in side-reaction pathways. Reactivity studies have shown that both the cationic and/or anionic component can engage in solvolysis reactions.[11,12] Specific relevant examples include activation of the C−H bonds in imidazolium ions, as well as hydrolysis of $[BF_4]$ or $[PF_6]$ salts to generate HF in situ.

Imidazolium-based ionic liquids are known to support many reactions that proceed well in acidic reaction conditions,[13−15] but the track record for ImILs as solvents for reactions involving strong bases is certainly less than stellar.[16−18] Indeed, recent reviews highlighted the rather unpredictable behavior of this solvent type.[19] Imidazolium ions have been shown to react under basic conditions to produce *N*-heterocyclic carbenes (NHCs)[20] as shown in Scheme 1. NHCs themselves are very reactive, highly basic, neutral six-electron species possessing a dicoordinate carbon atom with two nonbonding electrons.[21] They have strong $\sigma$-donor and poor $\pi$-acceptor characteristics, and have recently attracted attention in numerous applications in synthetic[22,23] and transition metal chemistry (Figure 1).[24,25]



M = Transition metal, lanthanide, actinide or main group element
Ln = CO, Cp, Cl, etc.
R = 2,4,6-trimethylphenyl, etc

**FIGURE 1.** Organometallic complexes of NHCs.

Even though imidazolium salts are reactive as solvent media, they have been used for many organometallic reactions[26] such as the preparation of new metal carbonyl complexes,[27] indium and tin catalysts,[28,29] and zinc reagents.[30,31] Deprotonation of the cationic component of ImILs can be important in some catalytic reactions[32−34] (i.e., it generates an active metal/NHC complex) but in other cases, such as in the Baylis−Hillman reaction (Scheme 2), the deprotonation results in a significant decrease in reaction yields.[17,18] ILs have been demonstrated as catalytically active in addition and cross-coupling reactions, respectively.[35,36]

Recently it has been reported that ionic liquids can serve as solvents for basic organometallic reagents, such as Grignard reagents. Specifically, ImILs can withstand the strong-base

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[7] Wilkes, J. S. *Green Chem.* **2002**, *4*, 73.

[8] (a) It should be noted that under specific conditions, some ILs are, in fact, combustible. However, the bulk properties of an IL are dramatically different than, for example, fine mists which in many ways are comparable to normal solvent vapors. (b) Smiglak, M.; Reichert, W. M.; Holbrey, J. D.; Wilkes, J. S.; Sun, L.; Thrasher, J. S.; Kirichenko, K.; Singh, S.; Katritzky, A. R.; Rogers, R. D. *Chem. Commun.* **2006**, 2554.

[9] Welton, T. *Chem. Rev.* **1999**, *99*, 2071.

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[11] Proton or hydrogen atom abstraction reactions are common in aqueous and nonaqueous media. In systems such as water these reactions lead to generation of $O_2$, $H_2$, or $OH^-$, and $H_3O^+$. In ILs, such reactions can also occur, but these lead to decomposition and contamination of the IL. We recognize, however, that these decompositions can often result in the formation of the truly active species in select reactions.

[12] (a) There have been numerous reports dealing with the hydrolysis of anions, particularly tetrafluoroborate and hexafluorophosphate. These reactions do cause significant problems and perhaps most important is the evolution of HF which can damage glass and metal. (b) Scammells, P. J.; Scott, J. L.; Singer, R. D. *Aust. J. Chem.* **2005**, *58*, 155.

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[15] (a) Imidazolium-based ionic liquids (ImILs), specifically tetrachloroaluminate (III) salts, have been classified as acidic or basic depending on the relative amount of $Cl^-/AlCl_3$ in the material—the anion $[Al_2Cl_7]^-$ is a source of $AlCl_3$ which is a good Lewis acid for catalysis. We use the term "acidic" to emphasize the high reactivity of the C−H fragment in ImILs, which, with strong bases, behave as protic acids. (b) Holbrey, J. D.; Seddon, K. R. *Clean Prod. Processes* **1999**, *1*, 223. (c) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391.

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[19] See, for example: Chowdhury, S.; Mohan, R. S.; Scott, J. L. *Tetrahedron* **2007**, *63*, 2363. Nair, V.; Bindu, S.; Sreekumar, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 5130.

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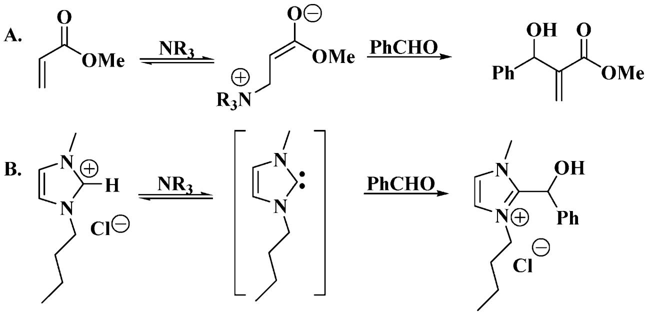
**SCHEME 2. (A) The Baylis-Hillman Reaction and (B) the Major Side Reaction that Occurs in ImIL between the Solvent and Benzaldehyde, Dramatically Decreasing the Yield of the Reaction**



conditions of the Grignard solutions when the acidic hydrogen site at the $C_2$ position on the imidazolium or imidazolinium ion has been protected or eliminated. This has been accomplished with a methyl,[37] isopropyl,[38] or phenyl[39] substituent at the vulnerable site. In most cases, the Grignard was added to the ImIL, but was not generated in situ. The choice of anion varied although two contained at least one triflimide unit, and thus contained an oxygen-based donor site, a feature that will be identified as key for the stability of Grignard solutions in IL solution.[38,39] The third, with the methyl-protecting group, employed a tetrafluoroborate anion that was successful in supporting the Grignard itself, and its generation, although only at elevated temperatures. A pyridinium-based ionic liquid was also used to engender a Grignard in solution within the same study.[37]

Studies on basic reagents in ionic liquids have been performed and will be presented here. These reactions can be achieved by using related phosphonium-based ionic liquids especially since the phosphonium cations are well-known to be more thermally robust than imidazolium cations.[40,41] In this paper it is shown that phosphonium ionic liquids (PhosILs) (1) can be used as solvents for Grignard reactions,[42,43] (2) can dissolve other important carbon centered ligands; (3) can be used as solvents for generating NHCs and for preparing their metal complexes, and (4) can be used as a solvent medium for the generation of Wittig reagents. Preliminary reports dealing with select topics have been the focus of earlier communications.[43,44] We note that in addition to acid/base deprotonation reactions, electron-transfer reactions can result in the decomposition of both organometallic species and the ionic liquid solvent. To this end, we have examined the electrochemistry of imidazolium and phosphonium ions and we have characterized by EPR spectroscopy a radical derived from the one-electron reduction of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride.

## Results and Discussion

**Phosphonium-Based Ionic Liquids.** Two phosphonium-based ionic liquids were chosen for the study of the chemistry of strong bases (Figure 2), namely, tetradecyl(trihexyl)phosphonium chloride (PhosIL-Cl) and tetradecyl(trihexyl)phosphonium decanoate (PhosIL-$C_9H_{19}COO$), which was prepared from PhosIL-Cl via an anion exchange reaction. PhosIL-$C_9H_{19}COO$ is somewhat more viscous than PhosIL-Cl, but overall, decanoate has much stronger ligand donor properties than chloride for the stabilization of metal sites. This effect will be described later.

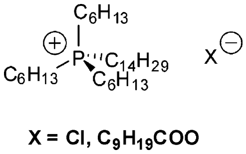


**FIGURE 2.** PhosILs used in this study.

**Purification of Phosphonium-Based Ionic Liquids.** It was found that commercially available PhosIL-Cl contains traces of residual phosphines (observed through NMR studies), HCl, and water. Also present are trace phosphine oxides as well as trace amounts of isobutylnitrile, derived from the radical addition step that generates the phosphines. Recognizing the sensitivity of organometallic reagents to these species, a method was designed to purify the PhosIL.

Excess HCl in the PhosIL is neutralized with aqueous sodium bicarbonate. Care should be exercised since there can be excessive foaming during this step. The ionic liquid layer is then washed vigorously with water and extracted using hexanes. Phosphine oxides can be easily removed by diluting the PhosIL with small amounts of hexanes and passing the solution through a short silica column. For the organometallic reactions described below, it was important to remove all traces of water by azeotropic distillation with toluene. The PhosIL can also be further dried at this stage with a small amount of solid potassium, but this treatment is not generally required. Isobutylnitrile is removed in the organic washes and distillation steps.

As noted above, the PhosIL can be dried with elemental potassium,[45] which suggests that unlike ImILs, PhosIL does not readily react with this *source* of the simplest base: the electron. This observation portends well for the stability of other bases and electron-rich molecules in the PhosIL. A word of caution is warranted: reaction of water with elemental potassium yields hydroxide ion, which does react with the PhosIL cation.

**Stability of Grignard Reagents in Phosphonium-Based Ionic Liquids.** The stability of the PhosIL in the presence of several different nucleophilic reagents was examined. Perhaps the most readily available carbon-based nucleophiles are commercial solutions of Grignard reagents in tetrahydrofuran (THF) ($pK_a = 45-50$). As a representative example of this important class of reagent, phenylmagnesium bromide (PhMgBr) was chosen for examination of its behavior in PhosIL. Anhydrous samples of PhosIL-Cl form clear solutions with low viscosity when mixed with commercially available 1 M PhMgBr in THF.[42] The solutions are air and moisture sensitive, but can be stored under an inert atmosphere such as argon or nitrogen. The reactivity of fresh PhosIL-Cl/Grignard reagent solutions with a THF:PhosIL-Cl ratio of 1:3 was tested by the addition of anhydrous bromine to give exclusive formation of bromobenzene, PhBr. To probe the persistence of the Grignard reagent

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**FIGURE 3.** A phosphorane, the anticipated product resulting from deprotonation of a PhosIL cation.

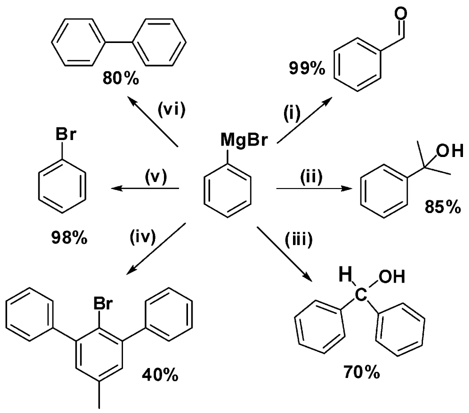
in PhosIL, the tests were repeated on month-old solutions. When the aged solution was treated with $Br_2$, 5% of biphenyl was detected along with bromobenzene. The presence of benzene was not observed in either case, indicating that a deprotonation reaction did not occur. Most importantly, deprotonation of the PhosIL to produce a phosphorane was not observed, as shown in Figure 3.

*Complete* removal of THF cosolvent from the PhosIL-Cl/Grignard solutions, as determined by $^{1}$H NMR spectroscopic studies, led to the formation of biphenyl and a variety of products that could be traced to the decomposition of PhosIL-Cl, including tetradecyl(dihexyl)phosphine and hexene. These products are formed by the reduction of the phosphonium ion presumably via an electron-transfer reaction. Also, we note here that similar preparations involving PhMgBr/THF solutions with PhosIL dicyanamide or PhosIL bis(trifluoromethylsulfonyl)imide resulted in immediate decomposition of the solution after mixing the reagents. Since the cations and reaction conditions were otherwise identical, this suggested that the anion of the ionic liquid plays a central role in the stabilization of the Grignard reagent (see below).

To test this hypothesis, solutions Grignard solutions in PhosIL devoid of ether were prepared and the absence of ether was indicated by spectroscopic studies. After adding a few drops of THF or toluene to tetradecyl(trihexyl)phosphonium *decanoate* to lower its freezing point and decrease viscosity, the ionic liquid was cooled to −78 °C and PhMgBr in THF was added to make a 1 M solution. The new PhosIL-$C_9H_{19}COO$/Grignard reagent solutions were allowed to warm to room temperature and stirred for 15 min. The color changed from pale yellow to orange-red with an intermediate faint blue color. This unusual blue color has previously been observed when two neighboring carbonyl groups of benzil make a stable intermediate radical anion with a Grignard reagent,[46] but no significant effect of the trace transient blue species was observed for the reactivity of the solution. THF or toluene was completely removed in vacuo to yield an *ether-free* Grignard solution, and this new solution showed no sign of decomposition over several months. It is proposed that the stability of these new solutions is the result of coordination between the magnesium atom of the Grignard reagent and the oxygen donor site of the decanoate anion[46] of PhosIL-$C_9H_{19}COO$, which replaces a similar metal−oxygen interaction when using ethereal solvent.[47]

All attempts to *generate* Grignard reagents in PhosIL failed, for reasons not clear at this time. It is speculated that it may be because the oxidative addition reaction of the magnesium metal into the carbon halide bond is slow, or an additional cosolvent must be added to the reaction mixture to facilitate this reaction. Recent reports, however, have shown that the oxidative addition step does proceed in pyridinium ionic liquids.[37] Adjunctly, it has been shown that magnesium metal can form a protective surface coating, which impeded reactions when exposed to PhosIL.[48]

**SCHEME 3. Reactions Performed in PhosIL-$C_9H_{19}COO$ without any Ethereal Cosolvent**[a]



[a] A few drops of either toluene or hexanes was added to reduce the viscosity of the IL. Reaction conditions: (i) DMF, stirred for 3 h; (ii) acetone, stirred for 3 h; (iii) benzaldehyde, stirred for 2 h; (iv) 2,6-dibromo-4-methyl-iodobenzene, stirred for 3 h, quenched with $Br_2$; (v) $Br_2$, stirred for 1 h; (vi) $CuCl_2$, stirred for 2 h.

It is interesting to note at this point that analogous reactions using phenyllithium produced a variety of PhosIL decomposition products including tetradecyl(trihexyl)phosphine and hexene, as identified by GC-MS studies. A similar observation was made by Handy when he noted the inability of imidazolium-based ionic liquids to support butyllithium.[38] The reasons for this difference in reactivity between the Grignard reagent and organolithium reagents are not obvious. For the Grignard reagents, there may be an outer-sphere mechanism where the Schlenk equilibrium[49] might be favorably influenced by the large excess of anions (strong donors) in PhosIL solution. Recently, we reported that the mode of reactivity for Grignard reagents, either as nucleophiles or as reducing agents, is strongly influenced by the solvent, whether it is ionic (PhosIL) or molecular (THF).[50] Finally, organolithium reagents tend to aggregate in solution and form clusters and we speculate that organolithium reagents may act as strong reducing agents through inner-sphere electron-transfer reactions, rather than the organolithium reagent behaving as a discrete hydrocarbyl transfer species.

**Reactivity of Grignard Reagents in Phosphonium-Based Ionic Liquids.** To test the tolerance of PhosIL to strong bases, a survey of Grignard reactions at room temperature was performed. Reactions included addition to carbonyl compounds (Scheme 3, i−iii), benzyne reactions (iv), halogenation (v), and coupling reactions (vi) in PhosIL-$C_9H_{19}COO$. The most interesting result came from the benzyne reaction (iv) because it suggests that the postulated *benzyne* intermediate is feasible in the PhosIL. GC-MS studies show that the benzyne intermediate does not abstract a hydrogen atom or proton from the PhosIL to form 3-methylbiphenyl. An added benefit for this system is the high heat capacity of PhosIL; therefore it is not necessary

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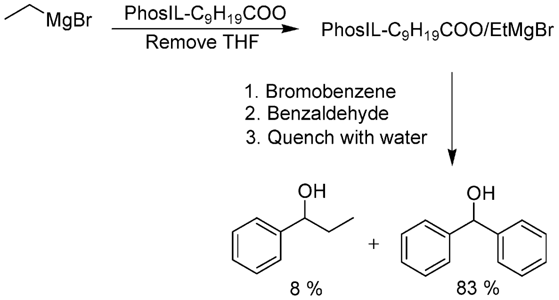
**SCHEME 4. Halogen/Magnesium Exchange Reaction between Ethylmagnesium Bromide and Bromobenzene in PhosIL-$C_9H_{19}COO$**



to cool the reaction solutions to the low temperatures often required for ethereal solutions.

The addition of water and hexanes to the reaction mixtures, as described above, results in the formation of a three-phase system, with the organic layer on top, ionic liquid in the middle, and the aqueous layer on the bottom. The products were isolated from the organic layer and analyzed by GC-MS. In some cases, the low yields reported in Scheme 3 reflect partitioning between the ionic liquid and the organic phase. Isolated yields can be markedly improved by successive extractions. Alternatively, in some cases, due to the high thermal stability of the PhosIL and the volatility of the products, distillation could be used to remove the products from the reaction mixtures. In all cases, PhosIL-$C_9H_{19}COO$ can be washed with water and hexanes, dried, and re-used, demonstrating the potential of these solvents to participate in recyclable, "green" processes.

Halogen/magnesium exchange reactions (Scheme 4) were also carried out in PhosIL-$C_9H_{19}COO$. For example, ethylmagnesium bromide in THF was added to cold PhosIL-$C_9H_{19}COO$ and the THF was removed under vacuum. Bromobenzene was added and the solution was stirred for 6 h. To probe the Mg/Br exchange reaction, benzaldehyde was then added and the mixture was stirred for an additional 16 h. Following an aqueous quench and extraction with dichloromethane, diphenylmethanol was obtained in 83% yield. A very small amount of 1-phenylpropan-1-ol (8%) was also obtained due to incomplete halogen/magnesium exchange reactions.

Halogen/magnesium exchange reactions appear to occur readily in PhosIL. A recent report on highly efficient reagents for Br/Mg exchange sheds some light on this kind of reaction.[51] It now appears likely that the highly polar (i.e., discrete ions) PhosIL media may stabilize polar "ate" complexes and, hence, also facilitate both the metal exchange reaction and increase the reactivity of the PhosIL/Grignard reagent solutions. The formation of the "ate" complex, although speculative, is consistent with both the Lewis acidity of diorganomagnesium species, reactivity studies, and the computational studies reported in the following section.

**A Computational Study on the Complexation of Arylmagnesium Species with $RCOO^-$.** As we reported recently, the reactivity of Grignard reagents in molecular and ionic liquids solvents is dramatically different. In molecular solvents Grignard reagents react dominantly as nucleophiles, whereas in ionic solvents electron-transfer reactions are preferred.[50] Recall that Grignard solutions are complex mixtures, with ArMgX, $Ar_2Mg$, and $MgX_2$ all possible species in solution. During our recent studies, evidence was obtained that suggested that the Schlenk equilibrium was strongly shifted so that in ionic liquid solvent $Ph_2Mg$ was the dominant species, whereas in molecular solvent PhMgBr was present in significant amounts.[50] With these results in hand we decided to probe computationally the complexation of $Ph_2Mg$ with carboxylate anions to appreciate more fully the structure of the apparently dominant species in solutions of Grignard reagents in PhosIL.

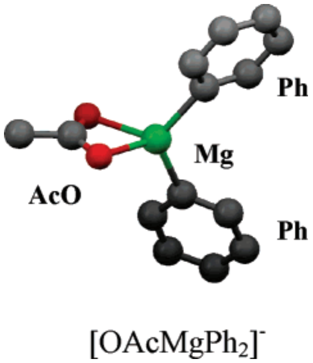


**FIGURE 4.** Calculated lowest energy structures for the reaction of diphenylmagnesium/acetate complex [$Ph_2Mg{-}O_2CCH_3$]. The net energy released for this reaction is 303 kJ/mol.

Calculations on the interactions of arylmagnesium species with acetate ions (as a model for decanoate) were performed. Computations were carried out on the individual components of the reaction mixtures, specifically diphenylmagnesium, acetate, phenylmagnesium bromide, and related complexes. The computational studies indicate that diphenylmagnesium prefers the twisted $D_{2d}$ form, although it should be noted that the barrier to rotation about the C−Mg−C axis to give the $D_{2h}$ transition structure is less than 3 kJ/mol, and is clearly likely to occur at room temperature. The calculated Mg−C bond length is 2.098 Å. The barrier to C−C rotation in the acetate ion ($AcO^-$) is much smaller, 0.05 kJ/mol, and neither of the two structures is clearly preferred. The C−O distance was calculated to be 1.234 Å. The barrier to phenyl rotation in the phenylmagnesium bromide−acetate complex is estimated to be 10 kJ/mol. For details of calculations consult the Experimental Section.

The binding of the first acetate to diphenylmagnesium is highly exothermic, at ca. $\Delta H = -303$ kJ/mol. The structure of this complex, shown in Figure 4, featuring a bidentate acetate ion, exhibits two Mg···O interactions (2.120 Å). This evidently makes the magnesium metal formally tetracoordinate, as perhaps is anticipated for a magnesium center. Note, also, that the second acetate binds *endothermically* with a value estimated to be $\Delta H = 120$ kJ/mol.

We propose that the strong interaction between the Mg center and the anion of the ionic liquid may be required for the stability of the solution and hence may suggest a reason for the apparent decomposition of the PhosIL/Grignard solution where the counterion is bis(trifluoromethylsulfonyl)imide or chloride. These anions are notoriously nonbasic and a weakly coordinating anion and, hence, may not stabilize $Ph_2Mg$ in ionic liquid solution.

**PhosIL and Neutral Bases of Interest to Organometallic Chemistry.** Some of the most basic neutral ligands are the carbenes with $pK_a$ values in the range of 22 to 24.[52,53] Highly basic solutions containing NHCs dissolved in PhosIL can be prepared by mixing the NHC with the PhosIL in the presence

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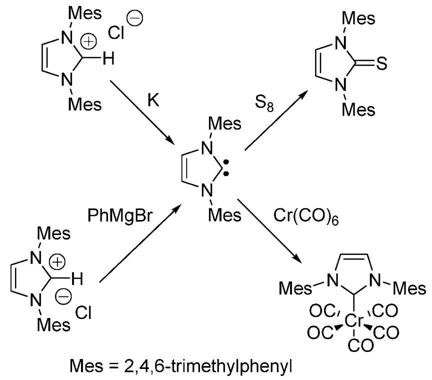
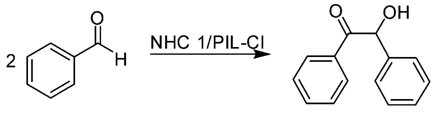
**SCHEME 5. Preparation and Reactivity of the Carbene 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (NHC 1), Synthesized in PhosIL-Cl**



**SCHEME 6. Benzoin Condensation of Benzaldehyde Catalyzed by NHC 1 in PhosIL-Cl**



of several drops of benzene, toluene, or THF. The addition of the cosolvent facilitates dissolution of the NHC, after which the cosolvent can be removed under vacuum with no observable effect on the stability of the resulting solution. Other strong neutral Lewis bases, such as triphenylphosphine and *tert*-butylisocyanide, were examined and were found by IR spectroscopic studies to be persistent in PhosIL.

Although difficulties were encountered during the attempted synthesis of Grignard reagents in PhosIL, the carbene 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (NHC 1**)** was readily synthesized by two different routes in PhosIL: (1) by reduction of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride using metallic potassium[45] and (2) by the treatment of the aforementioned imidazolium chloride with PhMgBr dissolved in a PhosIL (Scheme 5). Imidazolium ions labeled at the carbeneic carbons with $^{13}$C were used to provide unambiguous evidence for the formation of NHC 1 by the observation of the $^{13}$C NMR signal for the carbeneic carbon at 216 ppm. Further evidence was supplied by reactivity studies (see below). The PhosIL/NHC solutions are viscous and light brown in color. Surprisingly, these basic solutions are stable in excess of 1 month and are active for organic transformations. For example, NHC 1 in PhosIL catalyzes the benzoin condensation of benzaldehyde in 40% yield as shown in Scheme 6.[54]

The stability of the NHC in PhosIL was tested by surveying some well-established NHC chemistry with the *p*-block[55] and the *d*-block elements (Scheme 5). The products of these reactions were characterized in PhosIL-Cl using analytical techniques such as NMR, IR, and GC/MS. The NHC 1 solutions prepared in PhosIL-Cl behave as normal NHC solutions. Treatment of NHC 1 with $S_8$ produces 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-thione as indicated by $^{13}$C NMR spectroscopy and mass spectrometry ($m + 1 = 336.3$ amu).[56] NHCs coordinated to transition metal sites have attracted interest in catalysis, so the reactivity of NHC 1 in PhosIL-Cl was illustrated by reacting the solution with $Cr(CO)_6$. Displacement of one carbonyl occurs to afford IMesCr$(CO)_5$ as identified by IR spectroscopy.

**SCHEME 7. Kumada-Corriu Cross-Coupling Reaction in PhosIL-$C_9H_{19}$COO**

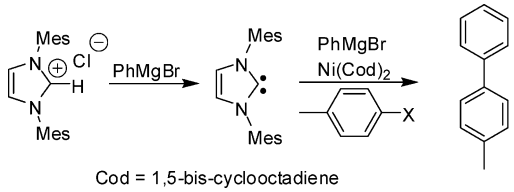
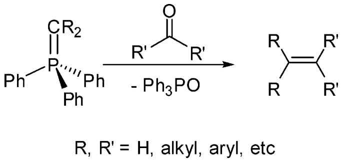


**TABLE 1. Coupling of Aryl-Grignard Reagents with Aryl Halides in the Presence of a Ni(0) Complex of NHC 1 in PhosIL-$C_9H_{19}$COO**

| aryl halide | MePh-Ph (%) | $Me_2Ph_2$ (%) |
|---|---|---|
| 4-fluorotoluene | 42 | 0 |
| 4-chlorotoluene | 88 | 0 |
| 4-bromotoluene | 73 | 25 |
| 4-iodotoluene | 74 | 22 |

**SCHEME 8. Reaction of the Wittig Reagent with Carbonyl Compounds To Form an Alkene**



The Kumuda−Corriu reaction was examined to illustrate the ability of Grignard reagents in PhosIL-$C_9H_{19}$COO to support carbene reactions. These reactions involve the coupling of aryl-Grignard reagents with aryl halides in the presence of a Ni(0) complex of NHC 1, as shown in Scheme 7.[57] The coupling reaction proceeds with high yield for 4-bromotoluene and 4-iodotoluene, although halogen/magnesium exchange reactions also occur with concomitant generation of ca. 25% 4,4′-dimethylbiphenyl as shown in Table 1. The reaction works best for chlorotoluene, and surprisingly even facilitates C−F bond activation in modest yield. The activation of C−F bonds is of great current interest as they are perhaps one of the most challenging bonds to activate.[58]

**Generation and Use of Wittig Reagents in PhosIL.** Synthetically, one of the most valuable classes of *carbon-based* nucleophiles are the phosphoranes, also known as Wittig reagents.[59] These molecules react readily with aldehydes and ketones to produce C−C double bonds (Scheme 8), from which other important reactions proceed. Wittig reagents, ranging from weakly basic, “stabilized” ylides (p$K_a$ of the conjugate acid ca. 8−11) to highly basic derivatives (p$K_a$ of $[Ph_3P-CH_3]$ ca. 22.5 in DMSO), are available, but their *generation* in ILs has not been reported.[60]

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**TABLE 2. Wittig Reactions in PhosIL-$C_9H_{19}COO^a$**

| PhosIL and base | Wittig precursor | RR′C=O | alkene | yield (%) |
|---|---|---|---|---|
| PhosIL-$C_9H_{19}COO$/PhMgBr | $[Ph_3PCH_2CH_3][Br]$ | benzaldehyde | PhCH=CHCH$_3$ | 96 |
| PhosIL-$C_9H_{19}COO$ + KOBu$^t$ | $[Ph_3PCH_2CH_3][Br]$ | benzaldehyde | PhCH=CHCH$_3$ | 88 |
| PhosIL-$C_9H_{19}COO$/PhMgBr | $[Ph_3PCH_3][Br]$ | benzaldehyde | PhCH=CH$_2$ | 86 |
| PhosIL-$C_9H_{19}COO$ + KOBu$^t$ | $[Ph_3PCH_3][Br]$ | benzaldehyde | PhCH=CH$_2$ | 94 |

[a] The yields reported for PhCH=CHCH$_3$ include both *E*/*Z* isomers.

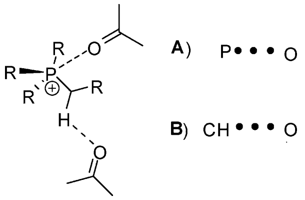

**FIGURE 5.** Possible interactions between a phosphonium ion and a carbonyl compound: (A) interaction between the quaternary phosphonium ion and oxygen of the carbonyl and (B) hydrogen bonding.

Generation of Wittig reagents was found to be feasible in PhosIL without observable decomposition of the solvent. For example, $[Ph_3PCH_2CH_3]^+[Br]^-$ can be deprotonated by PhosIL-$C_9H_{19}COO$/PhMgBr solutions or other bases such as potassium *tert*-butoxide suspended in PhosIL-$C_9H_{19}COO$ to form the nonstabilized phosphorane $Ph_3P{=}CHCH_3$. The product was identified by the appearance of a distinctive $^{31}P\{^1H\}$ resonance at 15 ppm.[61] A similar resonance is observed for samples of pure $Ph_3P{=}CHCH_3$ *dissolved* in PhosIL-$C_9H_{19}COO$. The resulting ylide is synthetically useful, and was used in Wittig reactions with aldehydes and ketones to generate an alkene as shown in Table 2. The byproduct of Wittig reactions is triphenylphosphine oxide, which was obtained as a white residue after the reaction, and was characterized by mass spectrometry ($M^+ = 278$ amu).

**Interaction of PhosIL with Basic Reagents.** Phosphonium ions have been used as catalysts in several reaction types[62,63] including phase transfer catalysis,[64,65] and quarternary phosphonium cations have been reported to activate carbonyl compounds.[66] It seems probable that this catalytic activity arises from interactions between the cation and basic substrates. To probe this interaction, some simple experiments were performed.

There are two probable types of interaction between the solute (carbonyl compound) and the solvent (phosphonium cation) (Figure 5), namely coordination to the quaternary cationic phosphorus site through a [P···O] interaction (Mode A) or through hydrogen bonding to the hydrogen α to the phosphonium cation [C−H···O] (Mode B).

The existence of [P···O] coordination would be consistent with the well-known strength of the P−O bond but formation of this interaction would be accompanied by a reorganization of the P-coordination sphere to a crowded, distorted, trigonal bipyramidal geometry, which should cause significant changes to the $^{31}P$ NMR spectrum. To probe the association between the ionic solvent and solute molecules, NMR titration experiments were performed. It was found that the addition of carbonyl compounds, such as benzaldehyde or propionaldehyde, to PhosIL-Cl had little effect on the $^{31}P$ NMR spectrum. This result, although not conclusive, suggests that the local coordination sphere of the phosphorus site has not been affected. Note that the interaction would be dynamic, but even in dynamic systems, such a change should be observable even as a small movement of the $^{31}P$ NMR resonance.

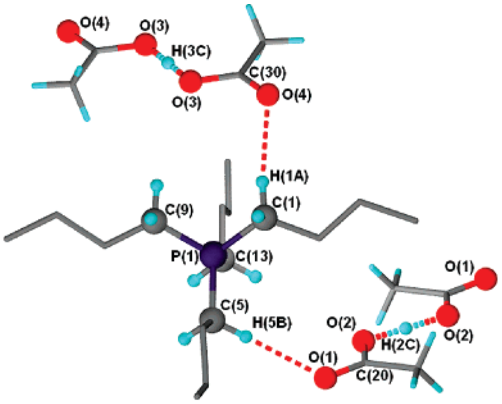

**FIGURE 6.** X-ray structure of tetrabutyl phosphonium acetate monoacetic acid. Selected bond lengths (Å) and angles (deg): O(1)−C(20) 1.229(2), O(2)−C(20) 1.286(3), O(3)−C(30) 1.287(2), O(4)−C(30) 1.235(2), O(2)···H(2C) 1.2245(14), O(2)···O(2) 2.449(3), O(3)···H(3C) 1.2256(14), O(3)···O(3) 2.451(3), O(1)···H(5B) 2.388, O(1)···C(5) 3.377, O(4)···H(1A) 2.452, O(4)···C(1) 3.437; O(2)···H(2C)···O(2) 180.00(15), O(3)···H(3C)···O(3) 180.00(15), C(5)−H(5B)···O(1) 178.25, C(1)−H(1A)···O(4) 173.19.

More interestingly, $^1H$ NMR studies indicate a *downfield* shift of the proton α to the phosphorus with increased concentration of the carbonyl compound. This observation suggests that the mode of association between solute and solvent likely involves a hydrogen bonding interaction, consistent with Mode B coordination. The shortest reported [cation···anion] contact for a phosphonium ion, as determined by a survey of the Cambridge crystallographic database, was a [C−H···O] hydrogen bond (1.935(5) Å) reported for the simple phenoxide salt $[Ph_3PCH_3]$-$[2,6\text{-}Ph_2C_6H_3O]$.[67] The aforementioned salt is not a good model for the systems under investigation, due to the differences between arylphosphonium and alkylphosphonium cations, and hence a crystalline sample of a salt composed of tetrabutylphosphonium acetate monoacetic acid was produced, as shown in Figure 6.

X-ray crystallographic studies revealed the expected tetrahedral phosphonium cation. The anion, however, is more interesting: the acetate and acetic acid fragments are indistinguishable, with a proton present at 50% occupancy on both O(2) and O(3). This proton is located equidistant between the

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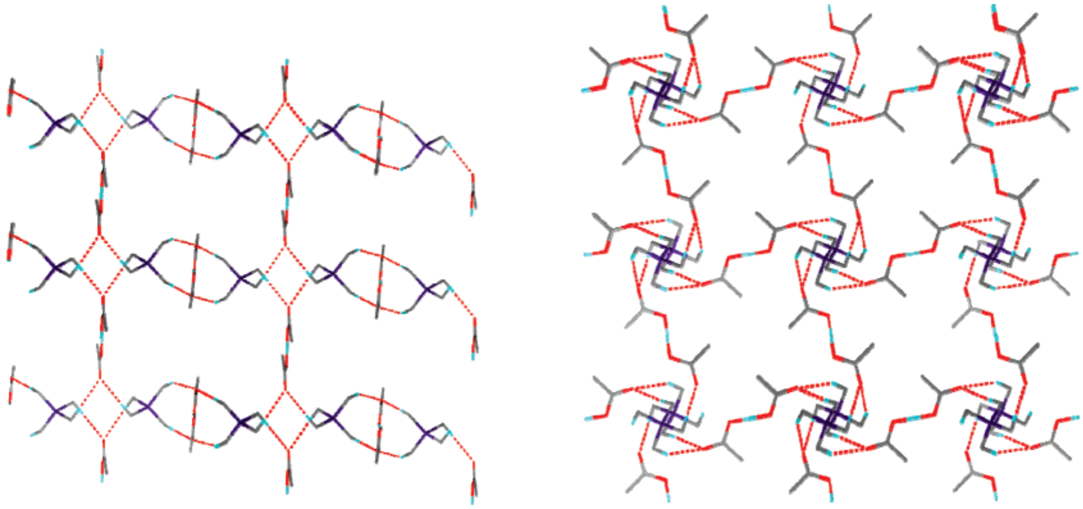

**FIGURE 7.** Three-dimensional network formed by [O−H···O] and [C−H···O] hydrogen bonds, viewed along the crystallographic *b* and *c* axes, respectively. For clarity, only the α carbon and hydrogens of each butyl are shown.

symmetry related C−O oxygen atoms, forming a strong[68] O−H···O hydrogen bond as shown in Figure 6. The C═O oxygen atoms each form a weak [C−H···O] hydrogen bond to the hydrogen α to the phosphonium cation, consistent with a Mode B interaction, as described above. Upon examination of the extended structure (Figure 7), it became apparent that all four alkyl chains are involved in this type of hydrogen bonding. This leads to the formation of an extensive three-dimensional, hydrogen-bonded network.

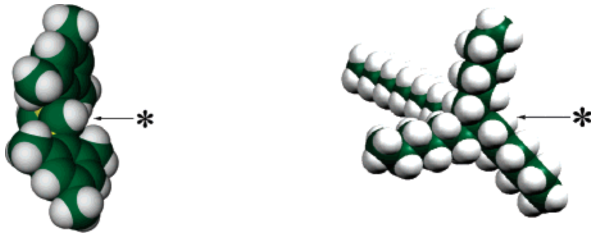

**FIGURE 8.** Space-filling diagram of 1,3-bis(2,4,6-trimethylphenyl)-imidazolium ion (left) and tetradecyl(trihexyl)phosphonium ion (right). Highlighted (*) are the reactive C−H fragments of the ions.

**Deprotonation and Proton Exchange: Occurrence and Reasoning.** Two, often competing, reactions can result in the decomposition of solvents, and of importance to this paper, to the decomposition of ions. These reactions are deprotonation reactions and electron-transfer reactions. It was initially thought that the hydrogen sites in the PhosIL were resistant to deprotonation, and a simple test was performed to examine this hypothesis. A solution of the PhosIL was prepared by dissolving a few drops of 50/50 $D_2O$ in ethanol-*d* containing a small amount of NaOD. Over a period of days, the $^1H$ signal for the α-$CH_2$ protons (ca. 2.3 ppm) decreased relative to the nonexchangeable protons on the PhosIL. This indicates that the resistance to deprotonation of the PhosIL is couched in terms *other than* the acidity of the $CH_2$ groups. This experiment clearly indicates that the proton on the phosphonium ion, although crowded, and contrary to our first expectation,[43] is indeed accessible by small bases.

There also appear to be steric reasons why deprotonation reactions occur more readily in ImILs than in PhosIL. The imidazolium ring is rigid whereas the alkyl chains on the phosphonium ions are flexible and thus provide more protection to the reactive proton. As shown in the space-filling diagram of 1,3-bis(2,4,6-trimethylphenyl)imidazolium ion (Figure 8, left) and tetradecyl(trihexyl)phosphonium ion (Figure 8, right), it is difficult to sterically shield the carbeneic site in the imidazolium ion, whereas in the tetradecyl(trihexyl)phosphonium ion there is considerable steric congestion and flexibility and hence the *access* to the reactive C−H site is diminished, although possible for small bases as observed for hydroxide.

The inertness of PhosIL toward reactions of bases therefore appears to have primarily a kinetic basis and for Grignards in the IL, it is largely anion dependent. For example, cosolvent-free solutions of Grignard reagents dissolved in ILs are persistent with O-donor anions, such as decanoate, whereas chloride and bistriflamide appear to be insufficiently strong enough bases to stabilize the metal-containing species in solution. Although it would be reasonable to expect that deprotonation of a phosphonium ion to produce phosphorane and a salt would be thermodynamically favored, evidence of this reaction was not observed with these bases. In the case of poor donor anions, such as chloride, when the cosolvent THF is stripped away, an electron-transfer reaction occurs producing phosphines and alkenes as products rather than the phosphorane. In IL solution where the Grignard reagent is persistent, such as in a decanoate solution, a bulky complex is formed between $Ph_2Mg$ and decanoate, an ion that possesses substantial steric bulk. This anion may not have access to the reactive protic site on PhosIL and hence bases such as Grignard reagents dissolved in PhosIL fail to react with the phosphonium component. Further support for this kinetic argument is provided by noting that $[Ph_3PCH_2CH_3]^+[Br]^-$ is deprotonated to form a phosphorane by PhosIL-$C_9H_{19}COO$/PhMgBr solutions or other bases such as potassium *tert*-butoxide, as shown by $^{31}P\{^1H\}$ NMR studies. These solutions exhibit a single $^{31}P\{^1H\}$ resonance at 15 ppm, consistent with the presence of $Ph_3P{=}CH(CH_3)$,[69] and also consistent with a known sample of the phosphorane dissolved in the phosphonium-based ionic liquid. In other words, for phosphonium ions, small bases are susceptible to reacting with

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**TABLE 3. Reduction Potential of 1.5 mM Imidazolium Ions and Phosphonium Ions Measured by Using a Platinum Working Electrode in DMSO (Scan Rates = 300 mV s$^{-1}$), Pt Coil Counter Electrode, and Ag/AgCl Reference Electrode**

| salt | reduction potential (V) |
|---|---|
| 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride | −2.23 |
| 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride | −2.28 |
| tetraethylphosphonium bromide | −2.06 |
| tetradecyl(trihexyl)phosphonium decanoate (PhosIL-$C_9H_{19}COO$) | −2.82 |
| tetradecyl(trihexyl)phosphonium chloride (PhosIL-Cl) | −2.93 |
| tetra-*n*-octylphosphonium bromide | −3.70 |

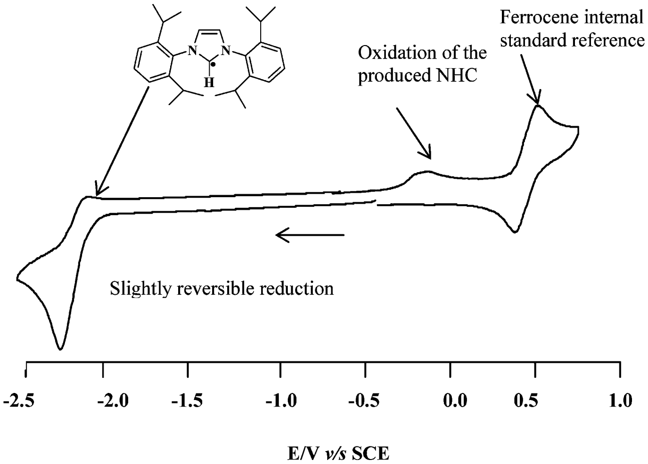

**FIGURE 9.** Cyclic voltammogram of 1,3-bis(2,6-diisopropylphenyl)-imidazolium chloride (1.66 mM) referenced to ferrocene/ferrocenium redox couple (internal standard) taken to be 0.475 vs SCE.

the PhosIL through deprotonation reactions whereas large bases are resistant to this reaction.

Thus, the inertness of the phosphonium cations in the PhosIL-Grignard solutions appears to have manifold reasons/causes. First of all, and most obvious is the bulky and flexible nature of the cation, which limits approach from external bases to the eight acidic hydrogen sites. Second, the bases, namely a decanoate complex of $Ph_2Mg$, is itself bulky and has difficulty approaching the α-hydrogen atoms of the phosphonium cation. Furthermore, the phosphonium ions are electron precise, i.e., eight electrons in four $\sigma$ bonds, and hence are more electrochemically robust than the unsaturated ions, specifically imidazolium ions. From a steric (kinetic) point of view, the acidic $C_2$ hydrogen is chemically more accessible than the phosphonium C−H. It also engages in electrochemical reactions that *appear* to be deprotonation reactions. These three features, the bulky tetrahedral cation, the bulky anion, and its electrochemical robustness, all collude to minimize detrimental side reactions from occurring in basic PhosIL solutions.

**Electrochemical Comparison of ImILs and Phosphonium Ions.** As shown by reactivity studies, phosphonium ionic liquids are more robust than ImILs toward bases and certain reducing agents and the difference in reactivity can be explained by the reduction potential of the ILs. Cyclic voltammetry of imidazolium and phosphonium salts has been studied before.[70,71] Reported here is the comparison of the reduction potentials of imidazolium salts and phosphonium salts with different lengths of alkyl chains. The cyclic voltammograms (CVs) using standard concentrations (1.5 mM) of the imidazolium and phosphonium salts in anhydrous and anoxic DMSO were carried out versus a standard calomel electrode (SCE) at 300 mV s$^{-1}$ with ferrocene as internal reference.

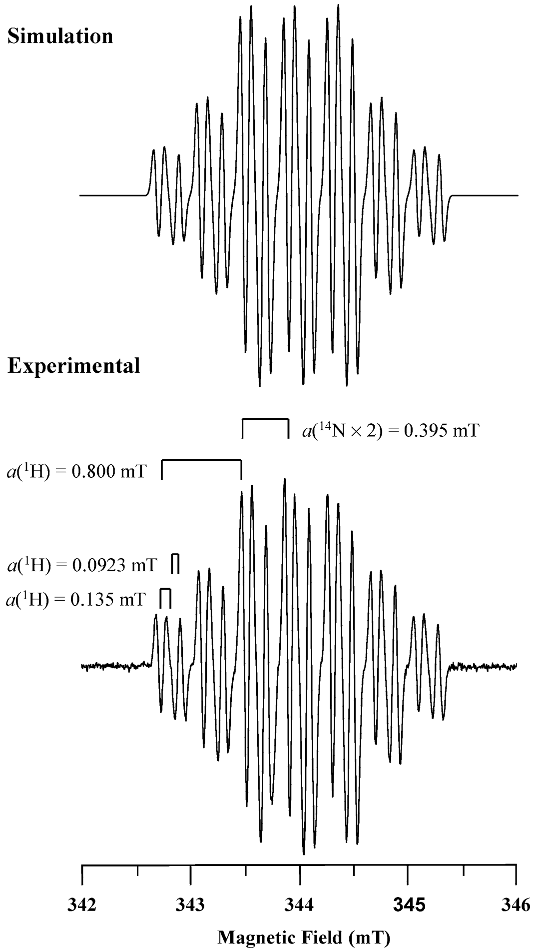

**FIGURE 10.** Experimental (bottom) and simulated (top) EPR spectra of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene neutral radical intermediate produced by reductive electrolysis: −2.3 V vs SCE of 1.66 mg/mL solution of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride in acetonitrile/0.1 M tetrabutylammonium hexafluorophosphate. Experimental spectral parameters: $\nu = 9.71$ GHz, scan time = 21 s, time constant = 5.12 ms, modulation amplitude = 0.05 mT, receiver gain = $2 \times 10^5$, average of 50 scans. Simulation parameters: $a(^{14}N \times 2) = 0.395$ mT, $a(^{1}H) = 0.800$ mT, $a(^{1}H) = 0.135$ mT, $a(^{1}H) = 0.0923$ mT, line width = 0.05 mT.

It was observed that the reduction of imidazolium salts generally occurs at a less negative potential than that of phosphonium salts and phosphonium salts possessing longer alkyl chains are harder to reduce. For example, tetra-*n*-octylphosphonium bromide has a more negative potential ($Ep_{red} = -3.70$ V) compared to tetradecyl(trihexyl)phosphonium chloride ($Ep_{red} = -2.93$ V) as shown in Table 3. Hence, since phosphonium ions have a higher reduction potential compared to ImILs, reduction of imidazolium salts using potassium metal can be carried out in PhosIL without decomposition of PhosIL. It is important to note that there is no reaction between the PhosIL and elemental potassium.

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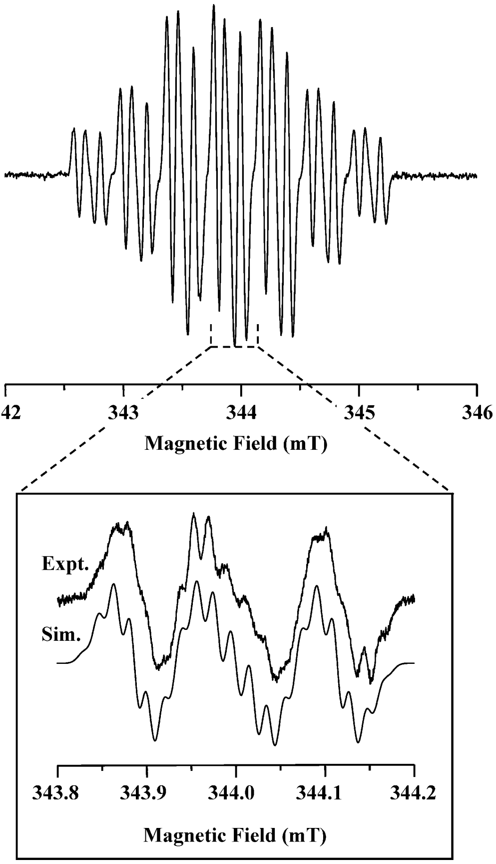

**FIGURE 11.** Close up of the central triplet in the EPR spectrum of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene neutral radical intermediate showing coupling with the phenyl hydrogens. Experimental spectral parameters: $\nu = 9.71$ GHz, scan time = 10.5 s, time constant = 5.12 ms, modulation amplitude = 0.01 mT, receiver gain = $2 \times 10^5$, average of 100 scans. Simulation parameters: $a(^1H) = 0.135$ mT, $a(^1H) = 0.0923$ mT, $a(^1H \times 2) = 0.021$ mT, $a(^1H \times 4) = 0.015$ mT, line width = 0.015 mT.

A qualitative coulometric analysis was obtained by comparing the peak currents of the ferrocene redox couple to the imidazolium cation reduction peak and this suggests that the reduction is a one-electron process. It is postulated that a neutral radical intermediate formed, which then collapsed to give the NHCs. Cyclic voltammetry and EPR studies were used to aid in the structural assignment of the radical intermediate.

CV studies of different imidazolium salts were carried out and it was observed that the reduction of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride was slightly reversible (Figure 9), suggesting that the radical formed has a longer lifetime compared to those of other imidazolium salts, which allowed for EPR studies.

A sample of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride was electrolyzed by applying a potential of −2.3 V for 5 min in acetonitrile (1.66 mM) under an inert atmosphere, with reference to a standard calomel electrode. The acetonitrile solution was then rapidly transferred to a quartz flat cell and the EPR spectrum was measured.

The main 21-line spectrum, shown in Figure 10, was reproduced very accurately by simulation and demonstrates that the electrochemically generated species contains radical-spin coupling to two equivalent nitrogen atoms ($^{14}N$, $I = 1$) and three inequivalent hydrogen atoms ($^1H$, $I = {}^1/_2$). The hyperfine couplings (mT) measured were as follows: $a(^{14}N \times 2) = 0.395$, $a(^1H) = 0.800$, $a(^1H) = 0.093$, and $a(^1H) = 0.137$. The $^{14}N$ couplings are from the ring nitrogen atoms and the largest $^1H$ coupling is assigned to the proton on $C_2$, the primary site of unpaired electron density. The two smaller proton couplings are assigned to the allylic protons on $C_4$ and $C_5$. Their distinct hyperfine couplings are consistent with nonplanarity of the ring due in large part to pyramidalization at the primary radical center. Overall, these observations show that the bulk of the electron density is positioned on the $C_2$-carbeneic carbon with delocalization onto the neighboring nitrogen heteroatoms and minor density on the backbone of the imidazole, thus consistent with the presence of the 1,3-bis(2,6-diisopropylphenyl)imidazolyl radical. Comparable results were obtained in a previous study where similar carbene reagents were reacted with muonium, $\mu$, a lighter “isotope” of hydrogen, to generate the neutral radical.[72] As shown in Figure 11, further resolution of the main EPR lines is possible. Simulation of this hyperfine structure shows couplings to 4 protons with $a(^1H) = 0.015$ mT and 2 with $a(^1H) = 0.021$ mT consistent with spin delocalization onto the phenyl rings of the diisopropylphenyl groups, and on the basis of the number of each type of proton these are assigned to the meta and para positions, respectively. The quality of the EPR data allow us to say with certainty that the species initially produced from the electrochemical reaction is the 1,3-diarylimidazolyl radical. We note that Nehta previously reported the formation of 1,3-dialkylimidazolyl radicals during the pulse radiolysis of ionic liquids and detected them by transient absorption spectroscopy (UV).[73]

## Conclusions

In this report it has been shown that some strongly basic carbon-centered reagents are compatible with PhosILs. Ether-free solutions of Grignard reagents can be prepared in PhosIL and they are stable for over 1 month at room temperature under an inert atmosphere with no observable decomposition. These Grignard solutions in PhosIL behave as normal Grignard reagents, i.e., undergo addition reaction to carbonyls. As well, 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride, which has a less negative potential than PhosIL, can be synthesized by reduction as well as deprotonation in PhosIL, and these solutions are persistent. The carbenes dissolved in the PhosIL can be used to prepare complexes of both main group and transition metals. Wittig reagents were also synthesized in the PhosIL and reacted with carbonyl compounds to make alkenes without any decomposition of the ionic liquid. These observations open up the use of PhosIL as a reliable reaction media for a wide variety of basic reagents. The problems associated with C−H activation in imidazolium ions by highly reactive bases are not observed for the PhosIL. Finally, a radical derived from the reduction of an imidazolium ion was detected and characterized by EPR spectroscopy.

In any solvent, there are two reactions one must be concerned with: the first is deprotonation and the second electron transfer. In the case of a PhosIL, a phosphorane (or Wittig reagent) would be the product of deprotonation and for an ImIL, a carbene. With respect to electron transfer, a phosphoryl or imidozyl radical would be expected dependent on the choice of IL; however, these are both reactive and thus transient. The absence

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of phosphoranes and phosphoryl in the PhosILs indicates that they are a suitable choice as solvent for strongly basic, carbon-centered reagents.

## Experimental Section

**1. General Experimental Procedures.** The experimental procedures are described in the Supporting Information.

**2. Synthetic Procedures. 2.1 Purification of Phosphonium Ionic Liquids.** Saturated aqueous sodium hydrogen carbonate (20 mL) was added to the PhosIL (120 mL) and the solution was stirred for 15 min. Vigorous foaming occurred. The solution was then washed with water (500 mL). The ionic liquid layer obtained was extracted using hexane (120 mL) and water (120 mL) in 3 × 40 mL aliquots. The ionic liquid was then dried by azeotropic distillation using toluene (20 mL), followed by exhaustive evacuation. $^{1}$H NMR spectroscopy showed the absence of water in the ionic liquid and $^{31}$P NMR spectroscopy (single peak at 33 ppm) showed the presence of only one type of phosphorus site and no residual phosphines present.

**2.2. Preparation of Stock Solutions of Ethereal Grignards in PhosIL-Cl.** Stock solutions of reaction media comprising Grignard reagents in PhosIL-Cl were prepared by mixing commercially available ethereal (i.e., in diethyl ether, tetrahydrofuran, etc.) solutions of Grignard reagents with PhosIL. Five milliliters of PhMgBr (1 M in THF) was added dropwise to 5 mL of PhosIL-Cl under an atmosphere of nitrogen and the solution was cooled at −78 °C. Ethereal solutions of Grignard reagents dissolved in PhosIL-Cl are air and moisture sensitive. These solutions show no significant sign of degradation after 1 month as shown by reactivity studies; however, upon complete removal of THF, decomposition of the phosphonium is observed.

**2.3. Reaction of PhosIL-Cl/Grignard with Bromine.** To an aliquot (5 mL) of 1-month-old 1 M PhosIL-Cl/Grignard reagent solution was added 1 equiv of $Br_2$ and the mixture was stirred for 1 h. The reaction was quenched with water (20 mL) and extracted with hexanes (20 mL). The extract was analyzed by GC-MS and the formation of phenylbromide was observed in addition to a small amount (5%) of biphenyl. Benzene was not detected indicating little degradation of the PhosIL-Cl/Grignard reagent solution.

**2.4. Generation of an Ether-Free Solution Composed of a Grignard Reagent Dissolved in PhosIL-$C_9H_{19}$COO.** To PhosIL-$C_9H_{19}$COO (5 mL) with a few drops of THF was added commercially available 1 M PhMgBr (5.0 mL) in THF at −78 °C. The mixture was stirred and warmed to room temperature. Tetrahydrofuran was removed in vacuo leaving a viscous pale yellow or orange solution to which a few drops of hexanes was added to reduce viscosity. Treatment of this solution with 1 equiv of either bromine or *N,N′*-dimethylformamide followed by quenching with saturated aqueous ammonium chloride and addition of water, followed by extraction with dichloromethane resulted in the formation of bromobenzene (98%) and benzaldehyde (99%), respectively, as determined by GC-MS studies.

**2.5. Addition Reaction of Grignard Reagents in PhosIL-$C_9H_{19}$COO.** A stock solution of 1 M PhosIL-$C_9H_{19}$COO and PhMgBr was prepared by mixing equal volumes of commercially available 1.0 M PhMgBr in THF with the ionic liquid, followed by removal of the THF under vacuum. Aliquots (5 mL) of the PhosIL-$C_9H_{19}$COO/Grignard reagent solution were treated with 1 equiv of reagents (e.g., aldehydes, ketone, DMF, etc.). The solutions were stirred under $N_2$ for 1−3 h. The reaction mixtures were quenched with saturated aqueous ammonium chloride (2 mL) followed by the addition of water (25 mL). Hexanes (20 mL) were added to establish a three-phase system and the products were extracted into the hexanes layer. Products were identified using NMR spectroscopy and the extracts were analyzed by GC-MS studies. Yields are reported in Scheme 3.

**2.6. Stability of Triphenylphosphine in PhosIL-Cl.** Triphenylphosphine (0.20 g, 0.76 mmol) was dissolved in PhosIL-Cl (2 mL) to give a clear colorless solution. This stability of triphenylphosphine in PhosIL-Cl was analyzed by $^{31}$P NMR (162 MHz): $\delta$ −4.8. The same chemical shift was observed after 2 months consistent with $^{31}$P NMR of triphenylphosphine in $CDCl_3$: $\delta$ −4.9.

**2.7. Stability of *tert*-Butylisocyanide in PhosIL-Cl.** A few drops of *tert*-butylisocyanide was added to PhosIL-Cl, and an IR study was carried out on the mixture. No degradation was observed (1 month) as indicated by the presence of a diagnostic stretch at 2133 (vs) ($N\equiv C$).

**2.8. Preparation of a Solution of 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, NHC 1, in PhosIL-Cl.** 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, NHC 1 (0.20 g, 0.66 mmol), was dissolved in PhosIL-Cl (2 mL) with the addition of toluene drops to aid the dissolution of the NHC. The toluene was then removed under vacuum. $^{1}$H NMR (THF-$d_8$, 400 MHz) $\delta$ 2.02 (s, 12 H), 2.30 (s, 6 H), 6.94 (s, 4 H), 7.04 (s, 2 H); $^{13}$C NMR (THF-$d_8$, 101 MHz) $\delta$ 18.0 (s,), 21.0 (s), 121.3 (s), 129.7 (s), 135.7 (s), 137.6 (s), 139.7 (s), 219.7 (s).

**2.9. Reduction of 1,3-Bis(2,4,6-trimethylphenyl)imidazolium Chloride with Potassium in PhosIL-Cl To Give 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, NHC 1.** 1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride[74] (2.00 g, 5.87 mmol) and an excess of potassium metal (0.35 g, 8.75 mmol), previously washed with anhydrous THF, were added to PhosIL-Cl (10 mL). The reaction mixture was heated at 80 °C under nitrogen for 24 h. Hexanes (10 mL) were added to the resulting suspension and the solution was filtered through Celite to remove the side product, potassium chloride. Evaporation to remove hexanes gave a reddish brown viscous residue that was characterized as a solution of PhosIL-Cl and NHC 1. $^{1}$H NMR (THF-$d_8$, 400 MHz) $\delta$ 2.08 (s, 12 H), 2.31 (s, 6 H), 6.96 (s, 4 H), 7.14 (s, 2 H); $^{13}$C NMR (THF-$d_8$, 101 MHz) $\delta$ 18.6 (s), 21.6 (s), 122.1 (s), 129.8 (s), 136.2 (s), 138.2 (s), 139.9 (s), 215.8 (s). These spectroscopic data are consistent with NHC 1 dissolved in PhosIL-Cl.

**2.10. Reaction of $^{13}$C-Labeled 1,3-Bis(2,4,6-trimethylphenyl)imidazolium Chloride with Phenylmagnesium Bromide in PhosIL-Cl.** 1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride (0.10 g, 0.29 mmol) was added to PhosIL-Cl (2 mL) to afford a creamy suspension to which 1.0 M PhMgBr (0.35 mL, 0.29 mmol) was added dropwise with stirring. The mixture turned to a clear yellow solution after being stirred for 15 min. $^{1}$H NMR (THF-$d_8$, 400 MHz) $\delta$ 2.18 (s, 12 H), 2.41 (s, 6 H), 7.15 (s, 4 H), 7.41 (s, 2 H); $^{13}$C NMR (THF-$d_8$, 101 MHz) $\delta$ 15.8 (s,), 21.3 (s), 130.2 (s), 130.6 (s), 136.9 (s), 137.1 (s), 143.6 (s), 219.7 (s). These spectroscopic data are consistent with NHC 1 dissolved in PhosIL-Cl.

**2.11. Preparation of 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-thione, IMes(S).** To an NHC/PhosIL solution prepared according to the method described above in subsection 2.8 (0.50 g, 1.64 mmol) in PhosIL-Cl (10 mL) was added sulfur (0.05 g, 1.64 mmol) followed by an amount of hexanes to decrease viscosity. The resulting mixture was stirred for 4 h at room temperature. More hexanes were then added (5 mL) and the mixture was filtered through Celite and the filtrate evaporated to remove hexanes leaving a viscous yellow residue. $^{1}$H NMR ($C_6D_6$, 400 MHz) $\delta$ 2.08 (s, 6 H), 2.32(s, 12 H), 6.66 (s, 2 H), 6.78 (s, 4 H); $^{13}$C NMR ($C_6D_6$, 101 MHz) $\delta$ 20.9 (s), 22.4 (s), 124.9 (s), 128.4 (s), 133.4 (s), 138.9 (s), 158.1 (s), 162.9 (s); MS (CI) *m/z* 336.3. These $^{13}$C NMR data for the C═S are consistent with previously reported data for IMes═S.[56]

**2.12. Preparation of Pentacarbonyl(1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)chromium, IMesCr(CO)$_5$ in PhosIL-Cl.** A solution of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene was prepared by dissolving NHC 1 (0.20 g, 0.91 mmol) in PhosIL-Cl (10 mL). Toluene (2 mL) was added to dissolve the NHC in PhosIL-Cl. The toluene was then removed under vacuum.

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The PhosIL-Cl solution of NHC 1 was treated with chromium hexacarbonyl (0.20 g, 0.91 mmol). A yellow precipitate was obtained. The mixture was warmed at 60 °C for 2 h. An IR study on the yellow precipitate contained diagnostic stretches at 2056 (s) and 1923 (vs) (CO) consistent with $IMesCr(CO)_5$.[75]

**2.13. Generation of Ethyltriphenylphosphorane in PhosIL.** Ethyltriphenylphosphonium bromide (0.20 g, 0.58 mmol) was dissolved in PhosIL-Cl and to it was added 1.0 M PhMgBr in THF (0.58 mL, 0.58 mmol) dropwise. The color of the solution changed from white to brick orange. $^{31}P$ NMR ($CD_2Cl_2$, 162 MHz): $\delta$ 15.6. These spectroscopic data are consistent with the formation of ethyltriphenylphosphorane in PhosIL-Cl. Similarly, ethyltriphenylphosphonium bromide is deprotonated in PhosIL-$C_9H_{19}COO$ Grignard stock solutions to produce ethyltriphenylphosphorane.

**2.14. Wittig Reactions: Formation of Methylstyrene in PhosIL-$C_9H_{19}COO$.** To a cold (−78 °C) sample of tetradecyl(trihexyl)phosphonium decanoate (5 mL) was added PhosIL-$C_9H_{19}$-COO, 1 M PhMgBr in THF (1.2 mL, 1.2 mmol), and the solution was allowed to slowly warm to room temperature. The THF was removed under vacuum, and to the resulting solution several drops of hexanes was added to reduce viscosity. Triphenylethylphosphonium bromide (0.4 g, 1.10 mmol) was then added to the solution. A color change from white to reddish orange was observed and the mixture was stirred under nitrogen for 1 h. $^{31}P\{^1H\}$ NMR showed a distinctive peak at 15.3 ppm for the deprotonation of triphenylethylphosphonium bromide to give ethyltriphenylphosphorane. Benzaldehyde (0.11 g, 1.10 mmol) was then added to the mixture and an instant color change from yellow to white was observed. The mixture was stirred for 2 h and then quenched with water. The product was extracted with dichloromethane, which was dried using anhydrous magnesium sulfate to give methylstyrene (96%) analyzed by GC-MS. Formation of $Ph_3PO$ was confirmed by mass spectrometry (278 amu).

**3. Computational Studies.** Calculations were performed using Gaussian 98,[76] using a stepping stone approach in which the geometries at the levels HF/STO-3G, HF/3-21G, HF/6-31G*, and HF/6-31+G* were sequentially optimized using default specifications. After each level, a frequency calculation was performed to verify the nature of the stationary point. Z-matrix coordinates constrained to the appropriate symmetry were used for efficiency, as any problems would manifest themselves by an imaginary mode orthogonal to the spanned Z-matrix space. The Hessian was also evaluated at the starting STO-3G geometry to aid convergence.

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**Supporting Information Available:** General experimental procedures and atomic coordinates for diphenylmagnesium, acetate and the acetate anion complex of diphenylmagnesium, as well as crystallographic data and a CIF file for tetrabutylphosphonium acetate monoacetic acid (CCDC 650492). This material is available free of charge via the Internet at http://pubs.acs.org.

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