

*Dedicated to Professor Luminița Silaghi-Dumitrescu
on the occasion of her 65th anniversary*

RHODIUM(I) COMPLEXES OF BISPHOSPHONITOCARBABORANE(12)S: A COMPUTATIONAL STUDY

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ABSTRACT. Density functional calculations indicate that, the steric and packing factors seem to play a much more significant role than the electronic effects in influencing the bending of the rhodium(I) complexes of bisphosphonitocarbaborane(12)s.

Keywords: *Rhodium(I) Complexes, Bisphosphonitocarbaborane(12)s, Density Functional Theory, Natural Bond Orbital Analysis*

INTRODUCTION

The rhodium(I) complexes **1–5** (Scheme 1) with various bisphosphonitocarbaborane(12) ligands are chloro-bridged dimers in which the Rh₂Cl₂ four-membered ring is either in a butterfly conformation (**1–4**) or planar (**5**) [1]. Density functional calculations were carried out to elucidate which factors determine the conformational preferences in these complexes.

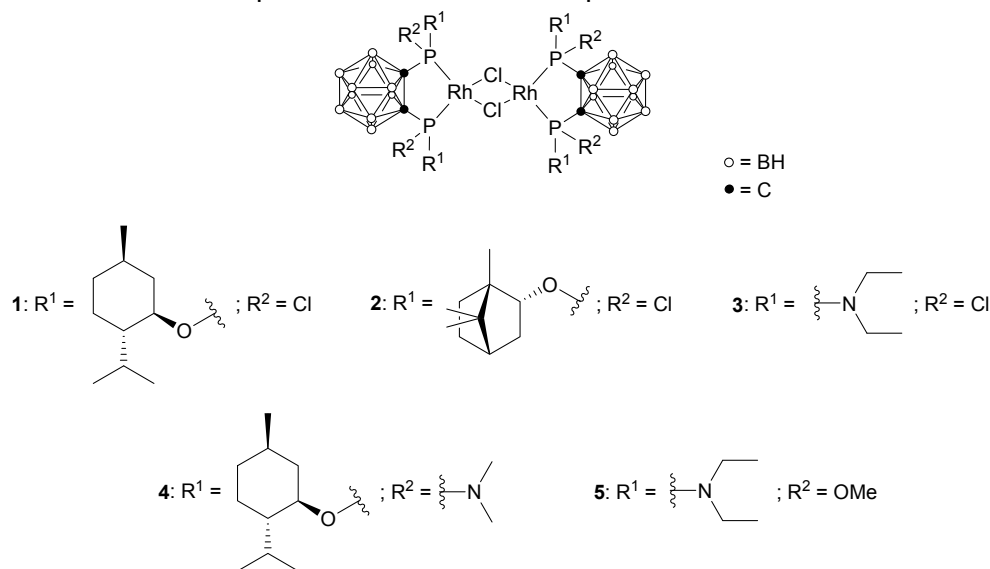
RESULTS AND DISCUSSION

Bis(phosphanes) are versatile ligands for late transition metals, which can be used in homogeneous catalysis. Due to the tunability of the steric and electronic properties, a range of different ligands has been employed over the last few decades. 1,2-Dicarba-*closo*-dodecaborane(12) [*ortho*-carbaborane(12)] is

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of interest as a C_2 -symmetric backbone for phosphanes. Tertiary phosphane derivatives were first obtained in 1963 by dilithiation of *ortho*-carbaborane(12) and subsequent reaction with chlorodiphenylphosphane [2]. Since then several derivatives with organophosphorus substituents have been prepared and their reactivity and coordination chemistry have been investigated. Several of these compounds have been applied in homogeneous catalysis [3]. Specifically, the corresponding rhodium complexes are of interest in homogeneous catalysis. We have, therefore, prepared several rhodium(I) bisphosphonitocarbaborane(12) complexes (**1–5**) (Scheme 1) which were shown by X-ray crystallography to be chloro-bridged dimers in which the Rh_2Cl_2 four-membered ring is either in a butterfly conformation (**1–4**) or planar (**5**) [1]. We here report the results of density functional calculations which allowed elucidating the factors determining the conformational preferences in these complexes.



Scheme 1. Chloro-bridged rhodium(I) bisphosphonitocarbaborane(12) complexes **1–5** [1].

A driving force for bending of such binuclear square-planar complexes of d^8 transition metal appears to be the donor–acceptor interactions between the d_z^2 electrons and empty p_z orbitals of the two metal atoms [4,5]. However, only for large degrees of bending is the $M \cdots M$ interaction attractive enough to make the molecule more stable in its bent form with $\theta < 140^\circ$. The fold angle θ is defined as the dihedral angle between the coordination planes of the two metal centers ($M-X-X-M$: $M = Ni, Pd, Pt, Rh, Ir$; $X = Cl, Br, I$). Steric factors can also have a major influence on the fold angle θ , as shown by an energy difference of $10 \text{ kJ}\cdot\text{mol}^{-1}$ between a planar and folded modification

of $[\{\text{Rh}(\mu\text{-Cl})(\text{H}_2\text{PCH}_2\text{PH}_2)\}_2]$ [6]. However, steric effects seem to be important in preventing bending only for bulky terminal ligands [7]. Furthermore, packing effects in the crystal may also be considered to play an important role in the degree of folding of the molecules [4,6].

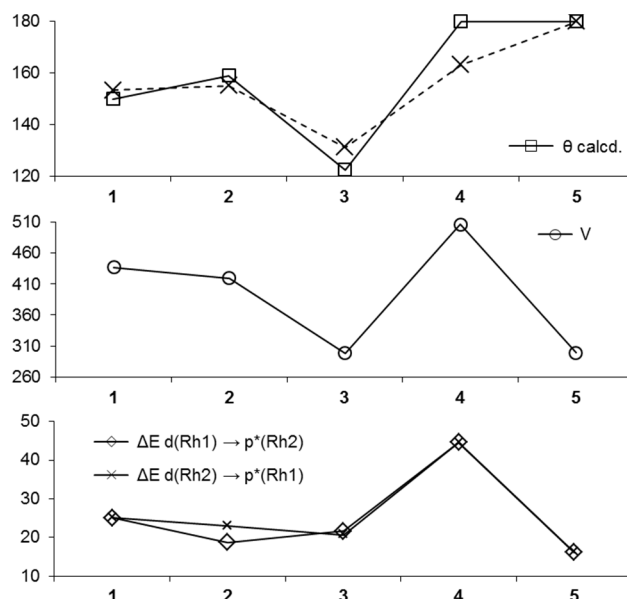


Figure 1. Optimized and experimental Rh–Cl–Cl–Rh fold angles θ (top, [°]), ligand volumes (middle, V , [cm³.mol⁻¹]) and second-order energy lowering values (bottom, ΔE , [kJ.mol⁻¹]) for rhodium complexes **1–5**.

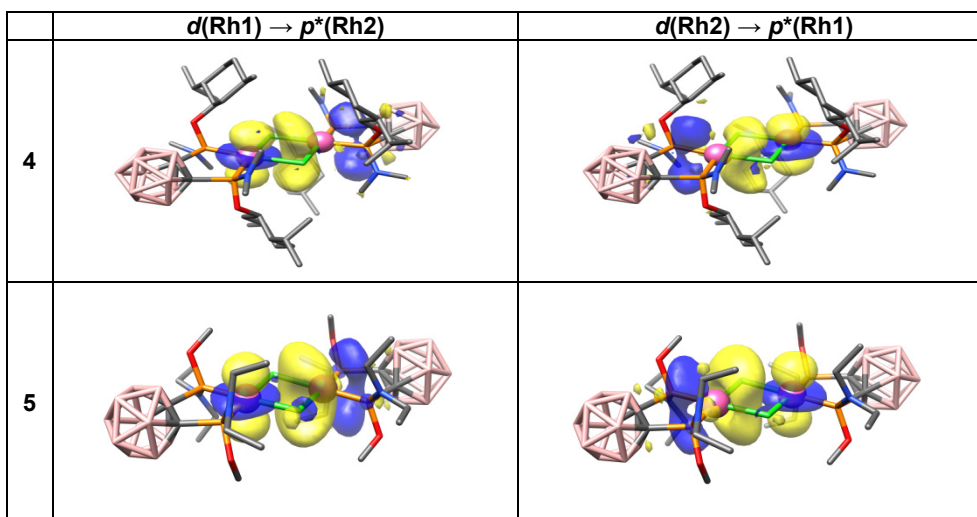
The optimized fold angles θ in complexes **1–4** correlate well with the calculated ligand volumes (Figure 1), indicating the significant influence of the steric factors on the bending of these complexes. The almost equal second-order energy lowering ($\Delta E^{(2)}$) values, in contrast with the decreasing fold angles θ in **1**, **2** and **3**, clearly indicate that the influence of $d \rightarrow p^*$ interactions on the level of bending is insignificant when compared with the effects of the steric factors. Complex **4** is perhaps the best example where steric and packing effects override electronic ones. Even though the crystal structure of **4** presents a bent Rh_2Cl_2 central unit, θ relaxes to 180° after optimization. On the other hand, the fold angle θ is unchanged or insignificantly altered after optimizing the structures of **1**, **2** and **3**. Thus, the bending observed in the crystal structure of **4** is only due to packing effects in the crystal and not caused by electronic effects. Furthermore, the bending in the optimized structure of **4** is sterically prohibited by the bulky ligands, in spite of the associated significant $d \rightarrow p^*$ interactions with the highest of all the $\Delta E^{(2)}$ values presented in Figure 1.

Finally, complex **5** stands out from the group with a planar Rh_2Cl_2 central unit in both the X-ray [1] and the optimized structure associated with a small ligand volume. The small ligand should allow the bending of **5**. However, the associated $d \rightarrow p^*$ interaction energies seems to be too weak to cause bending in **5**.

The values discussed above are summarized in Table 1. All in all, the steric and crystal packing effects seem to play a much more significant role than the electronic effects in influencing the bending of the rhodium complexes of the present study. This tendency of the bulky ligands to prevent bending is in good agreement with findings from previous studies [7].

Table 1. Optimized geometries and natural bond orbitals (NBO) involved in the $d \rightarrow p^*$ donor–acceptor interactions identified in **1–5**. Rh: pink, Cl: green, P: orange, O: red, N: blue, C: gray, B: tan. Hydrogen atoms are not shown.

	$d(\text{Rh1}) \rightarrow p^*(\text{Rh2})$	$d(\text{Rh2}) \rightarrow p^*(\text{Rh1})$
1		
2		
3		



CONCLUSIONS

Density functional calculations indicate that steric factors and packing seem to play a much more significant role than electronic effects in influencing the bending of the rhodium complexes **1–5**.

EXPERIMENTAL SECTION

The geometries of complexes **1–5** were optimized using the M06-L density functional [8] of the Gaussian 09 program package [9]. The calculations were performed using the LANL2TZ(f) basis set for Rh, the LANL08d basis set for P and Cl [10], along with the effective core potential of Hay and Wadt [11], obtained from the EMSL Basis Set Library [12]. For the remaining atoms, the D95V(d) basis set was used [13]. The existing $d \rightarrow p^*$ donor–acceptor interactions were identified with Natural Bond Orbital (NBO) analysis [14]. Additionally, the volume of one bisphosponito-carbaborane(12) ligand in each rhodium complex was also calculated. Images of the optimized structures and of the NBOs were rendered with the UCSF Chimera program package [15].

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