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Research paper

Spectroscopic and DFT assessment of bridging ligand effect on the structural and electronic properties of dinuclear iridium- and rhodium-based complexes

Saheed A. Popoola[a], Nisar Ullah[b], Abdulaziz A. Al-Saadi[b,*]

[a] Department of Chemistry, Islamic University of Madinah, Saudi Arabia
[b] Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

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ABSTRACT

A series of chloro-, amido-, and methoxo-bridged dinuclear complexes of iridium(I) and rhodium(I) was synthesized, and their coordination properties were assessed. Density functional theory (DFT) calculations, and infrared and Raman spectroscopies were employed to examine the metal-olefin and metal-bridging group interactions. The outcome of these studies revealed that the nature of bridging ligands does influence the electronic properties of these metal complexes. They also revealed that the amido-bridged complexes exercised the least metal-olefin interaction, while the methoxo-bridged complexes exhibited the most. The *p*-character in the hybrid orbitals of olefinic carbons was calculated to increase upon coordination, and the extent of increase can be linked to the group electronegativity of bridging ligands. Vibrational spectroscopy, supported with theoretical DFT approach, was useful and found consistent in assessing the pi and combined ($\pi + \sigma$) metal-olefin interactions in these dinuclear complexes.

1. Introduction

Organometallic compounds enjoy a resurgence of attention due to their importance in catalytic applications and bearing unique structural and electronic properties compared to regular covalent systems. On the other hand, olefins are considered a model of organic unsaturated ligands [1], and metal-olefin complexes are frequently used in a wide range of organic transformations such as hydrogenation, hydroformylation, hydrocarbonlyation, isomerization as well as metathesis both in the small scale and the industrial set-up [2–4]. The catalytic activity of a metal complex toward a desired transformation can be improved by thoroughly understanding the thermodynamics and electronic characteristics governing the metal-olefin interaction [2,3]. The strength of the metal-olefin interaction in organometallic complexes can be assessed with the help of useful tools including the Dewar-Chatt-Duncanson (DCD) model of metal-olefin bonding [1,3,5,6] as well as by the vibrational infrared and Raman spectroscopies [7–9].

Both sigma (σ) donation from the olefin's highest occupied molecular orbital (HOMO) to the metal's lowest unoccupied molecular orbital (LUMO) and π-acceptance from an occupied metal d_π orbital to a vacant antibonding ($\pi*$) olefin orbital [2,4] have greater influence on the olefinic character of the ligand [1,2,9]. Moreover, vibrational frequency shifts associated with some key bands, such as C=C stretching, in-plane CH bending, metal–carbon stretching and metal-bridging ligand stretching, could be employed to qualitatively evaluate σ- and π-type of interaction between the metal and the olefin ligand [7,10]. The magnitude of the vibrational shift is correlated with the extent of the metal-olefin interaction. Such a shift is associated with the coupling of the C=C stretching with the in-plane olefinic C−H bending modes (sometimes called band I and band II, respectively). Upon complexation, the C=C stretching is expected to shift to a lower frequency whereas the C−H bending shifts otherwise [7]. The extent of the joint frequency shifts of band I and band II has been used to measure the total ($\sigma + \pi$) metal-olefin interaction [7,10]. Moreover, the metal-olefin tilting vibrational mode caused by the movement of the olefinic carbon atoms into and out of the electron density region may be used to evaluate the π constituent of the metal-olefin coordination. Wertz and Moseley [7] have reported that the vibrational energy of the C−H rocking can be related to the magnitude of the electron density in the π constituent and, as such, the change in energy reflects the strength of the π component.

Of particular interest in dinuclear complexes is the nature of bridging atoms that influence their structural and electronic properties as well as metal–metal interaction [11]. The bridging atom size directly

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* Corresponding author.
E-mail address: asaadi@kfupm.edu.sa (A.A. Al-Saadi).

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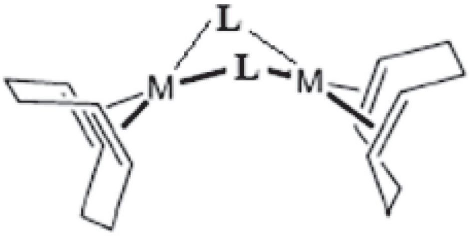
alters the metal centers closeness, while their flexibility plays an important role in the extent of the metal–metal interaction [12] which, in turn, has an impact on the metal-olefin coordination. In addition, the electronegativity of the bridging atom is one of the factors that controls the electron density on the metal center which subsequently dictates the metal–ligand interaction. Chloro-, alkoxy-, thioalkoxy- and parent-amido are among the radicals reported as efficient bridging ligands in dinuclear Rh and Ir complexes [13–16]. The parent-amido firmly bridges metals together in different dinuclear-based assemblies with 1,5-cyclooctadiene (COD) as a ligand [12,13]. The Ir–NH_2–Ir linkage has been proven to play a significant role in the concerted mechanism of iridium-based amido complexes in catalytic hydrogen transfer reactions [13,17]. Similarly, chloro- and methoxo-bridged complexes have served as precursor catalysts in transfer hydrogenation and other catalytic reactions [18–22].

Until now, the use of vibrational spectroscopy as a tool to elucidate the nature of the bridge coordination in dinuclear systems has not been extensively explored. When properly combined, vibrational methods along with proper theoretical approaches shall avail helpful evidences for organometallic chemists to understand mechanistic pathways of such types of complexes. In this work, we have prepared amido-, methoxo- and chloro-bridged dinuclear complexes of iridium and rhodium (**1**–**6**) with COD rings as an olefinic ligand (Fig. 1) and conducted a detailed structural and electronic examination using DFT calculations. Vibrational spectroscopic assessments of the metal-olefin interaction were performed by utilizing standard infrared and Raman techniques. The outcome reported herewith have been employed to shed some light on the nature of the intramolecular interaction and catalytic behavior of these complexes.

2. Methodology

2.1. Experimental

All chemicals were purchased from Sigma Aldrich and used as received without further purification. The synthesis of complexes **1**–**6** was accomplished under inert atmosphere using a schlenk-tube technique by employing literature known procedures [13,15,16,28]. Solvents used were distilled under argon before use. The mid-infrared spectra of 1,5-cyclooctadiene (COD) as well as complexes **1**–**6** (Figs. S1 and S2) were recorded on a NICOLET 6700 FT-IR using a single-reflection Attenuated Total Reflection (ATR) technique and KBr pellets, respectively. Raman spectra of COD and complexes (Figs. S3 and S4) were recorded on a NICOLET NXR FT-RAMAN MODULE in a 1-mm glass tube using a laser source of 1064 nm and 0.3 W power. Far-infrared spectra (Figs. S5 and S6) were collected after the complexes were sampled in polyethylene powder.



(**1**) M = Ir, L = NH_2
(**2**) M = Rh, L = NH_2
(**3**) M = Ir, L = OMe
(**4**) M = Rh, L = OMe
(**5**) M = Ir, L = Cl
(**6**) M = Rh, L = Cl

Fig. 1. Chemical structure of the *tilted* configuration of complexes **1**–**6**.

2.2. Computation

Ab initio density functional theory (DFT) calculations were performed using Gaussian 09 program [23]. The B3LYP approach [24–26] with a basis set of 6–311 + +G(d,p) for non-metal atoms was used to carry out the energy minimization, predict structural parameters, compute vibrational frequencies and explore natural bond orbitals of these complexes. The SDD pseudo potential was used to describe the orbitals of Rh and Ir with the inclusion of the D3 dispersion correction approach established by Grimme [27]. The choice of the B3LYP method together with the 6–311 + +G(d,p) basis set was based on their reliability for Ir and Rh metal-based complexes [28–33]. The calculated frequencies were scaled using reported scaling factors [29], whereas the reactivity parameters have been computed using the procedure described by Foresman and Frsich [34].

3. Results and discussion

3.1. Molecular symmetry and structure

The molecular symmetry of a metal complex plays a key role on its electronic properties and therefore is important in the design of catalytic systems. The overall symmetry of a binuclear-COD complex depends on the arrangement of the metal centers with respect to the bridging ligand as well as on the configuration the COD ring adopts. A square planar center by the metal ions and bridging atoms is characteristic for D_{2h} and C_{2h} configurations. On the other hand, in case of non-planar C_{2v} form, depicted in Fig. 1, an angle of less than 180° is adopted by the complex and hence is described as *tilted*. Based on available crystallographic data [13,36–38], the amido-bridged dinuclear complexes **1** and **2** maintain tilted C_{2v} symmetry with a folding angle of nearly 120°, whereas their methoxo-bridged counterparts **3** and **4** have strictly planar C_{2h} symmetry (Fig. 2). The chloro-bridged dinuclear complexes (**5** and **6)** were determined to adopt C_{2v} symmetry for the iridium and near-D_{2h} symmetry for the rhodium metal centers with folding angles of 109° and 170°, respectively (Fig. 2). The calculated DFT structures reproduced geometrical parameters of complexes **1**–**6** in fair agreement with the corresponding crystallographic data. The existing slight deviations are attributed mainly to the packing effect in the solid phase. An overview of some key structural parameters (Table 1) reveals that the amido and methoxo groups more significantly influence the metal-bridging ligand symmetry. The smaller size of oxygen in complexes **3** and **4** facilitates the planar geometry. In dichloro complexes, however, the effect of the type of the metal centers is a predominating factor which could be due to the appreciable electronegativity of chlorine atom. Although Cl atom is more electronegative than OCH_3 and NH_2 groups, its larger size resulted in a longer $M-L_{Bridg.}$ distance compared to OCH_3 or NH_2 counterparts. The symmetry of complexes **1**–**6** governs the intermetallic distance which was noticed in the tilted configuration to be up to 0.6 Å shorter compared to the planar/near-planar ones.

Careful analysis of the variation in M − C and C=C bond lengths (Table 1) and natural bond orbital (NBO) values (Table 2) manifests the extent of the back-bonding. Upon coordination, the π-character of the C=C bond becomes less significant in the iridium complexes (**1**, **3** and **5**) compared to their rhodium counterparts (**2**, **4** and **6**). The greater change in the C=C bond length in iridium complexes could be attributed to the more electropositive nature of iridium than rhodium; which