Investigation of a Mercury(II) Carbene Complex: Bis(1,3-dimethylimidazol-2-ylidene) mercury Chloride

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ABSTRACT

The reaction of 1,3-dimethylimidazolium chloride with $Hg(O_2CCH_3)_2$ afforded a bis(carbene)mercury(II) complex (2), which is characterized by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{15}N, and ^{199}Hg) and by single-crystal X-ray analysis. As a consequence of chloride-ion interaction with the mercury center, the C_2–Hg–C_2 angle in 2 is reduced to 161.4 (3)° compared to its near-linear value in complex 4 that contains perchlorate counterions. The C_2 resonance in the mercury complex 2 moves upfield by 36.96 ppm relative to the parent carbene (2), with a large $^1J_{HgC} = 2741.18$ Hz. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

We have previously reported the syntheses, characterizations, and isolation of stable nucleophilic carbenes that are very good synthons for studying previously inaccessible metal-carbene complexes [1–11]. Carbene-metal complexes have also been available by other indirect routes [12–32], so that a fair number of homoleptic bis(carbene) complexes are

now available for further study. We now report the synthesis and characterization of a bis(carbene)·mercury, which is obtained by one of the indirect methods starting from the corresponding imidazolium chloride. The structure and properties of this new complex provide an interesting comparison with the previously known adducts.

RESULTS AND DISCUSSION

The mercury-carbene complex is conveniently prepared in 89% yield by the reaction of 1,3-dimethylimidazolium chloride with $Hg(O_2CCH_3)_2$ (Equation 1).


$$(1)$$
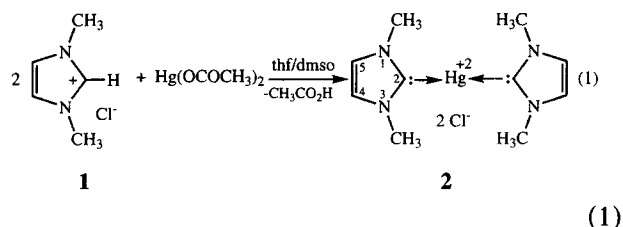
The formation of the carbene complex 2 may proceed through the free carbene (1,3-dimethylimidazol-2-ylidene, 3) by deprotonation of 1 with the mildly basic acetate anion (Scheme 1). The free carbene 3 is not sufficiently stable to be handled easily but has been observed in solution and even flash distilled as a neat liquid. Mild bases such as acetate do catalyze the H/D exchange (in D_2O) of the 2-proton
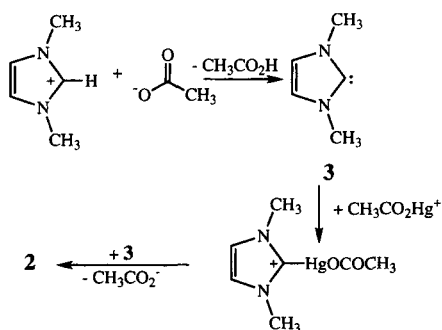

SCHEME 1

in imidazolium ions, which suggests that low equilibrium concentrations of the free carbenes can be generated under these mildly basic conditions [33]. A transient carbene generated under such conditions would be expected to react with an electrophilic mercury center. Direct mercuration of the imidazole ring in 1 is another possibility. However, the π centers at C_4 and C_5 are expected to be more basic than the C_2 position such that mercuration by this mechanism might occur at one of the two adjacent carbon centers (C_4 or C_5) similar to the result for direct iodination of imidazole [34]. Furthermore, the cationic imidazolium ring in 1 would seem to be too poorly nucleophilic for attack by an electrophilic mercury center.

The complex 2 is a stable colorless crystalline solid that is poorly soluble in most organic solvents. Methanol is a good solvent, but other polar solvents, such as acetonitrile and dimethylformamide, are not. Recrystallization of 2 can be accomplished from a mixture of methanol and tetrahydrofuran (thf). All the NMR spectroscopic measurements on 2 were performed on CD_3OD solutions. The spectral data for 2 and the related compounds are compiled in Table 1. The four-bond mercury-proton coupling is of higher magnitude ($^4J_{(HgH)} = 27.73$ Hz) for the rigidly held protons on the C_4 and C_5 carbons compared to the value for the $-NCH_3$ protons ($^4J_{(HgH)} = 9.32$ Hz) that is rotationally averaged. A similar trend is observed in the ^{13}C NMR spectra. The values are $^3J_{(HgC)}$ = 81.18 and 34.18 Hz for $C_{4(5)}$ and $-NCH_3$ carbons, respectively. This latter observation is probably the result of the E vs. Z arrangement about the $N-C_2$ bond. There is a substantial upfield shift of the C_2 resonance by 37 ppm (Table 1) compared to the parent carbene 3. This shift in the C_2 resonance is in accordance with the trend observed for other metal-carbene complexes (vide infra). The one-bond Hg-C coupling is quite high at 2741.18 Hz. Fairly large one-bond coupling constants also seem to be typical for the metal complexes of the imidazol-2-ylidenes.

The ^{15}N NMR spectrum of 2 shows a single resonance that is downfield by 3.64 ppm of the parent carbene.
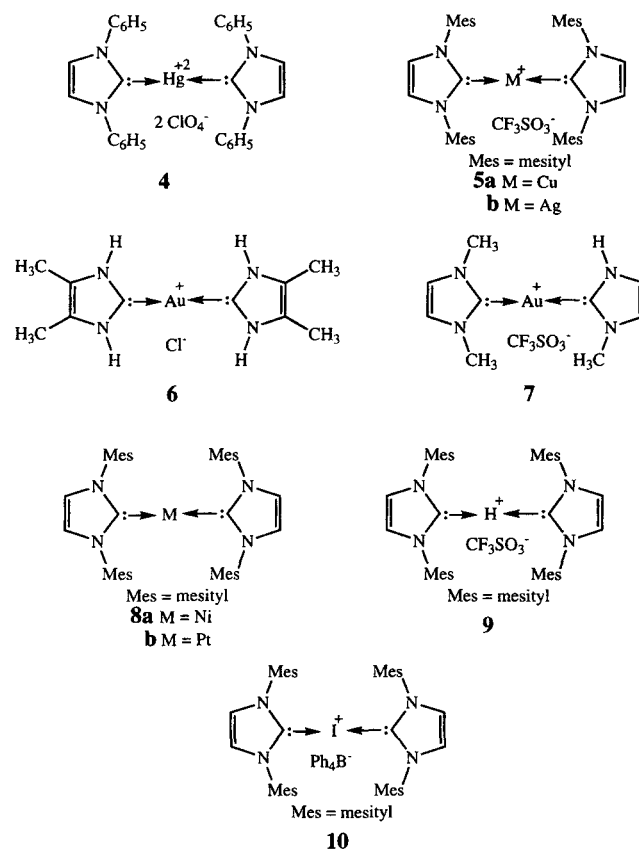
A single crystal of 2 that was suitable for X-ray crystallographic measurements was grown from a methanol/tetrahydrofuran solution. Selected bond lengths and angles for 2 and related compounds are given in Table 2. The structure of 2 is an interesting study of the complexities of polar space groups, and details about this are reported elsewhere [35]. The geometry of 2 is illustrated by the KANVAS [36] drawing in Figure 1. The solid-state structure of 2 is not cleanly a linear bis(carbene)·mercury complex. There are additional interactions between the mercury center and the associated chloride ions that distort the geometry toward a tetrahedral arrangement. As a consequence of these chloride ion interactions with the mercury center, the C_2-Hg-C_2 angle in 2 is substantially reduced to 161.4 (3)° compared to its value of 180° in the previously reported bis(carbene)·mercury complex 4 [37,38]. It should be noted that none of the other bis(carbene)complexes listed in Table 2 show such a large deviation from a linear geometry as is found in 2. The Cl-Hg-Cl angle in 2 is 86° with Cl-Hg distances of about 283 pm. One of the chlorides can be considered to be somewhat

TABLE 1   Selected NMR Chemical Shifts[a] in **2, 3, 5, 8, 9,** and **10**

Nucleus	3[b]	2[c]	5a	5b[d]	8a[e]	8b[e]	9[b]	10[f]
$^{13}C_2$	215.2	178.2 $^1J_{HgC} = 2741.2$	178.2	183.6 $^1J_{107AgC} = 188.0,$ $^1J_{109AgC} = 208.6$	193.2.2	197.5 $^1J_{PtC} = 1218.0$	176.1	155.2
$^{13}C_{4,5}$	120.5	125.6 $^3J_{HgC} = 81.2$	124.2	124.2 $^3J_{AgC} = 5.4$	118.1	118.6	123.9	126.6
$^1H_{4,5}$	6.92	7.51 $^4J_{HgH} = 27.7$	7.33	7.45[b] $^4J_{AgH} = 1.5$	6.01 (6.41)[b]	6.16 (6.66)[b]	7.53	7.22
$^{15}N_{1,3}$	−197.3	−193.7	−180.8	−179.1 $^2J_{107AgN} = 6.3,$ $^2J_{109AgN} = 7.2$	−193.2	−189.2	--	—
$^{199}Hg/^{109}Ag/^{195}Pt/^1H$	—	−933.5	—	642.4 $^4J_{AgH} = 1.7$	—	−1196.1	9.6	—

[a]References are $(CH_3)_4Si$, $NH_4{}^{15}NO_3$, $HgCl_2$, 5M $AgNO_3$, and K_2PtCl_4.
[b]In thf-d_8 solution.
[c]In methanol-d_4 solution.
[d]In pyridine-d_5 solution.
[e]In benzene-d_6 solution.
[f]In CD_3CN solution.

TABLE 2   Selected Bond Lengths (pm) and Angles (°) in **2** and Related Structures[a]

Property	1	2	4	5b	6	8a	8b	9	10
$r(C_2-N_{1(3)})$	132.3 (2),	133.1 (7),	134.0 (2),	135.6 (6),	132.8 (7)	137.5 (7)	138.0 (9)	135.9 (7)	133.3 (6)
	133.5 (2)	134.2 (7)	133.0 (1)	136.0 (6)	135.3 (9)	137.4 (7)	137.4 (10)	136.8 (7)	135.5 (6)
				135.2 (6)	132.2 (8)	138.1 (7)	138.3 (10)	132.9 (8)	134.2 (6)
				135.5 (6)	133.1 (8)	136.9 (7)	136.4 (10)	134.7 (7)	135.0 (6)
$r(C_4-C_5)$	134.6 (3)	136.5 (1)	136.0 (2)	133.0 (7)	134.7 (9)	134.2 (9)	130.9 (12)	134.4 (9)	133.3 (7)
				132.9 (7)	131.0 (10)	132.4 (9)	132.7 (12)	134.1 (9)	133.2 (7)
$r(N_{1(3)}-C_{5(4)})$	137.6 (2)	138.5 (8)	138.0 (2)	139.6 (6)	140.0 (8)	138.7 (8)	139.5 (10)	138.0 (8)	139.7 (6)
	137.9 (2)	138.6 (8)	140.0 (2)	139.8 (6)	138.1 (8)	137.8 (8)	140.5 (11)	137.3 (8)	139.6 (6)
				139.9 (6)	139.0 (9)	139.2 (8)	139.0 (10)	138.6 (8)	138.9 (6)
				139.0 (6)	139.8 (8)	139.3 (8)	138.4 (10)	134.6 (8)	139.5 (6)
$r(N_{1(3)}-R)$	146.5 (2)	145.0 (9)	143.0 (1)	143.7 (6)	—	144.6 (8)	143.5 (10)	144.8 (7)	145.0 (6)
	146.4 (2)	145.4 (8)	143.0 (2)	144.5 (7)		142.6 (8)	142.8 (10)	143.7 (7)	143.6 (6)
				143.4 (6)		142.7 (8)	142.8 (10)	146.9 (7)	144.7 (6)
				143.9 (6)		143.8 (8)	143.6 (10)	146.4 (8)	143.9 (6)
$r(C_2-M)$				206.7 (4)	201.2 (6)	182.7 (6)	195.9 (8)	210.1 (48)	228.6 (4)
	96 (1)	209.2 (5)	206.0 (1)	207.8 (4)	201.6 (6)	183.0 (6)	194.2 (8)	106.4 (47)	236.3 (4)
				103.6 (4)	104.2 (5)	101.5 (5)	103.1 (7)	101.2 (5)	106.2 (4)
$\theta(N_1-C_2-N_3)$	108.3 (1)	106.9 (5)	107.0 (1)	104.8 (4)	104.0 (5)	102.5 (5)	102.1 (7)	106.6 (6)	105.3 (4)
$\theta(C_{5(4)}-N_{1(3)}-C_2)$	109.0 (1)	110.1 (6)	111.0 (1)	111.1 (4)	111.9 (5)	112.4 (5)	110.5 (7)	114.0 (5)	110.2 (4)
	108.5 (1)		110.0 (1)	111.8 (4)	111.7 (5)	113.0 (5)	111.1 (7)	112.5 (5)	109.7 (4)
				110.6 (4)	112.4 (6)	111.5 (5)	111.2 (7)	109.3 (5)	110.9 (4)
				110.6 (4)	111.0 (6)	111.7 (5)	112.7 (7)	109.8 (6)	107.2 (5)
$\theta(N_{1(3)}-C_{5(4)}-C_{4(5)})$	107.0 (2)	106.1 (5)	106.0 (1)	107.6 (4)	105.7 (5)	106.6 (6)	108.4 (8)	104.9 (6)	107.1 (5)
	107.1 (2)	106.7 (5)		105.9 (5)	106.4 (6)	106.5 (6)	106.9 (8)	106.3 (6)	106.8 (5)
				106.7 (4)	105.8 (6)	107.1 (6)	107.4 (8)	107.4 (6)	106.6 (5)
				107.3 (4)	106.8 (6)	107.2 (6)	106.6 (8)	107.9 (6)	107.2 (5)
$\theta(C_2-N_{1(3)}-R)$	126.1 (1)	126.6 (5)	126.0 (1)	125.4 (4)	—	123.0 (5)	123.4 (6)	122.5 (5)	124.3 (4)
	125.1 (1)		127.0 (1)	124.3 (4)		123.0 (5)	124.1 (7)	123.1 (5)	124.8 (4)
				126.3 (4)		124.2 (5)	123.8 (7)	124.6 (5)	123.4 (4)
				124.6 (4)		125.3 (5)	123.3 (7)	122.4 (6)	122.9 (4)
$\theta(M-C_2-N_{1(3)})$	127 (1)	125.6 (4)	123.95	132.5 (3)	129.6 (5)	129.8 (4)	129.1 (6)	140 (2)	124.2 (4)
	125 (1)	127.5 (4)		123.7 (3)	126.1 (4)	128.7 (5)	127.7 (6)	119 (2)	129.6 (4)
				131.8 (4)	128.0 (5)	129.4 (5)	129.6 (6)	128 (2)	126.1 (3)
				123.4 (3)	128.1 (4)	128.0 (5)	128.2 (6)	126 (2)	128.5 (4)
$\theta(C_2-M-C_2)$	—	161.4 (3)	180	176.3 (2)	175.8 (2)	176.4 (3)	177.4 (3)	172.1 (20)	177.5 (2)

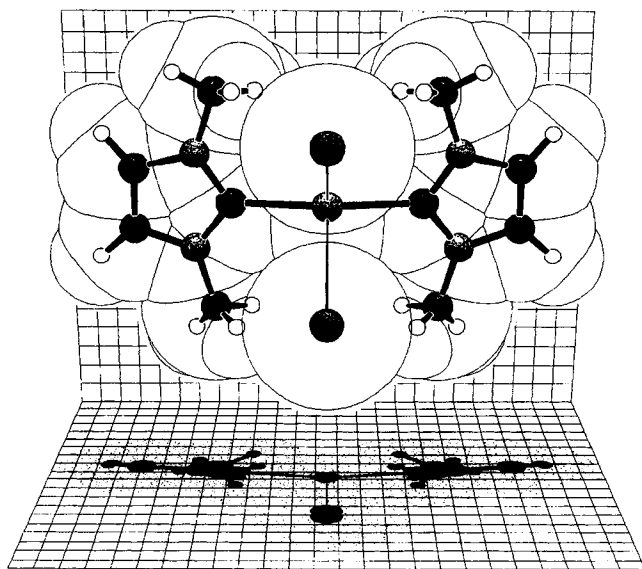[a]The numbering scheme for all compounds is as indicated for **1**. R = substituent on the nitrogen atom.

FIGURE 1 Drawing of the solid-state geometry of 2.

"bridging" and approaches a second mercury center at a distance of 366 pm. By comparison, the linear geometry found for **4** is probably the result of the less nucleophilic perchlorate ions and the additional steric bulk offered by the phenyl substituents on the nitrogens compared to the methyls in **2**. The remaining bond angles and bond lengths in **2** are fairly similar to those in **4**. The imidazole ring geometry in **2** is also close to that found for the imidazolium ion **1** [2]. The ring internal angle at C_2 in **1**, **2**, and **4** are all fairly similar and reflect a geometry that is more commonly found for carbene·main-group-element adducts.

The mercury complex **2** is closely related to a complex (**4**) that is formally derived from 1,3-diphenylimidazol-2-ylidene and mercury(II) perchlorate, as described earlier. There are other homoleptic bis(carbene) metal complexes of Cu [6] (**5a**), Ag [6] (**5b**), Au (6 [39] and 7 [40]), Ni [7] (**8a**), and Pt [7] (**8b**). Among the nonmetals, homoleptic bis(carbene) complexes have been reported for hydrogen [10] (**9**) and iodine [10] (**10**). These varied structures serve as useful comparisons for structural and spectroscopic data.

In general, a more carbenelike geometry is observed for the adducts of the transition metals (Table 2). This is reflected primarily by the more carbenelike (small) valence angle at the former carbene center. These homoleptic complexes also tend toward a near-linear geometry at the central atom, except when counterions are also interacting (as in **2**). One respect in which the mercury complexes differ from all the other complexes presented in Table 2 is the

slightly longer $C_4 = C_5$ double bond. The reason for this difference is unclear, but most other features for these homoleptic bis(carbene)·mercury complexes resemble their main group counterparts more than the transition metal analogs. From the data presented in Table 1, the complexes that retain the most carbenelike resonances for C_2 are the nickel and platinum complexes (**8a** and **8b**, respectively). In these complexes, C_4 and C_5 remain at somewhat higher fields, similar to the free carbenes. There is insufficient experimental data available on the gold complexes to relate their NMR spectral properties to the other complexes. For the three metal complexes where coupling data is available (Hg, Ag, and Pt), there is a trend to have fairly large one-bond couplings to these two-coordinate metal centers. In these cases, the respective $^1J_{MC}$ couplings are among the largest known for each of the metal centers.

SUMMARY

In summary, the bis(carbene)·mercury complexes seem to be more closely related to other main group element carbene adducts than to adducts of transition metals like nickel or platinum. There is a tendency of the mercury center in complexes like **2** and **4** to interact with other nucleophiles that could lead to interesting reactivity for the compounds. However, the level of reactivity at the mercury is probably far less than that observed for the related 14*e* two-coordinate nickel and platinum compounds (**8a** and **8b**, respectively).

EXPERIMENTAL SECTION

Reaction and manipulations were carried out under an atmosphere of dry nitrogen, either in a Vacuum Atmospheres dry box or using standard Schlenk techniques. Solvents were dried (using standard procedures) [41], distilled, and deoxygenated prior to use. Glasswares were oven-dried at 160°C overnight. The salt, 1,3-dimethylimidazolium chloride was prepared as previously described [42]. Mercury(II) acetate was purchased from Aldrich and used without further purification. The ^1H (300.75 MHz), ^{13}C (75.629 MHz), ^{15}N (30.484 MHz), and ^{199}Hg (53.777 MHz) NMR spectra were recorded on a GE Omega 300WB spectrometer. NMR references are $(CH_3)_4Si$ (^1H, ^{13}C), $NH_4^{15}NO_3$ (^{15}N), and $HgCl_2$(aq) (^{199}Hg). The ^{15}N DEPT experiment was run using standard DEPT sequence assuming a $J_{HN} = 7$ Hz with a θ pulse of 45°. Melting point was obtained on a Thomas–Hoover capillary apparatus and was not corrected. Elemental analysis was performed by Micro-Analysis, Inc., Wilmington, DE.

Synthesis of Bis(1,3-dimethylimidazol-2-ylidene)mercury Chloride (2)

In the dry box, a 100 mL round-bottom flask was charged with 1.00 g (7.55 mmol) of 1,3-dimethylimidazolium chloride and 25 mL of thf. To this solution was added 1.20 g (3.77 mmol) of $Hg(O_2CCH_3)_2$ and an additional 20 mL of thf followed by 1 mL of dimethyl sulfoxide. The mixture was stirred at room temperature for 24 hours. The solution was filtered and the precipitate washed with 2 × 10 mL of thf, and the solid obtained was dried under reduced pressure for 6–7 hours (1.57 g, 89.8% yield). The white product is soluble in methanol. High-quality crystals were obtained when a CD_3OD (1.5 mL) solution was mixed with 0.5 mL of thf and cooled to 5°C overnight. A pure sample gave mp 305.6°C. ^1H NMR (CD_3OD): δ 4.07 (s, 12 H, $^4J_{HgH}$ = 9.32 Hz, NCH_3), 7.51 (s, 4 H, $^4J_{HgH}$ = 27.73 Hz, CCH). ^{13}C NMR (CD_3OD): δ 38.83 (s, $^3J_{HgC}$ = 34.18 Hz, NCH_3), 125.62 (s, $^3J_{HgC}$ = 81.18 Hz, $C_{4,5}$), 178.24 (s, $^1J_{HgC}$ = 2741.18 Hz, C_2). ^{15}N NMR (CD_3OD): δ −193.66 (s). ^{199}Hg NMR (CD_3OD): δ −933.53 (s). Anal. calcd for $C_{10}H_{16}N_4Cl_2Hg$: C, 25.9; H, 3.5; N, 12.1. Found: C, 25.5; H, 3.4; N, 11.6.

X-ray Crystal Structure of Bis(1,3-dimethylimidazol-2-ylidene)mercury(II) Chloride (3)

Crystal Data. $C_{10}H_{16}N_4Cl_2Hg$, orthorhombic, spacegroup $Cmc2_1$ (No. 36), a = 1226.3 (3), b = 1293.4 (3), c = 912.7 (3) pm, from 25 reflections, T = −70°C, Z = 4, fw = 463.76, D_c = 2.128 g/cm^3, μ(Mo) = 109.89 cm^{-1}.

Crystal Description. Colorless, parallelpiped (0.23 × 0.23 × 0.26 mm), grown from a solution of CD_3OD and THF. A total of 6618 data were collected; $4.5° \leq 2\theta \leq 55.0°$; data octants + + +, + + −, + − +, + − −, − + +, − + −, − − +, − − −, ω-scan method, scan width = 1.30–2.20° ω, scan speed 2.00–5.00°/min, Enraf-Nonius CAD4 diffractometer with graphite monochromator using Mo $K\alpha$ radiation, typical half-height peak width = 0.15° ω, two standards collected 21 times, 1% fluctuation, 16.5% variation in azimuthal scan, corrected for absorption (azimuthal), range of transmission factors = 0.07–0.08, 1595 duplicates, 1.9% R merge, 889 unique reflections with $I \geq 3.0\ \sigma(I)$; the structure was solved by Patterson method, refinement by full-matrix least squares on F, scattering factors from *International Tables for X-ray Crystallography*, Vol. IV, including anomalous terms for Hg and Cl, biweight $a[\sigma^2(I) + 0.0009I^2]^{-1/2}$, (excluded 13); refined anisotropic: all nonhydrogen atoms, isotropic H; there were 113 pa-

rameters, data/parameter ratio = 7.75, final R = 0.021, R_w = 0.019, error of fit = 0.84, max Δ/σ = 0.03, largest residual density = 1.11e/Å^3.

Supplementary Material Available. A complete description of the X-ray crystallographic structure determination on **2** has been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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[36] This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institute der Universität Freiburg, Germany), which was modified by A. J. Arduengo III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50 pm grid, and the lighting source is at infinity, so that shadow size is meaningful.

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[42] These 1,3-disubstituted imidazolium chlorides are available by established procedures: A. J. Arduengo III: U.S. Patent 5 077 414, 1991. 1,3-Dimethylimidazolium chlorides are also available by alkylation of the appropriately substituted imidazole with 1.1 equiv. of methyl chloride in THF at room temperature (sealed bomb).