Journal of Molecular Catalysis A: Chemical 423 (2016) 85–91

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Synthesis, characterization and catalytic activity of stable [(NHC)H][$ZnXY_2$] (NHC = *N*-Heterocyclic carbene, X, Y = Cl, Br) species

Orlando Santoro[a], Fady Nahra[b], David B. Cordes[a], Alexandra M.Z. Slawin[a], Steven P. Nolan[b,c], Catherine S.J. Cazin[a,*]

[a] EaStCHEM School of Chemistry, University of St. Andrews, St Andrews KY16 9ST, UK
[b] Universiteit Gent, Department of Inorganic and Physical Chemistry, Krijgslaan 281, S-3, B-9000 Ghent, Belgium
[c] King Saud University, Department of Chemistry, College of Sciences, P.O. Box 2455, Riyadh 11451, Saudi Arabia

ARTICLE INFO

Article history:
Received 20 April 2016
Received in revised form 30 May 2016
Accepted 31 May 2016
Available online 4 June 2016

Keywords:
N-Heterocyclic carbenes
Zinc
Methylation
CO_2

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 CO_2 and $PhSiH_3$.

© 2016 Elsevier B.V. All rights reserved.

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 CO_2, 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—CO_2 adduct) [3–7]. Alternatively, the NHC salt can be directly reacted with diethylzinc, affording a mixed halide-ethyl complex [7][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][$ZnXY_2$] (X = Cl, Br) species. Such compounds were fully characterized and their catalytic activity in the methylation of amines with CO_2 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 $^{13}C\{^1H\}$ Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker–400 MHz or 300 MHz spectrometers using the residual solvent peak as reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm) at 298 K. 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

* Corresponding author.
E-mail address: ccazin@gmail.com (C.S.J. Cazin).

http://dx.doi.org/10.1016/j.molcata.2016.05.031
1381-1169/© 2016 Elsevier B.V. All rights reserved.

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][$ZnCl_3$] (**4a**)*

Colorless solid (368 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.14 (d, $^3J_{H–H}$ = 6.9 Hz, 12H, CH—CH_3), 1.31 (d, $^3J_{H–H}$ = 6.9 Hz, 12H, CH—CH_3), 2.53 (sept, $^3J_{H–H}$ = 6.9 Hz, 4H, C*H*—CH_3), 7.32 (d, $^3J_{H–H}$ = 7.7 Hz, 4H, C*H* phenyl), 7.55 (t, $^3J_{H–H}$ = 7.8 Hz, 2H, C*H* phenyl), 8.00 (s, 1H, H^2), 8.46 (s, 2H, H^4 and H^5). ^{13}C—{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 24.0 (s, CH—CH_3), 25.0 (s, CH—CH_3), 29.0 (s, *C*H—CH_3), 124.8 (s, *C*H Ar), 128.6 (s, *C*H Ar), 129.9 (s, C^{IV}), 132.2 (s, C^{IV}), 134.3 (s, C^2), 145.6 (s, C^4 and C^5). Anal. Calcd for $C_{27}H_{37}Cl_3N_2Zn$: 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][$ZnClBr_2$] (**4b**)*

Colorless solid (414 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.16 (d, $^3J_{H–H}$ = 6.9 Hz, 12H, CH—CH_3), 1.30 (d, $^3J_{H–H}$ = 6.9 Hz, 12H, CH—CH_3), 2.51 (sept, $^3J_{H–H}$ = 6.9 Hz, 4H, C*H*—CH_3), 7.33 (d, $^3J_{H–H}$ = 7.7 Hz, 4H, C*H* phenyl), 7.56 (t, $^3J_{H–H}$ = 7.8 Hz, 2H, C*H* phenyl), 8.19 (s, 1H, H^2), 8.37 (s, 2H, H^4 and H^5). ^{13}C—{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 24.1 (s, CH—CH_3), 24.4 (s, CH—CH_3), 29.1 (s, *C*H—CH_3), 124.9 (s, *C*H Ar), 128.3 (s, *C*H Ar), 129.8 (s, C^{IV}), 132.3 (s, C^{IV}), 134.9 (s, C^2), 145.4 (s, C^4 and C^5). Anal. Calcd for $C_{27}H_{37}Br_2ClN_2Zn$: 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][$ZnCl_3$] (**5a**)*

Colorless solid (363 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.18 (d, $^3J_{H–H}$ = 6.8 Hz, 12H, CH—CH_3), 1.40 (d, $^3J_{H–H}$ = 6.8 Hz, 12H, CH—CH_3), 3.14 (sept, $^3J_{H–H}$ = 7.3 Hz, 4H, C*H*—CH_3), 4.97 (s, 4H, H^4 and H^5), 7.25 (d, $^3J_{H–H}$ = 7.7 Hz, 4H, C*H* phenyl), 7.36 (s, 1H, H^2), 7.44 (t, $^3J_{H–H}$ = 7.8 Hz, 2H, C*H* phenyl). ^{13}C—{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 24.0 (s, CH—CH_3), 25.6 (s, CH—CH_3), 29.1 (s, *C*H—CH_3), 55.7 (s, C^4 and C^5), 125.0 (s, *C*H Ar), 129.5 (s, *C*H Ar), 131.5 (s, C^{IV}), 146.8 (s, C^{IV}), 156.6 (s, C^2). Anal. Calcd for $C_{27}H_{39}Cl_3N_2Zn$: 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][$ZnClBr_2$] (**5b**)*

Colorless solid (408 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.18 (d, $^3J_{H–H}$ = 6.8 Hz, 12H, CH—CH_3), 1.40 (d, $^3J_{H–H}$ = 6.8 Hz, 12H, CH—CH_3), 3.11 (sept, $^3J_{H–H}$ = 7.3 Hz, 4H, C*H*—CH_3), 4.94 (s, 4H, H^4 and H^5), 7.25 (d, $^3J_{H–H}$ = 7.7 Hz, 4H, C*H* phenyl), 7.38 (s, 1H, H^2), 7.44 (t, $^3J_{H–H}$ = 7.8 Hz, 2H, C*H* phenyl). ^{13}C—{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 24.1 (s, CH—CH_3), 25.6 (s, CH—CH_3), 29.1 (s, *C*H—CH_3), 55.6 (s, C^4 and C^5), 125.1 (s, *C*H Ar), 129.4 (s, *C*H Ar), 131.6 (s, C^{IV}), 146.7 (s, C^{IV}), 156.8 (s, C^2). Anal. Calcd for $C_{27}H_{37}BrCl_2N_2Zn$: 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][$ZnCl_3$] (**6a**)*

Colorless solid (370 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.14 (s, 12H, CH_3), 2.34 (s, 6H, CH_3), 7.01 (s, 4H, C*H* phenyl), 7.89 (s, 2H, H^4 and H^5), 8.71 (s, 1H, H^2). ^{13}C—{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 17.7 (s, *C*H$_3$), 21.3 (s, *C*H$_3$), 126.0 (s, C^{IV}), 129.9 (s, *C*H Ar), 130.6 (s, C^{IV}), 134.4 (s, C^{IV}), 136.4 (s, C^2), 141.3 (s, C^4 and C^5). Anal. Calcd for $C_{21}H_{25}Cl_3N_2Zn$: 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][$ZnClBr_2$] (**6b**)*

Colorless solid (428 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.10 (s, 12H, CH_3), 2.30 (s, 6H, CH_3), 6.96 (s, 4H, C*H* phenyl), 7.75 (s, 2H, H^4 and H^5), 9.01 (s, 1H, H^2). ^{13}C—{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 17.8 (s, *C*H$_3$), 21.2 (s, *C*H$_3$), 125.7 (s, C^{IV}), 129.8 (s, *C*H Ar), 130.5 (s, C^{IV}), 134.3 (s, C^{IV}), 136.6 (s, C^2), 141.2 (s, C^4 and C^5). Anal. Calcd for $C_{21}H_{25}Br_2ClN_2Zn$: 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][$ZnCl_3$] (**7a**)*

Colorless solid (315 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.15 (s, 6H, CH_3), 5.29 (s, 4H, C*H*—Ph), 5.59 (s, 2H, H^4 and H^5), 6.80 (m, 12H, C*H* Ar), 7.12–7.25 (m, 32H, C*H* Ar), 10.76 (s, 1H, H^2). ^{13}C—{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 21.9 (s, *C*H$_3$), 51.4 (s, *C*H$_3$—Ph), 123.8 (s, C^4 and C^5), 125.7 (s, C^{IV}), 127.0 (s, *C*H Ar), 127.1 (s, *C*H Ar),128.7 (s, *C*H Ar), 128.8 (s, *C*H Ar), 129.3 (s, *C*H Ar), 130.1 (s, *C*H Ar), 130.3 (s, *C*H Ar), 131.1 (s, *C*H Ar), 140.5 (s, C^{IV}), 141.5 (s, C^2), 141.9 (s, C^{IV}), 142.6 (s, C^{IV}). Anal. Calcd for $C_{69}H_{57}Cl_3N_2Zn$: 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][$ZnClBr_2$] (**7b**)*

Colorless solid (331 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.19 (s, 6H, CH_3), 5.13 (s, 4H, C*H*—Ph), 5.71 (s, 2H, H^4 and H^5), 6.80 (m, 12H, C*H* Ar), 7.10 (m, 8H, C*H* Ar), 7.15–7.20 (m, 16H, C*H* Ar), 7.26–7.30 (m, 8H, C*H* Ar), 10.11 (s, 1H, H^2). ^{13}C—{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ = 22.0 (s, *C*H$_3$), 51.5 (s, *C*H$_3$—Ph), 124.4 (s, C^4 and C^5), 127.2 (s, C^{IV}), 127.4 (s, *C*H Ar), 128.9 (s, *C*H Ar), 128.9 (s, *C*H Ar), 129.2 (s, *C*H Ar), 129.7 (s, *C*H Ar), 129.9 (s, *C*H Ar), 131.1 (s, *C*H Ar), 138.9 (s, *C*H Ar), 140.5 (s, C^{IV}), 141.5 (s, C^2), 141.9 (s, C^{IV}), 142.3 (s, C^{IV}). Anal. Calcd for $C_{69}H_{57}Br_2ClN_2Zn$: 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 CO_2

Under an argon atmosphere, a 3 mL vial was charged with **6b** (5 mol%), KO^{t}Bu (5 mol%) and CPME (2 mL). Substrate **8** (0.28 mmol, 1 equiv.) and $PhSiH_3$ (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 steal autoclave. The autoclave was sealed, purged twice with CO_2 and heated at 100 °C (oil bath) under CO_2 atmosphere (1 bar) for 20 h. 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 K_2CO_3 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 $ZnBr_2$ or $ZnCl_2$ in the presence of K_2CO_3 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 ^{1}H NMR spectra of the products showed the presence of the acidic H signal (N—C*H*—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 $ZnBr_2$ with K_2CO_3 and IPr*·HCl, IPr^{Cl}·HCl and IPr·HBr, respectively (IPr* = *N*,*N*′-bis-[2,6-bis-(diphenylmethyl)-4-methylphenyl]imidazol-2-ylidene, IPr^{Cl} = *N*,*N*′-bis-[2,6-(di-*iso*-propyl)phenyl]-4,5-dichloroimidazol-2-ylidene and IPr = *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 Fig. 1. In this species, two NHC moieties surround a tetrahedral $[ZnX_4]^{2-}$ unit, which acts as counterion [13]. Interesting short-contacts

Download English Version:

https://daneshyari.com/en/article/64528

Download Persian Version:

https://daneshyari.com/article/64528

Daneshyari.com