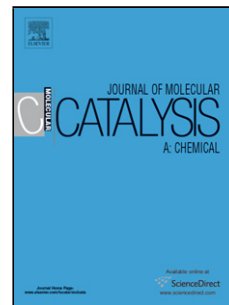


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Synthesis, characterization and catalytic activity of stable $[(\text{NHC})\text{H}][\text{ZnXY}_2]$ (NHC = *N*-Heterocyclic carbene, X, Y = Cl, Br) species

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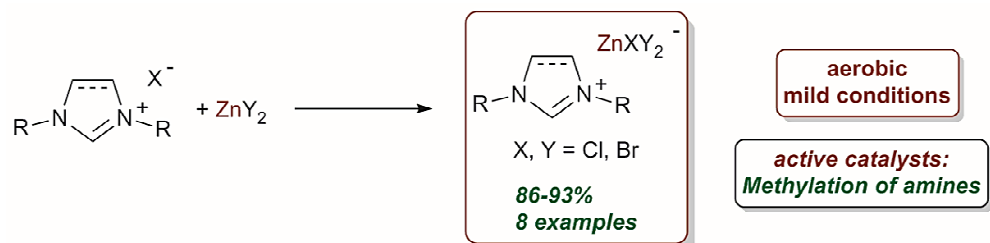
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Graphical Abstract



Highlights

- A library of stable [(NHC)H][ZnXY₂] species was synthesized
- The structure of the salts was unambiguously assessed by X-ray diffraction analyses
- The catalytic activity of the novel species was tested in the methylation of amines with CO₂ as carbon feedstock

Abstract

The synthesis and characterization of imidazol(in)ium-based zinc(II) halide salts are reported. These compounds present interesting structural features and exhibit high stability. Their catalytic activity was explored in the methylation of amines with CO₂ and PhSiH₃.

Keywords

N-Heterocyclic carbenes, Zinc, methylation, CO₂

1. Introduction

During the past decades, transition metal complexes bearing NHC ligands (NHC = *N*-Heterocyclic Carbene) have gained increasing attention. Indeed, these have shown to be efficient catalysts in several reactions as well as enabling interesting synthetic applications [1]. In order to develop more cost-effective processes, the use of complexes featuring inexpensive and Earth-abundant metals has been widely investigated [2]. In this context, Zn(II)-NHC complexes represent a remarkable example. They have shown to be particularly active in reactions involving the fixation of CO₂, such as the methylation of amines [3], or the synthesis of cyclic carbonates from epoxides [4]. In addition, they are employed in the synthesis of polyurethanes [5] and in the polymerization of *D,L*-lactide [6]. To date, the synthesis of Zn(II)-NHC complexes involves the addition of a free carbene to a zinc salt. The carbene can either be *a priori* isolated or generated *in situ* from an appropriate precursor (NHC salt or NHC-CO₂ adduct) [3-7]. Alternatively, the NHC salt can be directly reacted with diethylzinc, affording a mixed halide-ethyl complex [7b]. In spite of their general applicability, these procedures involve the use of sensitive and/or pyrophoric precursors and, consequently, require strictly anaerobic conditions. The development of a straightforward synthetic procedure leading to Zn(II)-NHC complexes would be most useful. Herein we report synthetic attempts towards Zn(II)-NHC complexes that led to the isolation of highly air- and moisture-stable [(NHC)H][ZnXY₂] (X = Cl, Br) species. Such compounds were fully characterized and their catalytic activity in the methylation of amines with CO₂ was investigated.

2. Experimental

2.1 General Considerations

All reactions were carried out in air unless otherwise stated. Chemicals were used as received unless otherwise noted. Dry solvents were obtained from a solvent purification system. ¹H and ¹³C-{¹H} Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker-400 MHz or 300 MHz spectrometers using the residual solvent peak as reference (CDCl₃: δ_H = 7.26 ppm, δ_C = 77.16 ppm) at 298K. Elemental analyses were performed by the London Metropolitan University.

2.2 General procedure for the synthesis of the zincates 4-7

A 20 mL vial was charged with the NHC·HCl (300 mg, 1 equiv.) and the zinc salt (1 equiv.). Tetrahydrofuran (5 mL) was added, the vial was sealed with a screw-cap and the reaction was

stirred at 60 °C for two hours. The mixture was allowed to reach room temperature and the

solvent was removed under reduced pressure to afford the desired product.

2.2.1 Synthesis of [IPrH][ZnCl₃] (4a)

Colorless solid (368 mg, 93%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 1.14 (d, ³J_{H-H} = 6.9 Hz, 12H, CH-CH₃), 1.31 (d, ³J_{H-H} = 6.9 Hz, 12H, CH-CH₃), 2.53 (sept, ³J_{H-H} = 6.9 Hz, 4H, CH-CH₃), 7.32 (d, ³J_{H-H} = 7.7 Hz, 4H, CH phenyl), 7.55 (t, ³J_{H-H} = 7.8 Hz, 2H, CH phenyl), 8.00 (s, 1H, H²), 8.46 (s, 2H, H⁴ and H⁵). ¹³C-{¹H} NMR (75 MHz, CDCl₃, 298 K): δ = 24.0 (s, CH-CH₃), 25.0 (s, CH-CH₃), 29.0 (s, CH-CH₃), 124.8 (s, CH Ar), 128.6 (s, CH Ar), 129.9 (s, C^{IV}), 132.2 (s, C^{IV}), 134.3 (s, C²), 145.6 (s, C⁴ and C⁵). Anal. Calcd for C₂₇H₃₇Cl₃N₂Zn: C, 57.77; H, 6.64; N, 4.99. Found: C, 57.84; H, 6.61; N, 5.05.

2.2.2 Synthesis of [IPrH][ZnClBr₂] (4b)

Colorless solid (414 mg, 90%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 1.16 (d, ³J_{H-H} = 6.9 Hz, 12H, CH-CH₃), 1.30 (d, ³J_{H-H} = 6.9 Hz, 12H, CH-CH₃), 2.51 (sept, ³J_{H-H} = 6.9 Hz, 4H, CH-CH₃), 7.33 (d, ³J_{H-H} = 7.7 Hz, 4H, CH phenyl), 7.56 (t, ³J_{H-H} = 7.8 Hz, 2H, CH phenyl), 8.19 (s, 1H, H²), 8.37 (s, 2H, H⁴ and H⁵). ¹³C-{¹H} NMR (75 MHz, CDCl₃, 298 K): δ = 24.1 (s, CH-CH₃), 24.4 (s, CH-CH₃), 29.1 (s, CH-CH₃), 124.9 (s, CH Ar), 128.3 (s, CH Ar), 129.8 (s, C^{IV}), 132.3 (s, C^{IV}), 134.9 (s, C²), 145.4 (s, C⁴ and C⁵). Anal. Calcd for C₂₇H₃₇Br₂ClN₂Zn: C, 49.87; H, 5.74; N, 4.31. Found: C, 50.04; H, 5.81; N, 4.45.

2.2.3 Synthesis of [SIPrH][ZnCl₃] (5a)

Colorless solid (363 mg, 92%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 1.18 (d, ³J_{H-H} = 6.8 Hz, 12H, CH-CH₃), 1.40 (d, ³J_{H-H} = 6.8 Hz, 12H, CH-CH₃), 3.14 (sept, ³J_{H-H} = 7.3 Hz, 4H, CH-CH₃), 4.97 (s, 4H, H⁴ and H⁵), 7.25 (d, ³J_{H-H} = 7.7 Hz, 4H, CH phenyl), 7.36 (s, 1H, H²), 7.44 (t, ³J_{H-H} = 7.8 Hz, 2H, CH phenyl). ¹³C-{¹H} NMR (75 MHz, CDCl₃, 298 K): δ = 24.0 (s, CH-CH₃), 25.6 (s, CH-CH₃), 29.1 (s, CH-CH₃), 55.7 (s, C⁴ and C⁵), 125.0 (s, CH Ar), 129.5 (s, CH Ar), 131.5 (s, C^{IV}), 146.8 (s, C^{IV}), 156.6 (s, C²). Anal. Calcd for C₂₇H₃₉Cl₃N₂Zn: C, 57.57; H, 6.98; N, 4.97. Found: C, 57.38; H, 6.83; N, 5.05.

2.2.4 Synthesis of [SIPrH][ZnClBr₂] (5b)

Colorless solid (408 mg, 89%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 1.18 (d, ³J_{H-H} = 6.8 Hz, 12H, CH-CH₃), 1.40 (d, ³J_{H-H} = 6.8 Hz, 12H, CH-CH₃), 3.11 (sept, ³J_{H-H} = 7.3 Hz, 4H, CH-CH₃), 4.94 (s, 4H, H⁴ and H⁵), 7.25 (d, ³J_{H-H} = 7.7 Hz, 4H, CH phenyl), 7.38 (s, 1H, H²), 7.44 (t, ³J_{H-H} = 7.8 Hz, 2H, CH phenyl). ¹³C-{¹H} NMR (75 MHz, CDCl₃, 298 K): δ = 24.1 (s, CH-CH₃), 25.6 (s, CH-CH₃), 29.1 (s, CH-CH₃), 55.6 (s, C⁴ and C⁵), 125.1 (s, CH Ar), 129.4 (s, CH Ar), 131.6 (s, C^{IV}), 146.7 (s, C^{IV}), 156.8 (s, C²). Anal. Calcd for C₂₇H₃₇BrCl₂N₂Zn: C, 49.72; H, 6.03; N, 4.29. Found: C, 49.60; H, 5.76; N, 4.77.

2.2.5 Synthesis of [IMesH][ZnCl₃] (6a)

Colorless solid (370 mg, 88%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 2.14 (s, 12H, CH₃), 2.34 (s, 6H, CH₃), 7.01 (s, 4H, CH phenyl), 7.89 (s, 2H, H⁴ and H⁵), 8.71 (s, 1H, H²). ¹³C-{¹H} NMR (75 MHz, CDCl₃, 298 K): δ = 17.7 (s, CH₃), 21.3 (s, CH₃), 126.0 (s, C^{IV}), 129.9 (s, CH Ar), 130.6 (s, C^{IV}), 134.4 (s, C^{IV}), 136.4 (s, C²), 141.3 (s, C⁴ and C⁵). Anal. Calcd for C₂₁H₂₅Cl₃N₂Zn: C, 52.86; H, 5.28; N, 5.87. Found: C, 52.93; H, 5.11; N, 5.93.

2.2.6 Synthesis of [IMesH][ZnClBr₂] (6b)

Colorless solid (428 mg, 86%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 2.10 (s, 12H, CH₃), 2.30 (s, 6H, CH₃), 6.96 (s, 4H, CH phenyl), 7.75 (s, 2H, H⁴ and H⁵), 9.01 (s, 1H, H²). ¹³C-{¹H} NMR (75 MHz, CDCl₃, 298 K): δ = 17.8 (s, CH₃), 21.2 (s, CH₃), 125.7 (s, C^{IV}), 129.8 (s, CH Ar), 130.5 (s, C^{IV}), 134.3 (s, C^{IV}), 136.6 (s, C²), 141.2 (s, C⁴ and C⁵). Anal. Calcd for C₂₁H₂₅Br₂ClN₂Zn: C, 44.56; H, 4.45; N, 4.95. Found: C, 44.61; H, 4.44; N, 5.13.

2.2.7 Synthesis of [IPr*H][ZnCl₃] (7a)

Colorless solid (315 mg, 92%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 2.15 (s, 6H, CH₃), 5.29 (s, 4H, CH-Ph), 5.59 (s, 2H, H⁴ and H⁵), 6.80 (m, 12H, CH Ar), 7.12-7.25 (m, 32H, CH Ar), 10.76 (s, 1H, H²). ¹³C-{¹H} NMR (75 MHz, CDCl₃, 298 K): δ = 21.9 (s, CH₃), 51.4 (s, CH₃-Ph), 123.8 (s, C⁴ and C⁵), 125.7 (s, C^{IV}), 127.0 (s, CH Ar), 127.1 (s, CH Ar), 128.7 (s, CH Ar), 128.8 (s, CH Ar), 129.3 (s, CH Ar), 130.1 (s, CH Ar), 130.3 (s, CH Ar), 131.1 (s, CH Ar), 140.5 (s, C^{IV}), 141.5 (s, C²), 141.9 (s, C^{IV}), 142.6 (s, C^{IV}). Anal. Calcd for C₆₉H₅₇Cl₃N₂Zn: C, 76.32; H, 5.29; N, 2.58. Found: C, 76.23; H, 5.17; N, 2.67.

2.2.8 Synthesis of [IPr*H][ZnClBr₂] (7b)

Colorless solid (331 mg, 89%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 2.19 (s, 6H, CH₃), 5.13 (s, 4H, CH-Ph), 5.71 (s, 2H, H⁴ and H⁵), 6.80 (m, 12H, CH Ar), 7.10 (m, 8H, CH Ar), 7.15-7.20 (m, 16H, CH Ar), 7.26-7.30 (m, 8H, CH Ar), 10.11 (s, 1H, H²). ¹³C-{¹H} NMR (75

MHz, CDCl₃, 298 K): δ = 22.0 (s, CH₃), 51.5 (s, CH₃-Ph), 124.4 (s, C⁴ and C⁵), 127.2 (s, C^{IV}), 127.4 (s, CH Ar), 128.9 (s, CH Ar), 128.9 (s, CH Ar), 129.2 (s, CH Ar), 129.7 (s, CH Ar), 129.9 (s, CH Ar), 131.1 (s, CH Ar), 138.9 (s, CH Ar), 140.5 (s, C^{IV}), 141.5 (s, C²), 141.9 (s, C^{IV}), 142.3 (s, C^{IV}). Anal. Calcd for C₆₉H₅₇Br₂ClN₂Zn: C, 70.54; H, 4.89; N, 2.38. Found: C, 70.45; H, 4.75; N, 2.51.

2.3 General procedure for the Zn-catalyzed *N*-methylation of amines with CO₂

Under an argon atmosphere, a 3 mL vial was charged with **6b** (5 mol%), KO^tBu (5 mol%) and CPME (2 mL). Substrate **8** (0.28 mmol, 1 equiv.) and PhSiH₃ (3 equiv.) were added and the vial was sealed with a septum cap. The septum cap was pierced with a syringe needle and placed into a six-slot steel autoclave. The autoclave was sealed, purged twice with CO₂ and

heated at 100 °C (oil bath) under CO₂ atmosphere (1 bar) for 20 hours. After this time the

reaction mixture was allowed to cool and the gas was carefully released. The reaction mixture was analyzed by gas chromatography (GC).

3. Results and Discussion

3.1 Synthetic attempts towards Zn(II)-NHC complexes

Recently, NHC complexes of gold(I) and copper(I) have been synthesized by reacting the corresponding imidazol(in)ium salts with the metal precursors in the presence of K₂CO₃ in air under mild conditions [8,9]. Based on these reports, attempts towards the synthesis of Zn(II)-NHC complexes were carried out using a similar strategy (Scheme 1) [10]. NHC salts were reacted with ZnBr₂ or ZnCl₂ in the presence of K₂CO₃ at 60 °C, under inert atmosphere [11]. Although full transformation of the starting NHC salt was achieved in all cases, the desired Zn(II)-NHC complexes were not obtained. The ¹H NMR spectra of the products showed the presence of the acidic H signal (N-CH-N) significantly shifted upfield, suggesting the formation of new imidazolium-based species [10].

Crystals suitable for X-ray analyses were obtained for compounds **1**, **2** and **3**, isolated from the reaction of ZnBr₂ with K₂CO₃ and IPr^{*}·HCl, IPr^{Cl}·HCl and IPr·HBr, respectively (IPr^{*} =

N,N'-bis-[2,6-bis-(diphenylmethyl)-4-methylphenyl]imidazol-2-ylidene, $\text{IPr}^{\text{Cl}} = \text{N,N'}$ -bis-[2,6-(di-*iso*-propyl)phenyl]-4,5-dichloroimidazol-2-ylidene and $\text{IPr} = \text{N,N'}$ -bis-[2,6-(di-*iso*-propyl)phenyl]imidazol-2-ylidene) [12]. X-ray analyses showed that the obtained compounds were the zincate salts and not the expected Zn(II)-NHC complexes. The molecular structure of **1** is reported in figure 1. In this species, two NHC moieties surround a tetrahedral $[\text{ZnX}_4]^{2-}$ unit, which acts as counterion [13]. Interesting short-contacts between imidazolium protons and halides of the zinc moieties were observed (*e.g.* H(1)-Br(1) 2.787 Å), which would probably justify the absence of deprotonation when K_2CO_3 is used. Compound **2** displayed structural features similar to **1** [14]. In this case, the anionic dimer $[(\text{ZnBr}_2\text{Cl})^-]_2$ is in contact with two IPr^{Cl} moieties. Short-contacts were found between the Cl atoms on the backbone of the NHC and the halides of the zinc anion.

Compound **3** exhibited a peculiar molecular structure (Figure 2). In this species, a tetrahedral $[\text{ZnBr}_4]^{2-}$ anion is surrounded by four IPr moieties. Short-contacts between the Br atoms and the hydrogen atoms on the backbone of the NHC were also observed (*e.g.* H(33)-Br(2) 2.726 Å) [15], further highlighting the stability of such species. Bond lengths and angles around the imidazole unit of compounds **1-3** are similar to those reported for the corresponding NHC salts [16].

3.2 Synthesis of a library of $[(\text{NHC})\text{H}][\text{ZnXY}_2]$ salts

Compounds **1-3** are considered analogues to the metallate intermediates obtained during the synthesis of Au(I)- and Cu(I)-NHC complexes *via* the reaction of NHC salts with gold and copper precursors in the absence of a base [8,9]. In order to generate a library of zincate salts that we could later use to generate the Zn(II)-complexes, we reacted various imidazol(in)ium salts with ZnCl_2 and ZnBr_2 in the absence of base (Scheme 2). In all cases full conversion to the corresponding zincates was observed.

All species were isolated in micro-analytically pure form and in good to excellent yields. Similarly to zincates **1-3**, the ^1H NMR spectra of these species displayed an upfield shift of the signal assigned to the acidic proton (N-CH-N) with respect to their corresponding $\text{NHC}\cdot\text{HX}$ salts [17]. Synthetic attempts towards Zn(II)-NHC complexes by treatment of these compounds with bases such as K_2CO_3 or KO^tBu were unsuccessful, further underlining the high stability of these salts [18]. Crystals suitable for X-ray analyses of **4a** and **5b** were obtained by slow diffusion of pentane into a saturated solution of the salts in chloroform [12]. Their molecular structures are reported in Figure 3 and Figure 4, respectively.

In both species, two $[\text{ZnX}_3]^-$ moieties are bound *via* bridging halides and interacting with two $[(\text{NHC})\text{H}]^+$ cations. Similarly to compound **2**, the sites of the anion in **5b** are partially occupied by both Cl and Br atoms. Short-contacts between the hydrogen atoms of the NHC backbone and the halides of the counterion have been observed in both structures. Bond lengths and angles of the NHC moieties are similar to those found in salts **1-3** [16]. It is clear that the structure of the zincates and the nature of the short-contacts are highly dependent on the NHC used (steric hindrance) and on the type of halides present on the zinc (mixed bromide-chloride, fully brominated or chlorinated). In addition, in the absence of K_2CO_3 , only $[(\text{ZnX}_3)_2]^-$ dimers were observed as counter-ions, which indicated that the base was probably responsible for the disproportionation of the $[(\text{ZnX}_3)_2]^-$ into the $[\text{ZnX}_4]^{2-}$ observed in compounds **1** and **3**.

3.3 Zn-catalysed methylation of amines with CO_2 as carbon feedstock

The catalytic activity of these interesting species was tested in the *N*-methylation of *N*-methylaniline (**8a**) using CO_2 (Table 1) [3,19]. Under the optimized conditions reported for $[\text{Zn}(\text{Cl})_2(\text{IPr})]$ [3], none of the zincates **4a-7a** were catalytically active (Table 1, entries 1-4) [20]. To our delight, in the presence of a catalytic amount of KO^tBu (5 mol%), the desired product **9a** was obtained (Table 1, entry 5). It should also be noted that mixed chloride-bromide salts performed better than their fully chlorinated or fully brominated analogues (Table 1, entries 5-13). In particular, in the presence of $[\text{IMesH}][\text{ZnClBr}_2]$ (**6b**) 80% conversion towards the desired methylated compound was obtained (Table 1, entry 12). Finally, by adding a further equivalent of PhSiH_3 , full conversion of the starting material was observed (Table 1, entry 14). With these optimal conditions in hand, an exploration of the substrate scope was undertaken (Scheme 3). While full conversion of *N*-methylaniline **8a** into **9a** was achieved, substrates **8b** and **8c** only afforded 66% and 64% conversion, respectively, into the corresponding methylated products. These results are in line with those reported for the same reaction catalyzed by $[\text{Zn}(\text{Cl})_2(\text{IPr})]$ [3].

Thus, these observations clearly indicate that the air- and moisture-stable zincates could be considered as viable alternatives to the highly sensitive well-defined Zn(II)-NHC systems. Primary amines were also investigated. Under the optimal conditions, 39% conversion towards the dimethylated compound **9d** was observed when aniline **8d** was used, whereas the more hindered 2,6-diisopropylaniline **8e** only afforded 9% conversion into the dimethylated product **9e**. Nevertheless, by doubling the amount of catalyst, KO^tBu and phenylsilane, in both cases, the formation of the dimethylated product drastically increased (48% for **9d** and 70% for **9e**).

Insights into the mechanism of this transformation can be obtained by analyzing the composition of the reaction mixtures for substrates **8d** and **8e** (Table 2). Under the standard conditions, the reaction mixture was composed of mono- and dimethylated amines (**I** and **III**) and by the carbamate **II**, with the latter being the major product in both cases (Table 2, entries 1 and 2).

When the amounts of catalyst, silane and base were doubled, the conversion of the substrate into **III** improved and the formation of carbamate **IV** was also observed (Table 2, entries 3 and 4).

A possible mechanism for this transformation, based on our observations and those of previous reports, is depicted in Scheme 4 [3,19]. The first step involves the incorporation of CO₂ into the primary aniline **8** affording carbamate **II**. The reduction of the latter under hydrosilylation conditions leads to the formation of the corresponding methylated aniline **I**. Similarly, the insertion of CO₂ into the methylated aniline **I** generates amide **IV**, whose reduction liberates the corresponding dimethylated compound **III**. Previous reports have also identified species **II** and **IV** as possible intermediates of this transformation. Moreover, the reduction of such carbonyl compounds under hydrosilylation conditions have also been shown to yield the desired methylated products **I** and **III** [3,19]. Considering this pathway, KO^tBu could have two roles: 1) assist the *in situ* formation of Zn(II)-NHC and 2) accelerate the hydrosilylation step. In fact, it has been shown that the use of a catalytic amount of an alkoxide salt has a positive effect on the rate of reduction of carbonyl compounds *via* hydrosilylation [21]. Both synthetic and computational works are ongoing in our laboratories in order to identify the actual catalytically active species and to obtain a better understanding of the mechanism of this transformation.

4. Conclusions

In conclusion, we have described the synthesis of [(NHC)H][ZnXY₂] species. These compounds present interesting structural and spectroscopic features. Their stability could be explained by taking into account the short-distance interactions between the imidazol(in)ium moieties and the central anion. In addition, these species were shown to be catalytically active in the methylation of amines with CO₂ and phenylsilane, proving to be stable alternatives to the highly air- and moisture-sensitive well-defined Zn(II)-NHC complexes. The mechanism of the methylation and other possible catalytic applications of these novel compounds are being investigated in our laboratories.

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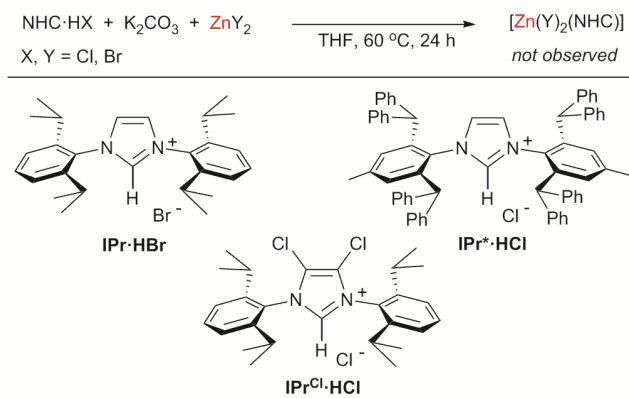
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References

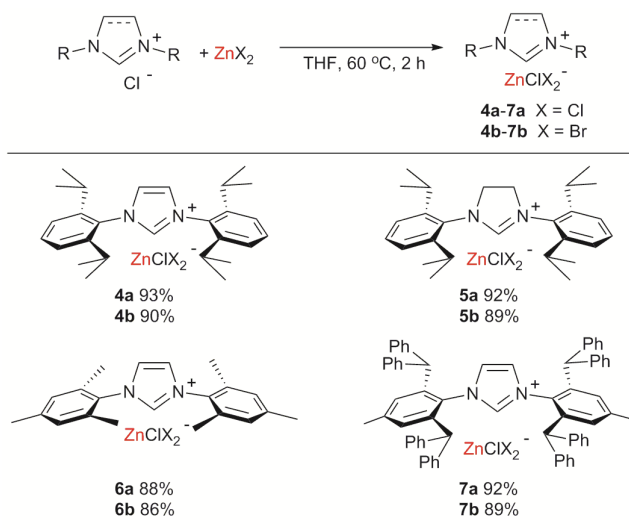
- [1] (a) S. P Nolan, *N-Heterocyclic Carbenes in Synthesis*, Wiley-VCH, New York (2006). (b) F. Glorius, *N-Heterocyclic Carbenes in Transition Metal Catalysis*, Topic in Organometallic Chemistry, Vol. 21. Springer-Verlag, Berlin-Heidelberg, (2007). (c) C. S. J. Cazin, *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*, Springer, London, (2011). (d) S. P. Nolan, *N-Heterocyclic Carbenes – Effective tools for Organometallic Synthesis*, Wiley-VCH, Mannheim, (2014). (e) F. E. Hahn, M. Jahnke, *Angew. Chem. Int. Ed.*, 47 (2008) 3122. (f) P. de Frémont, N. Marion, S. P. Nolan, *Coord. Chem. Rev.*, 253 (2009) 862. (g) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.*, 109 (2009) 3612. (h) T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.*, 49 (2010) 6940.
- [2] (a) M. S. Hill, G. Kociok-Köhn, D. J. MacDougall, *Inorg. Chem.*, 50 (2011) 5234. (b) F. Lazreg, F. Nahra, C. S. J. Cazin, *Coord. Chem. Rev.*, 293-294 (2015) 48. (c) J. D. Egbert, C. S. J. Cazin, S. P. Nolan, *Catal. Sci. Tech.*, 3 (2013) 912. (d) K. Gopalaiah, *Chem. Rev.*, 113 (2013) 3248. (e) B. D. Sherry, S. Fürstner, *Acc. Chem. Res.*, 41, (2008) 1500.
- [3] O. Jacquet, X. Frogneux, C. D. N. Gomes, T. Cantat, *Chem. Sci.*, 4 (2013) 2127.
- [4] Y. Li, P. Guan, L. Yang, Y. Shi, *Synlett*, 23 (2012) 1343.
- [5] B. Bantu, G. M. Pawar, K. Wurst, U. Decker, A. M. Schmidt, M. R. Buchmeiser, *Eur. J. Inorg. Chem.*, (2009) 1970.

- [6] T. R. Jensen, C. P. Schaller, M. A. Hillmyer, W. B. J. Tolman, *J. Organomet. Chem.*, 690 (2005) 5881.
- [7] (a) D. Wang, K. Wurst, M. R. J. Buchmeiser, *J. Organomet. Chem.*, 689 (2004) 2123. (b) S. Budagumpi, S. Endud, *Organometallics*, 32 (2013) 1537.
- [8] A. Collado, A. Gómez-Suárez, A. Martín, A. M. Z. Slawin, S. P. Nolan, *Chem. Commun.*, 49 (2013) 5541.
- [9] O. Santoro, A. Collado, A. M. Z. Slawin, S. P. Nolan, C. S. J. Cazin, *Chem. Commun.*, 49 (2013) 10483.
- [10] For further details, see Supporting Information, Section 3.1.
- [11] This methodology was first attempted under inert atmosphere because of the air-sensitivity of the expected Zn-NHC complexes. Although acetone was first used, it was later replaced by THF because the latter allowed an easier recovery of the product.
- [12] CCDC-1447299 (**1**), CCDC-1447302 (**2**), CCDC-1447301 (**3**), CCDC-1447298 (**4a**) and CCDC-1447300 (**5b**) contain the supplementary crystallographic data for this contribution.
- [13] Ideally, both Cl and Br partially occupy the sites of the anion; it was not possible to discriminate between the two halides in the refinement process.
- [14] For the molecular structure of **2**, see Supporting Information, section 6.
- [15] All H-Br contacts drawn are shorter than the sum of the van der Waals radii of H and Br.
- [16] A. J. Arduengo III, R. Krafczyk, R. Schmutzler, *Tetrahedron*, 55 (1999) 14523.
- [17] For further details, see Supporting Information, Section 2.
- [18] See Supporting Information, Table S1.
- [19] For more examples of *N*-methylation of amines with CO₂ see: (a) Y. Fang, X. Li, K. Junge, M. Beller, *Angew. Chem. Int. Ed.*, 52 (2013) 9568. (b) T. Beydoun, K. vom Stein, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.*, 52, (2013) 9554. (c) Y. Li, I. Sorribes, T. Yan, K. Junge, M. Beller, *Angew. Chem. Int. Ed.*, 52 (2013) 12156. (d) L. González-Sebastián, M. Flores-Alamo, J. J. García, *Organometallics*, 34 (2015) 763. (e) E. Blondiaux, J. Pouessel, T. Cantat, *Angew. Chem. Int. Ed.*, 53 (2014) 12186. (f) S. Das, F. D. Bobbink, G. Laurenczy, P. J. Dyson, *Angew. Chem. Int. Ed.*, 53 (2014) 12876. (g) O. Santoro, F. Lazreg, Y. Minenkov, L. Cavallo, C. S. J. Cazin, *Dalton Trans.*, 44 (2015) 18138.
- [20] See Supporting Information, Table S2.
- [21] T. Vergote, F. Nagra, A. Merschaert, O. Riant, D. Peeters, T. Leyssens, *Organometallics*, 33 (2014) 1953.

Figure Captions



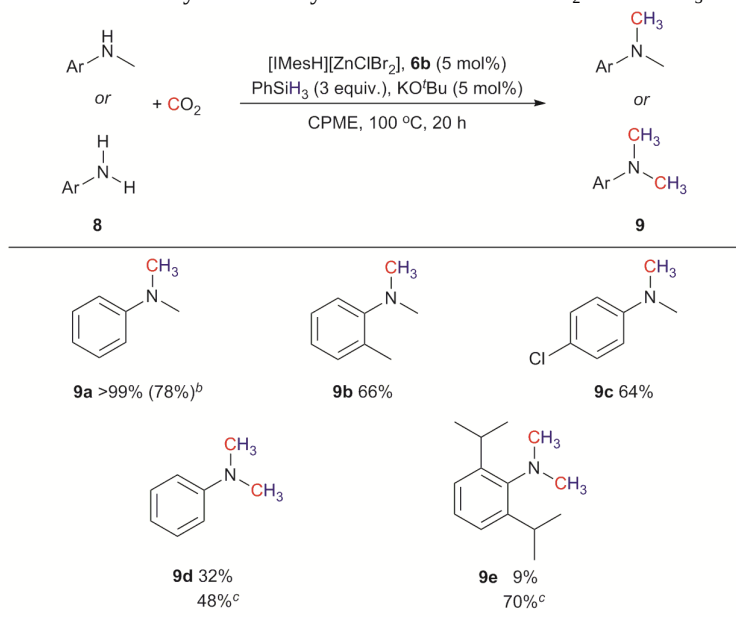
Scheme 1. Initial attempts towards Zn(II)-NHC complexes *via* the K_2CO_3 route.



Reaction conditions: NHC·HCl (300 mg, 1 equiv.), ZnX_2 (1 equiv.), THF (5 mL), 60 °C, 2 h. Isolated yields.

Scheme 2 Synthesis of $[(\text{NHC})\text{H}][\text{ZnClX}_2]$ species.

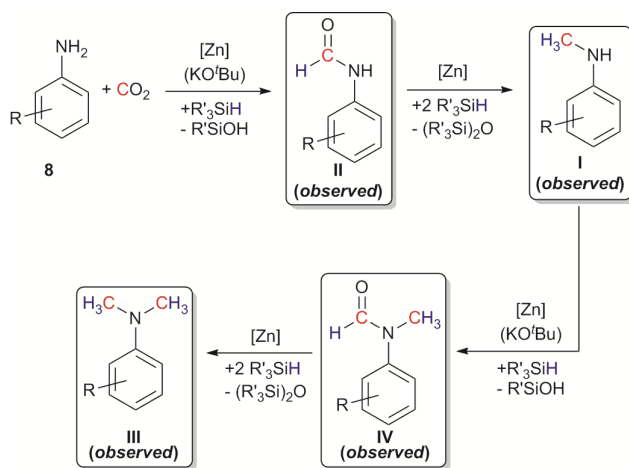
Scheme 3. Zn-catalyzed *N*-methylation of amines with CO₂ and PhSiH₃.^a



^aReaction conditions: **8** (0.28 mmol, 1 equiv.), PhSiH₃ (3 equiv.), **6b** (5 mol%), KO^tBu (5 mol%), CO₂ (1 bar), CPME (2 mL), 100 °C, 20 h. Conversions determined by GC, based on the substrate, minimum average of two reactions.

^bIsolated yield. ^cPhSiH₃ (6 equiv.), **6b** (10 mol%), KO^tBu (10 mol%).

Scheme 4. Proposed mechanism for the Zn-catalyzed *N*-methylation of amines with CO₂ and PhSiH₃ [3,19].



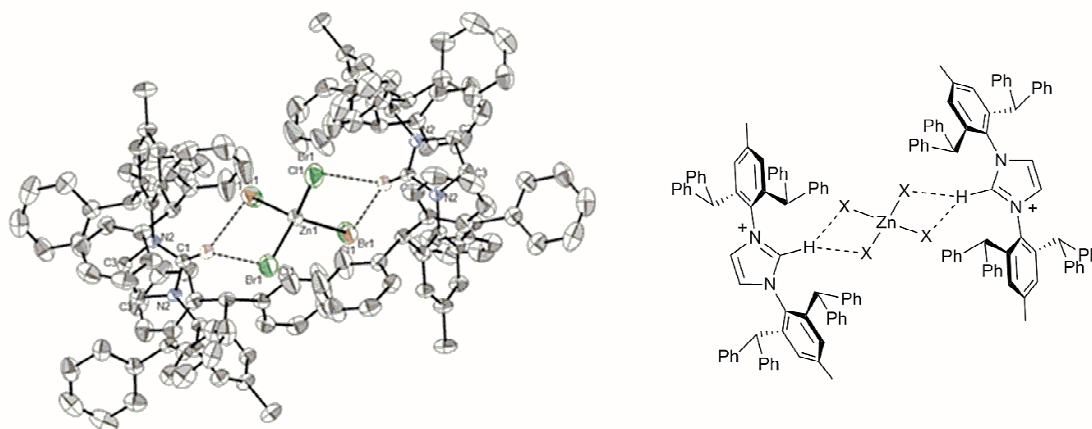


Fig. 1. Molecular structure of $[\text{IPr}^*\text{H}]_2[\text{ZnX}_4]$ (**1**) ($\text{X} = \text{Br}, \text{Cl}$). Ellipsoids are represented at the 50% probability level. Hydrogen atoms (except for N-CH-N) are omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) (esd): C(1)-N(2) 1.331(5), N(2)-C(3) 1.393(6), C(3)-C(4) 1.334(6), Zn(1)-Cl(1) 2.30(2), Zn(1)-Br(1) 2.397(3), N(2)-C(1)-N(5) 108.0(5), C(1)-N(2)-C(3) 108.9(4), N(2)-C(3)-C(4)-107.1(4), Cl(1)-Zn(1)-Cl(1) 111.8(7), Br(1)-Zn(1)-Br(1) 111.76(12).

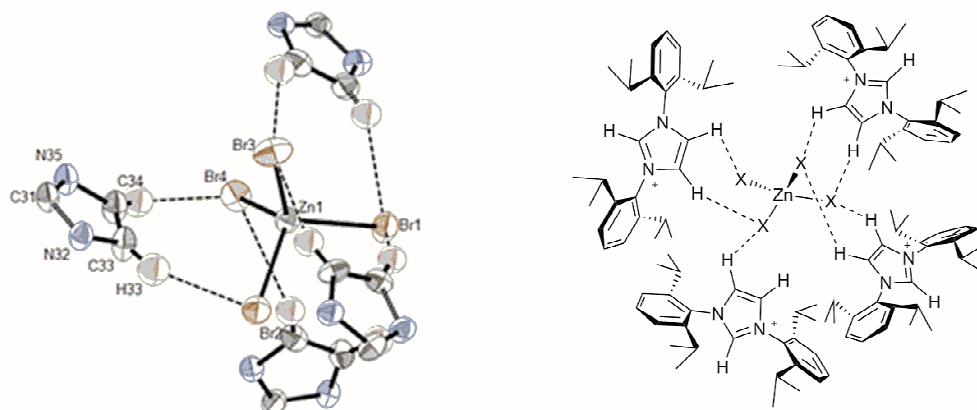


Fig. 2. Molecular structure of $[\text{IPrH}]_4[\text{ZnBr}_4][\text{ZnBr}_3]_2$ (**3**). Ellipsoids are represented at the 50% probability level. Hydrogen atoms (except for N-CH-CH-N), N-aryl substituents and two $[\text{ZnBr}_3]^-$ counter-ions are omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) (esd): C(31)-N(32) 1.312(10), N(32)-C(33) 1.391(11), C(33)-C(34) 1.352(13), Zn(1)-Br(1) 2.4297(13), N(32)-C(31)-N(35) 107.7(7), C(31)-N(32)-C(33) 110.4(7), N(32)-C(33)-C(34) 105.5(8), Br(1)-Zn(1)-Br(2) 107.94(5), Br(1)-Zn(1)-Br(4) 108.78(5).

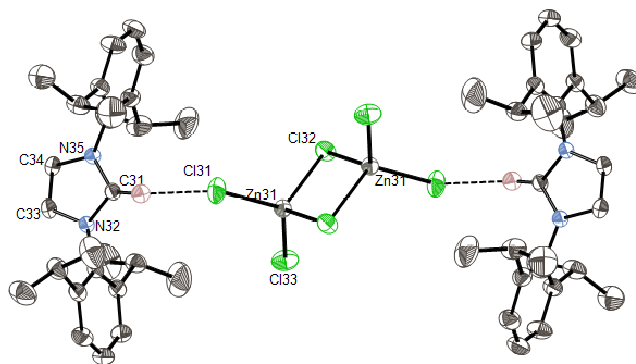


Fig. 3 Molecular structure of [IPrH][ZnCl₃] (**4a**). Ellipsoids are represented at the 50% probability level. Hydrogen atoms (except for N-CH-N) are omitted for clarity. Selected bond lengths (Å) and angles (°) (esd): C(31)-N(32) 1.334(3), N(32)-C(33) 1.381(2), C(33)-C(34) 1.340(4), Zn(31)-Cl(31) 2.2299(6), Zn(31)-Cl(32) 2.3316(8), N(32)-C(31)-N(35) 107.95(15), C(31)-N(32)-C(33) 108.87(18), N(32)-C(33)-C(34)-107.1(2), Cl(31)-Zn(31)-Cl(32) 114.45(3), Zn(31)-Cl(32)-Zn(31) 88.20(2).

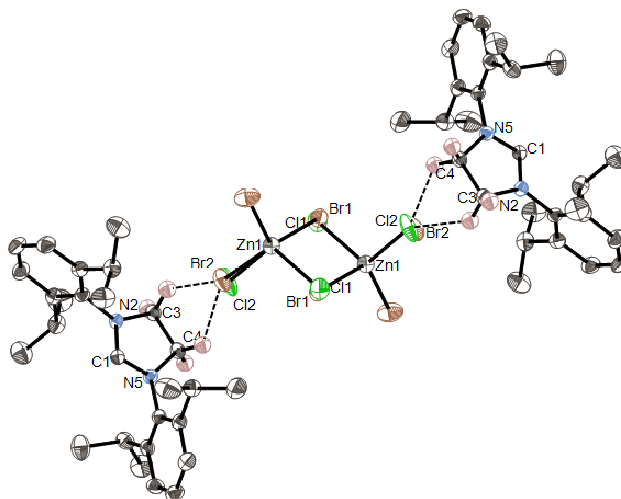


Fig. 4 Molecular structure of [SIPrH][ZnClBr₂] (**5b**). Ellipsoids are represented at the 50% probability level. Hydrogen atoms (except for N-CH₂-CH₂-N) are omitted for clarity. Selected bond lengths (Å) and angles (°) (esd): C(1)-N(2) 1.304(3), N(2)-C(3) 1.483(3), C(3)-C(4) 1.533(3), Zn(1)-Br(1) 2.442(7), Zn(1)-Cl(1) 2.381(10), N(2)-C(1)-N(5) 115.13(19), C(1)-N(2)-C(3) 109.56(17), N(2)-C(3)-C(4)-102.89(17), Br(1)-Zn(1)-Br(2) 109.9(2), Cl(1)-Zn(1)-Cl(2) 103.3(4), Zn(1)-Br(1)-Zn(1) 85.0(2), Zn(1)-Cl(1)-Zn(1) 86.7(3).

Table

Table 1 Optimization of the reaction conditions for the Zn-catalyzed *N*-methylation of **8a** with CO₂ and PhSiH₃.^a

Entry	[Zn]	Conversion (%) ^a
1	[IPrH][ZnCl ₃] (4a)	-
2	[SIPrH][ZnCl ₃] (5a)	-
3	[IMesH][ZnCl ₃] (6a)	-
4	[IPr*H][ZnCl ₃] (7a)	-
5 ^b	[IPrH][ZnCl ₃] (4a)	51
6 ^b	[SIPrH][ZnCl ₃] (5a)	-
7 ^b	[IMesH][ZnCl ₃] (6a)	65
8 ^b	[IPr*H][ZnCl ₃] (7a)	44
9 ^b	[IPrH][ZnClBr ₂] (4b)	58
10 ^b	[IPrH][ZnBr ₃] (3)	50
11 ^b	[SIPrH][ZnClBr ₂] (5b)	6
12 ^b	[IMesH][ZnClBr ₂] (6b)	80

¹³	[IPr*H][ZnClBr ₂] (7b)	50
¹⁴ ^{b,c}	[IMesH][ZnClBr ₂] (6b)	>99 (78)

Reaction conditions: **8a** (1 equiv.), PhSiH₃ (2 equiv.), [Zn] (5 mol%), CO₂ (1 bar), CPME (2 mL), 100 °C, 20 h. ^aConversions determined by GC based on **8a**, average of two runs. Isolated yield in parentheses.

^bKO^tBu (5 mol%). ^cPhSiH₃ (3 equiv.).

Table 2. Composition of the reaction mixtures for the methylation of primary amines with CO₂ catalyzed by **6b**.^a

Conversion ^a					
Entry	Substrate	I	II	III	IV
1	8d	10%	58%	32%	-
2	8e	2%	62%	9%	-
3 ^b	8d	6%	14%	48%	14%
4 ^b	8e	18%	4%	70%	6%

^aDetermined by GC based on the substrate, average of two runs. ^b**6b** (10 mol%), KO^tBu (10 mol%), PhSiH₃ (6 equiv.).