SYNTHESIS, CHARACTERIZATION AND THERMAL PROPERTIES OF IRON MATERIAL INCLUDING CARBODIIMIDE AND S-INDACENE STRUCTURES

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ABSTRACT

Iron carbodiimide materials have been prepared using transmetallation reaction from dilithium carbodiimide. The products were characterized by elemental analysis and infrared spectroscopy presenting the characteristic absorption of carbodiimide group (-NCN-). The partial oxidation of iron carbodiimide materials based on s-indacene ligand has shown a clear electronic delocalization observed by IR spectroscopy. The thermal degradation of these materials studied by thermogravimetric analyses (TGA), starts around 180-200°C.

INTRODUCTION

In the last decade, the chemistry of metallated carbodiimides (MNCN) group has been very developed because of its potential applications in the electronic and magnetic fields¹⁻¹¹. In the series of germylcarbodiimides, through the full study of the polycarbodiimidogermylene ($\text{Ge}_n\text{-NCN}$)¹², it has been found that this product shows a conductivity of 10^{-2} Scm^{-1} , and is classified as semiconductor material. This result has been explained by the presence of a high electronic delocalization in the polymer chain, due to the alternation of metal atoms and -N=C=N- electron rich spacers group¹²⁻¹⁵. An important interest has also been observed for the metallocarbodiimide chemistry using rare earth, transition and semi-metals for their potential magnetic, electronic and ceramics properties¹⁻⁶. For instances, in the case of magnetic properties, X. Liu⁵ and coworkers has described the preparation of MnNCN which has presented antiferromagnet behavior with an ordering temperature below 30 K. An example of properties, in the electronic fields, has been reported for CuNCN² which has been considered as a semi-conductor with a resistivity of about $1 \text{ k}\Omega\text{cm}$ at room temperature. Poly(silylcarbodiimides) compounds are examples of materials which could exhibit ceramics properties through thermolysis process. However, for (MNCN) materials including Mn, Fe, Co, Ni and Cu, the synthesis is quite difficult through metathesis reaction because at temperatures above 400°C, necessary for these reactions, such sensitive compounds decompose quickly. For instance, the degradation of CuNCN starts at 250°C. M. Krott and coworkers have recently described the synthesis and characterization of CoNCN and NiNCN materials¹⁶. They have shown in the case of Co and Ni that the synthesis is possible changing the synthetic route, using moderate temperatures and appropriate starting compounds.

Interested in metallated carbodiimides from many years^{8,12,13,17-20}, we have described the preparation and characterization of many compounds based on polygermylcarbodiimides. Most of them have been obtained by transmetallation reaction between organochlorogermene and dilithium carbodiimide LiNCNLi. Compared to others metal carbodiimides used as starting materials in metathesis reactions, dilithium carbodiimide LiNCNLi, which is obtained in situ from the addition of butyllithium on cyanamide, is a compound very reactive in solution and this explains why most of polygermylcarbodiimides have been prepared with temperatures lower than 100°C. In a first part of this paper, the results on the preparation and characterization of iron carbodiimide using dilithium carbodiimide LiNCNLi are presented and discussed.

As these materials are sensitive to the oxidation and the moisture, a way to protect metal centers is to use voluminous organic fragment. Few years ago, we have reported a general route to prepare tetra- and hexaalkylated-s-indacenes considered as voluminous ligand in the ferrocene chemistry. Besides, they are excellent delocalized systems and used to prepare metallocene complexes²¹⁻²⁵. In a second part of this work, the synthesis and characterization of new iron carbodiimides stabilized by polyalkylates-s-indacenes will be described.

In order to evaluate the thermal stability, thermogravimetric studies of these metallated carbodiimides materials have been realized and compared.

EXPERIMENTAL PART

All reactions were carried out under nitrogen and in dry solvents using standard Schlenk techniques. All organic and organometallic reagents were purchased from Aldrich and used without supplementary purification.

Infrared spectra were recorded on a Perkin Elmer 1600 FT instrument. C, H, N elemental analyses have been carried out with a Perkin Elmer PE 2400 elemental analyzer, whereas iron elemental analysis was determined on an Atomic Absorption Spectrometer Perkin Elmer 3100.

Thermogravimetric measurements were performed using a thermal analyser TGA Polymer Laboratories STA 625. Samples (2-3 mg) were placed inside aluminum pans and heated under flowing nitrogen (42 mL/min) ranging from 25 to 550 °C, at 10 °C/min, obtaining the corresponding thermal decomposition profiles. (Samples were dried under reduced pressure in a vacuum oven prior to measurements to eliminate all moisture traces).

Preparation of $[(\text{PPh}_3)_2\text{FeNCN}]_n$ - (**1**)

To a suspension of LiNCNLi¹⁷ (2.38 mmol) prepared from H_2NCN (0.1 g, 2.38 mmol) and *n*-BuLi (1.6 M in hexane, 3.0 mL, 4.8 mmol) in 10 mL of THF, a solution of FeCl_2 (0.30 g, 2.38 mmol) in 10 mL of THF was added at room temperature under stirring. After 4 hours of reaction at reflux, a solution of triphenylphosphine PPh_3 (1.26 g, 4.8 mmol) in 10 mL of THF was added. The reaction mixture was warmed 4 hours more at reflux. LiCl was eliminated immediately by filtration. A dark green powder of **1** precipitated on cooling. After filtration, 1.1g of **1** was isolated. Yield: 75%.

Preparation of $[(\text{PPh}_3)_2\text{Fe}(s\text{-indacene})\text{Fe}(\text{PPh}_3)_2\text{-NCN-}]_n$ **2** and **3**

First, according to a previously published procedure²³, dilithium derivative (1.19 mmol) of 2,6-diethyl-4,8-dimethyl-1,5-dihydro-s-indacene is prepared by the addition of *n*BuLi (1.6 M in hexane, 1.5mL, 2.40mmol) on 2,6-diethyl-3,4,7,8-tetramethyl-1,5-dihydro-s-indacene (0.28g, 1.19mmol) in 8 mL of THF at -60°C. The mixture was warmed to room temperature and a solution of acetylacetonate iron (II) $\text{Fe}(\text{acac})_2$ (0.60g, 2.38mmol) in 10 mL of THF was added at -60°C under stirring. The mixture was warmed to room temperature. A suspension of LiNCNLi (1.19 mmol) in 7 mL of THF is then added to the acacFe -tetraalkyl-s-indacene- Feacac solution at room temperature. After 5 hours under reflux and stirring, a solution of triphenylphosphine PPh_3 (1.26 g, 4.8 mmol) in 10 mL of THF was added and the reaction mixture was warmed 4 hours more at reflux. AcacLi and excess of PPh_3 were eliminated immediately by filtration. A brownish powder of **2** precipitated on cooling and was isolated by filtration. After filtration, 1.1g of **2** was obtained. Yield: 60%.

A similar procedure has been realized for the preparation of **3**, from a solution of dilithium derivative (1.19mmol) of 2,6-diethyl-3,4,7,8-tetramethyl-

1,5-dihydro-s-indacene in 8mL of THF, $\text{Fe}(\text{acac})_2$ (0.60g, 2.38mmol) in 10 mL of THF, LiNCNLi (1.19 mmol) in 7mL of THF and PPh_3 (1.26 g, 4.8 mmol) in 10 mL of THF. 0.81 g of **3** was obtained. Yield: 72%.

Oxidation of $[(\text{PPh}_3)_2\text{Fe}(s\text{-indacene})\text{Fe}(\text{PPh}_3)_2\text{-NCN-}]_n$ **2 and **3** : preparation of **4** and **5**.**

To **2** (0.27g, 0.30 mmol) and $[\text{Cp}_2\text{Fe}]\text{BF}_4$ (0.04g, 0.15mmol) is added 15 mL of THF. After 20 hours at room temperature under stirring, the precipitate identified as **4** is separated by filtration to eliminate Cp_2Fe which is very soluble in THF. Yield: 55%.

A similar procedure has been realized for the preparation of **5**, from **3** (0.30g, 0.31 mmol) and $[\text{Cp}_2\text{Fe}]\text{BF}_4$ (0.04g, 0.15mmol) in 15mL of THF. Yield: 60%.

RESULTS AND DISCUSSION

As it has been reported previously, it is possible to prepare germaniumcarbodiimides using dilithium carbodiimide LiNCNLi in transmetalation preparations. The main advantage of this transmetalation reaction is that these preparations are carried out at moderate temperature with excellent yields and at the same time, they can prevent degradation if the products are thermally unstable. Therefore, iron carbodiimide $(\text{FeL}_2\text{NCN})_n$ has been synthesized in the same way using dilithium carbodiimide LiNCNLi and dichloride iron in presence of triphenylphosphine PPh_3 which is used as a voluminous ligand in order to stabilize the iron center²⁶ (eq. 1).

The preparation of the product **1** has been obtained with good yields. Although the product **1** presents organic ligand, it does not show any solubility in classical organic solvent and does not melt under 350°C. However, the elemental analysis shown in the table 1 confirms the monomer structure with two PPh_3 ligands stabilizing the iron center. Besides, infrared analysis shows a characteristic absorption at 2076 cm^{-1} attributed to -N=C=N- bond. Despite the presence of bulky ligands of triphenylphosphine, $(\text{FeL}_2\text{NCN})_n$ is quite hygroscopic and it makes impossible to observe the characteristic infrared absorption of C-H aromatic bond. However, the infrared absorption of C=C aromatic bond present in the triphenylphosphine ligand, is observed around 1635 cm^{-1} (see table 2).

As it has been mentioned previously, the s-indacene ligand incorporated in organometallic compounds should allow to obtain materials with important electronic delocalization and because of their hindrance effect, it should protect metallic centers from undesired oxidation reactions and the moisture. Consequently, the design of organometallic compound including carbodiimide, s-indacene and iron, should lead to new materials with very interesting properties in the electronic and magnetic fields and especially with better chemical stability, due to the s-indacene ligands presence. We have developed few years ago the preparation of tetra- and hexaalkylsubstituted -1, 5-dihydro-s-indacene and characterized their dilithium derivatives²³, that allows polymerization reactions.

The preparation of the materials **2** and **3** are realized according the scheme 1: the preparation of the intermediate specie **I**₂ by the reaction of dilithium derivatives of polyalkylsubstituted -1, 5-dihydro-s-indacene **I**₁²³ and acetylacetonate iron (II) (scheme 1, ii) has been performed in the same conditions as it has been described for the preparation of 1,2,3,4,5-pentamethylcyclopentadienide-Iron (II)-(acetyl-acetonato) $\text{Cp}^*\text{Fe}_{II}(\text{acac})$ ²⁷. The specie **I**₂ is highly unstable and has to be used in situ and in solution, as in the case of $\text{Cp}^*\text{Fe}_{II}(\text{acac})$ compound. Then, the addition of the dilithium carbodiimide on **I**₂ gives the final products **2** or **3** (scheme 1, iii).

Scheme 1

The products **2** and **3** have been obtained with good yields and do not present any melting point under 350°C. Due to their insolubility in classical organic solvents, it was not possible to perform NMR studies. However, the monomer structures of **2** and **3**, stabilized by triphenyl phosphine ligand have been confirmed by elemental analysis (table 1) and IR spectra which show characteristic absorptions for NCN functional group (Table 2). Compared to material **1**, the iron carbodiimide materials **2** and **3** are less sensitive to the moisture and it has allowed the identification of the infrared absorption for the main bond present in these materials. The indacene groups involved in sandwich structures protect partially the Fe-NCN center from moisture.

Table 1: Elemental analysis for the compounds **1**, **2** and **3**.

	1		2		3	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
%C	71.6	72.1	72.4	72.9	72.8	73.2
%H	4.8	5.2	5.5	5.9	5.8	6.1
%N	4.5	4.7	3.1	3.5	3.0	3.3
%Fe	9.0	9.1	12.3	12.9	11.9	12.5

Table 2: FT-IR absorptions (KBr, cm^{-1}) for the compounds **1**, **2** and **3**.

Bond type	1	2	3
C-H aliph.	-	2960-2800	2960-2870
C-H arom.	-	3065	3067
NCN	2076	2080	2073
C=C	1635	1642	1639

In the chemistry of polyferrocene, the preparation of mixed valence compounds with Fe(II) and Fe(III) centers, by a partial and mild oxidation, is very important for the study of electronic delocalization. In our systems, a partial oxidation has been carried out for **2** and **3**, using $[\text{Cp}_2\text{Fe}]\text{BF}_4$ as oxidant agent, following the equation 2.

To determine if no decomposition occurred, the corresponding oxidized materials have been studied by IR spectroscopy. In the case of the compounds **2** and **3**, the analysis shows perfectly the characteristic IR absorption of the NCN group which has been shifted to lower value (see figure 1). In the series of germlycarbodiimides, a similar shift tendency of -NCN- IR absorption has also been observed for poly(dimesitylgermylcarbodiimides)¹⁷ $(\text{Mes}_2\text{GeNCN})_n$, poly(germylcarbodiimides)¹² $[(\text{Ge}(\text{NCN})_2)_n]$ and poly(germylenecarbodiimide)⁸

(GeNCN)_n. For (Mes₂GeNCN)_n compounds, the studies have shown that the IR absorption of the NCN is shifted to lower value with the increase of the degree of polymerization what allows to improve the electronic delocalization. As [(GeNCN)₂]_n and (GeNCN)_n materials present NCN IR absorptions around 2165 and 2105 cm⁻¹ respectively, the reason of this difference is explained by the delocalization of a lone pair into the vacant 4d orbitals of the germylene. With these antecedents, the IR spectroscopy results obtained for the compounds **2**, **4**, **3** and **5** shows a certain degree of electronic delocalization present in such systems.

The same experiment has been performed for the compound **1**. However, the treatment by [Cp₂Fe]BF₄ shows a decomposition of the material, confirmed by the disappearance of NCN absorption in IR analysis. As it has been observed in the case of (GeNCN)_n material¹², the decomposition is probably due to the rupture of Fe-N bond with the formation of dicyanodiazene NC-N=N-CN, from radical species ·NCN.

Figure 1: Infrared Spectra of neutral materials **2**, **3** and oxidized materials **4**, **5**.

New materials are usually submitted to studies of thermal degradation, before eventual and possible applications, in order to determine the temperature range where the materials are sensitive to degradations. The thermogravimetric analyses (TGA) of **1**, **2** and **3** have been performed and the figure 2 shows their respective TGA curves. For **1**, **2** and **3** carbodiimides iron materials, the first weight loss, that does not correspond to degradation, is observed around 100°C and attributed to the loss of water present in these hygroscopic materials. A similar thermal degradation is observed for **1**, **2** and **3** compounds and starts around 180°C-200°C. This degradation is probably due to the Fe-NCN bond rupture as **1**, **2** and **3** compounds have the same bond in their structure. NCN fragment decompose with the loss of nitrogen N₂ and cyanogen C₂N₂ as it has been reported⁷.

As s-indacene ligands decompose around 390°C, the last thermal degradation is observed for **2** and **3** around 340°C-360°C with bond rupture between Fe and s-indacene. In the case of **1**, the decomposition starts around 460°C and could be explained by a higher length chain for **1**. Indeed, a higher molecular weight is expected for **1**, because a poor steric hindrance is involved in the synthesis reaction, compared to **2/3**, where the s-indacene ligands are voluminous and make difficult the preparation of material with high molecular weight.

Figure 2: Thermal decomposition profiles of **1** (—), **2** (- -) and **3** (···).

CONCLUSION

To conclude, the preparation of iron carbodiimide from dilithium carbodiimide LiNCNLi, based on a simple transmetallation reaction, is possible using mild experimental conditions. The presence of s-indacene ligand makes these new iron carbodiimide materials less hygroscopic and through a partial oxidation of metal centers, an increase of conjugation in such systems is clearly observed. From this distinguishable characteristic, new properties could be expected in electronic fields. Besides, the thermal degradations of these new materials only start from 180°C-200°C, what could be used in broad range temperature applications.

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