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Synthesis, Structure, and Reactivity of Two-Coordinate Mercury Alkyl Compounds with Sulfur Ligands: Relevance to Mercury Detoxification

Jonathan G. Melnick, Kevin Yurkerwich, and Gerard Parkin*

Department of Chemistry, Columbia University, New York, New York 10027

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The susceptibility of two-coordinate mercury alkyl compounds of the type X−Hg−R (where X is a monodentate sulfur donor) towards protolytic cleavage has been investigated as part of ongoing efforts to obtain information relevant to understanding the mechanism of action of the organomercurial lyase, *MerB*. Specifically, the reactivity of the two-coordinate mercury alkyl compounds PhSHgR, [mim$^{Bu^t}$]HgR and {[Hmim$^{Bu^t}$]HgR}$^+$ (Hmim$^{Bu^t}$ = 2-mercapto-1-*t*-butylimidazole; R = Me, Et) towards PhSH was investigated, thereby demonstrating that the ability to cleave the Hg−C bond is very dependent on the nature of the system. For example, whereas the reaction of PhSHgMe with PhSH requires heating at 145 °C for several weeks to liberate CH_4, the analogous reaction of PhSHgEt with PhSH leads to evolution of C_2H_6 over the course of 2 days at 100 °C. Furthermore, protolytic cleavage of the Hg−C bond by PhSH is promoted by Hmim$^{Bu^t}$. For example, whereas the reaction of {[Hmim$^{Bu^t}$]HgEt}$^+$ with PhSH eliminates C_2H_6 at elevated temperatures, the protolytic cleavage occurs over a period of 2 days at room temperature in the presence of Hmim$^{Bu^t}$. The ability of Hmim$^{Bu^t}$ to promote the protolytic cleavage is interpreted in terms of the formation of a higher coordinate species {[Hmim$^{Bu^t}$]$_n$HgR}$^+$ that is more susceptible to Hg−C bond cleavage than is two-coordinate {[Hmim$^{Bu^t}$]HgR}$^+$. These observations support the notion that access to a species with a coordination number greater than two is essential for efficient activity of *MerB*.

Introduction

In view of the potent toxicity of organomercury compounds,[1] Nature has developed a detoxification procedure that is achieved by the combined action of two enzymes, namely *(i)* organomercurial lyase (*MerB*), which causes protolytic cleavage of the otherwise inert Hg−C bond, and *(ii)* mercuric ion reductase (*MerA*), which reduces Hg(II) to less toxic elemental mercury, Hg(0).[1,2] The active site of *MerB* features cysteine ligation[3] and, to emulate this aspect, we have employed the [S_3]-donor *tris*(2-mercapto-1-*t*-butylimidazolyl)hydroborato ligand, [Tm$^{Bu^t}$], to provide insight into the mechanism of action of the enzyme.[4] For example, we demonstrated that the Hg−C bonds of the *tris*(2-mercapto-1-*t*-butylimidazolyl)hydroborato mercury alkyl complexes [κ^1-Tm$^{Bu^t}$]HgR (R = Me, Et) are readily cleaved by a thiol (Scheme 1). The facility with which the Hg−C bonds are cleaved under mild conditions was proposed to be a consequence of the mercury center of two-coordinate [κ^1-Tm$^{Bu^t}$]HgR being able to access higher coordination numbers because of the multidentate nature of the [Tm$^{Bu^t}$] ligand.[4,5] Herein, we provide further evidence that supports this suggestion by describing the susceptibility of a series of linear two-coordinate mercury alkyl compounds with a common S−Hg−C coordination environment towards protolytic Hg−C bond cleavage by PhSH.[6]

Results and Discussion

X-ray diffraction studies on [κ^1-Tm$^{Bu^t}$]HgR indicate that only one of the sulfur donors of the [Tm$^{Bu^t}$] ligand coordinates to the mercury in the solid state, such that the metal adopts a

*To whom correspondence should be addressed. E-mail: parkin@columbia.edu.

(1) (a) Clarkson, T. W.; Magos, L. *Crit. Rev. Toxicol.* **2006**, *36*, 609–662. (b) Mutter, J.; Naumann, J.; Guethlin, C. *Crit. Rev. Toxicol.* **2007**, *37*, 537–549. (c) Clarkson, T. W. *Environ. Health Perspect. Suppl.* **2002**, *110*, 11–23. (d) Clarkson, T. W. *Crit. Rev. Clin. Lab. Sci.* **1997**, *34*, 369–403. (e) Langford, N. J.; Ferner, R. E. *J. Human Hypertens.* **1999**, *13*, 651–656. (f) Boening, D. W. *Chemosphere* **2000**, *40*, 1335–1351. (g) Magos, L. *Met. Ions Biol. Sys.* **1997**, *34*, 321–370. (h) Hutchison, A. R.; Atwood, D. A. *J. Chem. Crystallogr.* **2003**, *33*, 631–645. (i) Alessio, L.; Campagna, M.; Lucchini, R. *Am. J. Ind. Med.* **2007**, *50*, 779–787. (j) Clarkson, T. W.; Vyas, J. B.; Ballatorl, N. *Am. J. Ind. Med.* **2007**, *50*, 757–764. (k) Risher, J. F.; De Rosa, C. T. *J. Environ. Health* **2007**, *70*, 9–16. (l) Onyido, I.; Norris, A. R.; Buncel, E. *Chem. Rev.* **2004**, *104*, 5911–5929. (m) Ozuah, P. O. *Curr. Probl. Pediatr.* **2000**, *30*, 91–99.

(2) (a) Moore, M. J.; Distefano, M. D.; Zydowsky, L. D.; Cummings, R. T.; Walsh, C. T. *Acc. Chem. Res.* **1990**, *23*, 301–308. (b) Walsh, C. T.; Distefano, M. D.; Moore, M. J.; Shewchuk, L. M.; Verdine, G. L. *FASEB J.* **1988**, *2*, 124–130.

(3) Lafrance-Vanasse, J.; Lefebvre, M.; Di Lello, P.; Sygusch, J.; Omichinski, J. G. *J. Biol. Chem.* **2009**, *284*, 938–944.

(4) Melnick, J. G.; Parkin, G. *Science* **2007**, *317*, 225–227.

(5) (a) Stradeit, H. *Angew. Chem., Int. Ed. Engl.* **2007**, *46*, 2–5. (b) Miller, S. M. *Nat. Chem. Biol.* **2007**, *3*, 537–536. (c) Omichinski, J. G. *Science* **2007**, *317*, 205–206.

(6) Some of this research has been previously communicated. See reference 4.

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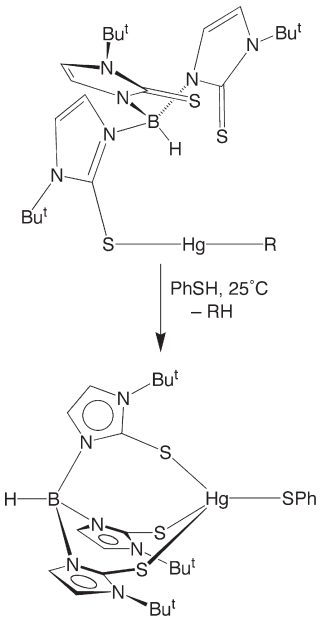
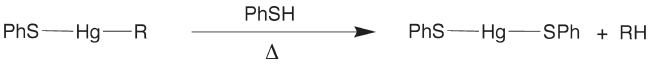
Scheme 1



linear two-coordinate S−Hg−C coordination geometry.[4] In view of the observation that two-coordinate mercury alkyl compounds of the type X−Hg−R are generally inert towards protolytic cleavage of the Hg−C bond,[7,8] the high reactivity of [κ^1-Tm$^{Bu^t}$]HgR towards PhSH (as a simple mimic for a cysteine S−H group) was attributed to the ability of mercury to access non-linear κ^2− or κ^3−isomers in which the Hg−C bond is more susceptible to cleavage.[4] In this regard, ^{1}H NMR spectroscopic studies demonstrate that [κ^1-Tm$^{Bu^t}$]HgR is fluxional and that higher coordination numbers are accessible.[4] To provide further evidence for the proposal that increased coordination number facilitates protolytic cleavage of Hg−C bonds, it was deemed appropriate to probe the reactivity of well-defined two-coordinate X−Hg−R complexes in which X is a strictly monodentate sulfur donor. Therefore, we report here the reactivity of a series of two-coordinate mercury alkyl compounds, namely, PhSHgR, [mim$^{Bu^t}$]HgR, and {[Hmim$^{Bu^t}$]HgR}$^+$ (Hmim$^{Bu^t}$ = 2-mercapto-1-*t*-butylimidazole), towards PhSH.

Reactivity of PhSHgR towards PhSH. As part of an investigation of thimerosal (sodium ethylmercury thiosalicylate), we have recently demonstrated that the phenylthiolate mercury alkyl complexes, PhSHgMe and PhSHgEt, possess two-coordinate linear geometries at mercury.[9,10] As such, these complexes provide suitable reference points to evaluate the reactivity of the Hg−C bond in organomercury compounds with a two-coordinate linear S−Hg−C coordination geometry. Significantly, despite the similar coordination geometries (Table 1), [κ^1-Tm$^{Bu^t}$]HgR and PhSHgR (R = Me, Et) react very differently towards PhSH. Thus, whereas the Hg−C bonds of [κ^1-Tm$^{Bu^t}$]HgR are cleaved

Scheme 2



rapidly by PhSH at room temperature,[4] the phenylthiolate complexes PhSHgR are inert under these conditions. At elevated temperatures, however, PhSH cleaves the Hg−C bond of PhSHgR (R = Me, Et) to give $(PhS)_2Hg$[11] and RH (Scheme 2).[12] The greater reactivity of [κ^1-Tm$^{Bu^t}$]HgR towards PhSH is, therefore, consistent with the notion that cleavage of the Hg−C bond is promoted by access to species with coordination numbers greater than two.

While the Hg−C bonds of both PhSHgMe and PhSHgEt are cleaved by PhSH, the facility of these reactions differ considerably, with the Hg−Et bond being considerably more susceptible to cleavage than that of the Hg−Me bond. For example, whereas PhSH protolytically cleaves the Hg−Et bond of PhSHgEt over a period of 2 days at 100 °C, the corresponding reaction of PhSHgMe proceeds only slowly at temperatures of about 145 °C. The greater reactivity of the Hg−Et bond relative to the Hg−Me bond in this system is noteworthy because protonolysis of RHgI by $HClO_4$ and H_2SO_4 exhibits the opposite trend, with the reactivity decreasing in the sequence Me > Et > Pr^i > Bu^t.[13] On the other hand, the ease of cleaving the Hg−R bond of a series of asymmetric dialkyl mercury compounds, RHgR′, by AcOH decreases in the irregular sequence Et > Pr^i > Me > Bu^t (for a common spectrator R′ group).[14] The observation that the preference for cleaving Hg−Me and Hg−Et bonds in RHgX molecules may be switched by varying X and/or the acid is particularly noteworthy, and it is evident that a detailed understanding of these effects is of considerable relevance to mercury detoxification.

Reactivity of [mim$^{Bu^t}$]HgR towards PhSH. While comparison of the reactivity of [κ^1-Tm$^{Bu^t}$]HgR and PhSHgR provides evidence that the additional sulfur donors of the [Tm$^{Bu^t}$] ligand are responsible for facilitating cleavage of the Hg−C bond, a better comparison is to evaluate the reactivity of [κ^1-Tm$^{Bu^t}$]HgR relative to a two-coordinate mercury alkyl complex that features a monodentate sulfur ligand that more closely resembles the [κ^1-Tm$^{Bu^t}$] ligand than does phenylthiolate. Therefore, we sought mercury alkyl compounds that incorporate the 2-mercapto-1-*t*-butylimidazolyl ligand, namely, [mim$^{Bu^t}$]HgR (R = Me, Et), which may be hypothetically regarded as being derived from [κ^1-Tm$^{Bu^t}$]HgR by dissociation of the neutral borane, HB(mim$^{Bu^t}$)$_2$ (Scheme 3). Such complexes are conveniently obtained via the reaction of RHgCl with Hmim$^{Bu^t}$ in aqueous NaOH solution (Scheme 4).[15] The

(7) (a) Kreevoy, M. M. *J. Am. Chem. Soc.* **1957**, *79*, 5927–5930. (b) Kreevoy, M. M.; Hansen, R. L. *J. Am. Chem. Soc.* **1961**, *83*, 626–630.

(8) Barone, V.; Bencini, A.; Totti, F.; Uytterhoeven, M. G. *Organometallics* **1996**, *15*, 1465–1469.

(9) Melnick, J. G.; Yurkerwich, K.; Buccella, D.; Sattler, W.; Parkin, G. *Inorg. Chem.* **2008**, *47*, 6421–6426.

(10) For simplicity, this description does not take into account the longer distance secondary Hg···S interactions that are often observed in mercury compounds.

(11) $(PhS)_2Hg$ has been previously reported. See, for example, (a) Carlton, L.; White, D. *Polyhedron* **1990**, *9*, 2717–2720. (b) Canty, A. J.; Kishimoto, R. *Inorg. Chim. Acta* **1977**, *24*, 109–122.

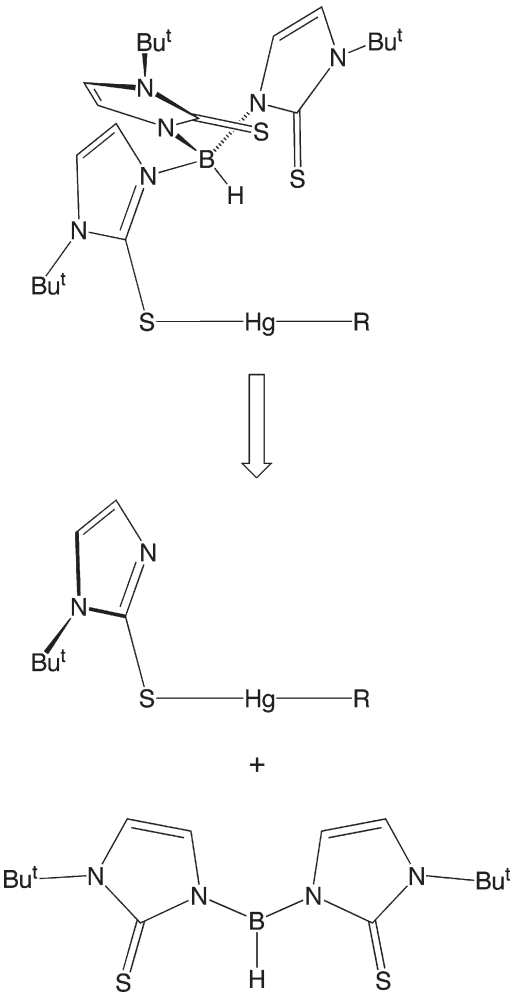
(12) PhSHgMe has been synthesized by reaction of MeHgCl with PhSH, but subsequent elimination of methane was not observed; however, the conditions employed were not reported. In contrast, PhSHgPh has been reported to react with PhSH to give $(PhS)_2Hg$ and PhH. See: Cross, R. J.; Jenkins, C. M. *Environ. Pollut.* **1975**, *8*, 179–184.

(13) Kreevoy, M. M.; Hansen, R. L. *J. Am. Chem. Soc.* **1961**, *83*, 626–630.

(14) Nugent, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5979–5988.

(15) The related methimazole complex (mim^{Me})HgMe has been reported. See: Norris, A. R.; Taylor, S. E.; Buncel, E.; Bélanger-Gariépy, F.; Beauchamp, A. L. *Can. J. Chem.* **1983**, *61*, 1536–1541.

Scheme 3



molecular structure of [mim$^{Bu^t}$]HgEt has been determined by X-ray diffraction (Figure 1), and the coordination geometry at mercury is comparable to that of [κ^1-Tm$^{Bu^t}$]HgEt (Table 1).

In contrast to the phenylthiolate derivatives, the 2-mercapto-1-*t*-butylimidazolyl complexes [mim$^{Bu^t}$]HgR react rapidly with PhSH at room temperature. However, instead of cleaving the Hg−C bond, PhSH cleaves the Hg−S bond to give PhSHgR (Scheme 4). The different reaction pathway is most likely a consequence of the presence of the sp^2 nitrogen lone pair on the [mim$^{Bu^t}$] ligand, protonation of which provides an alternative mechanism than one involving direct reaction with the Hg−C bond (Scheme 4). Supporting this suggestion, the proposed {[Hmim$^{Bu^t}$]HgR}$^+$ (R = Me, Et) intermediates may be synthesized independently via addition of Hmim$^{Bu^t}$ to [RHg][BF$_4$],[16] as illustrated in Scheme 5. The molecular structure of the ethyl derivative {[Hmim$^{Bu^t}$]HgEt}[BF$_4$] has been determined by X-ray diffraction (Figure 2) and the Hg−S and Hg−C bond lengths are similar to those of the neutral counterpart, [mim$^{Bu^t}$]HgEt (Table 1).

With respect to the reactivity of {[Hmim$^{Bu^t}$]HgR}[BF$_4$], it is significant that treatment of {[Hmim$^{Bu^t}$]HgR}[BF$_4$] with

(16) Brower, K. R.; Gay, B.; Konkol, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 1681–1685.

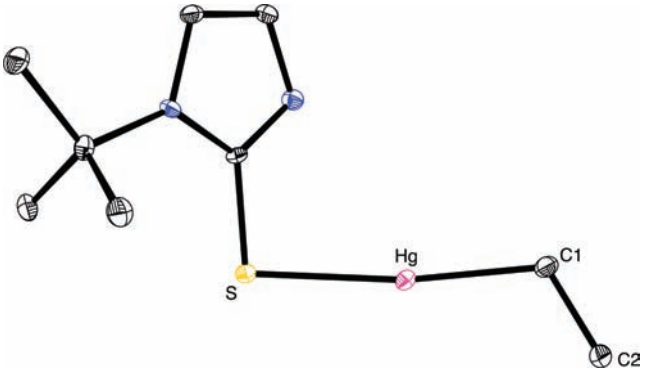
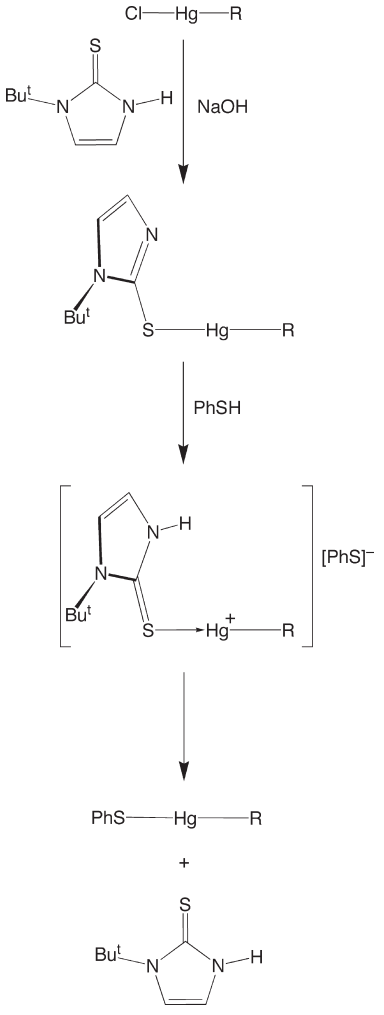


Figure 1. Molecular structure of [mim$^{Bu^t}$]HgEt.

Scheme 4



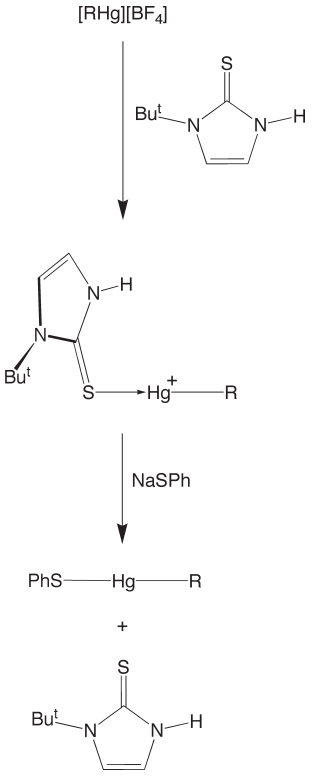
NaSPh generates PhSHgR (Scheme 5), thereby providing evidence for the second step of the proposed mechanism for the reaction of [mim$^{Bu^t}$]HgR with PhSH (Scheme 4).

Reactivity of {[Hmim$^{Bu^t}$]HgEt}[BF$_4$] towards PhSH. Since the Hmim$^{Bu^t}$ ligand of {[Hmim$^{Bu^t}$]HgR}$^+$ is not susceptible to protonation, {[Hmim$^{Bu^t}$]HgR}$^+$ cannot react with PhSH in a manner analogous to that of [mim$^{Bu^t}$]HgR, and the site of reactivity switches from the Hg−S bond to the Hg−C bond. Thus, treatment of {[Hmim$^{Bu^t}$]HgEt}$^+$ with PhSH results in elimination of C_2H_6 (Scheme 6). The initial

Table 1. Mercury Coordination Environments in Two-Coordinate Mercury Alkyl Complexes with Sulfur Donors

	Hg−C/Å	Hg−S/Å	S−Hg−C/deg	reference
$[\kappa^1\text{-Tm}^{Bu^t}]HgCH_3$	2.073(7)	2.396(2)	176.1(3)	4
$[\kappa^1\text{-Tm}^{Bu^t}]HgCH_2CH_3$	2.093(3)	2.405(1)	176.5(1)	4
$PhSHgCH_3$	2.068(6)	2.383(2)	176.6(2)	9
$PhSHgCH_2CH_3$	2.07(1)	2.369(2)	178.1(3)	9
$[mim^{Bu^t}]HgCH_2CH_3$	2.092(5)	2.377(1)	171.8(1)	this work
$\{[Hmim^{Bu^t}]HgCH_2CH_3\}[BF_4]$	2.088(3)	2.4098(7)	174.41(8)	this work
	2.085(3)	2.3874(7)	176.80(9)	

Scheme 5



mercury product is postulated to be $\{[Hmim^{Bu^t}]HgSPh\}^+$, although this species has not been isolated because of the existence of a subsequent exchange equilibrium that results in the formation of, inter alia, $\{[Hmim^{Bu^t}]_2Hg\}[BF_4]_2$, the molecular structure of which is shown in Figure 3. In addition, $(PhS)_2Hg$, the accompanying redistribution product, was identified by mass spectrometry (m/z = 421.1 $\{M + 1\}^+$).[11]

Protolytic Cleavage of PhSHgR and $\{[Hmim^{Bu^t}]HgR\}^+$ by PhSH is Promoted by $Hmim^{Bu^t}$. The observation that both neutral and cationic two-coordinate compounds, i.e., PhSHgR and $\{[Hmim^{Bu^t}]HgR\}^+$, are less susceptible to protolytic cleavage of the Hg−C bond than is $[Tm^{Bu^t}]HgR$ provides a strong indication that the more facile cleavage reaction of $[Tm^{Bu^t}]HgR$ is a consequence of the ability of the mercury center to access a higher coordination number, an effect which has been attributed to an increase in the negative charge on the carbon atom.[17] Further evidence to support the proposal that an increase in coordination number enhances protolytic

(17) Ni, B.; Kramer, J. R.; Bell, R. A.; Werstiuk, N. H. *J. Phys. Chem. A* **2006**, *110*, 9451–9458.

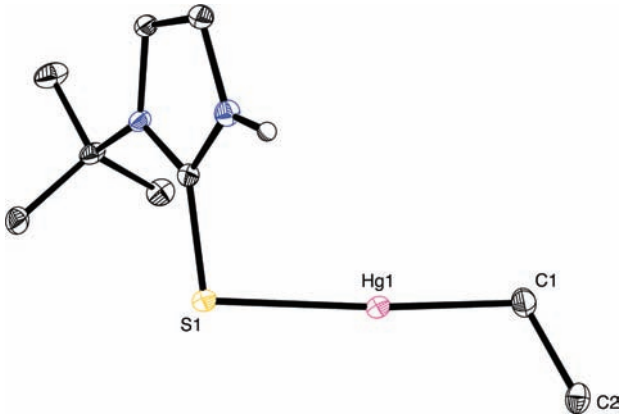
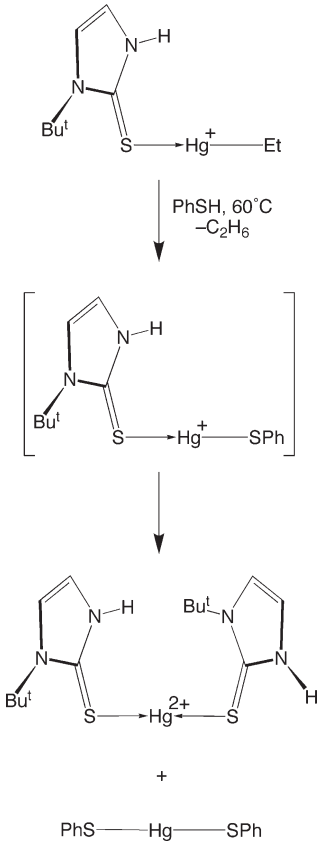


Figure 2. Molecular structure of $\{[Hmim^{Bu^t}]HgEt\}[BF_4]$ (only the cation is shown).

Scheme 6



cleavage of the Hg−C bond is provided by the observation that cleavage of the Hg−C bond of both PhSHgEt and $\{[Hmim^{Bu^t}]HgEt\}[BF_4]$ by PhSH is promoted by

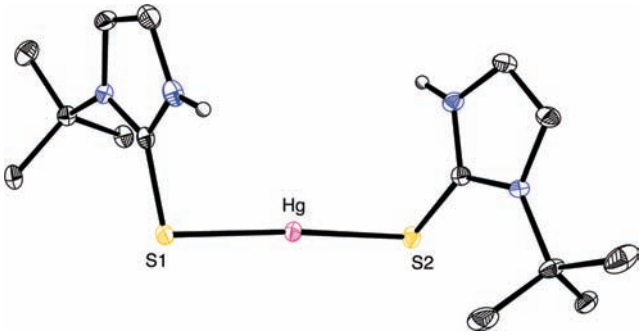
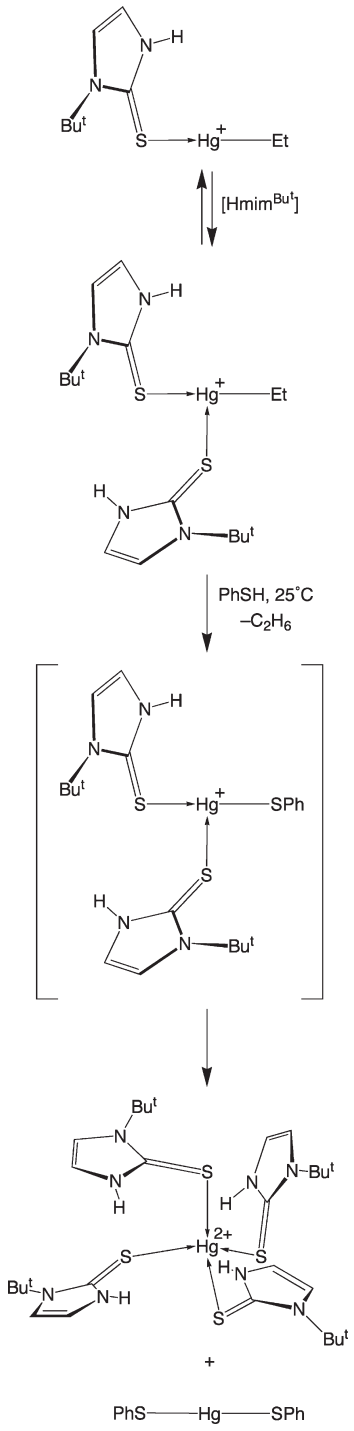


Figure 3. Molecular structure of $\{[Hmim^{Bu^t}]_2Hg\}[BF_4]_2$ (only the cation is shown).

addition of $Hmim^{Bu^t}$. For example, a mixture of PhSHgEt and PhSH readily eliminates ethane at room temperature in the presence of $Hmim^{Bu^t}$.[18,19] Likewise, $Hmim^{Bu^t}$ promotes elimination of ethane from a mixture of $\{[Hmim^{Bu^t}]HgEt\}[BF_4]$ and PhSH at room temperature (Scheme 7). Since $Hmim^{Bu^t}$ alone does not cleave the Hg−C bond under these conditions,[20] the ability of $Hmim^{Bu^t}$ to promote protolytic cleavage may be rationalized by the generation of higher coordinate species that are more susceptible to Hg−C protolytic cleavage than their two-coordinate counterparts.[21] Other studies also suggest that coordination of substrates to mercury enhances the susceptibility of protolytic cleavage of Hg−C bonds. For example, I^- catalyzes the protolytic cleavage of allyl mercury iodide,[22] while the nature of the buffer (i.e., formate, acetate, phosphate) has been shown to have an effect on the rate of protolytic cleavage of an aryl−mercury bond.[23]

Scheme 7



Support for the proposal that $Hmim^{Bu^t}$ is capable of coordinating to the mercury centers of PhSHgMe, PhSHgEt, and $\{[Hmim^{Bu^t}]HgMe\}^+$ is provided by the observation that the ^1H NMR spectroscopic signals for the mercury alkyl groups of these complexes shift in the presence of $Hmim^{Bu^t}$. For example, ^1H NMR spectra of PhSHgMe and PhSHgEt in the presence of variable concentrations of $Hmim^{Bu^t}$ are illustrated in Figures 4 and 5,[24] thereby demonstrating that $Hmim^{Bu^t}$

(18) In the presence of excess PhSH and $Hmim^{Bu^t}$, the mercury product could possibly be a dynamic mixture of $Hg(SPh)_2$, $[Hg(SPh)_3]^-$, $[Hg_2(SPh)_6]^{2-}$, and $[Hg(SPh)_4]^{2-}$. See: (a) Christou, G.; Folting, K.; Huffman, J. C. *Polyhedron* **1984**, *3*, 1247–1253. (b) Bowmaker, G. A.; Dance, I. G.; Harris, R. K.; Henderson, W.; Laban, T.; Scudder, M. C.; Oh, S.-W. *J. Chem. Soc., Dalton Trans.* **1996**, 2381–2388.

(19) In view of the observation that coordination of $Hmim^{Bu^t}$ has a significant effect on the facility of protolytically cleaving the Hg−C bond, it is possible that protolytic cleavage in the absence of this reagent does not occur with two-coordinate PhSHgR but occurs preferentially via low concentration species with higher coordination numbers, such as $PhSHgR(PhSH)$ or $[PhSHgR]_2$.

(20) At elevated temperatures (100 °C), a solution of PhSHgEt and $Hmim^{Bu^t}$ eliminates ethane.

(21) The three-coordinate intermediates are represented with a "T-shaped", rather than a "Y-shaped", geometry on the basis that the former type of structure is often observed in organomercury compounds.[a,b,c] Indeed, this geometry is observed in $[Tm^{Bu^t}]HgR$ upon consideration of the secondary bonding interaction involving one of the mercaptoimidazole groups.[d] Furthermore, DFT geometry optimization calculations on $\{[Hmim^{Bu^t}]_2HgCH_3\}^+$ indicate a structure in which the S−Hg−S and S−Hg−C angles are 89° and 157°, respectively, which are more in accord with a "T-shaped", rather than a "Y-shaped", geometry. Three-coordinate mercury compounds with "Y-shaped" geometries and 120° bond angles are, nevertheless, known in situations where the three ligands contribute equally to the bonding (e.g., $[Hg(SBu^t)_3]^-$).[e] (a) Casa, J. S.; García-Tasende, M. S.; Sordo, J. *Coord. Chem. Rev.* **1999**, *193*−*195*, 283–359. (b) Holloway, C. E.; Melnkk, M. *J. Organomet. Chem.* **1995**, *495*, 1–31. (c) Holloway, C. E.; Melnik, M. *Main Group Met. Chem.* **1994**, *17*, 799–885. (d) Reference 4. (e) Wright, J. G.; Natan, M. J.; MacDonnell, F. M.; Ralston, D. M.; O'Halloran, T. V. *Prog. Inorg. Chem.* **1990**, *38*, 323–412.

(22) Kreevoy, M. M.; Goon, D. J. W.; Kayser, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5529–5534.

(23) Gopinath, E.; Bruice, T. C. *J. Am. Chem. Soc.* **1987**, *109*, 7903–7905.

(24) Note that $^2J_{Hg-H}$ (235 Hz) for PhSHgMe does not change significantly in the presence of $Hmim^{Bu^t}$.

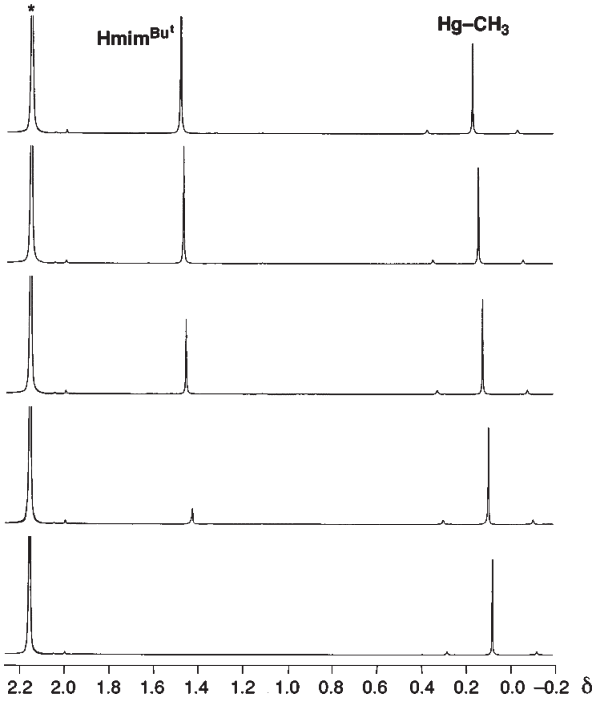


Figure 4. ^{1}H NMR spectra of PhSHgMe in the presence of increasing amounts of Hmim$^{Bu^t}$ (* = mesitylene internal reference).

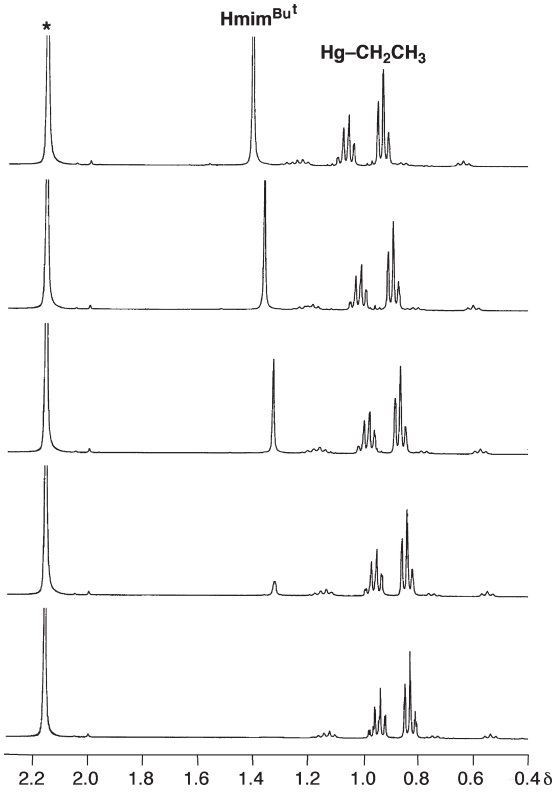


Figure 5. ^{1}H NMR spectra of PhSHgEt in the presence of increasing amounts of Hmim$^{Bu^t}$ (* = mesitylene internal reference).

binds rapidly, and reversibly, to the mercury centers of these two-coordinate compounds, such that the observed chemical shifts are a weighted average of two- and three-coordinate species.

In addition to ^{1}H NMR spectroscopy, ^{199}Hg NMR spectroscopy also provides evidence for coordination

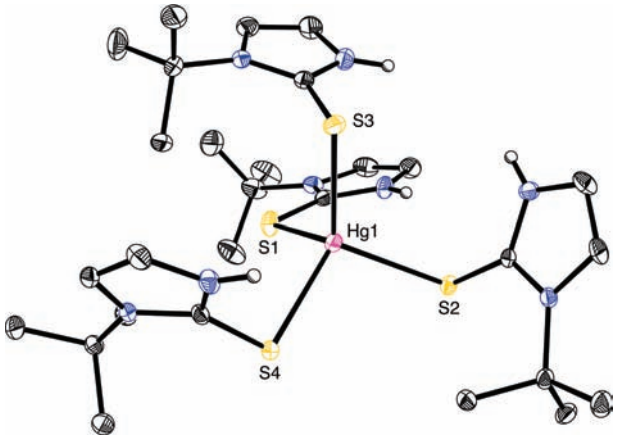


Figure 6. Molecular structure of {[Hmim$^{Bu^t}$]$_4$Hg}[BF$_4$]$_2$ (only the cation is shown).

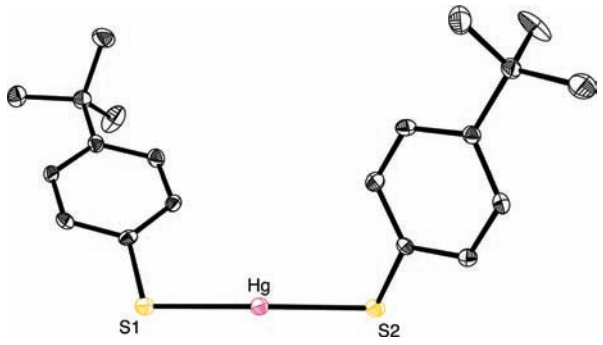


Figure 7. Molecular structure of [*p*-Bu^{t}C$_6$H$_4$S]$_2$Hg.

of Hmim$^{Bu^t}$ to PhSHgR. For example, the ^{199}Hg NMR spectroscopic signal for PhSHgMe progressively shifts from −557 ppm[25] to −540 ppm upon increasing the concentration of Hmim$^{Bu^t}$. Likewise, the ^{199}Hg NMR spectroscopic signal for PhSHgEt progressively shifts from −730 ppm[25] to −680 ppm in the presence of Hmim$^{Bu^t}$. O'Halloran and co-workers have noted that ^{199}Hg NMR chemical shifts of mercury thiolate complexes typically become deshielded as coordination number increases,[21e] and thus the observed variation of ^{199}Hg chemical shifts are in accord with coordination of Hmim$^{Bu^t}$ to PhSHgR generating three-coordinate species that are in rapid equilibrium with the two-coordinate species in solution.

Further evidence for the existence of three-coordinate mercury species in solution is provided by mass spectrometric studies that suggest that {[Hmim$^{Bu^t}$]$_2$HgSPh}$^+$ (m/z = 623.3)} is a component of the product mixture resulting from the reaction of {[Hmim$^{Bu^t}$]HgEt}[BF$_4$] with PhSH in the presence of Hmim$^{Bu^t}$, although ligand redistribution giving {[Hmim$^{Bu^t}$]$_4$Hg}[BF$_4$]$_2$ and (PhS)$_2$Hg[11] is facile (Scheme 7). Likewise, the corresponding reaction of {[Hmim$^{Bu^t}$]HgEt}[BF$_4$] with *p*-Bu^{t}C$_6$H$_4$SH in the presence of Hmim$^{Bu^t}$ liberates ethane and yields {[Hmim$^{Bu^t}$]$_4$Hg}[BF$_4$]$_2$

(25) The ^{199}Hg NMR chemical shifts for PhSHgR are within the range observed for two-coordinate mercury thiolate compounds. See references 9, 21d, and (a) Almagro, X.; Clegg, W.; Cucurull-Sánchez, L.; González-Duarte, P.; Traveria, M. *J. Organomet. Chem.* **2001**, *623*, 137–148. (b) Carlton, L.; White, D. *Polyhedron* **1990**, *9*, 2717–2720.

and [*p*-Bu^{t}C$_6$H$_4$S]$_2$Hg.[26] The molecular structures of {[Hmim$^{Bu^t}$]$_4$Hg}[BF$_4$]$_2$ (Figure 6) and [*p*-Bu^{t}C$_6$H$_4$S]$_2$-Hg (Figure 7) have been detemined by X-ray diffraction.[27] As expected, the Hg−S bond lengths in tetrahedral {[Hmim$^{Bu^t}$]$_4$Hg}$^{2+}$ (2.54 Å average) are substantially longer than the corresponding values in two-coordinate {[Hmim$^{Bu^t}$]$_2$Hg}$^{2+}$ (2.35 Å average). For comparison, these bond lengths are virtually identical to the mean values for two-coordinate (2.34 Å) and four-coordinate (2.55 Å) mercury thiolate compounds listed in the Cambridge Structural Database.[28]

Conclusions

In summary, comparison of the reactivity of the two-coordinate mercury alkyl compounds [κ^1-Tm$^{Bu^t}$]HgR, PhSHgR, [mim$^{Bu^t}$]HgR, and {[Hmim$^{Bu^t}$]HgR}$^+$ towards PhSH indicates that the susceptibility towards cleavage of the Hg−C bond is very dependent on the nature of the system. Thus, whereas the Hg−C bond of [κ^1-Tm$^{Bu^t}$]HgR is readily cleaved by PhSH at room temperature, the Hg−C bonds of PhSHgR and {[Hmim$^{Bu^t}$]HgR}$^+$ are inert under comparable conditions. On the other hand, [mim$^{Bu^t}$]HgR is reactive towards PhSH at room temperature, but it is the Hg−S bond that is preferentially cleaved to give PhSHgR. Although {[Hmim$^{Bu^t}$]HgEt}$^+$ does not react with PhSH at room temperature, addition of Hmim$^{Bu^t}$ promotes cleavage of the Hg−C bond, thereby supporting the notion that access to geometries with a coordination number greater than two is required for the efficient activity of *MerB*.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox and Schlenk techniques under a nitrogen or argon atmosphere. Solvents were purified and degassed by standard procedures. Reactions monitored by NMR spectroscopy were prepared in an NMR tube equipped with a J. Young valve. NMR spectra were measured on Bruker 300 DRX, Bruker 400 DRX and Bruker Avance 500 DMX spectrometers. ^{1}H NMR spectra are reported in ppm relative to SiMe$_4$ (δ = 0) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C$_6$D$_5$H, and 2.50 for d_6−Me$_2$SO).[29] ^{13}C NMR spectra are reported in parts per million relative to SiMe$_4$ (δ = 0) and were referenced internally with respect to the solvent (δ 128.06 for C$_6$D$_6$).[29] ^{199}Hg NMR chemical shifts are reported relative to HgMe$_2$ (δ = 0) but in view of the toxicity of the latter compound, the spectra were referenced externally with respect to HgI$_2$ (1 M in d^6-DMSO, δ = −3106).[30] Coupling constants are given in hertz. IR spectra were recorded as KBr pellets on a Nicolet Avatar DTGS spectrometer, and the data are reported in reciprocal centimeters. Mass spectra were obtained on a JMS-HX110/110 Double Focusing mass spectrometer using fast atom bombardment (FAB). Hmim$^{Bu^t}$,[31] PhSHgMe[9] and PhSHgEt[9] were obtained by the literature methods. HgI$_2$ (Aldrich), MeHgCl (Aldrich), EtHgCl (Strem), PhSH (Aldrich), PhSNa (Fluka) and AgBF$_4$ (Strem) were obtained commercially. ***Caution!*** *All mercury compounds are toxic and appropriate safety precautions must be taken in handling these compounds.*

Reactivity of PhSHgEt towards PhSH in the Presence and Absence of Hmim$^{Bu^t}$. (a) A solution of PhSHgEt (25 mg, 0.074 mmol) in C$_6$D$_6$ (0.7 mL) was treated with PhSH (20 μL) and heated at 100 °C for a period of 2 days. The solution was allowed to cool to room temperature, thereby depositing a white precipitate over a period of 3 days. The mother liquor was decanted, and the white solid was washed with pentane (2 × 1 mL) and dried in vacuo to give (PhS)$_2$Hg as a white solid (9 mg, 29%). (PhS)$_2$Hg was identified by comparison of the ^{1}H NMR spectrum of a solution in d_6−DMSO with that of an authentic sample.[11a] ^{1}H NMR (d_6−DMSO) 7.06 [t, 2H, $^3J_{H-H}$ = 7 Hz (C$_6$H$_5$S)$_2$Hg], 7.15 [t, 4H, $^3J_{H-H}$ = 7 Hz (C$_6$H$_5$S)$_2$Hg], 7.36 [d, $^3J_{H-H}$ = 4 Hz, 4H of (C$_6$H$_5$S)$_2$Hg]; ^{1}H NMR (C$_6$D$_6$) 6.85 [m, 6H of (C$_6$H$_5$S)$_2$Hg], 7.25 [m, 4H of (C$_6$H$_5$S)$_2$Hg].

(b) A solution of PhSHgEt (40 mg, 0.12 mmol) in C$_6$D$_6$ (3 mL) was treated with PhSH (40 μL) and mesitylene (10 μL) as an internal standard. The resulting solution was divided equally into four NMR tubes, to which three were treated with Hmim$^{Bu^t}$ (2 mg, 0.013 mmol; 10 mg, 0.064 mmol; 20 mg, 0.13 mmol), and the reactions were monitored by ^{1}H NMR spectroscopy. The formation of small quantities of C$_2$H$_6$ was observed immediately for all three samples which contained Hmim$^{Bu^t}$, but complete elimination required a period of several days: the mixture containing 2 mg of Hmim$^{Bu^t}$ went to completion over a period of 12 days at room temperature, while the mixtures containing 10 and 20 mg of Hmim$^{Bu^t}$ were complete after 1 week. In contrast, the solution to which no Hmim$^{Bu^t}$ was added proceeded to only about 50% conversion over a period of 2 weeks at room temperature, and complete elimination of C$_2$H$_6$ required heating for 1 day at 145 °C.

Reactivity of PhSHgMe towards PhSH in the Presence and Absence of Hmim$^{Bu^t}$. A solution of PhSHgMe (20 mg, 0.062 mmol) in C$_6$D$_6$ (1.5 mL) was treated with PhSH (20 μL) and mesitylene (20 μL) as an internal standard. The resulting solution was divided equally into two NMR tubes, to which one was treated with Hmim$^{Bu^t}$ (10 mg, 0.064 mmol). The reactions were heated at 145 °C and monitored by ^{1}H NMR spectroscopy. In the presence of Hmim$^{Bu^t}$, elimination of methane was complete after two days, whereas in the absence of Hmim$^{Bu^t}$, elimination of methane proceeded only to about 90% completion after 3 weeks.

Comparison of the Reactivity of PhSHgMe and PhSHgEt towards PhSH. A solution of PhSHgMe (10 mg, 0.031 mmol) and PhSHgEt (10 mg, 0.030 mmol) in C$_6$D$_6$ (0.7 mL) was treated with PhSH (20 μL) and mesitylene (20 μL) as an internal standard. The reactions were heated at 145 °C and were monitored by ^{1}H NMR spectroscopy, thereby demonstrating the complete formation of C$_2$H$_6$ after heating the solution for 1 day. In contrast, liberation of CH$_4$ required a period of 3 weeks.

Synthesis of [mim$^{Bu^t}$]HgMe. A solution of Hmim$^{Bu^t}$ (200 mg, 1.28 mmol) in aqueous NaOH (30 mL of 75 mM) was added to a suspension of MeHgCl (321 mg, 1.28 mmol) in water (20 mL)

(26) The dithiolate complex [*p*-Bu^{t}C$_6$H$_4$S]$_2$Hg can also be independently prepared via reaction of *p*-Bu^{t}C$_6$H$_4$SH with HgO, a method analogous to that for other Hg(SR)$_2$ complexes. See: Carlton, L.; White, D. *Polyhedron* **1990**, *9*, 2717–2720.

(27) For other structurally characterized (ArS)$_2$Hg compounds, see: (a) Alsaadi, B. M.; Sandström, M. *Acta Chem. Scand.* **1982**, *A36*, 509–512. (b) Gruff, E. S.; Koch, S. A. *J. Am. Chem. Soc.* **1990**, *112*, 1245–1247. (c) Block, E.; Brito, M.; Gernon, M.; McGowty, D.; Kang, H.; Zubieta, J. *Inorg. Chem.* **1990**, *29*, 3172–3181. (d) Kato, M.; Kojima, K.; Okamura, T.; Yamamoto, H.; Yamamura, T.; Ueyama, N. *Inorg. Chem.* **2005**, *44*, 4037–4044. (e) Chen, J. X.; Zhang, W.-H.; Tang, X.-Y.; Ren, Z.-G.; Zhang, Y.; Lang, J.-P. *Inorg. Chem.* **2006**, *45*, 2568–2580. (f) Ueyama, N.; Taniuchi, K.; Okamura, T.; Nakamura, A.; Maeda, H.; Emura, E. *Inorg. Chem.* **1996**, *35*, 1945–1951. (g) Chen, J.-X.; Zhang, W.-H.; Tang, X.-Y.; Ren, Z.-G.; Li, H.-X.; Zhang, Y.; Lang, J. P. *Inorg. Chem.* **2006**, *45*, 7671–7680. (h) Almagro, X.; Clegg, W.; Cucurull-Sánchez, L.; González-Duarte, P.; Traveria, M. *J. Organomet. Chem.* **2001**, *623*, 137–148.

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(31) Cassidy, C. S.; Reinhardt, L. A.; Cleland, W. W.; Frey, P. A. *J. Chem. Soc., Perkin Trans.* **1999**, *2*, 635–641.

over 15 min resulting in the immediate formation of a white precipitate. The suspension was stirred for 3 h, allowed to settle for 30 min, and filtered. The precipitate was dried in vacuo to give [mim$^{Bu^t}$]HgMe as a white powder (290 mg, 61%). ^{1}H NMR (C_6D_6) 0.42 [s, 3H, $^2J_{Hg-H}$ = 176 Hz, {$C_3N_2H_2$[$C(CH_3)_3$]S}-HgMe], 1.45 [s, 9H, {$C_3N_2H_2$[$C(CH_3)_3$]S}HgMe], 6.66 [br d, 1H, $^3J_{H-H}$ = 2 Hz, {$C_3N_2H_2$[$C(CH_3)_3$]S}HgMe], 6.92 [br d, 1H, $^3J_{H-H}$ = 2 Hz, {$C_3N_2H_2$[$C(CH_3)_3$]S}HgMe]. ^{13}C{^{1}H} NMR (C_6D_6) 8.6 [1C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgCH$_3$], 29.6 [3C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgMe], 55.8 [1C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgMe], 117.8 [1C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgMe], 125.9 [1C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgMe], 144.4 (tentative) [1C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgMe]. IR Data (KBr pellet, cm^{-1}): 3172 (w), 3111 (w), 2970 (m), 2908 (m), 1679 (w), 1561 (w), 1511 (m), 1475 (w), 1468 (w), 1447 (w), 1438 (w), 1417 (s), 1404 (m), 1393 (m), 1367 (s), 1343 (vs), 1297 (m), 1251 (vs), 1230 (m), 1221 (m), 1180 (w), 1141 (w), 1123 (vs), 1043 (s), 1021 (m), 914 (w), 843 (w), 817 (w), 771 (m), 720 (s), 690 (vs), 632 (w). Mass spectrum: m/z = 373.1 {M+1}$^+$.

Synthesis of [mim$^{Bu^t}$]HgEt. A solution of [Hmim$^{Bu^t}$] (200 mg, 1.28 mmol) in aqueous NaOH (30 mL of 40 mM) was added to a suspension of EtHgCl (339 mg, 1.28 mmol) in water (20 mL) over 15 min resulting in the immediate formation of a white precipitate. The suspension was stirred for 16 h, allowed to settle for 30 min, and filtered. The precipitate was dried in vacuo to give [mim$^{Bu^t}$]HgEt as a white powder (263 mg, 53%). Crystals of composition [mim$^{Bu^t}$]HgEt suitable for X-ray diffraction were obtained from CH_3CN. ^{1}H NMR (C_6D_6) 1.07 [t, 3H, $^3J_{H-H}$=8 Hz, {$C_3N_2H_2$[$C(CH_3)_3$]S}HgCH$_2$CH$_3$], 1.27 [q, 2H, $^3J_{H-H}$ = 8 Hz, {$C_3N_2H_2$[$C(CH_3)_3$]S}HgCH$_2$CH$_3$], 1.46 [s, 9H, {$C_3N_2H_2$[$C(CH_3)_3$]S}HgEt], 6.66 [br d, 1H, $^3J_{H-H}$ = 2 Hz, {$C_3N_2H_2$[$C(CH_3)_3$]S}HgEt], 6.93 [br d, 1H, $^3J_{H-H}$ = 2 Hz, {$C_3N_2H_2$[$C(CH_3)_3$]S}HgEt]. ^{13}C{^{1}H} NMR (C_6D_6) 13.8 [1C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgCH$_2$CH$_3$], 25.7 [1C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgCH$_2$CH$_3$], 29.6 [3C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgEt], 55.8 [1C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgEt], 117.7 [1C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgEt], 126.0 [1C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgEt], 144.7 [1C, {$C_2N_2H_2$[$C(CH_3)_3$]CS}HgEt]. IR Data (KBr pellet, cm^{-1}): 3165 (w), 3103 (w), 2988 (w), 2970 (m), 2926 (w), 2864 (w), 1683 (w), 1566 (w), 1476 (w), 1445 (w), 1418 (m), 1406 (m), 1394 (m), 1368 (s), 1338 (vs), 1295 (m), 1248 (vs), 1232 (m), 1178 (m), 1141 (m), 1123 (vs), 1044 (s), 1022 (s), 966 (w), 952 (w), 913 (w), 845 (w), 800 (m), 722 (s), 692 (vs), 682 (s), 633 (w). Mass spectrum: m/z = 387.1 {M + 1}$^+$.

Reactivity of [mim$^{Bu^t}$]HgMe towards PhSH. A solution of [mim$^{Bu^t}$]HgMe (10 mg, 0.027 mmol) in C_6D_6 (0.7 mL) was treated with PhSH (10 μL) and mesitylene (10 μL) as an internal standard. The reaction was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of PhSHgMe and Hmim$^{Bu^t}$ in quantitative yield over a period of 1.5 h.

Reactivity of [mim$^{Bu^t}$]HgEt towards PhSH. A solution of [mim$^{Bu^t}$]HgEt (10 mg, 0.027 mmol) in C_6D_6 (0.7 mL) was treated with PhSH (10 μL) and mesitylene (10 μL) as an internal standard. The reaction was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of PhSHgEt and Hmim$^{Bu^t}$ in quantitative yield over a period of 1.5 h. Over the period of a day, PhSHgEt reacts further with excess PhSH to yield $(PhS)_2Hg$ (see above).

Synthesis of {[Hmim$^{Bu^t}$]HgMe}[BF_4]. A mixture of MeHgCl (750 mg, 2.99 mmol) and $AgBF_4$ (582 mg, 2.99 mmol) was treated with CH_2Cl_2 (15 mL) resulting in the immediate deposition of a white precipitate. The suspension was stirred 3 h, allowed to settle for 30 min, and filtered into a solution of [Hmim$^{Bu^t}$] (466 mg, 2.98 mmol) in CH_2Cl_2 (15 mL). The resulting solution was stirred for 1 h and solvent removed in vacuo to give {[Hmim$^{Bu^t}$]HgMe}[BF_4] as a white powder (680 mg, 50%). ^{1}H NMR (C_6D_6) 0.48 [s, 3H, $^2J_{Hg-H}$ = 194 Hz, H{$C_3N_2H_2$[$C(CH_3)_3$]S}HgMe], 1.24 [s, 9H, H{$C_3N_2H_2$[$C(CH_3)_3$]S}HgMe], 6.15 [d, 1H, $^3J_{H-H}$ = 2 Hz, H{$C_3N_2H_2$[$C(CH_3)_3$]S}HgMe], 6.75 [d, 1H, $^3J_{H-H}$ = 2 Hz, H{$C_3N_2H_2$[$C(CH_3)_3$]S}HgMe], 12.07 [br, 1H, H{$C_3N_2H_2$[$C(CH_3)_3$]S}-HgMe]. ^{13}C{^{1}H} NMR (C_6D_6) 8.9 [1C, H{$C_2N_2H_2$[$C(CH_3)_3$]CS}HgCH$_3$], 28.6 [3C, H{$C_2N_2H_2$[$C(CH_3)_3$]CS}HgMe], 58.8 [1C, H{$C_2N_2H_2$[$C(CH_3)_3$]CS}HgMe], 118.4 [1C, H{$C_2N_2H_2$-[$C(CH_3)_3$]CS}HgMe], 119.8 [1C, H{$C_2N_2H_2$[$C(CH_3)_3$]CS}HgMe], 147.6 (tentative) [1C, H{$C_2N_2H_2$[$C(CH_3)_3$]CS}HgMe]. IR Data (KBr pellet, cm^{-1}): 3191 (m), 2981 (m), 2919 (m), 2736 (w), 1574 (s), 1469 (s), 1420 (m), 1374 (s), 1325 (m), 1246 (s), 1220 (s), 1139 (s), 1055 (s), 914 (m), 734 (m), 686 (m). Mass spectrum: m/z = 373.1 {M}$^+$ (M = {[Hmim$^{Bu^t}$]HgMe}).

Synthesis of {[Hmim$^{Bu^t}$]HgEt}[BF_4]. A mixture of EtHgCl (500 mg, 1.89 mmol) and $AgBF_4$ (367 mg, 1.89 mmol) was treated with CH_2Cl_2 (25 mL) resulting in the immediate deposition of a white precipitate. The suspension was stirred 3 h and filtered into a flask containing Hmim$^{Bu^t}$ (221 mg, 1.42 mmol). The resulting solution was stirred 1 h at room temperature, and the volatile components removed in vacuo. The residue was extracted into C_6H_6 (20 mL) and filtered. The volatile components were removed by lyophilization to give {[Hmim$^{Bu^t}$]HgEt}-[BF_4] as a white powder (480 mg, 72%). Crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a tetrahydrofuran (THF) solution of the compound. ^{1}H NMR (C_6D_6) 1.15 [s, 9H, H{$C_3N_2H_2$[$C(CH_3)_3$]S}Hg], 1.17 [m, 3H, HgCH$_2$CH$_3$], 1.61[m, 2H, H{$C_3N_2H_2$[$C(CH_3)_3$]S}HgCH$_2$CH$_3$], 6.33 [d, 1H, $^3J_{H-H}$ = 2 Hz, H{$C_3N_2H_2$[$C(CH_3)_3$]S}HgEt], 6.90 [d, 1H, $^3J_{H-H}$ = 2 Hz, H{$C_3N_2H_2$[$C(CH_3)_3$]S}HgEt], 12.27 [br, 1H, H{$C_3N_2H_2$[$C(CH_3)_3$]S}HgEt]. ^{13}C{^{1}H} NMR (C_6D_6) 13.8 [1C, H{$C_2N_2H_2$[$C(CH_3)_3$]CS}-HgCH$_2$CH$_3$], 28.5 [1C, H{$C_2N_2H_2$[$C(CH_3)_3$]CS}HgCH$_2$CH$_3$], 59.9 [1C, H{$C_2N_2H_2$[$C(CH_3)_3$]CS}HgEt], 119.7 [1C, H-{$C_2N_2H_2$[$C(CH_3)_3$]CS}HgEt], obscured by solvent [1C, H-{$C_2N_2H_2$[$C(CH_3)_3$]CS}HgEt], 145.1 [1C, H{$C_2N_2H_2$[$C(CH_3)_3$]CS}HgEt]. IR Data (KBr pellet, cm^{-1}): 3287 (m), 3183 (m), 3158 (m), 2984 (m), 2928 (m), 2868 (m), 2742 (w), 1730 (w), 1618 (w), 1577 (s), 1480 (m), 1460 (m), 1431 (w), 1408 (w), 1373 (m), 1338 (m), 1284 (w), 1250 (m), 1222 (s), 1182 (s), 1143 (vs), 1129 (s), 1106 (vs), 1068 (vs), 1044 (vs), 958 (s), 913 (m), 818 (w), 785 (w), 755 (s), 696 (m). Mass spectrum: m/z = 387.1 {M}$^+$ (M = {[Hmim$^{Bu^t}$]HgEt}).

Reactivity of {[Hmim$^{Bu^t}$]HgMe}$^+$ towards NaSPh. A mixture of {[Hmim$^{Bu^t}$]HgMe}[BF_4] (25 mg, 0.055 mmol) and NaSPh (10 mg, 0.076 mmol) was treated with C_6D_6 (0.7 mL). The reaction was monitored by using ^{1}H NMR spectroscopy which demonstrated the formation of PhSHgMe and Hmim$^{Bu^t}$ within 20 min at room temperature.

Comparison of the Reactivity of {[Hmim$^{Bu^t}$]HgEt}[BF_4] towards PhSH in the Presence and Absence of Hmim$^{Bu^t}$. A solution of {[Hmim$^{Bu^t}$]HgEt}[BF_4] (15 mg, 0.032 mmol) in C_6D_6 (1.5 mL) was treated with PhSH (15 μL) mesitylene (2 μL) as an internal standard. The solution was divided into two NMR tubes, to which one was treated with Hmim$^{Bu^t}$ (5 mg), and the two samples were monitored by ^{1}H NMR spectroscopy. For the sample that was treated with Hmim$^{Bu^t}$, ^{1}H NMR spectroscopy demonstrated the complete loss of the mercury ethyl signal and the formation of ethane over a period of 2 days. For the sample without added Hmim$^{Bu^t}$, ^{1}H NMR spectroscopy demonstrated that {[Hmim$^{Bu^t}$]HgEt}$^+$ was unperturbed, and there was no formation of ethane over a period of 2 days and only small amounts (<5%) could be detected after a period of 10 days at room temperature. However, quantitative elimination of ethane was achieved over a period of 10 days at 60 °C.

Synthesis of {[Hmim$^{Bu^t}$]$_2$Hg}[BF_4]$_2$. {[Hmim$^{Bu^t}$]HgEt}[BF_4] (15 mg, 0.032 mmol) was treated with a solution of PhSH (20 μL) in C_6D_6 (0.7 mL) and heated at 60 °C for a period of 3 days. A white precipitate was deposited upon cooling to room temperature. The mother liquor was decanted, and the solid was washed with pentane (2×0.5 mL) and dried in vacuo to give {[Hmim$^{Bu^t}$]$_2$Hg}[BF_4]$_2$ as a white powder (4 mg, 37% yield).

Table 2. Crystal, Intensity Collection, and Refinement Data

	[mim$^{Bu^t}$]HgEt	{[Hmim$^{Bu^t}$]HgEt}[BF_4]	{[Hmim$^{Bu^t}$]$_2$Hg}[BF_4]$_2$	{[Hmim$^{Bu^t}$]$_4$Hg}[BF_4]$_2$·0.25(C_6H_6)	[*p*-Bu^tC_6H_4S]$_2$Hg
lattice	monoclinic	monoclinic	monoclinic	triclinic	triclinic
formula	$C_9H_{16}HgN_2S$	$C_{18}H_{34}B_2F_8Hg_2N_4S_2$	$C_{14}H_{24}B_2F_8HgN_4S_2$	$C_{29.5}H_{49.5}B_2F_8HgN_8S_4$	$C_{20}H_{26}HgS_2$
formula weight	384.89	945.41	686.70	1018.72	531.12
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	7.0504(6)	17.7657(7)	8.429(1)	14.647(2)	6.128(3)
b/Å	7.4019(7)	10.9903(5)	12.910(1)	17.583(2)	12.040(6)
c/Å	21.629(2)	15.9175(7)	21.383(2)	19.839(2)	13.715(7)
α/deg	90.00	90.00	90.00	96.814(2)	87.132(7)
β/deg	91.331(1)	114.537(1)	98.8040(10)	111.056(2)	80.368(7)
γ/deg	90.00	90.00	90.00	113.285(2)	83.006(7)
V/Å^3	1128.42(18)	2827.2(2)	2299.4(4)	4172.6(8)	989.7(8)
Z	4	4	4	4	2
temperature (K)	125(2)	125(2)	125(2)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ (calcd.), g cm^{-3}	2.266	2.221	1.984	1.622	1.782
μ (Mo Kα), mm^{-1}	13.784	11.063	6.948	3.957	7.984
θ max, deg.	32.60	32.54	30.52	30.70	30.710
no. of data collected	18521	47848	36426	68377	15931
no. of data used	3924	9940	7028	25691	6068
no. of parameters	118	325	280	946	209
R_1 [$I > 2\sigma(I)$]	0.0314	0.0223	0.0275	0.0439	0.0435
wR_2 [$I > 2\sigma(I)$]	0.0678	0.0471	0.0584	0.0771	0.0646
R_1 [all data]	0.0506	0.0357	0.0394	0.0830	0.0783
wR_2 [all data]	0.0678	0.0509	0.0625	0.0866	0.0731
GOF	1.026	1.044	1.018	1.101	1.010

^{1}H NMR (C_6D_6) 1.25 [s, 18 H, {$HC_3N_2H_2$[C(CH_3)$_3$]S}$_2$Hg], 5.97 [t, 2H, J_{H-H} = 2 Hz, {$HC_3N_2H_3$[C(CH_3)$_3$]S}2Hg], 6.32 [t, 2H, J_{H-H}=2 Hz, {$HC_3N_2H_2$[C(CH_3)$_3$]S}$_2$Hg], 12.11 [br, 2H, {*N*−H$C_3N_2H_2$[C(CH_3)$_3$]S}$_2$Hg] (note: the chemical shifts are influenced by Hmim$^{Bu^t}$ because of exchange). The accompanying redistribution product, $(PhS)_2Hg$, was observed by ^{1}H NMR spectroscopic analysis of the sample prior to isolating {[Hmim$^{Bu^t}$]$_2$Hg}[BF_4]$_2$.

Synthesis of {[Hmim$^{Bu^t}$]$_4$Hg}[BF_4]$_2$. (a) A solution of {[Hmim$^{Bu^t}$]HgEt}[BF_4] (15 mg, 0.032 mmol) in C_6D_6 (0.7 mL) was treated with Hmim$^{Bu^t}$ (5 mg, 0.032 mmol) and PhSH (5 μL). Over a period of several days crystals of composition {[Hmim$^{Bu^t}$]$_4$Hg}[BF_4]$_2$ suitable for X-ray diffraction were deposited. The formation of $(PhS)_2Hg$ and ethane was demonstrated by ^{1}H NMR spectroscopy. ^{1}H NMR for {[Hmim$^{Bu^t}$]$_4$Hg}[BF_4]$_2$ (C_6D_6): 1.47 [s, 36H, {$HC_3N_2H_2$[C(CH_3)$_3$]S}$_4$Hg], 5.95 [d, J_{H-H} = 2 Hz, 4H of {$HC_3N_2H_3$[C(CH_3)$_3$]S}$_4$Hg], 6.06 [d, J_{H-H} = 2 Hz, 4H, {$HC_3N_2H_2$[C(CH_3)$_3$]S}$_4$Hg], 12.1 [br, 4H of {*N*−H$C_3N_2H_2$[C(CH_3)$_3$]S}$_4$Hg] (note: the chemical shifts are influenced by Hmim$^{Bu^t}$ because of exchange).

(b) A solution of {[Hmim$^{Bu^t}$]HgMe}[BF_4] (5 mg, 0.011 mmol) in C_6D_6 (0.7 mL) was treated Hmim$^{Bu^t}$ (5 mg, 0.032 mmol) and PhSH (5 μL). The solution was heated at 110 °C for a period of 2 weeks resulting in the formation of {[Hmim$^{Bu^t}$]$_4$Hg}[BF_4]$_2$.

Reactivity of {[Hmim$^{Bu^t}$]HgEt}[BF_4] towards *p*-Bu^tC_6H_4SH in the Presence and Absence of Hmim$^{Bu^t}$]. A solution of {[Hmim$^{Bu^t}$]-HgEt}[BF_4] (12 mg, 0.03 mmol) and mesitylene (10 μL) in C_6D_6 (1.5 mL) was treated with *p*-Bu^tC_6H_4SH (20 μL). The solution was split into two NMR tubes, one of which contained Hmim$^{Bu^t}$ (3 mg, 0.02 mmol). The solution to which Hmim$^{Bu^t}$ was added reacted over a period of 1 day at room temperature to eliminate ethane and generate [*p*-Bu^tC_6H_4S]$_2$Hg and {[Hmim$^{Bu^t}$]$_4$Hg}[BF_4]$_2$, as demonstrated by ^{1}H NMR spectroscopy. In contrast, in the absence of additional Hmim$^{Bu^t}$, elimination of ethane was very slow, with <10% after 3 days at room temperature. The sample was heated at 60 °C, resulting in about 60% conversion over 12 days. Complete elimination of ethane was achieved by heating at 110 °C for 3 h, and [*p*-Bu^tC_6H_4S]$_2$Hg and {[Hmim$^{Bu^t}$]$_2$Hg}$_2$[BF_4] were identified by ^{1}H NMR spectroscopy.

^{1}H NMR Spectroscopic Evidence for Reversible Binding of Hmim$^{Bu^t}$ to PhSHgMe. (a) A solution PhSHgMe (7 mg, 0.02 mmol) in C_6D_6 (0.7 mL) was treated with mesitylene (10 μL) and successive portions of Hmim$^{Bu^t}$ (4 × 2 mg, 0.01 mmol). The resulting solution was monitored by ^{1}H NMR spectroscopy, thereby demonstrating that the chemical shift of the mercury methyl signal is a function of the concentration of Hmim$^{Bu^t}$ (0 mg Hmim$^{Bu^t}$, δ_{CH_3} = 0.081; 2 mg Hmim$^{Bu^t}$, δ_{CH_3} = 0.099; 4 mg Hmim$^{Bu^t}$, δ_{CH_3} = 0.126; 6 mg Hmim$^{Bu^t}$, δ_{CH_3} = 0.145; 8 mg Hmim$^{Bu^t}$, δ_{CH_3} = 0.172) because of rapid and reversible coordination of Hmim$^{Bu^t}$.

(b) A solution PhSHgMe (about 50 mg, 0.15 mmol) in C_6D_6 (0.7 mL) was treated with successive portions of Hmim$^{Bu^t}$ (2 × 10 mg, 0.06 mmol). The resulting solution was monitored by ^{199}Hg NMR spectroscopy, thereby demonstrating that the chemical shift of the mercury signal is a function of the concentration of Hmim$^{Bu^t}$ (0 mg Hmim$^{Bu^t}$, −557 ppm; 10 mg Hmim$^{Bu^t}$, −542 ppm; 20 mg Hmim$^{Bu^t}$, −540 ppm).

^{1}H NMR Spectroscopic Evidence for Reversible Binding of Hmim$^{Bu^t}$ to PhSHgEt. (a) PhSHgEt (7 mg, 0.02 mmol) in C_6D_6 (0.7 mL) was treated with mesitylene (10 μL) and successive portions of Hmim$^{Bu^t}$ (4 × 2 mg, 0.01 mmol). The resulting solution was monitored by ^{1}H NMR spectroscopy, thereby demonstrating that the chemical shifts of the mercury ethyl signals are a function of the concentration of Hmim$^{Bu^t}$ (0 mg Hmim$^{Bu^t}$, δ_{CH_2} = 0.944, δ_{CH_3} = 0.825; 2 mg Hmim$^{Bu^t}$, δ_{CH_2} = 0.958, δ_{CH_3} = 0.837; 4 mg Hmim$^{Bu^t}$, δ_{CH_2} = 0.986, δ_{CH_3} = 0.863; 6 mg Hmim$^{Bu^t}$, δ_{CH_2} = 1.019, δ_{CH_3} = 0.8923; 8 mg Hmim$^{Bu^t}$, δ_{CH_2} = 1.066, δ_{CH_3} = 0.930).

(b) A solution PhSHgEt (200 mg, 0.59 mmol) in C_6D_6 (0.7 mL) was treated with successive portions of Hmim$^{Bu^t}$ (2 × 25 mg, 0.16 mmol). The resulting solution was monitored by ^{199}Hg NMR spectroscopy, thereby demonstrating that the chemical shift of the mercury signal is a function of the concentration of Hmim$^{Bu^t}$ (0 mg Hmim$^{Bu^t}$, −730 ppm; 25 mg Hmim$^{Bu^t}$, −684 ppm; 50 mg Hmim$^{Bu^t}$, −680 ppm).

^{1}H NMR Spectroscopic Evidence for Reversible Binding of Hmim$^{Bu^t}$ to {[Hmim$^{Bu^t}$]HgMe}$^+$. A solution of {[Hmim$^{Bu^t}$]Hg-Me}[BF_4] in C_6D_6 was titrated with a solution of Hmim$^{Bu^t}$ in C_6D_6 and was monitored by ^{1}H NMR spectroscopy. Evidence for rapid reversible binding is provided by the observation that the signals due to the [mim$^{Bu^t}$] and alkyl groups shift, while no signals due to uncoordinated Hmim$^{Bu^t}$ are observed.

Synthesis of [*p*-Bu^tC_6H_4S]$_2$Hg. HgO (1.00 g, 4.62 mmol) was treated with a solution of *p*-Bu^tC_6H_4SH (1.59 mL, 9.3 mmol) in EtOH (30 mL). The resulting orange suspension turned white over

a period of 1 h and was stirred for an additional 3 h at room temperature. After this period, the mixture was filtered and the precipitate was washed with EtOH (30 mL) and dried in vacuo to give [*p*-Bu^{t}C$_6$H$_4$S]$_2$Hg as a white powder (2.30 g, 94% yield). Crystals of composition [*p*-Bu^{t}C$_6$H$_4$S]$_2$Hg suitable for X-ray diffraction were obtained from CH_3CN. ^{1}H NMR (C_6D_6) 1.15 [s, 18H, [*p*-Bu^{t}C$_6$H$_4$S]$_2$Hg], 6.99 [d, $^3J_{H-H}$ = 8 Hz, 4 H [*p*-Bu^{t}C$_6$H$_4$S]$_2$Hg], 7.33 [d, $^3J_{H-H}$ = 8 Hz, 4 H [*p*-Bu^{t}C$_6$H$_4$S]$_2$Hg]. ^{13}C NMR (C_6D_6) 31.4 [6 C, [*p*-{(CH_3)$_3$C}C$_6$H$_4$S]$_2$Hg], 34.4 [2 C [*p*-{(CH$_3$)$_3$C}C$_6$H$_4$S]$_2$Hg], 126.4 [4 C SCC$_4$H$_4$CBu^t], 131.0 [2 C SCC$_4$H$_4$CBu^t], 133.2 [4 C SCC$_4$H$_4$CBu^t], 149.2 [2 C SCC$_4$H$_4$CBu^t]. IR Data (KBr pellet, cm^{-1}): 3071 (w), 2961 (vs), 2901 (m), 2866 (m), 1491 (s), 1461 (m), 1396 (m), 1361 (m), 1268 (m), 1200 (w), 1119 (s), 1080 (w), 1009 (m), 829 (m), 820 (m), 807 (m), 737 (m), 722 (w). Mass spectrum: m/z = 530.6 {M }$^+$.

(32) (a) Sheldrick, G. M. *SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1981. (b) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

X-ray Structure Determinations. Single crystal X-ray diffraction data were collected on either a Bruker Apex II diffractometer or a Bruker P4 diffractometer equipped with a SMART CCD detector. Crystal data, data collection, and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.10).[32]

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Supporting Information Available: Experimental details, computational data, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.