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Bonding situation and stability of η^1- and η^6-bonded heteroarene complexes $M(\eta^1\text{-}EC_5H_5)_6$ and $M(\eta^6\text{-}EC_5H_5)_2$ (M = Cr, Mo, W; E = N, P, As, Sb, Bi) ☆

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This paper is dedicated to Professor Christoph Elschenbroich on the occasion of his 70th birthday.

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ABSTRACT

Density functional calculations at the BP86/TZ2P level are reported for the pseudo-octahedral heteroarene complexes $M(\eta^1\text{-}EC_5H_5)_6$ and for the sandwich complexes $M(\eta^6\text{-}EC_5H_5)_2$ (M = Cr, Mo, W; E = N, P, As, Sb, Bi). The complexes $M(CO)_6$ and $M(\eta^6\text{-}C_6H_6)_2$ have been calculated for comparison. The nature of the metal–ligand interactions was analyzed with the EDA (energy decomposition analysis) method. The calculated bond dissociation energies (BDE) of $M(\eta^1\text{-}EC_5H_5)_6$ have the order for $E = P > As > N > Sb \gg Bi$ and for $M = Cr < Mo < W$. All hexaheteroarenes bind more weakly than CO in $M(CO)_6$. Except for pyridine, which is the weakest η^6-bonded ligand, the trend in the BDE of the $M(\eta^6\text{-}EC_5H_5)_2$ complexes is opposite to the trend of the $M(\eta^1\text{-}EC_5H_5)_6$ complexes $NC_5H_5 < PC_5H_5 < AsC_5H_5 < SbC_5H_5 < BiC_5H_5$. The opposite trend is explained with the different binding modes in $M(\eta^6\text{-}EC_5H_5)_2$ and $M(\eta^1\text{-}EC_5H_5)_6$. The bonding in the former complexes mainly takes place through the π electrons of the ligand which are delocalized over the ring atoms while the bonding in the latter takes place through the lone-pair electrons of the heteroatoms E. The Lewis basicity of the group-15 heterobenzenes EC_5H_5 becomes weaker for the heavier elements E. The occupied π orbitals of the heterobenzene ring become gradually more polarized toward the five carbon atoms in the heavier arenes EC_5H_5 which induces stronger metal-carbon bonds in $M(\eta^6\text{-}EC_5H_5)_2$ and weaker metal-E bonds. The EDA calculations show that the nature of the $M\text{-}EC_5H_5$ bonding in $M(\eta^1\text{-}EC_5H_5)_6$ is similar to the M–CO bonding in $M(CO)_6$. Both types of bonds have a slightly more covalent than electrostatic character. The π orbital interactions in the chromium and molybdenum complexes of CO and heterobenzene are more important than the σ interactions. This holds true also for the tungsten complexes of CO and the lighter heteroarenes while the σ- and π-bonding in the heavier $W(\eta^1\text{-}EC_5H_5)_6$ species have similar strength. The EDA results also show that the nature of the bonding in the sandwich complexes $M(\eta^6\text{-}EC_5H_5)_2$ is very similar to the bonding in the bis-benzene complexes $M(\eta^6\text{-}C_6H_6)_2$. The orbital interactions contribute for all metals and all arene ligands about 60% of the attractive interactions while the electrostatic attraction contributes about 40%. The largest contribution to the orbital term comes always from the δ orbitals. The calculations predict that the relative stability of the sandwich complexes $M(\eta^6\text{-}EC_5H_5)_2$ over the octahedral species $M(\eta^1\text{-}EC_5H_5)_6$ increases when E becomes heavier and it increases from W to Mo to Cr when E = N, P, As.

1. Introduction

Heteroarenes of the group 15 elements EC_5H_5 (E = N–Bi) [1–4] are ambient ligands which can either bind η^1 via the σ-lone electron pair of atom E or η^6 through the six π electrons of the aromatic ring. The coordination chemistry of this class of ligands has systematically been investigated in experimental studies of Elschenbroich [5–13] with the focus on the preparation of neutral compounds. The results show that the phosphinine ligand prefers the η^6-binding mode in complexes with early metals of the first transition metal row while in complexes of late transition metals η^1 coordination via the lone pair is favored [5–7]. The group-6 metals chromium and molybdenum which are in the middle of the transition metals rows are particularly interesting because they exhibit a diverse binding mode with heteroarene ligands. Both coordination modes are experimentally observed for group-6 metals chromium [8–11] and molybdenum [12–14]. So far, for tungsten only η^1-complexes with phosphinine and arsenine are experimentally verified [12,15]. The arsenine complexes of the group-6 elements are particularly interesting, because they exemplify the dichotomy of the bonding behaviour of the heteroarenes.

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Chromium binds to arsenine in the η^6-mode exclusively, molybdenum exhibits both options η^1 and η^6, while for tungsten only the η^1 coordination is observed [8,14].

Previously, we reported on the η^1-bonding properties of EC_5H_5 in Lewis acid-base complexes with H_3B–L and H_2B^+–L and compared them with CO [16]. For EC_5H_5 not only the expected σ-donation in H_2B^+-L was found, but the calculations also suggested a significant amount of out-of-plane $\pi_\perp$-donation for all heteroarenes which was more than three times as strong as for CO which is a very weak π-donor [17].

In this paper, we expand our studies to transition metal complexes of EC_5H_5 and compare their bonding properties with CO in η^1-complexes while the η^6-complexes are compared with benzene as ligand. The group-6 transition metals are ideal candidates for this study as they are known to bind with both binding modes towards the heteroarenes. Firstly, we will discuss the η^1- and then the η^6-bonding mode separately. This will be followed by a discussion of the reason for the preference of one mode over the other depending on the metal and/or the heteroatom in EC_5H_5.

2. Methods

The geometries and bond dissociation energies have been calculated at the non-local DFT level of theory using the exchange functional of Becke [18] and the correlation functional of Perdew [19] (BP86). Scalar relativistic effects have been considered using the zero-order regular approximation (ZORA) [20]. Uncontracted Slater-type orbitals (STOs) were used as basis functions for the SCF calculations [21]. The basis sets for all atoms have triple-zeta quality augmented with two sets of polarization functions, i.e. two p functions on hydrogen, two d functions on the main-group elements and two f functions on the metals. An auxiliary set of s, p, d, f and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle [22]. This level of theory is denoted BP86/TZ2P. The latter calculations were carried out with the program package ADF 2003.01 [23]. All structures which are reported here are energy minima on the BP86/TZ2P potential energy surface by calculations of the Hessian matrices which have no imaginary frequencies.

The nature of the metal–ligand bonding has been investigated through the energy partitioning analysis (EDA) of the program package ADF based on the EDA method of Morokuma [24] and the extended transition state (ETS) partitioning scheme of Ziegler [25]. In the EDA method the bond dissociation energy D_e between the interacting fragments is partitioned into several contributions which can be identified as physically meaningful entities. In the present case the fragments are the naked transition metal M in the electronic reference singlet state with the proper valence configuration (η^1: $(n)s^0(n-1)[d_{xy}\ d_{xz}\ d_{yz}]^6\ [d_{z^2} d_{z^2-y^2}]^0$; η^6: $(n)s^0(n-1)[d_{z^2} d_{z^2-y^2} d_{xy}]^6\ [d_{xz}\ d_{yz}]^0$) and the ligand cages. The latter are $(EC_5H_5)_6$ for the η^1-bonded complexes and $(EC_5H_5)_2$ for the η^6-bonded species. We also calculated the hexacarbonyls $M(CO)_6$ where the ligand cage is the set of the six CO ligands $(CO)_6$. In the EDA, D_e is first separated into two major components ΔE_{prep} and ΔE_{int}:

$$-D_e = \Delta E_{prep} + \Delta E_{int}. \tag{1}$$

ΔE_{prep} is the energy which is necessary to promote the fragments from their equilibrium geometry to the geometry which they have in the complex and from the electronic ground state to the reference state. In the present case, the former applies only for the ligand cage while the latter applies only for the metal atoms. ΔE_{int} is the instantaneous interaction energy between the fragments in the molecule. Note that it is ΔE_{int} and not D_e which should be used to identify the nature of the chemical bond. The interaction energy ΔE_{int} can be divided into three components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{pauli} + \Delta E_{orb}. \tag{2}$$

ΔE_{elstat} gives the electrostatic interaction energy between the fragments which are calculated with a frozen electron density distribution in the geometry of the complex. It can be considered as an estimate of the *electrostatic* contribution to the bonding interactions. The second term ΔE_{Pauli} in Eq. (1) gives the repulsive four-electron interactions between occupied orbitals. ΔE_{Pauli} is calculated by enforcing the Kohn-Sham determinant of the molecule which results from superimposing the fragments to be orthonormal through antisymmetrization and renormalisation. The stabilizing orbital interaction term ΔE_{orb} is calculated in the final step of the analysis when the Kohn–Sham orbitals relax to their final form. The orbital term ΔE_{orb} can be considered as an estimate of the *covalent* contributions to the attractive interactions. Thus, the ratio $\Delta E_{elstat}/\Delta E_{orb}$ indicates the electrostatic/covalent character of the bond. The latter term can be partitioned further into contributions by the orbitals which belong to different irreducible representations of the interacting system. This makes it possible to calculate e.g. the contributions of and bonding to a covalent multiple bond. More details about the method can be found in Ref. [23b]. Reviews of EDA results for metal–ligand bonds have been reported in reference [26].

3. Geometries and dissociation energies

3.1. $M(\eta^1\text{-}EC_5H_5)_6$ complexes

The optimized structures of the $M(\eta^1\text{-}EC_5H_5)_6$ (M = Cr, Mo, W; E = N, P, As, Sb, Bi) complexes have a pseudo-octahedral geometry with T_h-symmetry. Due to technical restrictions in the ADF package the T_h symmetry group cannot be applied. In the actual geometry optimization we used D_{2h} symmetry for the calculation of the heteroarene complexes. Inspection of the finally optimized geometries showed that they have T_h symmetry. The most important bond lengths and bond angles of $M(\eta^1\text{-}EC_5H_5)_6$ are shown in Table 1

Table 1
Calculated bond lengths [Å] and bond angles [°] of $M(\eta^1\text{-}EC_5H_5)_6$ with E = N, P, As, Sb, Bi at D_{2h} symmetry[a] at the BP86/TZ2P level. Experimental values in *italics*.

	N	P	As	Sb	Bi
Cr					
Cr–E	2.081	2.276 *2.265(10)*[b]	2.406	2.594	2.717
E–C2	1.376	1.747	1.867	2.063	2.159
C2–C3	1.386	1.392	1.388	1.388	1.384
C2–C4	1.400	1.399	1.402	1.404	1.406
C2–E–C2′	113.9	101.0	98.6	94.1	91.7
D_e	79.4	135.1	85.4	75.0	15.5
Mo					
Mo–E	2.170	2.410 *2.381 (8)*[c]	2.518	2.692	2.793
E–C2	1.380	1.745	1.866	2.061	2.156
C2–C3	1.386	1.392	1.388	1.388	1.384
C2–C4	1.401	1.399	1.402	1.404	1.406
C2–E–C2′	114.2	101.2	98.7	94.2	91.9
D_e	130.4	191.0	143.6	128.7	72.3
W					
W–E	2.153	2.408 *2.378(10)*[c]	2.512	2.690	2.787
E–C2	1.384	1.745	1.865	2.060	2.155
C2–C3	1.384	1.392	1.388	1.388	1.384
C2–C4	1.402	1.399	1.402	1.404	1.406
C2–E–C2′	114.0	101.4	99.0	94.5	92.2
D_e	177.3	241.1	188.0	169.5	107.1

[a] ADF is not able to use T_h symmetry; however, complexes are practically T_h even though D_{2h} symmetry had to be applied.
[b] Ref. [8].
[c] Ref. [12].