

Research article



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SYNTHESIS OF DIALKYL-(SILA AND GERMA)-IMIDAZOLIDINES OF N, N' DI(FERROCENYL) METHYLENE

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ABSTRACT:

New compounds of imidazolidines substituted germanium and tin have been synthesized in good yield by reaction between group 14 and the lithium salts of the corresponding ligands. Mass spectrophotometry and NMR 1H, 13C studies show the stabilization of the generated transient cations by ferrocenyl groups, particularly in the elements of group 14.

KEY WORDS:germanium/ Tin/ N-ligands/ imidazolidines

INTRODUCTION:

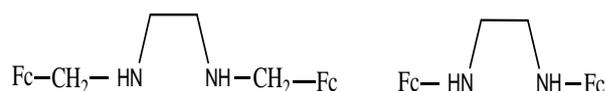
Since after the discovery of germylene by Lappert and coworkers in 1976, germanium received significant interest because of their essential importance as well as their rich chemistry. For example, the stabilizing effect (steric and electronic) of the ferrocenyl group in (N-heterocycles) system. We have the desired result of new ligands in which the introduction of this group could play an equivalent role. Species N-heterocyclic divalent which are the equivalent of carbenes of Arduengo¹ offer interesting possibilities especially by the wide variety of substituents that can be introduced on the nitrogen atom. In stoichiometric and catalytic processes, bimetallic complexes may have higher reaction rates and could lead to transformations that do not occur with

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mononuclear species¹, the most frequently used patterns are β -diketimines² with properties tunable by varying the substituent at the γ -carbon of the ligand backbone. By contrast, the new ligands, which may formally be considered as a stabilizing group in the N-heterocyclic shape, have been much less investigated.

Germynes and stannylens³ with ferrocenyl related to nitrogen atom either directly or via a methyl group. Herein we report the preparation of the first complexes based germanium and tin and their characterization. Also, some reactions were carried out in order to gain insights into the chemical behavior of these species. We chose two diamines:



Scheme 1.

MATERIALS AND METHODS:

Synthesis of N, N'-di (trimethylsilyl)-N, N'-di (ferrocenylmethyl) ethylene diamine.

A solution of *o*-t-BuLi (2.27 mmol) in pentane (1.5M) was added slowly to a solution of 1,6-diferrocenyl 2,5-diazahexane 0.46 g (1.00 mmol) in 6 mL of THF at -78°C . The mixture was warmed to room temperature and then stirred for 30 min. Then the mixture is cooled to -78°C and 0.22 g (2.02 mmol) of Me_3SiCl in 2 ml of THF is added. The yellow solution was warmed to room temperature and stirred for 3 hours. The solvent is then evaporated and treated with 10 mL of toluene and then filtered residue. The filtrate is then concentrated to dryness taken up in pentane. After filtration and drying, compound 1 is obtained as a yellow precipitate 0.44 g (72%).

M.P: 75°C

RMN ^1H (CDCl_3):

0.04 (s, 18H, $(\text{CH}_3)_3\text{Si}$)

2.54 (s, 4H, CH_2CH_2)

3.64 (s, 4H, FcCH_2)

4.11 (s, 18H, C_5H_5 et C_5H_4)

RMN ^{13}C (CDCl_3):

0.27 ($(\text{CH}_3)_3\text{Si}$)

45.51 ($\text{CH}_2\text{-CH}_2$)

47.69 (FcCH_2)

67.70 (C_5H_4)

68.38 (C_5H_5)

69.38 (C_5H_4)

87.48 (C_5H_4 , Cquat)

Mass spectrometry (IE, 70 eV), m/z :

$[\text{M}]^+ = 600$ (2%)

$[\text{M-Fc-CH}_2]^+ = 401$ (7%)

Synthesis of 2,2-(dimethyl)-1,3-di (ferrocenylmethyl) silaimidazolidine

A solution of *o*-t-BuLi (1mmol) in pentane (1.5M) was added slowly to a solution of 1,6-diferrocenyl 2,5-diazahexane 0.20 g (0.44mmol) in 6 mL of THF at -78°C . The mixture was warmed to room temperature and then stirred for 30 min. Then the mixture was cooled to -78°C and 0.06 g (0.44 mmol) of Me_2SiCl_2 in 2 ml of THF is added. The yellow solution was warmed to room temperature and then stirred for 2 hours. The solvent is then evaporated and the residue treated with 10 mL of toluene and filtered. The filtrate is concentrated to dryness and then taken up in benzene. After filtration and drying, the compound 2a is obtained as a yellow precipitate: 0.16 g (71%).

M.P: 200°C

RMN ¹H (CDCl₃):-0.12 (s, 6H, (CH₃)₃Si)2.90 (s, 4H, CH₂CH₂)3.64 (s, 4H, FcCH₂)4.04 (s, 4H, C₅H₄)4.08 (s, 10H, C₅H₅)4.14 (s, 4H, C₅H₄)**RMN ¹³C** (CDCl₃):1.02 ((CH₃)₂Si)46.57 (CH₂-CH₂)49.63 ((FcCH₂)68.56 (C₅H₄)68.87 (C₅H₅)68.99 (C₅H₄)84.04 (Cquat, C₅H₄)**Mass spectrometry** (IE, 70 eV), m/z :[M]⁺ = 512 (40%)[M-Fc-CH₂]⁺ = 313 (3%)**Elementary analysis:** C₂₆H₃₂N₂Fe₂Si

% Calculated: C, 60.94; H, 6.25

% found: C, 59.47 ; H, 6.30

Synthesis of 2,2 (dimesityl) -1,3-di (ferrocenylmethyl) silaimidazolidine

A solution of *o*t-BuLi (0.79mmol) in pentane (1.5M) was added slowly to a solution of 1,6-diferrocenyl 2,5-diazahexane 0.16 g (0.35mmol) in 6 mL of THF at -78°C. The mixture was warmed to room temperature and then stirred for 30 min. Then the mixture was

cooled to -78°C and 0.12 g (0.35 mmol) of Mes₂SiCl₂ in 2 ml of THF is added. The yellow solution was warmed to room temperature and then stirred for 2 hours. The solvent is then evaporated and the residue treated with 10 mL of toluene and filtered. The filtrate is concentrated to dryness and

then the residue filtered; the filtrate is concentrated to dryness. Analysis by ¹H NMR showed the presence of 43% of expected product 2b and 52% of ferrocenyldiazahexane. It was not possible to separate these two compounds.

RMN ¹H (CDCl₃):2.25 (s, 12H, *o*-CH₃)2.36 (s, 6H, *p*-CH₃)2.76 (s, 4H, CH₂-CH₂)3.65 (s, 4H, FcCH₂)4.12 (s, 8H, C₅H₄)4.20 (s, 10H, C₅H₅)6.85 (s, 4H, C₆H₂)**Mass spectrometry** (IE, 70 eV), m/z :[M]⁺ = 720 (5%)[M-Mes]⁺ = 601 (3%)**Synthesis of 2,2-(diethyl) -1,3-di (ferrocenylmethyl) germimidazolidine**

A solution of *o*t-BuLi (1.18mmol) in pentane (1.5M) was added slowly to a solution of 1,6-diferrocenyl 2,5-diazahexane 0.24 g (0.53mmol) in 6 mL of THF at -78°C. The mixture was warmed to room temperature and then stirred for 30 min. Then 0.11 g (0.53 mmol) of Et₂GeCl₂ in 2 ml of THF was added. The yellow solution was warmed to room temperature and stirred for 2 hours. The solvent is then evaporated and treated with 10 mL of toluene and then filtered residue. The filtrate is concentrated to dryness and taken up in hexane. After filtration and drying, the compound 2c is obtained in a yellow precipitate: 0.25 g (80%).

M.P: 190°C (déc.)

RMN ^1H (CDCl_3): 1.25 (t, 6H, $J = 7.8$ Hz, CH_3)

1.56 (q, 4H, $J = 7.8$ Hz, $\text{CH}_3\text{-CH}_2$)

2.78 (s, 4H, $\text{CH}_2\text{-CH}_2$)

3.53 (s, 4H, FcCH_2)

4.11 (s, 8H, C_5H_4)

4.20 (s, 10H, C_5H_5)

RMN ^{13}C (CDCl_3): 7.30 (CH_3)

15.53 (CH_2)

47.29 ($\text{CH}_2\text{-CH}_2$)

48.37 (FcCH_2)

68.39 (C_5H_4)

68.62 (C_5H_5)

68.79 (C_5H_4)

84.96 (C_5H_4 , Cq)

Mass spectrometry (IC, NH_3) :

$[\text{M} + \text{H}]^+ = 587$ (93%)

$[\text{M-Et}]^+ = 557$ (20%)

Synthesis of 2,2 (dimesityl) -1,3-di (ferrocenylmethyl) germainimidazolidine

A solution of *o*-t-BuLi (1mmol) in pentane (1.5M) was added slowly to a solution of 1,6-diferrocenyl 2,5-diazahexane 0.20 g (0.44mmol) in 6 mL of THF at -78°C . The mixture was warmed to room temperature and then stirred for 30 min. Then the mixture was cooled to -78°C and then 0.17 g (0.44 mmol) of $\text{Mes}_2\text{GeCl}_2$ in 2 ml of THF was added. The yellow solution was warmed to room temperature and then stirred for 2 hours. The solvent is then evaporated and the residue treated with 10 mL of toluene and filtered. The filtrate is concentrated to dryness and the compound 2d is obtained as a yellow precipitate: 0.25 g (77%).

M.P: 210°C

RMN ^1H (CDCl_3):

2.32 (s, 12H, *o*- CH_3)

2.42 (s, 6H, *p*- CH_3)

2.84 (s, 4H, $\text{CH}_2\text{-CH}_2$)

3.65 (s, 4H, FcCH_2)

3.96 (s, 8H, C_5H_4)

4.01 (s, 10H, C_5H_5)

6.87 (s, 4H, C_6H_2)

RMN ^{13}C (CDCl_3):

21.12 et 21.48 (*p*- CH_3)

23.74 (*o*- CH_3)

49.75 ($\text{CH}_2\text{-CH}_2$)

50.35 (FcCH_2)

67.23 (C_5H_4)

68.30 (C_5H_5)

68.42 (C_5H_4)

128.70 (C_6H_2)

135.42, 138.51, 142.50 (C_6H_2 , Cq)

Masse spectrometry(IE, 70 eV), m/z :

$[\text{M}]^+ = 766$ (67%)

$[\text{M-Mes}]^+ = 647$ (7%)

Synthesis of 2,2-(dichloro) -1,3-di (ferrocenylmethyl) germainimidazolidine

A solution of GeCl_4 0.10g (0.44mmol) was added slowly to a solution of 1,6-diferrocenyl 2,5-diazahexane 0.20 g (0.44mmol) and 0.10 g (0.44 mmol) of Et_3N in 5 mL of toluene at 25°C , the mixture was stirred 12 hours at room temperature. After filtration (removal of $\text{Et}_3\text{N.HCl}$), the volatiles were removed under reduced pressure. Analysis by ^1H NMR shows the presence of compound 3 (45%).

RMN ^1H (CDCl_3):

3.01 (s, 4H, $\text{CH}_2\text{-CH}_2$)

3.88 (s, 4H, FcCH_2)

4.20 (s, 18H, $\text{C}_5\text{H}_5\text{etC}_5\text{H}_4$)

Synthesis of N,N'-di(ferrocenylmethyl)diazagerma(II) cyclopentane:

A solution of germylene Lappert^{9,10} 0.19g (0.48mmol) in 5 mL of toluene, was added slowly to a solution of 1,6-diferrocenyl 2,5-diazahexane 0.22 g (0.48mmol) in 5 mL of toluene at room temperature. The solvent is evaporated and treated with 10 mL of pentane and filtered residue. The filtrate is concentrated to dryness. Analysis by proton NMR showed the presence of 0.16 g of 4 (85%).

RMN ^1H (CDCl_3):

2.77 (sl, 4H, CH_2CH_2)

3.51 (sl, 4H, FcCH_2)

4.13 (sl, 18H, C_5H_5 et C_5H_4)

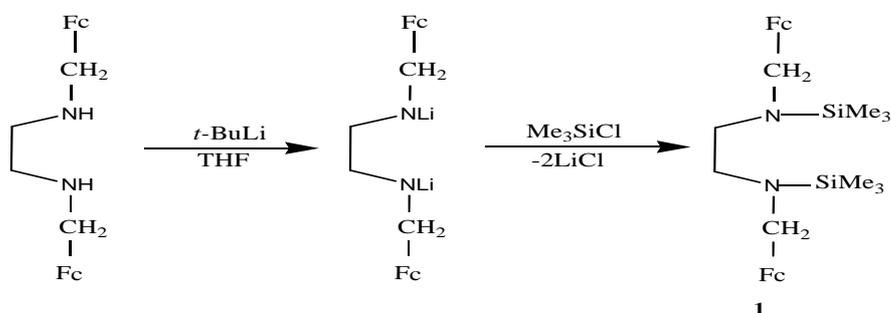
Masse spectrometry (IC, NH_3) m/z :

$[\text{M-H}]^+ = 529$ (4%).

RESULTS AND DISCUSSION:

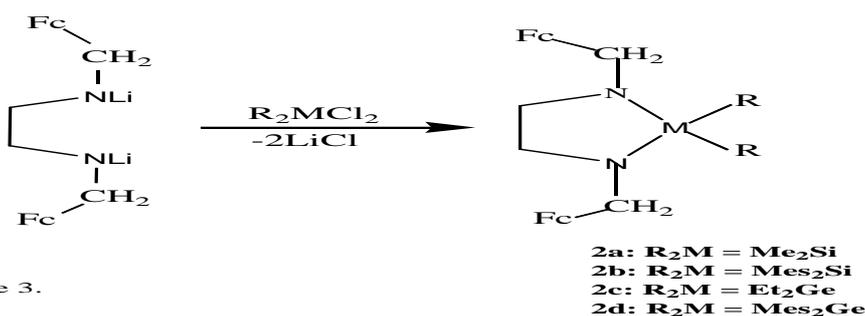
Synthesis of metal heterocyclic from N, N'-di(ferrocenyl)methylethylenediamine.

The first tests were carried out cyclization from this synthesis. Although the electronic effect of the ferrocenyl group can be reduced by presence of a CH_2 fragment, this pattern still retains its full potential kinetics stabilization by steric effect, since recently a stable FcCH_2PH_2 phosphine was reported in the litterature⁴. The lithiation reaction is carried out quickly by the action of two equivalents of *t*-BuLi in THF at low temperature (-78°C). The addition of Me_3SiCl gives the exclusive formation of disilylated derivative.



scheme 2.

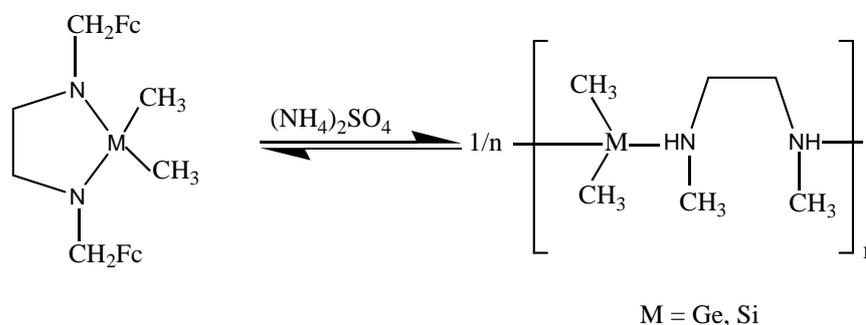
From the organodichlorosilanes and germanes, we were able to get the corresponding cycloadducts with good yields.



scheme 3.

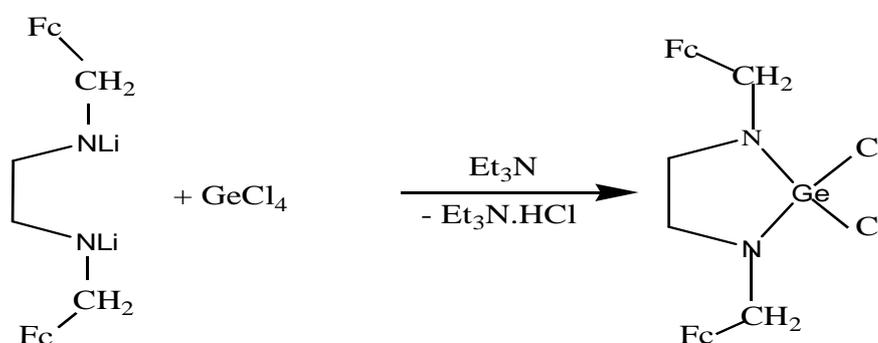
However, note that formation of oligomers when R = Me, or Et. These derivatives have been reported in the literature and the authors

consider certain conditions (presence of ammonium sulfate) a balance with cyclic⁵ form.



The presence of bulky groups on the metal 14 like mesityl group allows the stabilization of these heterocycles, the addition of tetrachlorogermane on the same diaminolithien leads to total decomposition of N-ferrocenyldiamine. We tried a reaction in deshydrochloratation in presence of an amine⁶.

In fact, the reaction is not selective and leads to the formation of about 50% of the correspond cycloadduct, the study by proton NMR is consistent with these structures in particular equivalence (C₅H₅).



scheme 4.

3

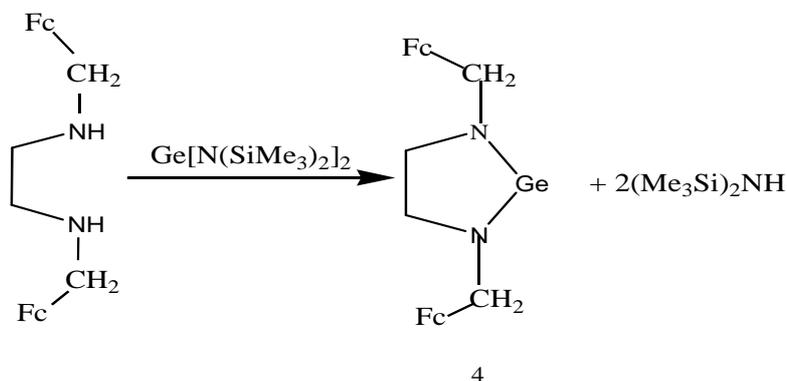
As against, there are two types of protons in (C₅H₄) are equivalent and both have similar values. For example, for the compound 2a, we observe:

$\delta_{C_5H_5}$ at 4.08 ppm and 4.04 ppm in $\delta_{C_5H_4}$ and 4.14 ppm. The carbon-13 NMR confirms these results with the presence of three peaks: $\delta_{C_5H_5}$ $\delta_{C_5H_4}$ to 68.87 ppm and 68.56 to 68.99 and then the characteristic ipso carbon 84.04

ppm. The Mass spectrometry, we observed all the molecular peaks. Depending on the nature of the metal used 14, the loss of the substituent R carried by the metal 14 or loss of ground CH₂Fc fragmentations are the most commonly observed.

N-heterocycles divalent metal

Transamination^{5,7} reaction, with Lappertgermylene was conducted in toluene at 45°C for 2 hours we observed the



scheme 5.

These results show that the heterocyclization reactions from N, N'-Diferrocenylmethylethylenediamine leads to a stable adducts to metal 14 (oxidation degree IV), the corresponding divalent species are more difficult to synthesize and could not be identified.

Bildstein et al⁸ have also encountered the same difficulties in the synthesis of carbene analogues, only with the corresponding silver complexes have been isolated. The authors discuss the steric hindrance and the electronic effect to explain the impossibility to access to N-heterocyclic carbenes with a ferrocenyl carried by the nitrogen atoms.

CONCLUSION:

The synthesis of diamines with a group ferrocenyl directly linked a CH₂ group; we have also developed their reactions with heterocyclisation Group 14 elements (silicon, and germanium) in the oxidation degree IV. While dialkylsila- dialkylgerma and-imidazolidines from N, N'-di (ferrocenyl) methylethylenediamine are stable, serial divalent, whatever the used

formation of compound 4 (scheme 5). Identified by ¹H NMR and mass spectrometry, chemical ionization [M + 1] = 529 However, these reactions are not complete, there is always start germylene.

(metallationreaction of transamination or dehydrochlorination), we observe the formation of mainly polymers. It appears that the steric hindrance of the ferrocenyl group promotes the intermolecular reactions.

REFERENCES:

- 1) Sola, E.; Bakmutov, V. I.; Torres, F.; Elduque, A.; Lopez, J. A.; Lahoz, F. J.; Werner, H.; Oro, L. A. *Organometallics* 1998, **17**, 683.
- 2) L. Bouget-Merle, M. F. Lappert, J. R. Seven, *Chem. Rev.* 2002, **102**, 3031-3065.
- 3) O. Köhl, *Coord. Chem. Rev.* (2004) **248**, 411.
- 4) N.J. Goodwin, W. Henderson, B.K. Nicholson, J. Fawcett, D.R. Russel, *J. Chem. Soc. Dalton Trans* (1999) 1785.
- 5) C.H. Yoder, J.J. Zuckerman, *J. Am. Chem. Soc.*(1966) **88**, 4831.
- 6) W.A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B.
- 7) T. Gans-Eichler, D. Gudat, K. Nättinen, M. Nieger, *Chem. Eur. J.* (2006) **12**, 1162.
- 8) B. Bildstein, M. Malaun, H. Kopacka, K. Wurst, M. Mitterböck, K-H. Ongara, G.

- Opromolla, P. Zanello, *Organometallics* (1999) **18**, 4325.
- 9) M.J.S. Gynane, D.H. Harris, M.F. Lappert, P.P. Power, P. Rivière, M. Rivière-Baudet, *J. Chem. Soc. Dalton* (1977) 2004.
- 10) E.W. Neuse, M.G. Meirim, N.F. Blom, *Organometallics* (1988) **7**, 2562.

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