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Synthesis and Organocatalytic Applications of Imidazol(in)ium-2-thiocarboxylates

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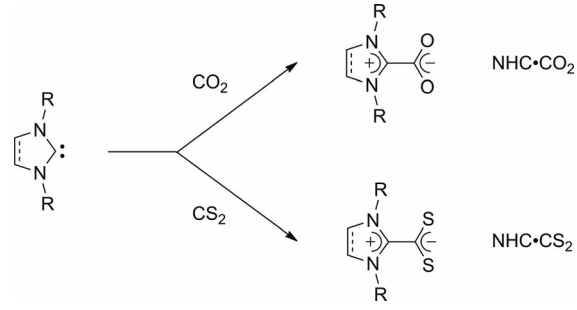
Keywords: Condensation reactions / Carbenes / Organocatalysis / Transesterification / Zwitterions

Five imidazol(in)ium-2-thiocarboxylates bearing cyclohexyl, mesityl, or 2,6-diisopropylphenyl substituents on their nitrogen atoms were prepared from the corresponding imidazol(in)ium chlorides or tetrafluoroborates in a one-pot, two-step procedure involving the in situ generation of free N-heterocyclic carbenes (NHCs) with a strong base followed by trapping with carbonyl sulfide. The resulting NHC·COS zwitterions were isolated in high yields and characterized by IR and NMR spectroscopy. The molecular structure of SIMes·COS was determined by X-ray diffraction analysis. Experimental data and DFT calculations indicated that the negative charge on the thiocarboxylate anion is preferentially delocalized on the sulfur atom. Thermogravimetric analysis showed that the NHC·COS zwitterions undergo thermolysis at temperatures ranging between 110 and 180 °C in the solid state. They are also rather labile in solution. Unlike the related NHC·CS_2 betaines, which are highly stable, crystalline materials, they displayed the same type of behavior as the analogous carboxylate adducts, which readily lose their CO_2 moiety upon heating or dissolution. Thus, imidazol(in)ium-2-thiocarboxylates acted as convenient NHC precursors in two model organocatalytic transformations. Of the five thiocarboxylates examined, ICy·COS was the most efficient at promoting the acylation of benzyl alcohol with vinyl acetate, whereas SIMes·COS afforded the highest activity in benzoin condensation.

Introduction

Since they were first isolated by Arduengo et al. in 1991,[1] stable N-heterocyclic carbenes (NHCs) built on the imidazole ring system have been embraced with an overwhelming enthusiasm by those involved in organic synthesis and organometallic chemistry.[2] Owing to their strong donor properties and wide structural diversity, these divalent carbon species have challenged or replaced phosphanes as versatile, neutral ligands in transition-metal complexes,[3] as well as main group elements,[4] lanthanides, and actinides.[5] Because they behave as powerful nucleophilic agents, stable carbenes are also used as reagents[6] and organocatalysts in the synthesis of fine chemicals[7] and in polymer chemistry.[8] Transesterification, cycloaddition, nucleophilic aromatic substitution, and acylation are classes of reactions that have already benefited from the participation of NHCs in stoichiometric or catalytic amounts, sometimes in an asymmetric fashion.[9]

In particular, owing to their high nucleophilicity, imidazol(in)-2-ylidenes readily add to a wide range of organic compounds, including allenes, ketenes, or heteroallenes of the X=C=Y type.[10] Upon reaction with carbon dioxide, they form inner salts, which can be stored and handled with no particular precautions (Scheme 1).[11–13] Such NHC·CO_2 zwitterions are rather labile in solution and act as convenient surrogates to air- and moisture-sensitive free carbenes in organometallic synthesis[14] and organocatalysis.[15] For instance, we have successfully used imidazol(in)ium-2-carboxylates as NHC ligand precursors in the synthesis of various second-generation ruthenium–alkylidene catalysts in olefin metathesis,[16] whereas other groups have developed several new major organocatalytic processes based on these zwitterions for carbon dioxide fixation reactions.[17]



Scheme 1. Synthesis of imidazol(in)ium-2-carboxylates and -dithiocarboxylates.

Betaines are also obtained when carbon disulfide reacts with NHCs or precursors thereof (Scheme 1).[18,19] The NHC·CS_2 adducts differ from the NHC·CO_2 series in that the dithiocarboxylate moiety shows no significant lability upon reaction with metals.[10] The coordination chemistry

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of these stable zwitterions remained almost unexplored until 2009, when a report based on ruthenium–arene complexes provided strong experimental evidence for the formation of cationic species of the [RuCl(*p*-cymene)(S_2C·NHC)]$^+$ type, in which the dithiocarboxylate group acts as a κ^2-*S*,*S*′ chelating ligand.[20] Further investigations on ruthenium– or osmium–alkenyl compounds confirmed this binding mode, although the most bulky imidazolium-2-dithiocarboxylates under scrutiny displayed non-innocent behavior in some instances, thereby allowing unexpected migration of the alkenyl fragment to take place.[21] In 2010, the inorganic chemistry of NHC·CS_2 zwitterions was extended to the synthesis of gold(I) complexes and gold nanoparticles.[22] In catalysis, these betaines were first employed in 2004 to promote the cyanosilylation of aldehydes.[23] Chiral enantiopure versions of these organocatalysts were subsequently applied to the asymmetric synthesis of β-lactams by the Staudinger reaction.[24]

In view of the rich chemistry exhibited by NHC·CO_2 and NHC·CS_2 betaines, and the marked differences between these two types of compounds, we launched a program to investigate the structural properties and reactivity of the related NHC·COS zwitterions. To the best of our knowledge, such adducts have never been described in the literature. In this contribution we report on the synthesis and characterization of five new imidazol(in)ium-2-thiocarboxylates bearing alkyl or aryl substituents on their nitrogen atoms. We also explore their potential in organocatalysis in acylation/transesterification reactions and benzoin condensation.

Results and Discussion

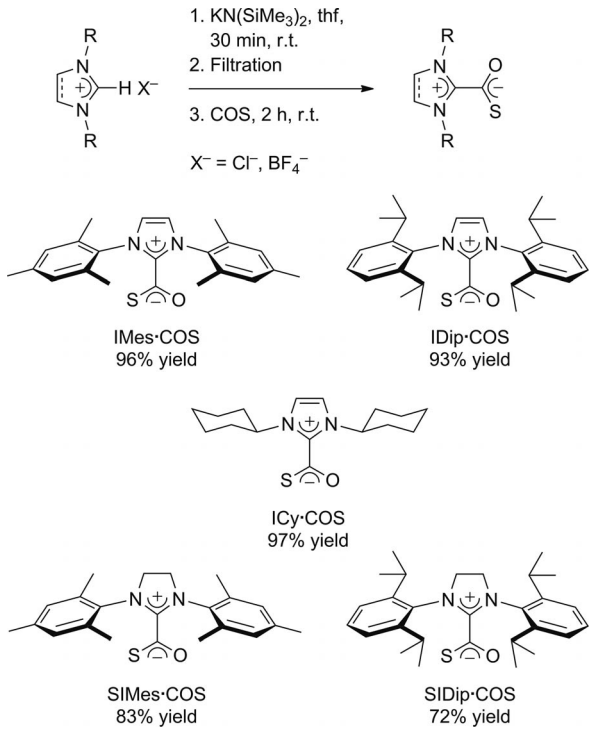
Preparation of Carbonyl Sulfide

Although it is commercially available from various industrial gas suppliers, carbonyl sulfide (also known as carbon oxysulfide) may be conveniently generated on a small preparative scale by hydrolysis of inorganic thiocyanates with mineral acids.[25] A particularly straightforward method involving the use of potassium thiocyanate and sulfuric acid as common, inexpensive starting materials was described as early as 1887 [Equation (1)].[26] We optimized and updated this procedure to match current laboratory practices (see the Experimental Section). The main contaminant, carbon dioxide, was removed by passing the gaseous product through concentrated aqueous sodium hydroxide followed by drying with concentrated sulfuric acid.[27] To displace oxygen, which might interfere with free carbenes in the next step, the whole apparatus was flushed with argon prior to the addition of KSCN. By using this protocol, a low-pressure feed of COS suitable for organic synthesis was obtained under the exclusion of air and moisture.

$$KSCN + 2\ H_2SO_4 + H_2O \rightarrow KHSO_4 + NH_4HSO_4 + COS\uparrow \quad (1)$$

Synthesis and Characterization of Imidazol(in)ium-2-thiocarboxylates

The in situ protocol that we had devised for trapping free carbenes with either carbon dioxide[28] or carbon disulfide[19] was again employed to obtain a set of five representative NHC·COS zwitterions bearing alkyl or aryl groups on the nitrogen atoms (Scheme 2). Imidazol(in)ium chlorides or tetrafluoroborates served as starting materials and were deprotonated with potassium bis(trimethylsilyl)amide. To ease contact between the reaction partners and to speed up the reaction, the base was dissolved in toluene and added to the imidazol(in)ium salts suspended in THF. After 30 min, the inorganic byproducts (KCl or KBF_4) were filtered off and excess carbonyl sulfide was bubbled into the solutions of free carbenes. Precipitation of the desired imidazol(in)ium-2-thiocarboxylates began after a few minutes, but the reagents were allowed to react for 2 h to ensure quantitative conversion. A simple workup involving partial solvent evaporation and filtration in air afforded imidazol(in)ium-2-thiocarboxylates in high yields and purities. Dimesitylimidazolium-2-thiocarboxylate (IMes·COS) was isolated as a bright-yellow microcrystalline powder, whereas its saturated heterocyclic analogue (SIMes·COS) and zwitterions bearing 2,6-diisopropylphenyl (IDip·COS and SIDip·COS) or cyclohexyl groups (ICy·COS) on the nitrogen atoms are less colored, with shades ranging from off-white to yellow-orange. Of note, the corresponding carboxylate inner salts are always white solids, whereas the dithiocarboxylate betaines are usually bright orange-red.



Scheme 2. Synthesis of the imidazol(in)ium-2-thiocarboxylates used in this work.

The five NHC·COS adducts were characterized by IR and NMR spectroscopy. The ^{1}H NMR spectra mainly revealed the disappearance of the strongly deshielded (9–11 ppm) formamidinium protons characteristic of the start-

ing materials whereas the ^{13}C NMR spectroscopic data showed the emergence of a new resonance at around 190 ppm due to the incorporation of a thiocarboxylate group into the products (Table 1). Note that the chemical shift of this latter resonance is almost exactly intermediate between those determined for the corresponding carboxylate and dithiocarboxylate zwitterions despite variations in the solvents used for acquiring the NMR spectroscopic data. Indeed, the values determined experimentally for δ(COS) in this study were correctly predicted by averaging the $\delta(CO_2)$ and $\delta(CS_2)$ values recorded previously for NHC·CO_2 and NHC·CS_2 betaines, provided that a correction of around +2 ppm was applied. This simple additivity rule might be useful for NMR predictive purposes.

Table 1. ^{13}C NMR chemical shifts (in ppm) of CXY in various NHC·CXY zwitterions at 298 K.

NHC	$\delta(CO_2)$[a]	$\delta(CS_2)$[b]	$[\delta(CO_2) + \delta(CS_2)]/2$	δ(COS)
ICy	154.3[c]	226.0[d]	190.2	192.2[e]
IMes	152.8[c]	221.6[c]	187.2	189.7[e]
IDip	152.3[e]	219.7[d]	186.0	188.2[e]
SIMes	153.6[c]	222.7[d]	188.2	190.7[e]
SIDip		219.8[d]		189.0[e]

[a] Data from ref.[28] [b] Data from ref.[19] [c] Solvent: [D_6]DMSO. [d] Solvent: $CDCl_3$. [e] Solvent: CD_2Cl_2.

The FTIR spectra of the five NHC·COS adducts were recorded in KBr pellets. Apart from the various C–H stretching vibration bands located between 2850 and 3100 cm^{-1}, the most intense absorptions originate from the N_2C^+ and COS^- groups (Table 2). In some instances these bands are further split into two components. The former endocyclic unit gives rise to a strong asymmetric stretching vibration band located at around 1480 cm^{-1}. This wavenumber is very similar to those recorded previously for the corresponding NHC·CO_2[28] and NHC·CS_2 adducts.[19] It is indicative of a CN double-bond character, which can be easily rationalized by assuming contributions of the canonical forms $^+$N=C–N and N–C=N$^+$.[29] The spectra present two characteristic absorptions for the CO and CS subunits of the thiocarboxylate groups. The CS stretching vibration band is in the fingerprint region of the IR spectrum between 917 and 1050 cm^{-1}, whereas the CO group affords a significantly more intense absorption, the position of which varies between 1524 and 1559 cm^{-1} (Table 2). It must be stressed that all these assignments are tentative and should be regarded with caution. In particular, the IR spectra of SIMes·COS and SIDip·COS exhibit different patterns compared with those of other NHC·CXY zwitterions. Hence they are difficult to interpret with certainty even with the help of DFT calculations. For the sake of comparison, the asymmetric stretching vibration bands of the CO_2^- and CS_2^- groups recorded previously for NHC·CO_2 and NHC·CS_2 betaines are also listed in Table 2. These data show that both the CO and CS vibrations of the thiocarboxylate inner salts are shifted to lower frequencies relative to those of symmetrical carboxylate and dithiocarboxylate compounds.

Table 2. IR stretching vibration bands (in cm^{-1}) of various NHC·CXY zwitterions.[a]

NHC	$\tilde{\nu}$(CO)	$\tilde{\nu}$(CN)	$\tilde{\nu}$(CS)	$\tilde{\nu}(CO_2)$[b]	$\tilde{\nu}(CS_2)$[c]
ICy	1524	1484, 1450	954	1663	1058
IMes	1532	1486, 1464	917	1675	1052
IDip	1531	1479	937	1679	1058
SIMes	1545	1483	1050, 1037	1683	1064
SIDip	1559, 1538	1465, 1445	1045	1683	1080

[a] Spectra were recorded in KBr pellets. [b] Data from ref.[28] [c] Data from ref.[19]

Although the recrystallization of NHC·CO_2 compounds is hampered by the labile and sometimes hygroscopic nature of these adducts,[11,12,30] NHC·CS_2 betaines display a remarkable tendency to form millimeter-long crystals simply by evaporating a solution in acetonitrile in the open air.[19] The NHC·COS adducts exhibited intermediate behavior. Thus we were able to grow crystals of SIMes·COS suitable for X-ray diffraction analysis (XRD) by slowly evaporating an acetonitrile solution of this zwitterion in the open air at room temperature, but the yield was low and significant decomposition occurred, most likely due to the loss of COS. Analysis of the molecular structure depicted in Figure 1 revealed that the C1–N1 and C1–N2 bond lengths are almost equivalent and equal to 1.32 Å, whereas the C2–C3 distance is 1.511(2) Å. This indicates significant C=N double-bond character with no further conjugation with the single C–C bond of the heterocyclic backbone, in good agreement with the absorption observed at 1483 cm^{-1} for the N_2C^+ unit by IR spectroscopy (see above). The mesityl groups are almost perpendicular to the central imidazolinium ring, which prohibits any electronic communication between these aromatic substituents and their nitrogen holders as further evidenced by rather long N1–C5 and N2–C4 distances of around 1.44 Å. Altogether, these data are in line with those recorded previously for other salts or zwitterions featuring the 1,3-dimesitylimidazolinium cation.[19,31,32]

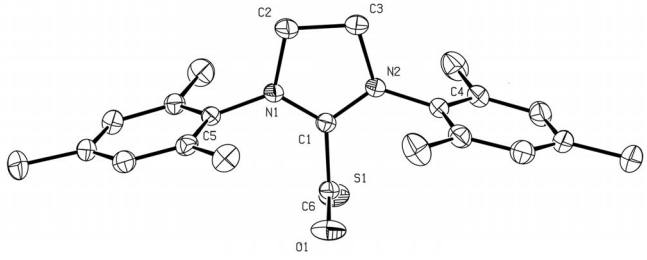
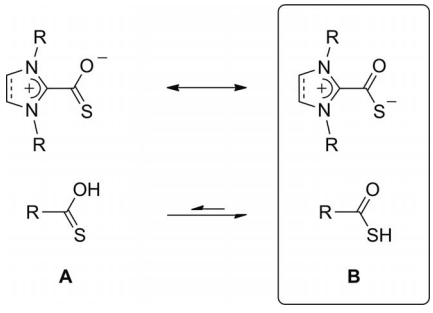


Figure 1. ORTEP plot of SIMes·COS with thermal ellipsoids drawn at the 30% probability level (hydrogen atoms have been omitted for the sake of clarity). Selected bond lengths [Å] and angles [°]: C1–C6 1.5237(16), C6–O1 1.2173(16), C6–S1 1.6761(14), C1–N1 1.3203(17), C1–N2 1.3240(16), C2–C3 1511(2), N1–C5 1.4387(17), N2–C4 1.4381(17), N1–C1–N2 112.03(11), O1–C6–S1 131.09(10), N1–C1–C6–S1 94.96(14), C1–N1–C5–C15 86.69(17), C1–N2–C4–C7 –79.10(18).

Like most NHC·CO_2 and NHC·CS_2 betaines investigated so far by XRD,[10] SIMes·COS displays an almost perpendicular arrangement between its cationic and anionic

moieties with a N1–C1–C6–S1 torsion angle of 94.96(14)° (Figure 1). Through-space attractive Coulomb interactions between the imidazol(in)ium C1 carbon atom and the lone pair of electrons on the thiocarboxylate moiety might explain this conformation.[29] In addition, steric hindrance caused by the bulky mesityl groups should further stabilize the orthogonal disposition of the N_2C^+ and COS^- units. At 131.09(10)°, the O1–C6–S1 angle is rather atypical as it closely matches those recorded for carboxylate,[12,13] dithiocarboxylate,[19] or even diselenocarboxylate groups.[29] Much more valuable information can be extracted from the bond lengths within the CXY unit. Thus, the C–O distance in SIMes·COS is significantly shorter than in SIMes·CO_2 [1.2173(16) vs. 1.2277(17) Å].[32] Conversely, the C–S bond length increases from 1.662(17) to 1.6761(14) Å when switching from SIMes·CS_2[19] to SIMes·COS. These data reveal a strengthening of the CO bond and a weakening of the CS bond in the COS adduct compared with the corresponding carboxylate and dithiocarboxylate inner salts. Hence, we conclude that the negative charge of the thiocarboxylate anion is preferentially delocalized on the sulfur atom (Scheme 3). DFT calculations performed at the B3LYP/6-31G(d,p) level of theory using the Gaussian 09 program[33] confirmed that the HOMO of SIMes·COS is located mainly on this heteroatom with only a minor contribution from the oxygen orbitals (Figure 2). These results are in good agreement with previous spectroscopic and computational studies of thiocarboxylic acids, which suggested that the thiol form (**B**) predominates over the thioxo tautomer (**A**) in nonpolar solvents and in the solid state (Scheme 3).[34]



Scheme 3. Relationship between charge delocalization in the imidazol(in)ium-2-thiocarboxylates and tautomerism in thiocarboxylic acids.

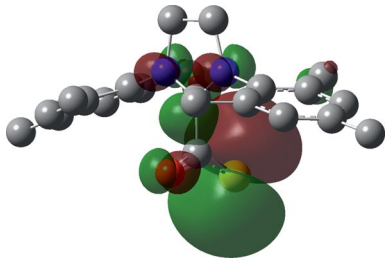


Figure 2. HOMO of SIMes·COS determined by DFT calculations at the B3LYP/6-31G(d,p) level of theory.

To complete their characterization and to probe their thermal stability, we carried out thermogravimetric analyses (TGA) of the five NHC·COS adducts (Figure 3). The presence or absence of a C=C double bond in the heterocyclic backbone did not significantly alter the onset of the decomposition, which was chiefly determined by the nature of the substituents on the nitrogen atoms. ICy·COS began to lose weight at around 110 °C, IDip·COS and SIDip·COS at around 150 °C, whereas IMes·COS and SIMes·COS resisted degradation up to around 180 °C. The same trends have previously been observed for the corresponding series of carboxylate adducts,[28] whereas a different sequence was noted for the dithiocarboxylates, with thermal stabilities increasing in the order IMes·CS_2 < SIDip·CS_2 < ICy·CS_2 < IDip·CS_2 < SIMes·CS_2.[19] These data must, however, be regarded with caution as they might be affected by the crystallinity of the NHC·CS_2 samples used for TGA measurements.

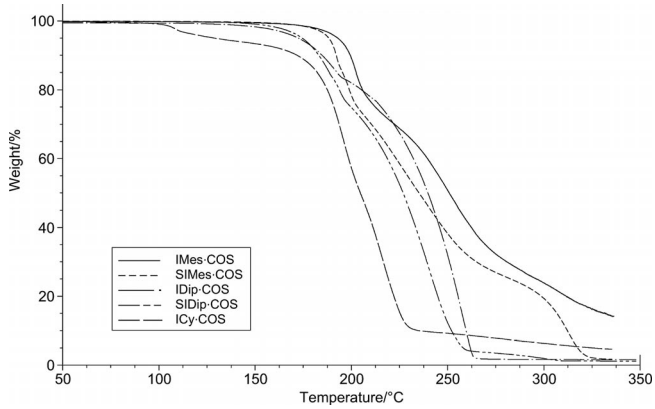


Figure 3. TGA curves of the five imidazol(in)ium-2-thiocarboxylates used in this work.

More reliable information was obtained by comparing the TGA curves of zwitterions sharing the same imidazol(in)ium moiety but with a different anionic fragment, namely, CO_2, COS, or CS_2. Comparison of the decomposition profiles of the betaines derived from IDip is particularly illustrative as the carboxylate adduct of this NHC is known to undergo clean decarboxylation leading to the intermediate formation of the free carbene.[12,13,28] Accordingly, the TGA curve recorded for this compound distinctively levels off after a 10.2% weight loss between 110 and 150 °C, which corresponds to the elimination of CO_2 (Figure 4). Thermolysis of IDip·COS began at about 140 °C with a deflection point detected at 194 °C (theoretical weight loss for COS: 13.4%; found: 15.4%). In contrast, the dithiocarboxylate inner salt resisted decomposition until 210 °C but completely degraded thereafter without any visible transition step. The other four imidazol(in)ium derivatives in our investigation did not afford such clear-cut results, however, the decomposition curves of the NHC·COS betaines always matched more closely those of the NHC·CO_2 adducts than those of their NHC·CS_2 counterparts.

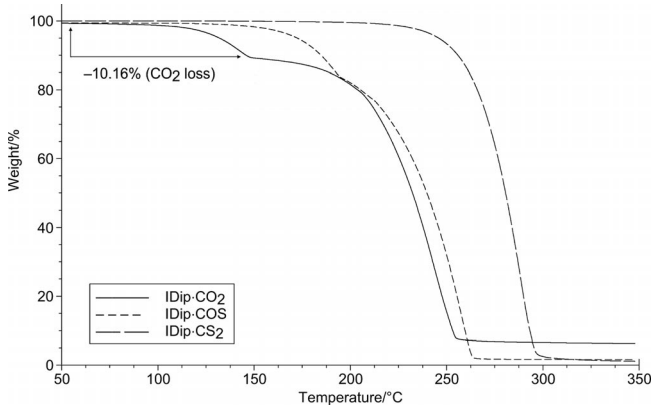
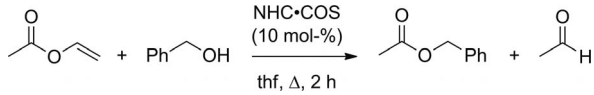


Figure 4. Comparison of the TGA curves recorded for 1,3-bis(2,6-diisopropylphenyl)imidazolium-2-carboxylate, -thiocarboxylate, and -dithiocarboxylate zwitterions.



(2)

Table 3. Isolated yields (%) of products[a] obtained by acylation of benzyl alcohol with vinyl acetate and by benzoin condensation catalyzed by various NHC·COS zwitterions.

Catalyst	Acylation reaction[b]	Benzoin condensation[c]
ICy·COS	100	23
IMes·COS	96	78
IDip·COS	96	40
SIMes·COS	78	99
SIDip·COS	40	55

[a] After purification by column chromatography. [b] Experimental conditions: Benzyl alcohol (9.66 mmol), vinyl acetate (11.93 mmol), organocatalyst (1 mmol), THF (5 mL), 2 h, reflux. [c] Experimental conditions: Benzaldehyde (9.85 mmol), organocatalyst (1 mmol), THF (5 mL), 4 h, reflux.

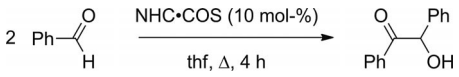
Organocatalysis with NHC·COS Zwitterions

Based on the TGA results described above for solid-state compounds, we reasoned that imidazol(in)ium-2-thiocarboxylates should be labile enough to release free carbenes into solution provided that suitable thermal activation is applied. Hence, we decided to test them as NHC precursors for two simple organocatalytic transformations.

In a first series of experiments, we performed the acylation of benzyl alcohol with a slight excess of vinyl acetate (1.2 equiv.) in the presence of NHC·COS zwitterions [0.1 equiv.; Equation (2)]. Nolan and co-workers had already chosen this model reaction in their initial assessment of free NHCs as nucleophilic catalysts for acylation/transesterification processes[35] before successfully extending the procedure to secondary alcohols[36] and phosphorus esters.[37] Very recently, Gnanou, Taton and their co-workers used the same synthesis of benzyl acetate to probe the activity of poly(NHC)s and their CO_2 adducts as recyclable polymer-supported organocatalysts.[38] Like the French team, we decided to carry out preliminary tests in THF under reflux conditions, which favor the dethiocarboxylation of the inner salts. After 2 h, a quantitative transformation had occurred with ICy·COS (Table 3). The two other imidazolium-based catalyst precursors under scrutiny, IMes·COS and IDip·COS, were almost equally active, whereas their saturated counterparts, SIMes·COS and SIDip·COS, afforded significantly lower yields of the pure product. These results are in line with the previous observations of Nolan and co-workers, who noted that imidazol-2-ylidenes bearing *N*-alkyl substituents, such as ICy, performed better than the *N*-aryl derivatives IMes and IDip, which were in turn much more active than the corresponding *N*,*N*′-diarylimidazolin-2-ylidenes SIMes and SIDip.[35] An increased nucleophilicity of the carbene was held responsible for its higher activity. Indeed, several experimental and theoretical studies have shown that the Tolman electronic parameter (TEP),[39] which provides a quantitative measurement of the donor properties associated with NHC or phosphane ligands, varies in the order ICy < IMes < IDip ≈ SIMes < SIDip.[40,41]

To better assess the efficiency of 1,3-dicyclohexylimidazolium-2-thiocarboxylate in the acylation of benzyl alcohol with vinyl acetate, we carried out further tests under more demanding conditions. We were pleased to note that heating was not required to achieve high catalytic activities with this NHC precursor. In fact, benzyl acetate was isolated in quantitative yield after 2 h irrespective of whether the reaction was carried out in a closed vessel at room temperature or in THF at reflux by using 10 mol-% of ICy·COS. The existence of an equilibrium between this zwitterion and its neutral constituents in solution most likely accounts for this situation. When the proportion of organocatalyst was incrementally decreased, a progressive slowdown of the transformation occurred, but full conversion was eventually achieved in any case. Thus, it took 4 h to reach completion with 5 mol-% of betaine, 12 h with 1 mol-% of betaine, and 24 h with 0.5 mol-% of betaine.

In a second series of experiments, we investigated the so-called benzoin condensation reaction, that is, the self-condensation of benzaldehyde to yield the aromatic β-keto alcohol known as benzoin (2-hydroxy-1,2-diphenylethanone) [Equation (3)]. Ever since Breslow postulated the intervention of carbenes in a biomimetic thiazolium-mediated benzoin condensation,[42] this C–C bond-forming reaction, which also creates a new stereogenic center, has become a benchmark for evaluating the catalytic potential of chiral heteroazolium salts and their respective NHCs.[43] In this study, we were only interested in demonstrating the feasibility of organocatalysis with NHC·COS zwitterions. Therefore no asymmetric induction was considered. The five betaines under investigation were added to a solution of benzaldehyde in THF and the mixture was heated at reflux for 4 h under an inert atmosphere. By using 10 mol-% of the catalyst precursor, an almost quantitative yield of product was obtained with SIMes·COS (Table 3). In this transformation, we noted that the activities of the various imidazol(in)ium zwitterions roughly paralleled their thermal stabilities determined by TGA (cf. Figure 3), although we have no rationale for this observation.



(3)

In sharp contrast with the acylation/transesterification process, there was a significant decrease in activity when the reaction mixture was kept at room temperature instead of being heated at reflux. Under these conditions the isolated yield of benzoin did not exceed 29% after reaction for 24 h with SIMes·COS. Control experiments performed with free 1,3-dimesitylimidazolin-2-ylidene (10 mol-%) at room temperature for 24 h and at 80 °C for 4 h led to quantitative yields of 2-hydroxy-1,2-diphenylethanone in both cases. These results are not trivial because the activity of *N*,*N*′-diarylimidazol(in)ium salts in benzoin-type condensation and Stetter reactions is usually poor compared with thiazolium salts and is hardly documented in the literature.[38,44] From these experiments it can be inferred that heat favors the release of active species from the zwitterionic catalyst precursor, but is not required to trigger benzoin condensation in the presence of free carbene.

Conclusion and Perspectives

In this study we have shown that NHCs derived from imidazol(in)ium salts react with carbonyl sulfide in the same way as they do with carbon dioxide or carbon disulfide. Thus, a set of five representative imidazol(in)ium-2-thiocarboxylate inner salts were prepared by using a one-pot, two-step procedure involving the in situ generation of free carbenes with a strong base followed by trapping with COS. The resulting NHC·COS zwitterions were isolated in high yields and characterized by IR and NMR spectroscopy. Their thermal stability was monitored by TGA. In addition, the molecular structure of SIMes·COS was determined by X-ray diffraction analysis. Experimental data and DFT calculations indicate that the negative charge of the thiocarboxylate anion is preferentially delocalized on the sulfur atom.

Unlike the NHC·CS_2 betaines, which are highly stable, crystalline materials with melting points above 230 °C,[19] the NHC·COS zwitterions are rather labile in solution and undergo thermolysis at temperatures ranging between 110 and 180 °C in the solid state. Thus, they were expected to display the same type of behavior as the analogous carboxylate adducts that readily lose their CO_2 moiety upon heating or dissolution. Indeed, we successfully employed imidazol(in)ium-2-thiocarboxylates as convenient NHC precursors for two model organocatalytic transformations. Among the five compounds examined, ICy·COS is the most efficient at promoting the acylation of benzyl alcohol with vinyl acetate and SIMes·COS afforded the highest activity in benzoin condensation.

To complement the present work and to gain further insight into the coordination chemistry of imidazol(in)ium-2-thiocarboxylates, we have started to explore the reactivity of these zwitterions with transition-metal compounds. A first report focusing on the use of these oxygen–sulfur mixed donors for the preparation of gold(I) complexes has already appeared.[45] Further investigation of the ability of NHC·COS betaines to act as ligands for ruthenium–arene catalysts are underway and will be reported in due course.

Experimental Section

General: Unless otherwise specified, all the syntheses were carried out under dry argon using standard Schlenk techniques. Solvents were distilled from appropriate drying agents and deoxygenated prior to use. Silica gel 60 (60 Å pore size, 0.063–0.2 mm particle size) supplied by Biosolve was used for column chromatography. Petroleum ether refers to the fraction of b.p. 40–60 °C. Imidazol(in)ium salts ICy·HBF_4, IMes·HBF_4, IDip·HCl, SIMes·HCl, and SIDip·HCl were prepared according to literature methods.[46] All other chemicals were obtained from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded at 298 K with a Bruker DRX 400 spectrometer operating at 400.13 and 100.62 MHz, respectively. Chemical shifts are listed in parts per million downfield from TMS and are referenced to solvent peaks or TMS. Infrared spectra were recorded with a Perkin–Elmer Spectrum One FT-IR spectrometer. Thermogravimetric analyses were performed under nitrogen with a TA Q500 instrument using a dynamic heating ramp. Elemental analyses were carried out in the Laboratory of Pharmaceutical Chemistry at the University of Liège.

Preparation of Carbonyl Sulfide: A two-necked 100 mL round-bottomed flask equipped with a magnetic stirring bar and a rubber septum was charged with 40% aqueous sulfuric acid (70 mL). By using a glass adapter and plastic tubing, the remaining neck was connected to two Dreschel bottles containing, successively, 33% aqueous sodium hydroxide and 95% sulfuric acid. The whole apparatus was purged of air by bubbling argon through the septum for a few minutes before a degassed, saturated aqueous solution of potassium thiocyanate (5 mL) was added through a syringe into the reaction flask. The formation of a precipitate and evolution of carbonyl sulfide began soon after. A small positive pressure of argon was maintained throughout the experiment to ensure a steady flow of COS and to prevent any backflow into the washing train.

Preparation of Imidazol(in)ium-2-thiocarboxylates: An oven-dried 100 mL round-bottomed flask equipped with a magnetic stirring bar and capped with a three-way stopcock was charged with imidazol(in)ium chloride or tetrafluoroborate (5 mmol) and dry THF (50 mL). A 0.5 M solution of potassium bis(trimethylsilyl)amide in dry toluene (12 mL, 1.20 g, 6 mmol) was added with a cannula. The resulting yellow suspension was stirred for 30 min at room temperature. It was allowed to settle and the supernatant solution was filtered through Celite under an inert atmosphere into a two-necked 100 mL round-bottomed flask equipped with a magnetic stirring bar and capped with a three-way stopcock. The solid was rinsed with dry THF (10 mL). Next, a slow stream of argon containing carbonyl sulfide was bubbled into the carbene solution for 2 h at room temperature. A precipitate appeared within a few minutes. After 2 h, the solvent was concentrated to around 10 mL under high vacuum and the resulting suspension was then exposed to air. The precipitate was filtered through a Büchner funnel, washed with *n*-pentane (3 × 10 mL), and dried under high vacuum.

1,3-Dicyclohexylimidazolium-2-thiocarboxylate (ICy·COS): Yellow powder (1.42 g, 97% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.99 (s, 2 H, Im-$C_{4,5}$), 4.60 (m, 2 H, CHN), 2.19–2.10 (d, 4 H, Cy), 1.87–1.84 (d, 4 H, Cy), 1.72–1.69 (d, 2 H, Cy), 1.57–1.36 (m, 8 H, Cy), 1.24–1.13 (m, 2 H, Cy) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2):

δ = 192.2 (COS), 145.9 (Im-C_2), 115.8 (Im-$C_{4,5}$), 58.4 (CHN), 33.6 (Cy), 25.7 (Cy), 25.5 (Cy) ppm. IR (KBr): $\tilde{\nu}$ = 3145 (m), 3110 (m), 3083 (m), 2933 (s), 2858 (s), 1664 (m), 1567 (m), 1524 (s), 1484 (s), 1450 (s), 1347 (m), 1304 (m), 1274 (w), 1264 (w), 1252 (m), 1203 (m), 1173 (m), 1144 (m), 1070 (m), 1031 (w), 1006 (w), 989 (m), 954 (s), 897 (m), 855 (w), 819 (m) cm^{-1}. $C_{16}H_{24}N_2OS$ (292.44): calcd. C 65.71, H 8.27, N 9.58, S 10.96; found C 64.14, H 8.22, N 9.49, S 10.99.

1,3-Bis(2,4,6-trimethylphenyl)imidazolium-2-thiocarboxylate (IMes·COS): Bright-yellow powder (1.75 g, 96% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.05 (s, 2 H, Im-$C_{4,5}$), 7.03 (s, 4 H, *m*-CH), 2.35 (s, 6 H, *p*-CH_3), 2.24 (s, 12 H, *o*-CH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 189.7 (COS), 146.6 (Im-C_2), 141.4 (*p*-C), 136.0 (*o*-C), 131.5 (*i*-C), 129.9 (*m*-CH), 120.7 (Im-$C_{4,5}$), 21.4 (*p*-CH_3), 18.3 (*o*-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3165 (m), 3112 (m), 3076 (m), 2968 (m), 2917 (m), 2857 (m), 2738 (w), 1677 (w), 1607 (m), 1556 (m), 1532 (s), 1486 (s), 1376 (m), 1227 (s), 1176 (m), 1162 (s), 1080 (m), 1035 (m), 1010 (m), 954 (m), 917 (s), 853 (s) cm^{-1}. $C_{22}H_{24}N_2OS$ (364.50): calcd. C 72.49, H 6.64, N 7.69, S 8.80; found C 71.72, H 6.74, N 7.74, S 8.79.

1,3-Bis(2,6-diisopropylphenyl)imidazolium-2-thiocarboxylate (IDip·COS): Pale-orange powder (2.09 g, 93% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.53 [t, ^3J(H,H) = 7.6 Hz, 2 H, *p*-CH], 7.32 [d, ^3J(H,H) = 7.8 Hz, 4 H, *m*-CH], 7.09 (s, 2 H, Im-$C_{4,5}$), 2.71 [sept., ^3J(H,H) = 6.8 Hz, 4 H, C*H*$(CH_3)_2$], 1.34 [d, ^3J(H,H) = 6.7 Hz, 12 H, CH_3], 1.18 [d, ^3J(H,H) = 6.9 Hz, 12 H, CH_3] ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 188.2 (COS), 147.5 (Im-C_2), 146.6 (*o*-C), 131.7 (*p*-CH), 131.3 (*i*-C), 125.0 (*m*-CH), 121.6 (Im-$C_{4,5}$), 29.7 [*C*H$(CH_3)_2$], 25.7 (CH_3), 23.2 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3148 (m), 3107 (m), 3071 (s), 2963 (s), 2931 (m), 2870 (m), 1679 (m), 1595 (m), 1531 (s), 1479 (s), 1383 (m), 1362 (m), 1330 (m), 1273 (w), 1257 (w), 1217 (m), 1170 (m), 1131 (w), 1105 (w), 1061 (m), 1019 (m), 950 (m), 937 (s), 801 (s) cm^{-1}. $C_{28}H_{36}N_2OS$ (448.66): calcd. C 74.96, H 8.09, N 6.24, S 7.15; found C 73.75, H 8.09, N 6.32, S 8.46.

1,3-Bis(2,4,6-trimethylphenyl)imidazolinium-2-thiocarboxylate (SIMes·COS): Pale-yellow powder (1.52 g, 83% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.94 (s, 4 H, *m*-CH), 4.15 (s, 4 H, Im-$C_{4,5}$), 2.46 (s, 12 H, *o*-CH_3), 2.28 (s, 6 H, *p*-CH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 190.7 (COS), 162.3 (Im-C_2), 140.6 (*p*-C), 137.0 (*o*-C), 131.0 (*i*-C), 130.1 (*m*-CH), 49.8 (Im-$C_{4,5}$), 21.3 (*p*-CH_3), 18.4 (*o*-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2953 (m), 2916 (m), 2860 (m), 1666 (w), 1608 (m), 1545 (s), 1483 (m), 1377 (m), 1269 (s), 1216 (m), 1200 (m), 1050 (m), 1037 (m), 898 (m), 860 (m) cm^{-1}. $C_{22}H_{26}N_2OS$ (366.52): calcd. C 72.09, H 7.15, N 7.64, S 8.75; found C 71.85, H 7.19, N 7.59, S 8.96.

1,3-Bis(2,6-diisopropylphenyl)imidazolinium-2-thiocarboxylate (SIDip·COS): Off-white powder (1.62 g, 72%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.43 [t, ^3J(H,H) = 7.8 Hz, 2 H, *p*-CH], 7.25 [d, ^3J(H,H) = 7.8 Hz, 4 H, *m*-CH], 4.20 (s, 4 H, Im-$C_{4,5}$), 3.27 [sept., ^3J(H,H) = 6.7 Hz, 4 H, C*H*$(CH_3)_2$], 1.41 [d, ^3J(H,H) = 6.7 Hz, 12 H, CH_3], 1.30 [d, ^3J(H,H) = 6.9 Hz, 12 H, CH_3] ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 189.0 (COS), 162.6 (Im-C_2), 147.9 (*o*-C), 131.2 (*i*-C), 130.8 (*p*-CH), 125.4 (*m*-CH), 52.4 (Im-$C_{4,5}$), 29.8 [*C*H$(CH_3)_2$], 26.4 (CH_3), 24.0 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3061 (m), 3023 (m), 2967 (s), 2929 (s), 2868 (s), 1684 (m), 1592 (s), 1559 (s), 1538 (s), 1507 (s), 1465 (s), 1445 (m), 1383 (m), 1364 (m), 1281 (s), 1185 (m), 1105 (m), 1045 (s), 936 (m), 901 (s), 807 (s) cm^{-1}. $C_{28}H_{38}N_2OS$ (450.68): calcd. C 74.62, H 8.50, N 6.22, S 7.11; found C 73.71, H 8.49, N 6.30, S 8.56.

X-ray Crystal Structure Determination: Data were collected at 293 K with a Gemini diffractometer (Oxford Diffraction Ltd.) equipped with a Ruby CCD detector using an Enhance (Mo) X-ray source. Data collection program: CrysAlis CCD (Oxford Diffraction Ltd.); data reduction: CrysAlis RED (Oxford Diffraction Ltd.); structure solution: SHELXS;[47] structure refinement (on F^2): SHELXL-97;[48] data analysis: PLATON.[49] A multi-scan procedure was applied to correct for absorption effects. Hydrogen atom positions were calculated and refined isotropically by using a riding model.

Crystal Data for SIMes·COS: Yellow-orange crystals (from MeCN) with dimensions 0.35 × 0.2 × 0.1 mm, monoclinic, $P2_1/c$, a = 7.31250(10), b = 16.7232(4), c = 17.3693(4) Å, β = 107.0(2)°, V = 2031.25(7) Å^3, Z = 4, $\rho_{calcd.}$ = 1.198 g cm^{-3}, $F(000)$ = 784, λ(Mo-K_α) = 0.71073 Å, θ_{max} = 32.83°, 6726 independent reflections (R_{int} = 0.0219), 4021 observed reflections [$I > 2\sigma(I)$], μ = 0.172 mm^{-1}, 241 parameters, R_1 (all data) = 0.0917, R_1 (observed data) = 0.0506, S = GoF = 0.926, Δ/s.u. = 0.001, residual ρ_{max} = 0.276 e Å^{-3}, ρ_{min} = –0.289 e Å^{-3}.

CCDC-828719 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Organocatalytic Acylation Reaction: A two-necked 25 mL round-bottomed flask equipped with a magnetic stirring bar, a three-way stopcock, and a reflux condenser topped with a gas bubbler was charged with an imidazol(in)ium-2-thiocarboxylate (1 mmol), benzyl alcohol (1 mL, 9.66 mmol), vinyl acetate (1.1 mL, 11.93 mmol), and dry THF (5 mL). The reaction mixture was heated at 80 °C in an oil bath for 2 h under an inert atmosphere. After cooling to room temperature, the volatiles were removed on a rotary evaporator. The residue was purified by flash chromatography on silica gel using a 19:1 (v/v) mixture of petroleum ether and ethyl acetate as eluent. Pure benzyl acetate was isolated as a colorless oil. The ^{1}H NMR spectroscopic data and R_f value matched those of an authentic commercial sample.

Organocatalytic Benzoin Condensation: A two-necked 25 mL round-bottomed flask equipped with a magnetic stirring bar, a three-way stopcock, and a reflux condenser topped with a gas bubbler was charged with an imidazol(in)ium-2-thiocarboxylate (1 mmol), benzaldehyde (1 mL, 9.85 mmol), and dry THF (5 mL). The reaction mixture was heated at 80 °C in an oil bath for 4 h under an inert atmosphere. After cooling to room temperature, the reaction was quenched with water (50 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The organic phases were gathered, dried with $MgSO_4$, and the solvents evaporated under vacuum. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and diethyl ether (10:1, v/v, then 1:1, v/v) as eluent. Pure benzoin was isolated as a white solid. The ^{1}H NMR spectroscopic data and R_f value matched those of an authentic commercial sample.

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