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Theoretical aspects of the bonding in acetylide-bridged organometallic dinuclear complexes

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Abstract

The electronic and geometrical structures of a variety of acetylide-bridged organometallic dinuclear complexes $(ML_n)_2(\mu\text{-}C_2)$ (M = Sc, Ti, W, Ru, Pt) are analysed and compared by use of extended Hückel and density functional-theory calculations. It is established that all the studied complexes feature the ethyne valence structure, except the titanium species for which resonance forms of ethyne-type and cumulenic-type must be invoked to rationalise its structure. Results indicate that the σ-bonded framework is similar in all complexes and mainly governs the metal–carbon bonding in these species. In all cases but the titanium compound, the σ-type M–C is hardly complemented by π-back-donation from the metals into acceptor C_2 orbitals. The peculiar energy and composition of the HOMOs, which are in general metal–carbon antibonding and carbon–carbon bonding for the metals at the right of the periodic table, can allow the observation of cumulenic structures upon oxidation. ***To cite this article: N. Ouddaï et al., C. R. Chimie 8 (2005)***.

Résumé

Les structures géométriques et théoriques de divers complexes organométalliques à pont acétylure de formule $(ML_n)_2(\mu\text{-}C_2)$ (M = Sc, Ti, W, Ru, Pt) sont analysées et comparées à l'aide de calculs en méthodes de Hückel étendue et de la fonctionnelle de la densité. Il est montré que tous les composés étudiés peuvent être décrits à l'aide d'une formule de Lewis de type acétylénique, à l'exception d'une espèce au titane, pour laquelle les deux formes résonantes acétylénique et cumulénique sont nécessaires pour rationaliser sa structure. Les calculs montrent que le mode de liaison σ est similaire dans tous les composés et gouverne majoritairement la liaison métal–carbone. Dans tous les cas, excepté le composé au titane, le retour π des atomes métalliques vers les orbitales acceptrices du ligand C_2 est quasiment absent. L'énergie et la composition des orbitales moléculaires les plus hautes occupées, qui sont antiliantes métal–carbone et liantes carbone–carbone pour les composés de la droite du tableau périodique, laissent entrevoir la possibilité d'espèces cumuléniques après oxydation. ***Pour citer cet article : N. Ouddaï et al., C. R. Chimie 8 (2005)***.

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1. Introduction

C_2 is a peculiar simple diatomic molecule [1]. Taken alone, it is not very stable although it can be generated in a carbon arc, is found in comets, or is responsible for the blue light we see in flames. It looks like a dumbbell in which the two carbon atoms are separated from 1.24 Å in the ground state. Such a molecule can easily be stabilised by other atoms or group of atoms. In the realm of organic chemistry, it is contained in ethane, ethene, and acetylene, molecules which are the archetypical references for carbon–carbon single (1.54 Å), double (1.34 Å), and triple (1.20 Å) bonds, respectively. C_2 units are also found in solid state chemistry [2], with different C–C separations depending on its formal electron count, leading to their interpretation as deprotonated ethyne, ethane or acetylene. For instance, a triple bond (1.19 Å) is assumed in CaC_2 ($Ca^{2+}C_2^{2-}$). In $Gd_2Cl_2C_2$ [$(Gd^{3+})_2(Cl^-)_2(C_2^{4-})_2$] [3], the C–C distance in the C_2 units which reside in octahedral cavities is 1.36 Å, corresponding to a double bond. A C–C single bond (1.47 Å) is observed in $Gd_{10}Cl_{18}C_4$ clusters, compatible with the presence of C_2^{6-} fragments within octahedral metallic cages [$(Gd^{3+})_{10}(Cl^-)_{18}(C_2^{6-})_2$] [2b,4]. C_2 can also be observed in numerous molecular organometallic compounds [5]. C_2 can span two mononuclear metal fragments as in $[ScCp^*{}_2]_2(\mu\text{-}C_2)$ ($Cp^* = C_5Me_5$) [6]. Five metallic atoms are caught in huddling around an exposed C_2 fragment in the cluster $Ru_5(CO)_{11}(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(\mu_5\text{-}\eta^4{:}\eta^5\text{-}C_2)$ [7]. C_2 can also be fully encapsulated in a metallic cage as in $[Co_6Ni_2(CO)_{16}(\mu_8\text{-}\eta^6{:}\eta^6\text{-}C_2)]^{2-}$ [8].

As in organic or solid state chemistry, the C–C bond length largely varies in these organometallic systems, and different electronic structures can be assigned on the basis of the C–C distance, which can be related to those in acetylene, ethene or ethane or as well. A carbon–carbon separation corresponding to a triple bond is observed in $[ScCp^*{}_2]_2(\mu\text{-}C_2)$ [6] (1.22 Å) or $[Ru(CO)_2Cp]_2(\mu\text{-}C_2)$ [9] (1.19 Å) complexes, whereas the C–C bond length of 1.37 Å measured in the binuclear species $[Ta(t\text{-}Bu_3SiO)_3]_2(\mu\text{-}C_2)$ [10] is more consistent with a C–C double bond. A C–C distance of 1.38 Å observed in $[W(t\text{-}Bu_3O)_3]_2(\mu\text{-}C_2)$ is rather assigned to a single bond [11]. C–C bond distances are generally more spread out when the number of metal atoms around the C_2 unit increases as in $Ru_5(CO)_{11}(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(\mu_5\text{-}C_2)$ ($d_{C-C} = 1.305$ Å) or $[Co_6Ni_2(CO)_{16}(\mu_8\text{-}C_2)]^{2-}$ ($d_{C-C} = 1.48$ Å) previously mentioned. The analogy between this type of compounds and purely organic or inorganic compounds is then less straightforward. Nevertheless, theoretical studies carried out on these high-nuclearity species by Halet and coworkers have shown that the bonding of C_2 with its metallic host follows the Dewar–Chatt–Ducanson model, resulting from an important forward electronic donation from occupied orbitals of the C_2 fragment toward acceptor metallic molecular orbitals (MO), but also from a back-donation from metallic orbitals into vacant C_2 orbitals [12]. Such a bonding mode is in turn comparable to that previously established for acetylenic complexes [13] and absorbed acetylene on metallic surfaces [14].

Following these previous studies carried out on encapsulated and exposed C_2-containing organometallic compounds [12], we have recently investigated the bonding and electronic structure of dinuclear $(ML_n)_2(\mu\text{-}C_2)$ complexes in which the C_2 entity is both end-capped by a metallic fragment. These compounds are of interest being thought as models for molecular-scale wires [5]. We report in this paper the main results obtained via extended Hückel theory (EHT) and density functional-theory (DFT) calculations on homometallic compounds containing metal fragments with π-acceptor ligands such as $[Ru(CO)_2Cp]_2(\mu\text{-}C_2)$ [9] which have been little studied [15,16]. Dinuclear compounds with π-donor ligands such as $[W(t\text{-}Bu_3O)_3]_2(\mu\text{-}C_2)$ have not been considered, having been extensively studied previously [10b,11b,17].

2. Structural considerations and electron counts

Several homo- and hetero-dinuclear $(ML_n)_2(\mu\text{-}C_2)$ complexes have been structurally characterised. They are reported in Table 1. In all those with π-acceptor