A DFT INVESTIGATION OF THE STRUCTURAL AND ELECTRONIC PROPERTIES OF Co(I) AND Rh(I) HALF-SANDWICH COMPLEXES WITH HETEROAROMATIC π LIGANDS

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Co(I) and Rh(I) half-sandwich complexes of the heteroaromatic 1,2-azaborolyl and 3a,7a-azaborindenyl anions with the ancillary ligand COD (1,5-cyclooctadiene) are designed by using accurate state-of-the-art Density Functional Theory (DFT) calculations. Their structural and electronic properties are compared to those of the analogous compounds containing the classic hydrocarbon isoelectronic ligands, *i.e.* cyclopentadienyl and indenyl anions. A comparison is made between the catalytic ability of $(\eta^5\text{-C}_5\text{H}_5)$-Co and (1,2-azaborolyl)-Co fragments toward alkyne [2+2+2] cyclizations, a class of reactions of paramount importance in industrial and pharmaceutical research for the synthesis of substituted benzenes, polycyclic and heterocyclic compounds, by theoretically addressing the fundamental mechanistic steps.

INTRODUCTION

In cyclopentadienyl (Cp, **1**) and indenyl (Ind, **2**) anions the replacement of one of the C-C π-bonds of the cyclopentadienyl moiety by an isoelectronic B-N π-bond leads to interesting heteroaromatic ligands, *i.e.* 1,2-azaborolyl (Ab, **3)** and 3a,7a-azaborindenyl (Abi, **4**) anions, which, after the pioneering studies of Schmid,[1] have been recently synthesized by Fu[2] and Ashe[3]; these species are shown in Scheme 1.

1   **2**   **3**   **4**
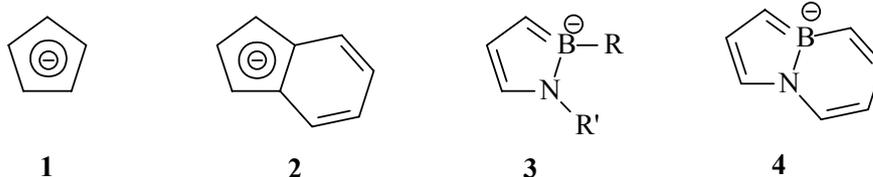
Scheme 1

Zr(IV) complexes of **3** (R=C$_6$H$_5$, R'=CH$_3$CH$_2$) and **4** were found to display a higher activity as Ziegler-Natta catalysts for the polymerization of olefins than the analogous **1** and **2** derivatives.[3c] This result prompted us to model half-sandwich Co(I) and Rh(I) complexes of **3** and **4**, with the aim of investigating how the bonding mode and the reactivity of these d^8 nuclei can be modulated by adjusting their electronic environment. A comparison is made with Co(I) and Rh(I) complexes of classic **1** and **2** hydrocarbon ligands, which are well known catalyst precursors for a very important class of reactions, *i.e.* the trimerization of alkynes to benzene or, more in general, the co-trimerization of alkynes and other unsaturated molecules to afford a variety of heteroaromatic compounds.[4] Schmid[1b] has reported some reactions of the AbCo fragment with alkynes to give arenes.

This computational study has been carried out by employing accurate state-of-the-art Density Functional Theory (DFT) methods.[5]

RESULTS AND DISCUSSION

Full geometry optimizations of the half-sandwich Co(I) and Rh(I) complexes shown in Scheme 2 have been carried out without any constraint.

1a: M=Co, L₂=COD
1b: M=Rh, L₂=COD
1c: M=Co, L =C₂H₂
1d: M=Rh, L=C₂H₂

2a: M=Co, L₂=COD
2b: M=Rh, L₂=COD

3a: M=Co, L₂=COD
3b: M=Rh, L₂=COD
3c: M=Co, L =C₂H₂
3d: M=Rh, L =C₂H₂

4a: M=Co, L₂=COD
4b: M=Rh, L₂=COD

R : N(CH₃)₂
R': CH₃

Scheme 2

1a, 1b and **2b** have been carefully compared to the corresponding crystallographic structures taken from the CSD.[6] The good agreement between the experimental and computed geometries (Figure 1) enhances our confidence in the reliability of the geometries which have not been determined yet.

The C-C distances of the coordinated aromatic and heteroaromatic anions are almost unaffected by replacing the CoCOD⁺ fragment with the RhCOD⁺ fragment. When passing from Co to Rh the relevant structural differences are the increased distances between the metal and the centroid of the five membered ring Q (Table 1) and between the metal and the ancillary ligand COD (Figure 1).
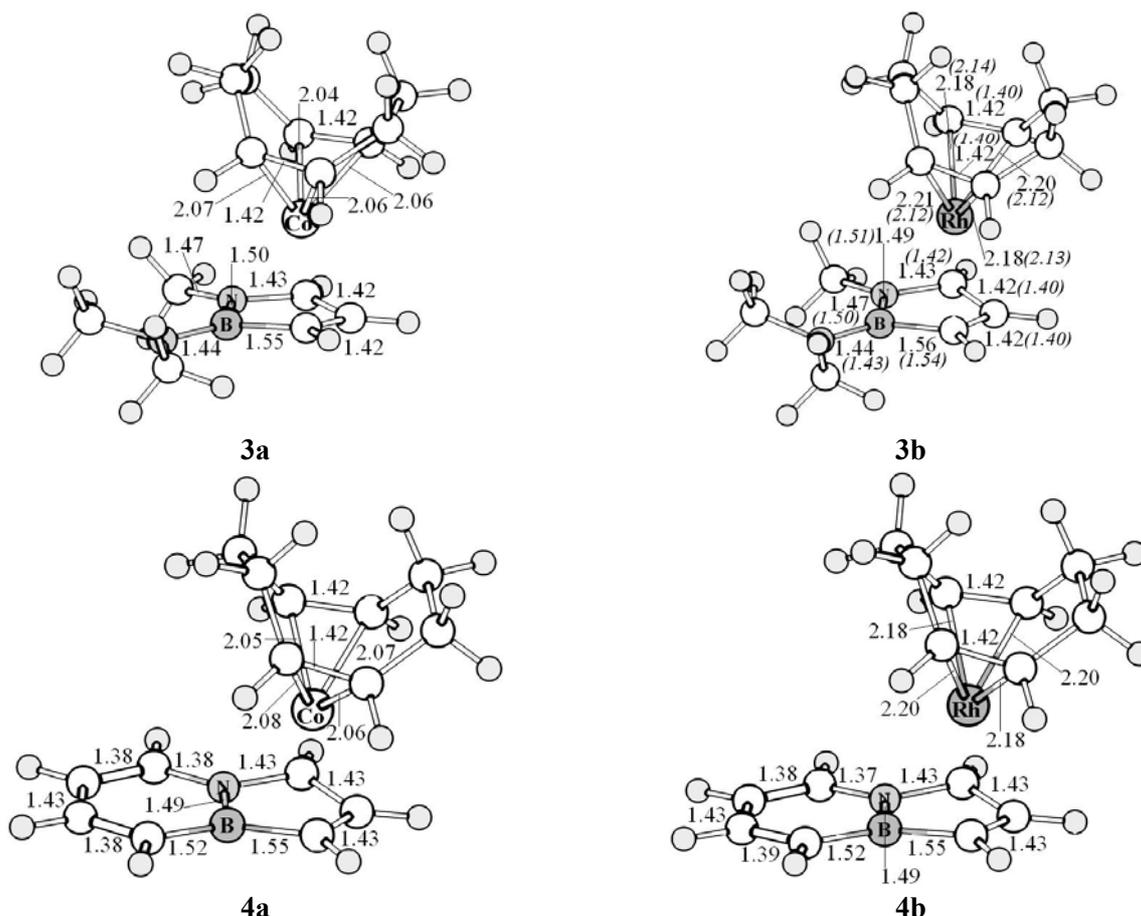

1a

1b

2a

2b

Fig. 1 – DFT optimized geometries of Co(I) and Rh(I) complexes containing the aromatic ligands **1**, **2**, **3** and **4** and the ancillary ligand COD. For sake of clarity the metals, B and N atoms of the five membered rings are labelled. The bracketed numbers in italics refer to the crystallographic structures indicated in the caption of Table 1.

Table 1

Ring slippage parameters (Å), metal-ring distances (Å) and folding angles (°)

	1a	1b	1c	1d	2a	2b	3a	3b	3c	3d	4a	4b
M-Q[a]	1.78 (1.72)[d]	2.03 (1.91)[e]	1.78	1.98	1.83	2.06 (1.93)[f]	1.84	2.08 (1.96)[g]	2.04	2.23	1.86	2.08
Δ[b]	0.044 (0.031)[d]	0.063 (0.047)[e]	0.031	0.060	0.21	0.25 (0.15)[f]	0.25	0.33 (0.27)[g]	0.52	0.54	0.29	0.33
FA[c]	3 (2)[d]	5 (3)[e]	2	4	8	11 (9)[f]	10	13 (12)[g]	16	16	12	14

[a] Q denotes the centroid of the five membered ring. [b] Ring slippage parameter defined as $\Delta=1/2[(M-C4+M-C5)-(M-C1+M-C3)]$; in **2** complexes C4 and C5 are denoted C3a and C7a respectively; in **3** and **4** complexes C4 and C5 must be replaced with B and N respectively. [c] Folding angle defined as the angle between the planes C1-C2-C3 and C1-C3-C4-C5 (C1-C3-C3a-C7a for **2** complexes and C1-C3-B-N for **3** and **4** complexes). [d] Crystallographic values from Ref. 7a [e] Crystallographic values from Ref. 7b. [f] Crystallographic values from Ref. 7c. [g] Crystallographic values of the similar compound (η^4-Cyclo-octa-1,5-diene)-(η^5-1-t-butyl-2-di-isopropylamino-1,2-azaborolyl)-rhodium from Ref. 7d.

More important variations can be noticed by inspecting the metal-ligand hapticity. A pure η^5 coordination, with five equivalent M-C bonds, is not observed even in **1** derivatives. In fact, the metal-Cp anti-bonding interaction present in a filled molecular orbital of **1a** and **1b** can be slightly relieved by the slippage of the ML_2 unit,

which is accompanied by folding of the ring.[8] In Ind complexes, the distorted $\eta^3+\eta^2$ bonding mode is more pronounced. In fact, the nodal properties of the Ind π system introduce an asymmetry which is not present in the Cp π orbitals (the hinge carbons do not contribute to all of them).[9] In addition, slippage from η^5 to η^3 coordination in Ind

complexes favours the aromatic character of the benzene ring. As a consequence, the two bonds of the metal to the hinge carbons are longer and weaker and both the slippage parameter and the folding angle of the five membered ring are more pronounced in **2a** and **2b** than in **1a** and **1b** (Table 1). These structural features are commonly invoked to explain the higher reactivity of Ind complexes compared to Cp complexes ("indenyl effect").[10] In the analogous heteroaromatic compounds the replacement of two carbon atoms with boron and nitrogen breaks severely the symmetry of the five membered ring. Thus the slippage and the folding angle are much higher in **3a** and **4a** than in **1a** and **2a**, and increase further when passing from Co to Rh, *i.e.* from **3a** to **3b** and from **4a** to **4b**. Interestingly, in presence of the heteroaromatic ligand **3**, the hapticity values are similar to those obtained in presence of the Ind ligand **2** and slightly increase when ligand **4** is used. This geometric feature of the ground state of the derivatives of the ligands **3** and **4** might be important for the reactivity of the Co(I) and Rh(I) heteroaromatic complexes.

In Figure 2 a scheme of the energy levels is shown. On the basis of the HOMO-LUMO gap a trend of relative stability of the complexes can be established. Rh(I) derivatives of **1** and **2** are more stable than the analogous Co(I) derivatives: **2b** (2.841 eV) > **1b** (2.755 eV) > **1a** (2.094 eV) ≈ **2a** (2.092 eV). The complexes with the heteroaromatic ligand **3** have larger HOMO-LUMO gaps than the corresponding complexes of ligand **1**, while the HOMO-LUMO gap slightly decreases by replacing **2** with **4**. Rh(I) derivatives are always more stable than Co(I) derivatives: **3b** (2.89 eV) > **4b** (2.752 eV) > **3a** (2.278 eV) > **4a** (2.01 eV).
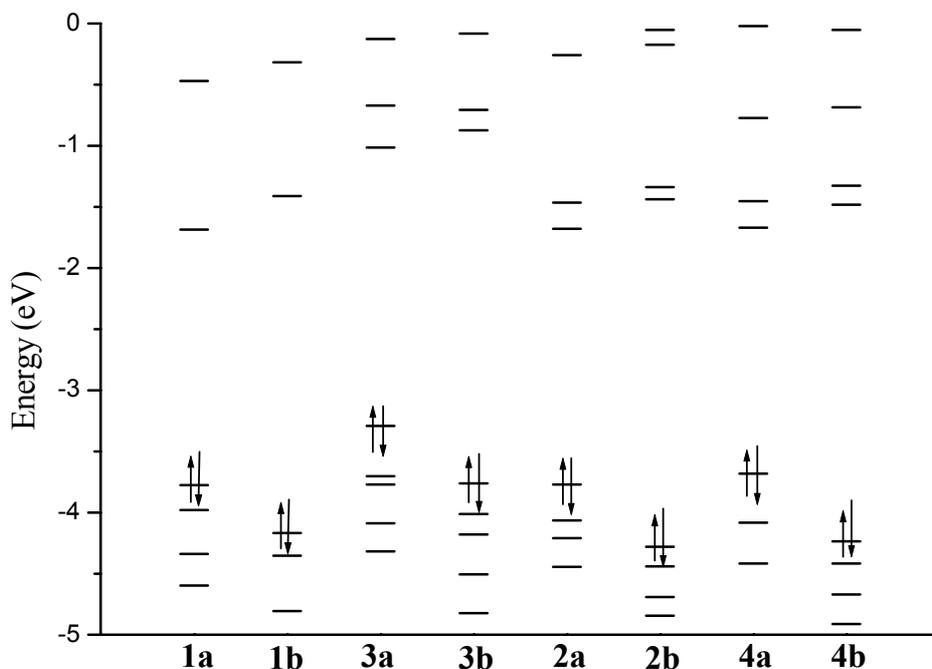

Fig. 2 – Energy levels of the Co(I) and Rh(I) complexes of **1**, **2**, **3** and **4** with the ancillary ligand COD.

Interestingly, the replacement of **1** with **3** changes significantly the MOs energies; in contrast when passing from **2** to **4** the effect is almost negligible, in analogy with the trends observed in the structural parameters of Table 1. While the bonding mode of Cp and Ind anions to several different transition metals has been extensively described,[8-9] the compounds with the heteroaromatic π ligands deserve some scrutiny. The filled π molecular orbitals of **3** and **4** are shown in Figure 3; the empty levels are involved mainly in backbonding from the metal orbitals and are not crucial for the following analysis. The π molecular orbitals of the Cp anion transform as A2, E1 and E2 (in C_{5v} symmetry). The degeneracy of both the filled E1 and the empty E2 levels of **1** is not possible in **3** where the two couples of MOs split. The loss of symmetry is evident also in the π system of **4**, to which N contributes more in the filled levels and B in the empty ones.
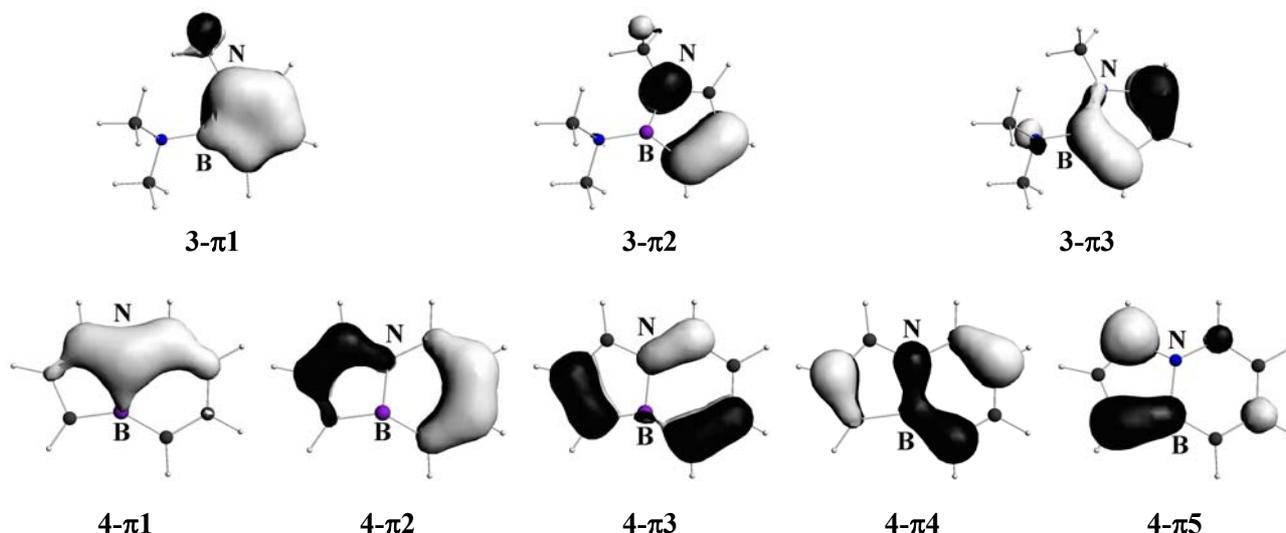
3-π1   **3-π2**   **3-π3**

4-π1   **4-π2**   **4-π3**   **4-π4**   **4-π5**

Fig. 3 – Filled Kohn-Sham π molecular orbitals of **3** and **4** anions. Density: 0.05 $(ea_0^{-3})^{1/2}$.

In Co(I) and Rh(I) **1** complexes the metal z^2 can combine with A2; xy and x^2-y^2 have δ symmetry and remain non bonding or may interact weakly with the E2 levels of **1**; xz and yz may combine with the E1 levels of **1** and, since the metals have eight d electrons, an anti-bonding combination is necessarily occupied. In **1a** this filled anti-bonding level, in which the metal yz (35%) combines with an E1 level of **1**, is the HOMO-1, stabilized by an empty Co py contribution (5%). The HOMO is formed mainly by the metal x^2-y^2 (52%) and xy (22%) and combined in bonding fashion (δ symmetry) with an E2 orbital of **1** (Figure 4 A). The two highest occupied levels of **1b** have analogous composition, but their energy order is inverted, and the mixing with the empty Rh py level is significantly smaller. The HOMO of **1b** is shown in Figure 4 B. The LUMO of **1a** (Figure 4 C) is the anti-bonding combination of the metal xz (47 %) with an E1 level of the Cp anion; the LUMO of **1b** has analogous composition. When the π orbitals of **3** bond to the MCOD$^+$ fragment, mixing occurs. In the HOMOs of **3a** and **3b** (Figure 4 D) N pz clearly contributes to the metal ligand repulsion, with consequences in the strong hapticity distortion of the **3** derivatives. The metal d contribution to these MOs comes mainly from xy. The LUMO of **3a** (Figure 4 E) is strongly destabilized; it is composed by the metal yz (30%) and xz (14%) oriented in anti-bonding fashion with both the ring and the COD double bonds; the LUMO of **3b** has analogous composition. As shown in Figure 2, the destabilization of the LUMOs is the main responsible for the large HOMO-LUMO gaps of **3** derivatives.

The HOMO of **2a** is mainly formed by the metal x^2-y^2 and is essentially non bonding; in contrast, in the HOMO of **2b** a participation of the indenyl π system is found. In fact, in the two highest occupied levels of **2b** contributions from metal xz, x^2-y^2 and z^2 mix and combine with $3\pi_s$ of the ligand (Figure 4 F-G). The LUMOs of both **2a** and **2b** are formed by the metal yz combined in anti-bonding fashion with the filled $2\pi_a$ level of the indenyl anion. The topology of the HOMOs (Figure 4 H-I) and the LUMOs of **4a** (Figure 4 J) and **4b** is rather similar to those of **2a** and **2b** respectively. It is worth noticing that there is an important contribution of N to metal-ligand repulsion in HOMO-1 of **4a** and in HOMO of **4b**.

The complexes **1a**, **1b**, **2a** and **2b** are employed as catalyst precursors for the reaction of alkynes cyclotrimerization.[4] The fundamental research of Wakatsuki and Yamazaki,[11a-b] Bönnemann[11c-d] and Vollhardt[11e-f] has assessed that, in particular, the CpCo fragment is the catalyst of primary choice for the synthesis of pyridines and pyridine derivatives. The catalytically active species is generated by the substitution of the olefin ancillary ligand with two alkynes. We have studied the first step of cobalt catalyzed alkyne cycloaddition starting from **1a** and **3a**. COD can be displaced thermally or photochemically; in general, for CpCo complexes, the reaction occurs in mild conditions.[12] On the basis of the changes in Gibbs free energy computed at 298.15 K the COD substitution reaction is easier in **3a** than in **1a**, *i.e.* 3.8 Kcal mol^{-1} and 6.0 Kcal mol^{-1}.
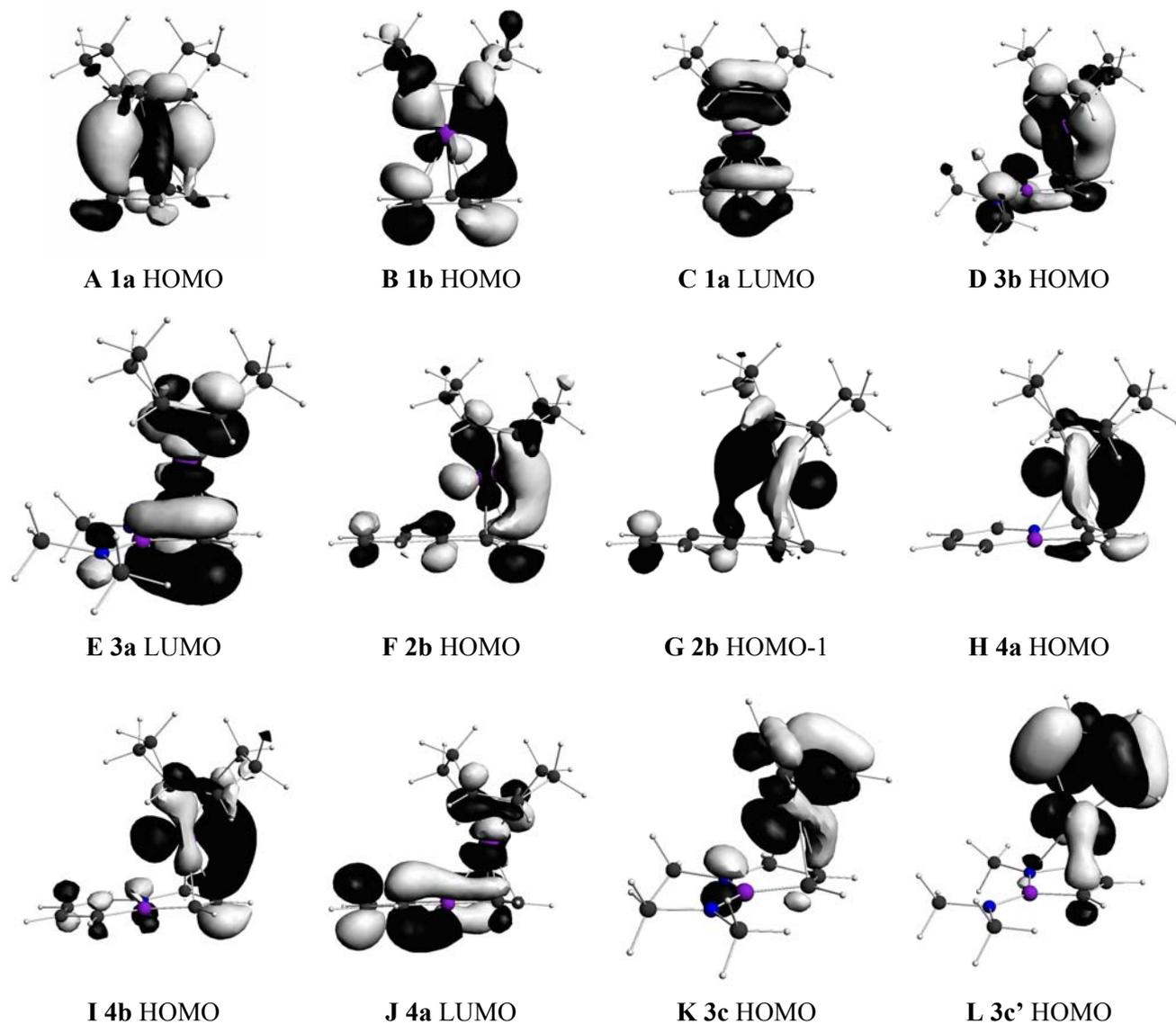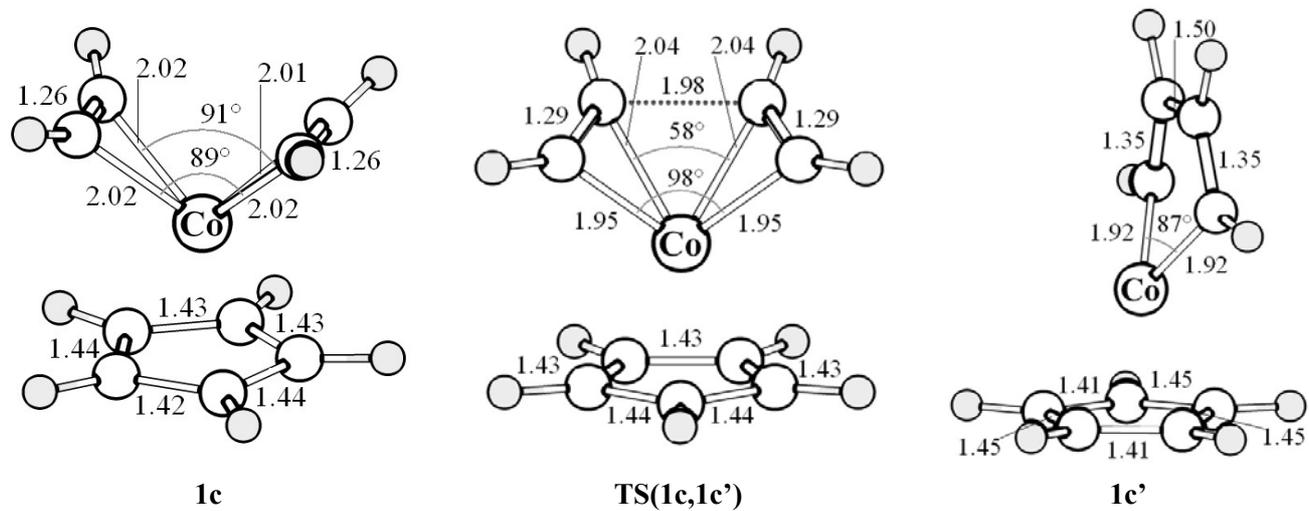
A 1a HOMO   **B 1b** HOMO   **C 1a** LUMO   **D 3b** HOMO

E 3a LUMO   **F 2b** HOMO   **G 2b** HOMO-1   **H 4a** HOMO

I 4b HOMO   **J 4a** LUMO   **K 3c** HOMO   **L 3c'** HOMO

Fig. 4 – Selected frontier Kohn-Sham molecular orbitals of the studied complexes. Density 0.02 $(ea_0^{-3})^{1/2}$.

1c   **TS(1c,1c')**   **1c'**

3c   **TS(3c,3c')**   **3c'**
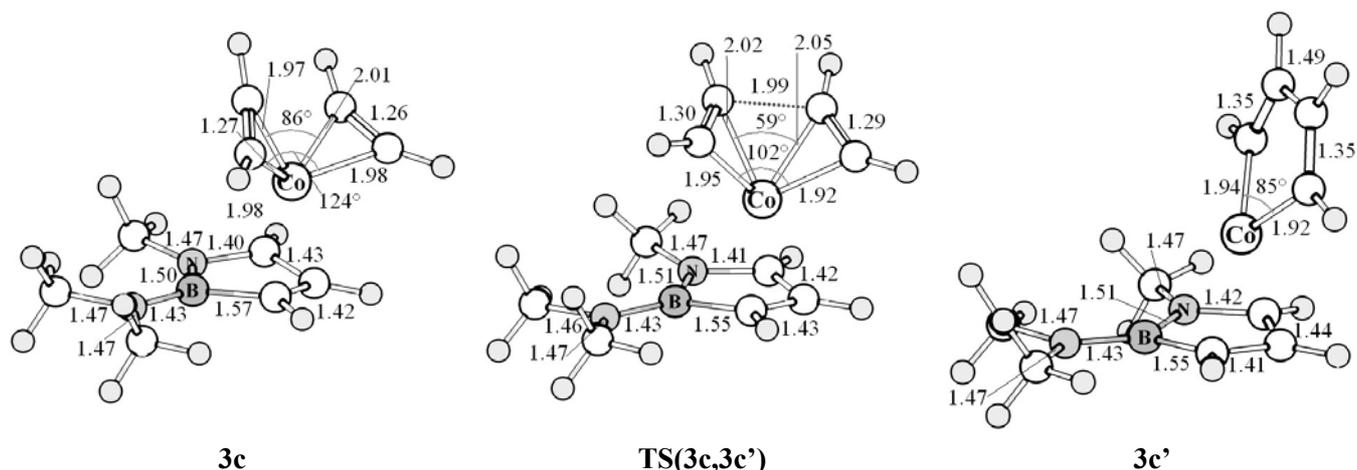
Fig. 5 – DFT optimized geometries of the intermediates and the transition state of the first step of alkyne trimerization process catalyzed by the fragments CpCo and AbCo. For sake of clarity the metal, B and N atoms of the five membered rings are labelled.

Once the alkyne complexes **1c** and **3c** are formed, it is consolidated that the formation of a cobaltacycle by oxidative coupling of the acetylene ligands is the rate determining step of the catalytic mechanism (Figure 5). The geometric parameters of the cobaltacycle **1c'** nicely compare with those reported previously by other authors at HF[13] and B3LYP[14] level of theory. The cycle is tilted by 20° with respect to the axis defined by the metal and the centroid of the Cp ring and is appreciably folded by 29°. The conversion **1c-1c'** is exothermic by 10.5 Kcal mol^{-1}. The transition state **TS(1c,1c')** is located 11.7 Kcal mol^{-1} above **1c** (v= -409 cm^{-1}). In **3c** the acetylene ligands are significantly tilted off of the plane parallel to the heteroaromatic ligand, in an arrangement favourable to the formation of the metallacycle **3c'**. The activation enthalpy for the formation of **3c'** is slightly less than the barrier for the formation of **1c'**, *i.e.* 10.7 Kcal mol^{-1}. Interestingly, the metallacycle portion of **TS(3c,3c')** (v= -423 cm^{-1}) is structurally very similar to that of **TS(1c,1c')**, but the conversion **3c-3c'** is more exothermic than the conversion **1c-1c'**, *i.e.* 18.1 Kcal mol^{-1}, due to the involved hapticity variation. In fact, while in **3c** the metal coordination is nearly allylic and the Cp ring is significantly folded, *i.e.* 16°, in **3c'** the folding angle is reduced to 8° (10° in **TS(3c,3c')**) and a stabilizing interaction between Co and N sets (Figure 4 K-L), with consequences on the Co-N distance which changes from 2.70 to 2.22 Å.

EXPERIMENTAL PART

Computational methods

All the geometry optimizations were performed with the software ADF 2006.01[16] without any constraint. Scalar

relativistic effects were taken into account using the zeroth order regular approximation (ZORA) formalism.[17] The BLYP functional[18] was employed. Slater type orbitals (STOs) of triple-ζ quality augmented with one set of polarization functions were used (TZP). Small frozen core approximation was used for Rh up to 3d, for Co up to 2p, for B, C and N up to 1s. For single point calculations another set of polarization functions was added (TZ2P). The stationary nature of the minima was confirmed by running frequency calculations. The normal modes of the minima have all positive frequencies; for the saddle points a single imaginary frequency was computed and the associated normal mode was analysed to ensure that the correct transition state was found. The values of the enthalpies and Gibbs free energies have been calculated at 298.15 K.

CONCLUSIONS

This description of Co(I) and Rh(I) complexes of the heteroaromatic ligands **3** and **4** highlights their peculiar structural and electronic features, which have important consequences on their reactivity. In particular, 1,2-azaborolyl-cobalt fragment displays good catalytic properties for the [2+2+2] alkyne cycloaddition, which nicely compare to those of the efficient CpCo analog. Further experimental and theoretical investigation is prompted on metal complexes of **3** and **4**, in particular (i) to assess the effects of different substituents of B and N on the structural and electronic properties of the derivatives of **3** and more in general (ii) to test the chemoselectivity and the regioselectivity of the metal complexes of **3** and **4** when employed in catalytic processes. A systematic study on the mechanism of alkyne cyclotrimerization catalyzed by different Rh(I) half-sandwich complexes is currently under theoretical investigation.[15]

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