Journal of Organometallic Chemistry 715 (2012) 1–4

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

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

Communication

Quantum chemical characterization of magnesium carbenoids

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ARTICLE INFO

Article history:
Received 23 January 2012
Received in revised form
23 March 2012
Accepted 5 April 2012

Keywords:
Carbene
Density functional theory calculation
Magnesium carbenoid
Natural bond orbital analysis
Quantum chemical calculation
Substitution reaction

ABSTRACT

Magnesium carbenoids, in which the magnesium and chlorine atoms are connected to the same carbon atom, are both nucleophilic and electrophilic. To elucidate their unconventional reactivity, density functional theory calculations were performed on magnesium carbenoids using the 6-311++G(d,p) basis set at the B3LYP level. Molecular orbital calculations were also performed on model compounds to determine their electronic structures. The C—Cl bond lengths of magnesium carbenoids were longer than those of the corresponding organic chlorides by 0.07–0.11 Å, and the bond angles around the carbenoid carbon atom deviated from those of standard *sp*^{3}- and *sp*^{2}-hybridized carbon atoms. Natural bond orbital analysis of the model compounds indicated that their unconventional reactivity and unusual structures were due to the increased *s*-character of the carbenoid carbon atom in the C—Mg bond and the increased *p*-character of the carbenoid carbon atom in the C—Cl bond.

1. Introduction

α-Haloorganometallic compounds, also referred to as metal carbenoids, are reactive intermediates that react similarly to carbenes [1–4]. Metal carbenoids have been widely used to construct C—C bonds via cyclopropanation, C—H insertion, C—C insertion, and 1,2-shift. Previously, we developed an efficient method for the generation of magnesium carbenoids using aryl 1-chloroalkyl sulfoxides **1** and aryl 1-chlorovinyl sulfoxides **2** as key precursors (Scheme 1) [5,6]. Magnesium—sulfoxide exchange of sulfoxides **1** and **2** with Grignard reagents took place at low temperature to afford (1-chloroalkyl)magnesium chlorides **3** and (1-chlorovinyl) magnesium chlorides **4**. During the course of our studies on the synthetic applications of magnesium carbenoids, we found that magnesium carbenoids could act as both nucleophiles and electrophiles. For example, when magnesium carbenoids such as (1-chloroalkyl)-, (1-chlorocyclopropyl)-, and (1-chlorovinyl)magnesium chlorides were quenched with water, protonated compounds were obtained (Scheme 1, Eqs. (1) and (3)) [7–9]. In contrast, magnesium carbenoids reacted with various nucleophiles to expel chloride, providing substituted products (Scheme 1, Eq. (2)) [9–11]. Furthermore, the substitution reaction of (1-chlorovinyl) magnesium chlorides **4** with nucleophiles, such as organometallic reagents and lithium amides, proceeded at the alkenyl carbon atom to afford multi-substituted alkenes; however, the substitution reaction does not generally occur at the alkenyl carbon atom (Scheme 1, Eq. (4)) [7,12–15]. The unusual reactivity of magnesium carbenoids is difficult to understand based on the electronic theory of organic chemistry. Quantum chemical calculations of magnesium carbenoids would provide important clues on the unconventional reactivity of magnesium carbenoids [13,16–18]. Herein, we report the quantum chemical characterization of magnesium carbenoids.

2. Calculation

Density functional theory (DFT) calculations were performed with Gaussian 03 software [19], and the geometries were fully optimized in the gas phase without any symmetry constraints at the B3LYP/6-311++G(d,p) level [20–22]. Frequency calculations at the same level were performed to determine if the structures corresponded to energy minima (no imaginary frequencies). Natural bond orbital (NBO) analysis was performed at the B3LYP/6-311++G(d,p) level using NBO version 3.1, which is a program contained in the Gaussian 03 package [23]. A typical σ bond A—B can be described as: $\sigma_{A-B}=C_A(sp^m)_A + C_B(sp^n)_B$ where C_A and C_B are polarization coefficients for the A- and B-centered hybrids $(sp^m)_A$ and $(sp^n)_B$. C_A^2 and C_B^2 are proportional to electron density at the A- and B-hybrids with $C_A^2 + C_B^2 = 1$ [24]. When A is more electronegative than B, $C_A^2 > 0.5 > C_B^2$. Polarization coefficients of carbon

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Abbreviations: DFT, density functional theory; NBO, natural bond orbital; LUMO, lowest unoccupied molecular orbital; HOMO, highest occupied molecular orbital.

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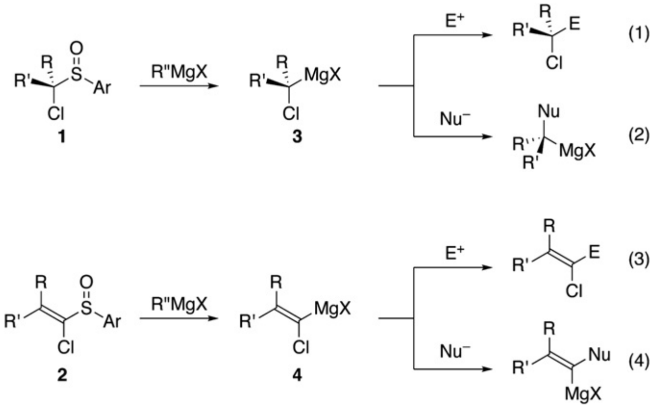
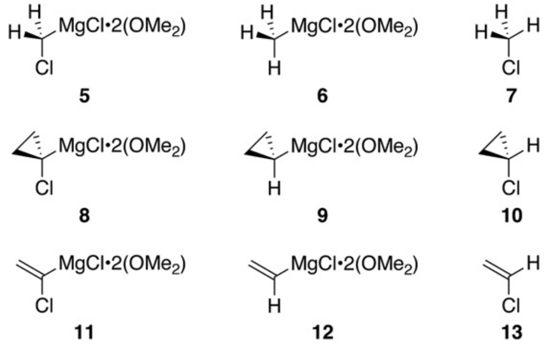
doi:10.1016/j.jorganchem.2012.04.028



Scheme 1. Generation of magnesium carbenoids **3** and **4** from sulfoxides **1** and **2** via magnesium–sulfoxide exchange and the reaction of **3** and **4** with electrophiles and nucleophiles.



Scheme 2. Structures of magnesium carbenoids **5**, **8**, and **11** and related compounds.

atoms bearing magnesium and/or chlorine atoms are shown in Table 2. Jmol program was used to draw the molecular structures and molecular orbitals [25].

3. Results and discussion

3.1. Molecular geometries

Initially, the geometric optimization of (chloromethyl)magnesium chloride bis(dimethyl ether) (**5**), (1-chlorocyclopropyl) magnesium chloride bis(dimethyl ether) (**8**), and (1-chlorovinyl) magnesium chloride bis(dimethyl ether) (**11**) was performed using the 6-311++G(d,p) basis set at the B3LYP level with Gaussian software (Scheme 2, Fig. 1). The optimized parameters of model compounds **5**, **8**, and **11** are listed in Table 1. Closely associated organomagnesium compounds [methylmagnesium chloride bis(dimethyl ether) **6**, cyclopropylmagnesium chloride bis(dimethyl ether) **9**, and vinylmagnesium chloride bis(dimethyl ether) **12**] and organic chlorides (chloromethane **7**, chlorocyclopropane **10**, and chloroethene **13**) were also calculated to compare the structural parameters.

The C–Cl bond lengths of magnesium carbenoids **5** (1.88 Å), **8** (1.88 Å), and **11** (1.86 Å) were longer than those of the corresponding organic chlorides **7** (1.81 Å), **10** (1.79 Å), and **13** (1.75 Å) by 0.07–0.11 Å. Another geometrical feature of magnesium carbenoids **5**, **8**, and **11** was the deviation of bond angles around the carbenoid carbon atom from the typical bond angles of sp^3- and sp^2-hybridized carbon atoms. For example, the Cl1–C1–H1 angle (102.8°) of **5** was smaller than that of model compound **7** (108.3°), and the torsion angle of H2–H1–C1–Mg (128.0°) in **5** was much different from that of H1–H2–C1–Cl1 (107.4°) in **5**, indicating that magnesium carbenoid **5** adopted a bent geometry. Similar trends were observed in the torsion angles of (1-chlorocyclopropyl)magnesium chloride **8**. The bond angle of C2–C1–Mg in **11** was 129.4° and was larger than the typical bond angle of sp^2 carbon atoms by approximately 9°. The structural features of model compounds **5**, **8**, and **11** were consistent with those observed in the X-ray molecular structures of magnesium carbenoid and lithium carbenoids [26–28].

3.2. NBO analysis

NBO analysis of model compounds **5**–**13** was conducted to elucidate their electronic structures (Table 2), and the hybridization of carbon atoms bearing magnesium and/or chlorine atoms in model compounds **5**–**13** was determined. The percent *s*-character of the carbon atom in the C–Mg bond of (chloromethyl)magnesium chloride **5** was equal to 30.53% and was greater than that of methylmagnesium chloride **6** (25.04%). In contrast, the *p*-character of the carbon atom in the C–Cl bond of magnesium carbenoid **5** was 82.98% and was greater than that of chloromethane **7** (79.55%). Similarly, an increase in the *s*-character of the carbenoid carbon atom in the C–Mg bond and the *p*-character of the carbenoid carbon atom in the C–Cl bond was observed in magnesium carbenoids **8** and **11**. Therefore, the extension of the C–Cl bond lengths in magnesium carbenoids **5**, **8**, and **11** can be attributed to an increase in the *p*-character of the carbenoid carbon atom in the C–Cl bond. The feeble C–Cl bonds facilitate substitution reactions

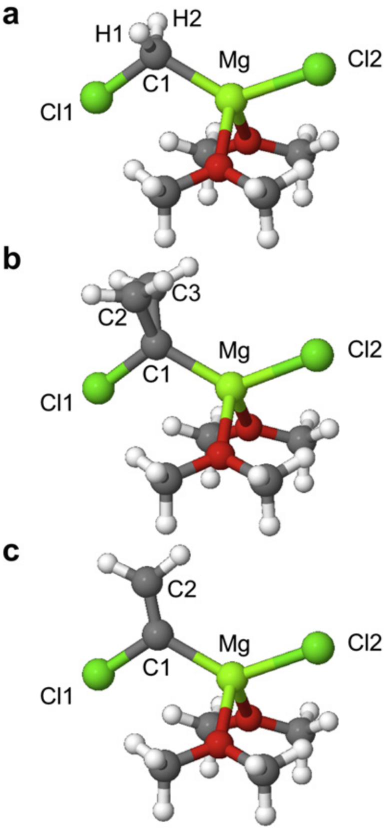


Fig. 1. Optimized geometries of model compounds calculated at the B3LYP/6-311++G(d,p) level: (a) (chloromethyl)magnesium chloride bis(dimethyl ether) (**5**); (b) (1-chlorocyclopropyl)magnesium chloride bis(dimethyl ether) (**8**); and (c) (1-chlorovinyl)magnesium chloride bis(dimethyl ether) (**11**).