Expedient Synthesis of Bis(imidazolium) Dichloride Salts and Bis(NHC) Complexes from Imidazoles using DMSO as a Key Polar Additive

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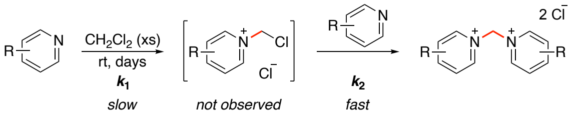
Supporting Information Placeholder

ABSTRACT: A general approach for the synthesis of bis(imidazolium) dichloride salts from imidazoles and dichloroalkanes is reported. Typical limitations of this reaction for the formation of methylene-bridged derivatives are addressed herein through the use of an excess CH_2Cl_2 in the presence of DMSO as a polar cosolvent, significantly improving conversion rates presumably via stabilization of the initial S_N2 transition state. The method was also shown to be applicable to the formation of bis(pyridinium) dichloride salts from pyridine derivatives, and to the direct synthesis of metal-bis(NHC) complexes from imidazoles.

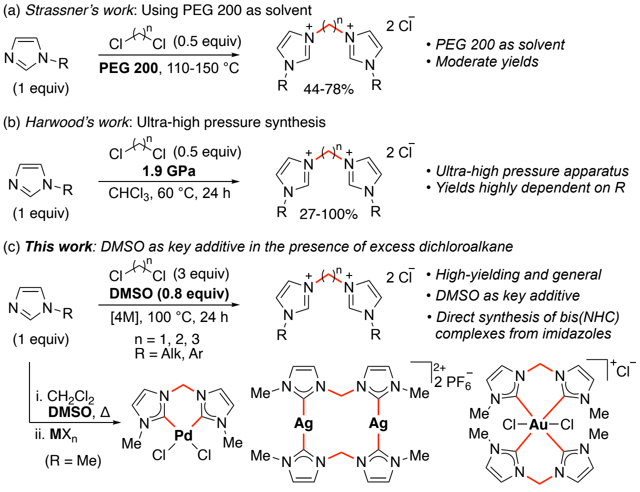
Metal-bis(carbene) complexes, typically synthesized from the corresponding bis(azolium) dihalide salts, constitute robust and highly effective catalysts in a wide range of chemical transformations[1,2,3] including cross-coupling reactions,[3a-d] imine reduction,[3e] redox alkylation,[3f-g] C–H/C–X activation,[3h-l] Nazarov cyclization,[3m] water oxidation[3n] and carbon dioxide reduction processes.[3o] Moreover, certain iridium(III)-bis(NHC) complexes have been identified as anti-cancer agents,[4] while gold analogues were previously employed as halide sensors.[5] The corresponding bis(azolium) salts have also been studied as ionic liquids[6] and as thermochromic and photoluminescent materials,[7] often accessed from the dichloride derivatives via anion exchange. While bis(azolium) dichloride salts are widely used in organic and organometallic chemistry, their efficient access from *N*-substituted imidazoles has been seriously impeded by the poor electrophilicity of 1,1-dichloroalkanes such as dichloromethane in nucleophilic substitution processes. Indeed, known routes to access these salts typically lack generality and practicality, requiring either prolonged heating in PEG 200 as solvent (Scheme 1a)[3a] or the use of an ultra-high pressure apparatus (Scheme 1b),[8] where yields were found to drastically decrease with longer *N*-alkyl substituents. After taking a closer look at these procedures, we noted that a common feature involve the use of stoichiometric dichloromethane as electrophile rather than a large excess, presumably to avoid isolation of the mono-alkylated *N*-chloromethyl imidazolium intermediate instead of the desired bis(azolium) salt.[3a,8,9] Due to the poor electrophilicity of dichloromethane, these reactions are often run at temperatures well above its boiling point in sealed vessels to prevent loss of this limiting reagent during the reaction, making the procedures difficult to reproduce on different scales. While the kinetic profiles of these transformations are not well-known, analogous processes involving pyridine derivatives as nucleophiles have previously been thoroughly investigated (eq 1).[10,11]



(1)

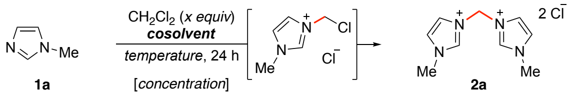
Particularly, Wamser and co-workers determined that the second substitution step is so much faster than the first one that the *N*-chloromethyl pyridinium chloride intermediate cannot be observed or isolated even when a large excess of dichloromethane was employed, and only the final bis(pyridinium) dichloride salt is obtained.[10a] Cognizant of the fact that *N*-alkyl imidazoles and pyridine derivatives possess similar nucleophilicities,[12] we reasoned that an analogous kinetic profile might be operative, potentially allowing the use of excess dichloromethane in the production of bis(azolium) dichloride salts as well. Herein, we report an expedient and general method for the formation of bis(imidazolium) dichloride salts via the use of an excess CH_2Cl_2 in the presence of DMSO as a key polar additive (Scheme 1c). The method could be extended to the production of bis(pyridinium) dichloride salts with excellent efficiency, and the subsequent addition transition metal salts was shown to lead to the production of various metal-bis(NHC) complexes directly from imidazoles. Considering the ubiquity of bis(azolium) salts and bis(NHC) complexes,[1-7] this practical approach should find utility in future research endeavors involving these species.

Scheme 1. Synthetic Methods to Bis(azolium) Dichloride Salts



Our initial studies focused on the formation of bis(imidazolium) salt **2a** from *N*-methylimidazole (**1a**) in the presence of an excess of dichloromethane (Table 1). A number of cosolvents were first evaluated at 70 °C for their ability to improve initial conversion rates of the transformation, presumably via stabilization of the polar S_N2 transition state leading to the *N*-chloromethyl imidazolium intermediate (entries 1-13).[13] Remarkably, such a species was never observed in any case, in accordance with our hypothesis stating that the second substitution step is likely significantly faster than the first one, in analogy to the formation of bis(pyridinium) dichloride salts (*vide supra*).[10a] From all cosolvents evaluated, DMSO proved to be superior (entry 13), and increasing both the temperature and concentration led to a significant improvement in yields (entries 14-21). Notably, while the absence of DMSO led to comparable yields at low conversions (see entry 2 vs 13-14), the beneficial effect of such a polar additive became more apparent at higher temperatures (see e.g., entry 19 vs 20), to the point where full conversion could not be reached in a reasonable time in the absence of this cosolvent. Under the optimized conditions, bis(imidazolium) salt **2a** could be obtained in 94% isolated yield and the procedure could be applied on multigram scale with similar efficiency (see entry 21 and Scheme 2, **2a**).

Table 1. Optimization of the Cosolvent and Reaction Conditions

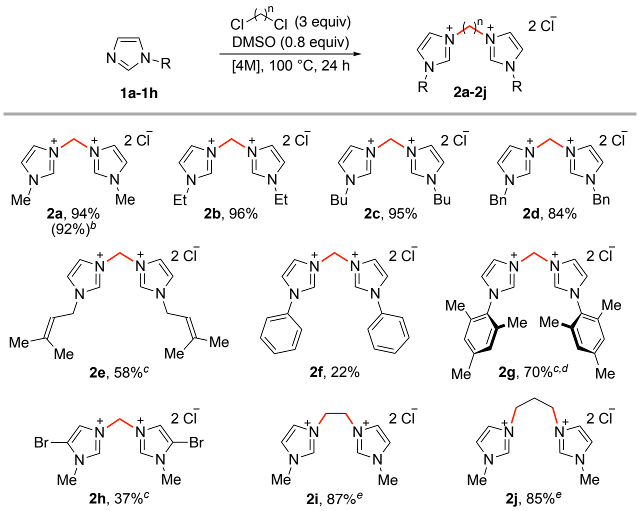


entry	CH_2Cl_2 equiv	cosolvent	temp. (°C)	conc. (M)	yield (%)[a]
1	7.8	-	70	2.0	7
2	3.0	-	70	5.2	15
3	3.0	Et_2O	70	2.0	4
4	3.0	DMF	70	2.0	7
5	3.0	*i*-PrOH	70	2.0	3
6	3.0	H_2O	70	2.0	1
7	3.0	MeCN	70	2.0	5
8	3.0	PhMe	70	2.0	2
9	3.0	1,4-dioxane	70	2.0	3
10	3.0	THF	70	2.0	2
11	3.0	PC[b]	70	2.0	8
12	3.0	DME	70	2.0	13
13	3.0	DMSO	70	2.0	16
14	3.0	DMSO	70	4.0	21
15	3.0	DMSO	80	4.0	43
16	3.0	-	80	5.2	29
17	3.0	DMSO	90	2.0	55
18	3.0	DMSO	90	3.0	76
19	3.0	DMSO	90	4.0	84
20	3.0	-	90	5.2	67
21	**3.0**	**DMSO**	**100**	**4.0**	**98 (94)**[c]

[a]Yield determined by ^1H NMR using 1,3,5-trimethoxybenzene as standard. [b]PC: propylene carbonate. [c]Isolated yield in parentheses.

In this procedure, the resulting insoluble precipitate **2a** is simply washed with diethyl ether at the end of the reaction to remove the DMSO additive, excess dichloromethane and any trace of unreacted imidazole, directly affording the pure product as a white solid without the need for further purification. With these conditions in hand, a number of imidazole derivatives were evaluated in the reaction, leading to considerable steric, electronic and functional variability in the bis(imidazolium) dichloride salts obtained (Scheme 2). The presence of longer alkyl chains at the 1-position of the imidazole substrate had little to no effect on the reaction outcome, affording excellent yields in all cases (**2a**-**2d**). Notably, this is in contrast with some other methods such as Harwood's high pressure protocol (see Scheme 1b),[8] where a significant decrease in yield was observed with *N*-alkyl substituents longer than methyl. *N*-prenylimidazole was also found to be compatible in the reaction (see **2e**), affording an alkene as functional handle for potential future derivatizations. As previously observed in other systems,[3h] less nucleophilic *N*-phenylimidazole proved to be more challenging in this transformation (see **2f**), while *N*-mesitylimidazole **1g** could afford a good yield of the corresponding bis(imidazolium) dichloride **2g** when the reaction was run at 110 °C for 48 hours. This significant variability in the efficiency of *N*-arylimidazoles to perform as effective nucleophiles is potentially due to the steric effect exerted by the ortho-methyl substituents, leading to deconjugation of both aromatic rings and thus a more nucleophilic imidazole ring in **1g**. Dibrominated bis(azolium) salt **2h** could also be obtained using this protocol, albeit in lower yield due to significant decomposition observed in the reaction conditions, requiring recrystallization in methanol to obtain the pure product.[13] The use of longer dichloroalkanes such as 1,2-dichloroethane (see **2i**) and 1,3-dichloropropane (see **2j**) afforded very good yields of the corresponding bis(imidazolium) dichloride salts when the electrophiles were used in stoichiometric amount. Notably, using an excess (3 equiv) of dichloroalkane in those two cases afforded a significant amount of undesired *N*-chloroalkyl imidazolium intermediate, highlighting the distinct kinetic profile of those reactions as compared with the use of dichloromethane as electrophile.

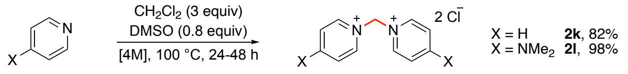
Scheme 2. Scope of Accessible Bis(imidazolium) Dichloride Salts[a]



[a]All yields correspond to yields of isolated product on a 4.0 mmol scale of imidazoles **1a**-**1h**. [b]Isolated yield on a 20 mmol (1.64 g) scale of imidazole **1a**. [c]Reaction was performed for 48 h. [d]Reaction was performed at 110 °C. [e]0.5 equiv dichloroalkane was used.

Our optimized conditions could also be extended to pyridine derivatives as substrates with high efficiency, affording the corresponding bis(pyridinium) dichloride salts **2k-2l** in good to excellent yields (Scheme 3). This practical method should find significant utility, considering the widespread use of these compounds either as organic dications and reaction additives,[14] linkers in materials chemistry,[15] organic oxidants,[16] or as aldehyde equivalents.[17]

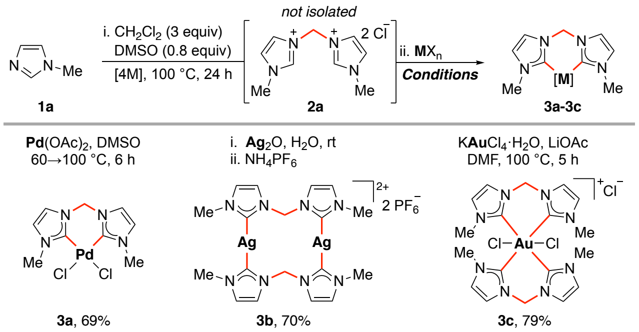
Scheme 3. Extension of the Method to Bis(pyridinium) Salts[a]



[a]All yields correspond to yields of isolated product on a 4.0 mmol scale of pyridine or DMAP.

Due the simplicity of the method developed, we sought to evaluate its compatibility with the direct formation of metal-bis(carbene) complexes using modified literature conditions (Scheme 4).[3a,h,18]

Scheme 4. Direct Assembly of Bis(NHC) Metal Complexes from Imidazole 1a and Dichloromethane[a]



[a]All yields correspond to yields of isolated product from imidazole **1a** (2–4 mmol scale).

For example, following our reaction, a solution of $Pd(OAc)_2$ in DMSO was added to the resulting mixture and heated for 6 hours, affording Pd(II) complex **3a** in good overall yield in a single pot from imidazole **1a**.[3a] Notably, this complex is known to be an effective catalyst for various cross-coupling reactions[3a-c] and C–H activation processes.[3i-k] Alternatively, the sequential addition of water, Ag_2O and NH_4PF_6 to the crude mixture led to the one-pot formation of dinuclear Ag(I) complex **3b** in 70% overall yield,[18a] which constitutes a versatile intermediate towards various Cu(I)-, Rh(III)-, Au(III)- or Ir(III)-bis(NHC) complexes via simple transmetallation.[4,5a,18a,19] Finally, Au(III)-NHC complex **3c**, previously studied for its halide-sensing properties,[5a] could be accessed in high overall yield via the addition of $KAuCl_4$ and LiOAc to the crude product **2a**.[18b] It is noteworthy that the overall yields observed herein for complexes **3a-3c** are comparable (<3% difference) with the reported yields starting from preformed **2a**,[3a,h,18a-b] highlighting the general compatibility of our method with a variety of known metalation procedures.

In summary, we report a general and expedient method for the synthesis of bis(imidazolium) dichloride salts via the use of DMSO as a key polar additive, and the process could be extended to the formation of versatile bis(pyridinium) dichloride salts difficult to access otherwise. Moreover, the conditions developed are shown to be compatible with subsequent metal-carbene formation, leading to the direct synthesis of various metal-bis(NHC) complexes from imidazoles. Considering the widespread utility of these salts in a variety of research fields,[1-7] this practical approach should find considerable utility for the rapid and efficient access to such derivatives.

ASSOCIATED CONTENT

Supporting Information

Experimental details and spectroscopic data.

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Notes

The authors declare no competing financial interest.

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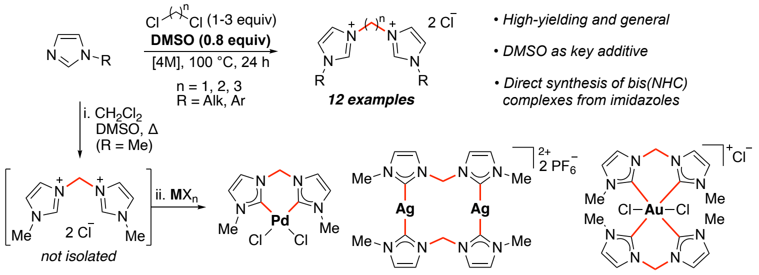
TOC GRAPHIC



- *High-yielding and general*
- *DMSO as key additive*
- *Direct synthesis of bis(NHC) complexes from imidazoles*