Journal of Organometallic Chemistry 696 (2011) 622–631

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

DFT calculation and AIM-analysis of the substituent influence on the structure of (1-azabuta-1,3-diene)tetracarbonyliron(0) complexes

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ARTICLE INFO

Article history:
Received 26 August 2009
Received in revised form
7 September 2010
Accepted 19 September 2010
Available online 29 September 2010

Keywords:
Carbonyliron(0) complexes
1-Azabuta-1,3-dienes
Substituent influence
Coordination modes
DFT calculations
Topology of charge density

ABSTRACT

1-Azabuta-1,3-dienes can coordinate to the tetracarbonyliron(0) moiety in four ways, to form (1-azabuta-1,3-diene)tetracarbonyliron(0) complexes with the ligand bonded in an η^2 fashion through the alkene, η^2 coordinated through its C═N bond, σ-bonded to the lone pair of the nitrogen atom, or η^3 coordinated through the C═C–C moiety under concomitant coupling of the imine nitrogen with one of the carbonyl ligands to a carbamoyl species. In the experiment, the equilibrium between these species strongly depends on factors such as the nature of the substituents at the ligand, the solvent and the temperature. In this work, DFT calculations (B3LYP/LANL2DZ/6-31G* and 6-311++G**) and an AIM-analysis of the topology of the charge density were used to investigate the influence of the substituents at the 1-azabuta-1,3-diene ligand on the structural, electronic and energetic properties of these constitutional isomers. In most cases, the calculations correctly predict the observed structure, even in situations where the energy differences between related species are rather small. Substituents larger than CH_3 at N and H at C2 disfavour the structures with an η^2 coordination to the C═N bond to such an extent that they cease to exist as minimum energy structures. Also the σ-*N* forms distort significantly with the introduction of substituents at N or C2 and become energetically less favourable. The geometries of the η^2-alkene form do not change much upon substitution, whereas the η^3 form tolerates steric strain best and becomes most favourable when the substituent at C2 is large. The activation barrier between the η^2-alkene and the η^3-allyl form is low (7.5–1.4 kcal/mol) and allows for an equilibration between these species. The conversion of the η^2-alkene into the σ-*N* form requires almost complete dissociation of the ligand from the $Fe(CO)_4$ moiety. Accordingly, its activation barrier is higher (approx. 14 kcal/mol) and fairly independent of the nature of the substituents at the azabutadiene ligand.

1. Introduction

Iron carbonyl complexes play an important role in organometallic chemistry, as synthetic precursors, auxiliaries or catalysts [1]. A particularly rich chemistry and a high degree of structural fluxionality is observed in iron carbonyl complexes bearing additional π-ligands such as dienes, oxadienes or azadienes [2]. In $Fe(CO)_3$(1-azabuta-1,3-diene) complexes, for example, a turnstile-type rotation of the carbonyl ligands has been noticed [3], and the $Fe(CO)_3$ moiety is capable of migrating from one face of the 1-azabuta-1,3-diene ligand to the other [4]. Strong bases can induce a number of reactions, in which a change of the coordination mode of the 1-azabuta-1,3-diene ligand takes place. Thus, the deprotonation of the substituent at C2 converts 1-azabuta-1,3-diene complexes into 2-amino-1,3-butadiene complexes [5]. The carbonyl ligands can also get involved in reactions, as in the addition of phenyllithium to the coordinated imino carbon of the azabuta-1,3-diene where a ligand slippage is accompanied by a nucleophilic attack of the nitrogen at one of the coordinated carbonyl ligands. Alkylation of the intermediate leads to η^2-alkene-alkoxycarbene complexes [6]. Methyllithium is able to convert one of the carbonyls into an acyl ligand which then adds to the terminal carbon of the 1-azabuta-1,3-diene. In a subsequent insertion reaction a pyrrole derivative is formed [7]. A remotely related synthesis of dihydropyrrol-2-ones from 1-azabuta-1,3-dienes with CO and ethylene has been achieved with $Ru_3(CO)_{12}$ as a catalyst [8]. In this reaction, pyrroles were observed as side products and a mechanistic pathway for their formation has been proposed [9]. With 1,4-diazabuta-1,3-dienes, a formal [2 + 2 + 1] cycloaddition can be catalysed with $Ru_3(CO)_{12}$ or with $Fe_2(CO)_9$, although the turnover numbers are lower in the latter case [10]. The underlying reaction mechanism, the

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doi:10.1016/j.jorganchem.2010.09.036

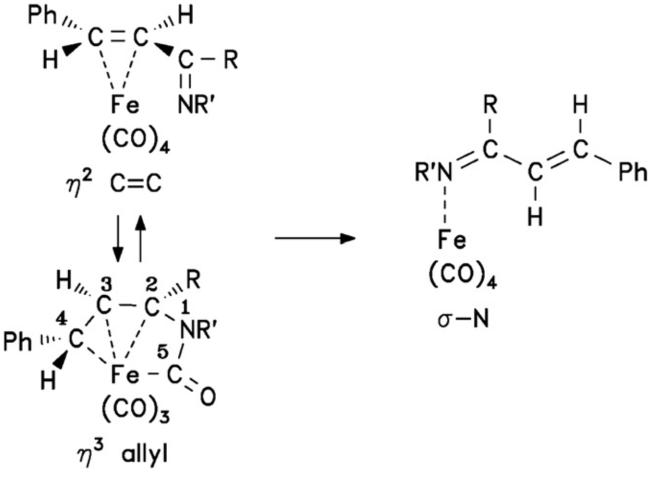
regioselectivity and substituent influence of this reaction has been studied in much detail with DFT methods [11].

Complexes of the type Fe(CO)$_4$(1-azabuta-1,3-diene) are relatively stable intermediates on the way to the well-known (1-azabuta-1,3-diene)tricarbonyliron(0) compounds [12]. They can be prepared by reaction of Fe$_2$(CO)$_9$ with a 1-azabuta-1,3-dienes [13], or by treatment of (1-oxabuta-1,3-diene)tricarbonyliron(0) complexes with BF$_3$ or acetylinium tetrafluoroborate and subsequent reaction of the adduct with a primary amine [14]. The 1-azabuta-1,3-diene ligands bind to the tetracarbonyliron(0) moiety by η^2 coordination through the C=C bond, by σ-coordination through the lone pair of the nitrogen atom, or in an η^3-fashion to the C=C–C moiety under concomitant coupling of the imine nitrogen with one of the carbonyl ligands to a carbamoyl species. Nesmeyanov [12c,d] proposed the existence of an equilibrium between the η^2 olefin and the η^3-allyl species, as shown in Scheme 1, and the ratio in which these species exist depends strongly on the nature of the substituents at the ligand, the solvent and the temperature.

If the substituent at the imine carbon of the 1-azabuta-1,3-diene is a hydrogen atom, conversion into the σ-*N* bound species occurs easily [12b] and the conversion possibly involves the intermediacy of a η^2-C=N coordinated species. This coordination mode has been considered although no experimental evidence for its existence has been found so far [13]. Overall, the ligand slippage and carbonyl insertion reactions involved in the interconversion of the different Fe(CO)$_4$(1-azabuta-1,3-diene) isomers are interesting from a mechanistic point of view because they can be considered as model systems for potential intermediate steps in stoichiometric or catalytic reactions such as the ones mentioned above. In the present work, DFT calculations (B3LYP/LANL2DZ/6-31G* and 6-311++G**) and an AIM-analysis of the topology of the charge density were used to study the mechanism of interconversion between the different forms and also the influence of the substitution pattern on the structural features of the individual isomers and their position on the potential energy surface.

2. Computational methods

Calculations were carried out with the PC GAMESS version [15] of the GAMESS(US) quantum chemistry package [16]. Results were visualised with MOLDEN [17] and MOLEKEL [18]. Molecular geometries were fully optimised using the B3LYP hybrid functional [19], in an implementation which is based on the VWN1 formula [20]. The LANL2DZ basis set [21] was used for the iron atom and 6-31G* [22] for all other atoms. Harmonic vibrational frequencies were computed for all stationary points in order to characterise them as local minima (no imaginary frequency) or transition states (only one imaginary frequency exists). Reaction pathways were traced from the transition states towards both directions along the imaginary mode of vibration using the algorithm developed by Gonzáles and Schlegel [23]. All transition states were found to correctly connect the reactants and products. The relative energies were zero-point energy corrected. The B3LYP/LANL2DZ/6-31G* optimised geometries were used for B3LYP/6-311++G** [24] single point calculations with the GAUSSIAN 03 programme suite [25]. The topological analysis of the charge density was performed with the programs AIMPAC [26] and MORPHY [27]. Critical points were located using the eigenvector following method as implemented in the programs. The respective wave function input files were generated with GAUSSIAN 03 from B3LYP single point calculations with the full electron basis set 6-311++G** at all atoms including iron. The core potential basis set LANL2DZ was not used here because the lack of an explicit description of the core electrons can distort the charge density in the vicinity of the nuclei so that the properties of critical points near the iron center may be poorly reproduced [28,29].



Scheme 1. Experimentally observed structures of Fe(CO)$_4$(1-azabuta-1,3-diene) complexes and interconversion between them.

3. Results and discussion

This work focuses on Fe(CO)$_4$(1-azabuta-1,3-diene) complexes in which the 1-azabuta-1,3-diene carries aliphatic substituents with moderate electron donating properties and increasing steric demand at the imine C and N atoms (**1**: R = H, R′ = Me, **2**: R = Me, R′ = Me; **3**: R = H, R′ = ^{t}Bu; **4**: R = Me, R′ = ^{c}Hx and **5**: R = ^{t}Bu, R′ = Me), as shown in Scheme 2. The complexes **1a**–**h** have been studied previously to some extent, by means of the same computational method [30], and are shown in Fig. S1 of the Supplementary Material.

Each of the 1-azabuta-1,3-diene complexes of the type **a**–**h** were geometry optimised and the absolute and relative energies are given in Table 1. In the case of ligands **2**–**5**, only the η^2-alkene, η^3-allyl, C-acyl and σ-*N* coordinated species **a**–**d**, **g** and **h** exist as energetic minima on the potential energy surface, and their structures are shown in Figs. 1–4. All attempts to locate structures **e** and **f** in which the ligand coordinates in an η^2 mode through the C=N bond failed, and instead, the σ-*N* coordinated species was obtained in the course of the geometry optimisation. With ligand **1**, however, all species **a** – **h** converged into energetic minima structures [30], although the η^2-C=N forms **1e/f** were relatively high in energy. Complex **1e** was by 9.4 kcal/mol less stable than its σ-*N* coordinated counterpart **1g**, and for **1f** the difference was 14.6 kcal/mol. From this, we concluded that the activation barrier for the conversion into the σ-*N* form must be low, to eventually vanish when larger substituents are introduced into the 1-azabuta-1,3-diene. Likewise, the comparatively long Fe–C2 bond [30] in **1e/f** suggests that minor steric strain could easily cause this bond to break. In order to verify this hypothesis, the transition states and intrinsic reaction path for the conversion of **1e** into **1g** were calculated, and the results are shown in Figs. 5 and 6.

The reaction occurs in one step consisting of five distinct stages, as shown in Fig. 6. The structural changes accompanying the different stages of the IRC are depicted in Fig. S2 of the Supplementary Material. During phase [A], the 1-azabuta-1,3-diene ligand rotates to move the C2=N1 moiety out of the equatorial plane. The angle between the plane through the Fe–N1–C2 atoms and the plane through the iron atom and the equatorial carbonyl ligands thereby increases from 15° in **1e** to approximately 26° at stride −4.5 on the reaction coordinate. This process requires less