Journal of Saudi Chemical Society (2017) **21**, 198–204

King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Intra-ring haptotropic rearrangements of $Mn(CO)_3$ in fluorenyl ligands

Souhila Laib, Nadia Ouddai *

Laboratoire de chimie des matériaux et des vivants: Activité, Réactivité, Department of Chemistry, Faculty of Science, University Hadj Lakhdar, Batna 05000, Algeria

Received 7 August 2014; revised 1 May 2015; accepted 7 May 2015
Available online 28 May 2015

KEYWORDS

Density functional theory DFT;
Intra-ring haptotropic rearrangements;
Aromaticity;
Manganesetricarbonyl complexes

Abstract Geometric parameters, and intra-ring haptotropic rearrangements π–π (intra-ring-HRs) $\eta^5 \rightleftharpoons \eta^3$ of the manganesetricarbonyl complexes $(\eta^5\text{-9-R-}C_{13}H_8)Mn(CO)_3$, R = Bu^t and Ph in 18e zero-valence are carried out using density functional theory DFT at PBE/TZP level. The calculated activation barriers to $\eta^5 \rightleftharpoons \eta^3$ intra-ring HR in $(\eta^5\text{-9-R-}C_{13}H_8)Mn(CO)_3$, R = Bu^t and Ph are (28.5 and 69.5 kcal.mol^{-1} respectively). The compute of HOMA and FLU indexes indicates the reduction of aromaticity when going from free to coordinated complex. The energy decomposition analysis reveals the dominant ionic character in manganese–Cp bond in the presence of covalent contribution.

1. Introduction

The ability of organometallic compounds to undergo intramolecular rearrangement involving cleavage of some chemical bonds and formation of others was an exciting discovery made more than 50 years ago already [1,2]. The interaction between the transition metal moiety and the aromatic ligand, results in an important specific feature of their structures as well as dynamic properties [3]. Recently, the ability of such complexes to catalyze many organic reactions [4] and to activate some positions in ligands, can be used in the synthesis of difficult -to- access organic derivatives [5].

There were several approaches to the classification of different types of rearrangements in organometallic compounds: sigmatropic rearrangement (rupture/formation of σ-bonds) was studied first [6–8] and haptotropic rearrangement (rupture and formation of π-bonds). A large number of haptotropic rearrangements in aromatic ligands were disclosed and qualitatively studied [9,10] for many other transition metals including Mo, W, Rh, Pd, Ir, Ni, Mn, Fe, Zr, Ru, and Os. There are two kinds of haptotropic rearrangements: intra-ring [11] haptotropic (when the metal fragment changes its π-coordination to the organic ligand within the same ring) and inter-ring [9] haptotropic (involving migration of organometallic group from one of the aromatic ring to the other). The intra-ring haptotropic rearrangement IRHR was studied experimentally and theoretically for various organometallic compounds. First example of IRHR is occupied by η^2-complexes of transition metal, e.g., Ni [11], Os [12], Rh [13], Re [14], etc complexes with polyaromatic ligands (e.g., naphthalene, anthracene,

* Corresponding author.
Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jscs.2015.05.005

octafluoronaphthalene). They also exhibit η^2, η^2-intra-ring HRs [15,16] with low activation barriers (5–10 K cal.mol^{-1}).

Yarmolenko et al. proposed a reaction mechanism $\eta^5 \rightleftharpoons \eta^3$ of the fluorenyl ligand in η^5-fluorenylmanganesetricarbonyl complexes (Scheme 1) by cyclic voltammetry in THF and varying the temperature condition (usually within −90° to 40 °C) [17]. Reactivity of the species and the potentials of peaks on cyclic voltammograms in $\eta^5 \rightleftharpoons \eta^3$ IRHR are compared with different temperatures.

The present study explores the reaction mechanism of IRHRs in order to understand the interaction of the π-electron distribution of organometallic fragments with the metal center.

In the first step, we studied the geometrical parameters (distances, angles) on two model complexes using the density functional theory calculation (DFT), after we examined the reaction mechanism pathway of the IRHRs; also we have computed the indices of aromaticity based on the measure of electronic delocalization in aromatic molecules. Finally, we analyzed the nature of the bond between $Mn(CO)_3$ fragment and the fluorenyl ligand using the energy decomposition analysis.

2. Computational methods

DFT calculation were performed with the Amsterdam Density Functional ADF program developed by Baerends et al. [18] on models (η^5-9-Bu^t-$C_{13}H_8$)$Mn(CO)_3$ and (η^5-9-Ph-$C_{13}H_8$)$Mn(CO)_3$. Electron correlation was treated within general gradient approximation (GGA), scalar relativistic effects were considered at the level of zero-order regular approximation (ZORA) [19] with a TZP and the basis set superposition error (BSSE). The bonding interactions have been analyzed by means of Morokuma-type energy decomposition analysis (decomposition of the bonding energy into the Pauli (exchange repulsion, total steric interaction, and orbital interaction terms) [20] developed by Ziegler and Rauk for DFT methods; incorporated in ADF [21].

For these complexes, we compute the indices of aromaticity, the harmonic oscillator model of aromaticity (HOMA) index [22,23] and the aromatic fluctuation index (FLU) [24].

3. Results and discussion

3.1. Geometrical analysis

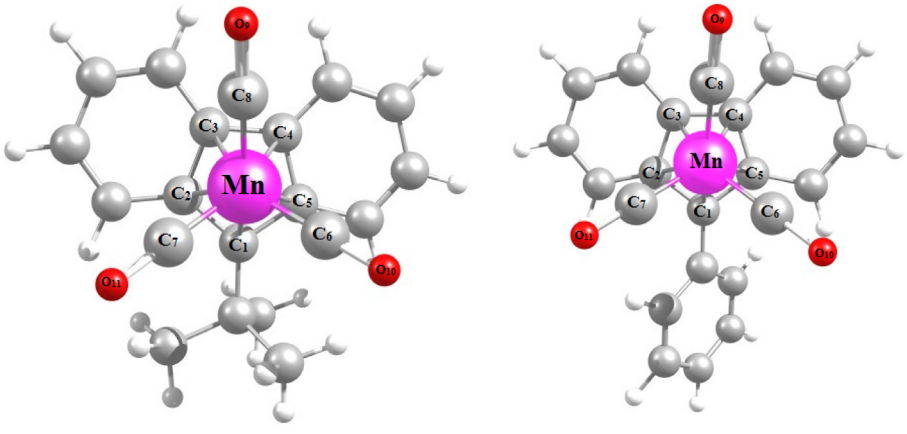
Two models of fluorenyl manganesetricarbonyl complexes (Fig. 1) containing two ligands of different nature R = Bu^t and Ph, the η^5-structure corresponds to the 18-electron manganese complexes. Geometries of manganesetricarbonyl complexes are described by the DFT method, optimized structures and selected geometries of these complexes are given in Table 1.

Analysis of bond orders indicates that these complexes are totally symmetric in η^5-coordinated molecules, with the position of the $Mn(CO)_3$ unit slightly shifted (1.865 Å for (η^5-9-Bu^t-$C_{13}H_8$)$Mn(CO)_3$ complex and 1.864 Å for (η^5-9-Ph-$C_{13}H_8$)$Mn(CO)_3$ complex respectively) from the ring in (η^5-9-R-$C_{13}H_8$)$Mn(CO)_3$ center, indicating that $Mn(CO)_3$ group slightly changes the geometry of the fluorenyl ligand when the substitute is changed. A large value of Mn–C(Cp) bond (π-interaction) can be seen easily in the two complexes compared with the experimental value of a simple bond Mn–C (2.095 Å) [25]. The C_1–C^t_{Bu} bond distance is longer by 0.058 Å than the C_1–C_{Ph} bond distance. In (η^5-9-Bu^t-$C_{13}H_8$)$Mn(CO)_3$ the angles of bonds do not differ significantly from those in the second complex.

$$[(\eta^5\text{-9-R-}C_{13}H_8)Mn(CO)_3] \overset{-e}{\rightleftharpoons} [(\eta^5\text{-9-R-}C_{13}H_8)Mn(CO)_3]^{\cdot} \rightleftharpoons [(\eta^3\text{-9-R-}C_{13}H_8)Mn(CO)_3]^{\cdot} \overset{-e}{\rightleftharpoons} [(\eta^3\text{-9-R-}C_{13}H_8)Mn(CO)_3]^{2-}$$

18e 17e 19e 18e

Scheme 1 Reaction mechanism $\eta^5 \rightleftharpoons \eta^3$ of the fluorenyl ligand in η^5- fluorenylmanganesetricarbonyl complexes.



(η^5-9-Bu^t-$C_{13}H_8$)$Mn(CO)_3$ (η^5-9-Ph-$C_{13}H_8$)$Mn(CO)_3$

Figure 1 Optimized geometrical structures of (η^5-9-R-$C_{13}H_8$)$Mn(CO)_3$ R=Bu^t and Ph complexes.