

Penta- and heteropentadienyl ligands coordinated to beryllium

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Abstract In this work we have performed a systematic study of new organometallic complexes containing penta- and heteropentadienyl ($\text{CH}_2\text{CHCHCHX}$, $\text{X}=\text{CH}_2$, O, NH, S) ligands coordinated to beryllium. Calculated complexes were studied using the density functional theory (PBE) in combination with the 6-311++G(3d,2p) basis set. The coordination number on the beryllium atom varies according to the type of ligand. Pentadienyl ligand shows hapticities η^1 and η^5 , while heteropentadienyl ligands display η^1 and η^2 hapticities. A Wiberg bond indices study was performed in order to get information about their bond orders.

Keywords Beryllium complexes · DFT · Heterodienyl ligands · Organometallic chemistry

Introduction

Beryllium is the second lightest metal and its chemistry is predicted to be the richest amongst the alkaline earth metals due to its greater tendency for covalent bonding [1]. Some research with this element focuses on structural and mechanistic properties [2–4], and has recently been relying more on computational rather than experimental studies [5–9].

On the other hand, the chemistry of the anions: pentadienyl [10–14], and their analogues oxo- [15–18], aza [15, 19–22],

and thiapentadienyl [23–26], are well-established ligands for transition-metals complexes [18, 27]. They have attracted attention due to their enhanced chemical reactivity or even to serve as catalysts because of a variety of accessible η^1 , η^3 , and η^5 bonding.

Based on the above, nowadays there are new organoberyllium compounds with a $\text{Be}(\eta^5\text{-C}_5\text{R}_5)$ ($\text{R}=\text{H}$, Me) fragment [28–30]. Recently, the synthesis of binuclear metallocenes with acyclic pentadiene ($\eta^5\text{-C}_5\text{H}_7$) and cycle phosphole ($\eta^5\text{-C}_5\text{H}_4\text{P}$) ligands has been reported [31].

As we can see, the structural features and coordination modes of the pentadienyl and heteropentadienyl ligands are reported specially with transition metals, however systematic study of geometries, stability and reactivity for alkali or main group chemistry heterodienyl complexes has not very well studied, even though they are quite common reagents in organic and organometallic chemistry [14, 32–41]. Generally, the main group elements have smaller atomic diameter compared with those transition metal elements, and the former tend to form complexes with low hapticity.

The main objective of this work is to understand the structural arrangement and the chemical behavior of the beryllium atom with pentadienyl and heteropentadienyl ligands. This study was carried out using the density functional theory (PBE) in combination with the 6-311++G(3d,2p) basis set.

Computational details

The geometry of all structures was fully optimized by using the Perdew–Burke–Ernzerhof (PBE) [42, 43] exchange-correlation functional in combination with the 6-311++G(3d,2p) basis set using the GAUSSIAN 09 software package. Their vibrational frequencies were calculated with the same level of theory. Charges and Wiberg bond indices were computed from a natural bond orbital analysis (NBO) [44]. Results were visualized with the Chemcraft program v1.6. The PBE functional has

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already been extensively evaluated, showing good results in several molecular systems containing elements of the second row of the periodic table [45–49].

Results

The dienyl compounds used in this study are those called pentadienyl [$\text{CH}_2=\text{CHCH}=\text{CHCH}_2$] and heteropentadienyl [$\text{CH}_2=\text{CHCH}=\text{CHX}$], where one terminal $-\text{CH}_2$ group of pentadienyl was exchanged by O, NH or a S atom, which will give the oxo-, aza- or thiapentadienyl ligands respectively. Figure 1 shows the optimized geometries of those ligands, which adopt different conformations, U, W, S1 or S2 (sick); the S2 conformation is only for heteropentadienyl ligands. For all cases the most stable conformation is a W-shaped structure.

Relative energies and bond distances are given in Table 1. For pentadienyl ligand the sickle-shaped and U conformation are less stable by about 2.56 and 2.59 kcal mol⁻¹, respectively. The S2-shaped conformation for oxo- and azapentadienyl ligands is less stable by about 3.62 and 4.89 kcal mol⁻¹, respectively. Also the U-shaped structure for thiapentadienyl is less stable by 4.58 kcal mol⁻¹.

The C-C bond distances for terminal bonds ($\text{H}_2\text{C}-\text{C}_1$, C_3-C_4) in pentadienyl ligand are shorter than the internal bonds, (C_1-C_2 , C_2-C_3), 1.37 Å vs 1.41 Å. The oxopentadienyl compounds display a typical $\text{C}=\text{O}$ bond length 1.25 Å, as well as the corresponding aza- and thiapentadienyl ligand, $\text{HN}-\text{C}_1$ and $\text{S}-\text{C}_1$, 1.31 and 1.70 Å.

When these ligands interact with a beryllium cation, Be(II), their shapes become different. The optimized geometries of pentadienylberyllium are shown in Figs. 2 and 3. On the half sandwich complex ($\eta^5-\text{C}_5\text{H}_7$)Be($\eta-\text{C}_5\text{H}_7$) (**1**), the pentadienyl

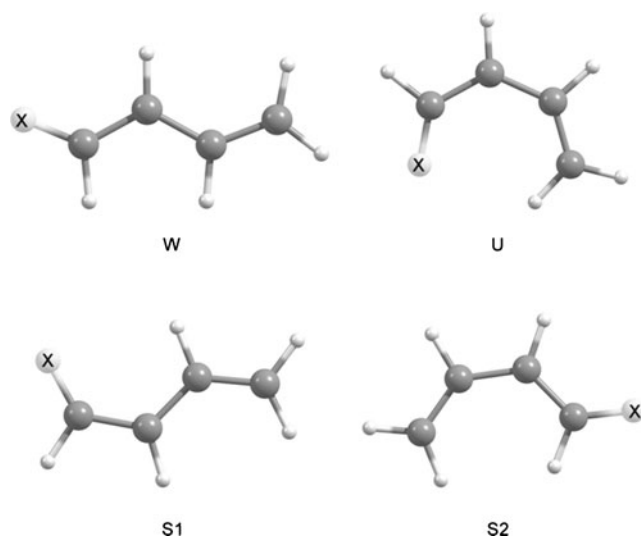


Fig. 1 Conformations adopted by dienyl ligands ($\text{X}=\text{CH}_2$, NH, O and S)

Table 1 Bond distances (Å) and relative energies (kcal mol⁻¹) for free ligands

Shape (X)	X-C1	C1-C2	C2-C3	C3-C4	Relative energy
W (CH_2)	1.37	1.41	1.41	1.37	0.00
S1=S2 (CH_2)	1.37	1.41	1.41	1.37	2.56
U (CH_2)	1.37	1.41	1.41	1.37	2.59
W (NH)	1.31	1.40	1.41	1.37	0.00
S1 (NH)	1.31	1.41	1.41	1.36	2.21
S2 (NH)	1.31	1.41	1.42	1.37	3.62
U (NH)	1.31	1.41	1.42	1.37	3.27
W (O)	1.25	1.40	1.41	1.36	0.00
S1 (O)	1.25	1.40	1.42	1.36	1.60
S2 (O)	1.25	1.40	1.43	1.36	4.89
U (O)	1.25	1.40	1.43	1.36	4.07
W (S)	1.70	1.37	1.43	1.35	0.00
S1 (S)	1.71	1.37	1.43	1.35	1.45
S2 (S)	1.70	1.37	1.44	1.35	4.17
U (S)	1.70	1.37	1.44	1.35	4.58

ligands are coordinated in U-shaped (pentacoordinated) and W-shaped (monocoordinated).

The charge distribution for complex **1** displays high negative values on terminal carbon atoms of the mono- and pentahapto ligands (CX, C4 and C5, C9). In fact, all carbon atoms of the U-shaped ligand donate charge to beryllium, but the main contributors are those atoms of the ends with values of -0.548 and -0.576 . Similarly, the electron density of the monocoordinated pentadienyl ligand is donated through the terminal methylene (CX), which has a value of -0.944 . The W-shaped ligand coordinated displays a conjugated short-long-short-long pattern (C_1-C_2 1.34, C_2-C_3 1.45, C_3-C_4 1.35, and C_4-C_5 1.47 Å), (see Fig. 3), which is different with the corresponding free ligand that displays a short-long-long-short pattern (CH_2-C_1 1.37, C_1-C_2 1.41, C_2-C_3 1.41, and C_3-C_4 1.37 Å), Table 1.

The obvious question now is, why both pentadienyl ligands do not form sandwich complexes such as those found by Su and Sheu [50]? Those complexes (LMML) are formed by two U pentadienyl ligands and two berylliums as central atoms. The authors found a sandwich structure with both alternate pentadienyl ligands and with a η^5 -coordination. This explains clearly why our system, structure **1**, does not form the sandwich structure, and is due to steric effects. In the case of the sandwich of Su and Sheu, both ligands are far from each other due to a Be-Be bond, while our system is monometallic forming a half sandwich complex.

On the other hand, we have also found the most stable structures for complexes with heteropentadienyl ligands having O, N and S atoms of many calculated structures. These structures are shown in Figs. 2 and 3. Ligands in ($\eta^2-\text{C}_4\text{H}_5\text{NH}$)Be(NHC_4H_5) (**2**), ($\eta^2-\text{C}_4\text{H}_5\text{O}$)Be(OC_4H_5) (**3**), and

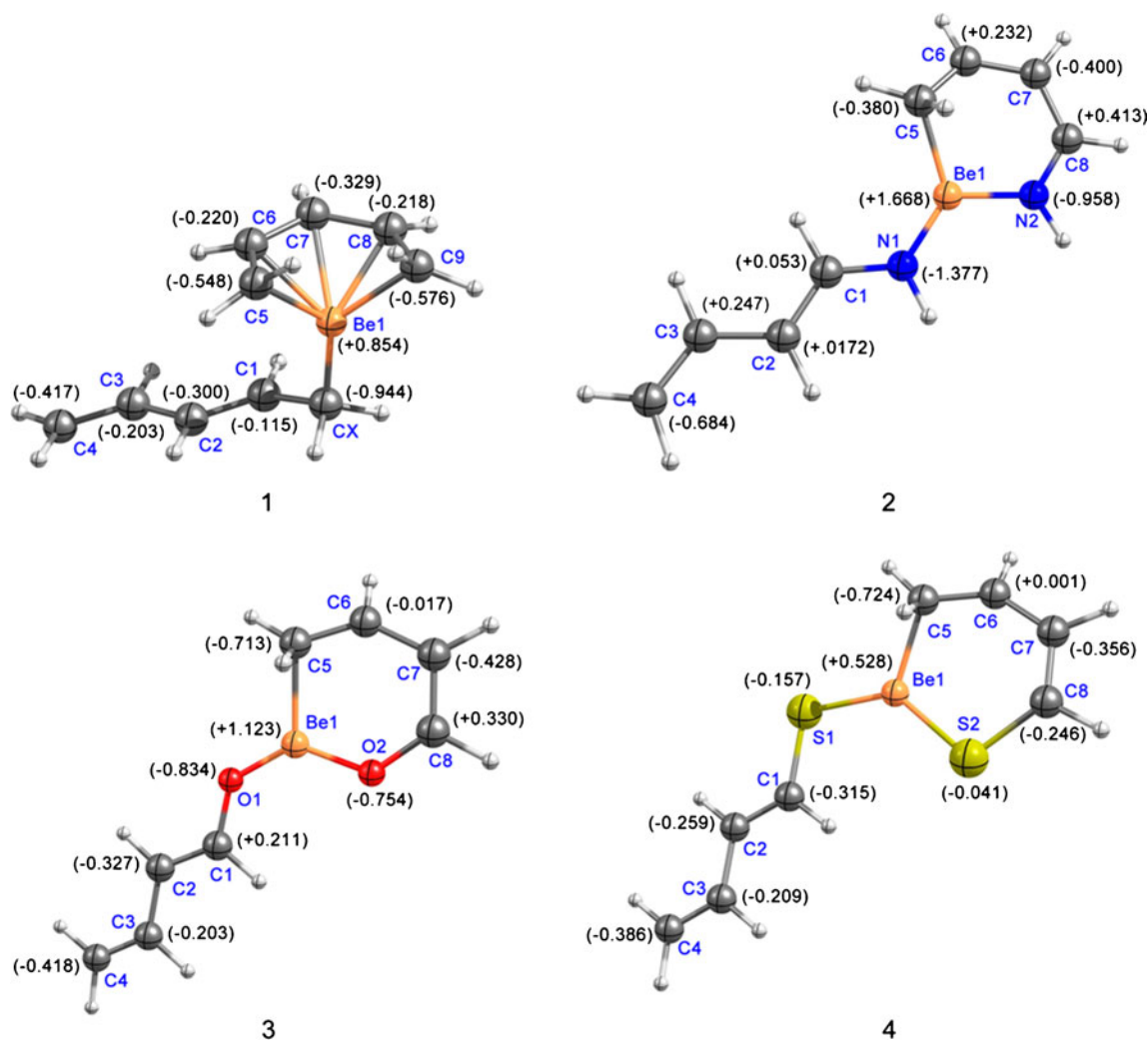


Fig. 2 Natural charges in terms of natural populations analysis (NPA) for structures 1–4

(η^2 -C₄H₅S)Be(C₄H₅S) (**4**) compounds have the same conformation similarly to structure **1**, but different forms of coordination. In these structures, the U-shaped ligands are η^2 coordinated by terminal CH₂ group and heteroatom forming a beryllacycle, while the W-shaped ligands are η^1 coordinated. The explanation to this is if one takes into account the electronegativity of the N, O and S atoms (3.04, 3.44, 2.58), compared with the electronegativity, using the Pauling scale [51], of the carbon atom (2.55).

The beryllium atom in complexes **2**, **3**, and **4** is tricoordinated, the heteroatoms offer more electron density to the metallic center, this is the reason why the Be1-N1 (1.63 Å), Be1-O1 (1.53 Å) bonds are shorter than Be-C1 (1.80 and 1.88 Å) bonds of the metallacycle fragment in each structure, except for the B1-S1 (2.00 Å) bond in structure **4**, Fig. 3. Lengths of the corresponding Be-N bonds, for Be-N1 1.56 Å and Be-N2 1.63 Å, are shorter than those for structures L₂Be-NH₃ (1.782–1.737 Å) [52], imidazole-BeR₂ (1.719–1.707 Å) [8] and β -diketiminato dimers of beryllium (1.67 Å

[6]. It is important to note that charge values of the coordinated atoms to beryllium in structures **2–4** are higher than any other atom, Fig. 3.

Regarding the adjacent carbon atoms of the heteroatom coordinated on **2** (nitrogen) and **3** (oxygen) structures, they displayed positive values, because all the electron density of adjacent carbon atoms is engaged with the coordinating atoms and is somewhat similar to an aldehyde group. In both structures we can see the N2-C8 and O2-C8 distances with values of 1.32 and 1.29 Å, respectively.

When we compare the bond distances from those ligands coordinated to the beryllium atom with their respective free ligands, we found some changes, for example, for complex **1**, in the W-shaped ligand two bond lengths increase (X-C1 and C2-C3 by 0.10 and 0.04 Å, respectively) and two bond lengths decrease (C1-C2 and C3-C4 by 0.06 and 0.03 Å, respectively) compared with its free ligand. Values of bond distances in the U-shaped are not significant. The explanation for this could be that all carbon atoms are interacting with

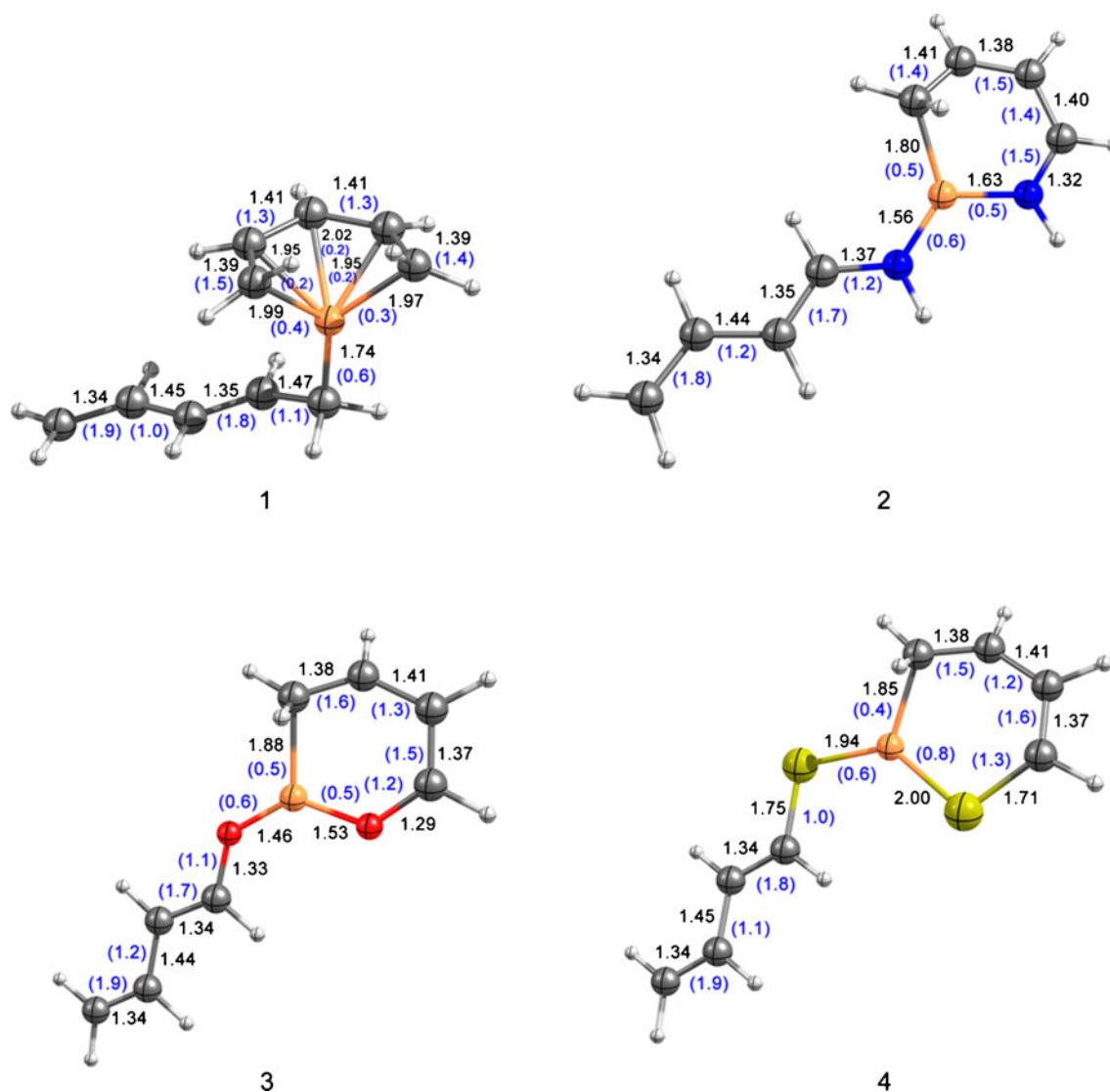


Fig. 3 Bond lengths (Å) and Wiber bond indices (blue color) for structures 2–4

the beryllium atom, while the W-shaped ligand is only monocoordinated.

One the other hand, in order to obtain more evidence about all bond orders, the Wiberg bond indices (WBIs) were determined from natural bond orbital analysis (NBO) [44]. In structure **1**, the C-C WBIs for the U-shaped ligand have similar values (1.3–1.5). These values are in good agreement with the bond distances shown in Fig. 3 (1.39 and 1.41 Å). It is interesting to note that all bond orders around the beryllium atom have values less than 1, this is due to the weak interaction from both ligands. In the monocoordinated ligand, X-C and C-C bonds have alternated values of bond orders close to 1 and 2.

For structures 2–4, in monocoordinated ligands, the bond orders have the same behavior in terms of alternating double bonds with values close to 1 and 2 (Fig. 3). For metallacycle, in structure **2**, the WBIs suggest an electron delocalization in

the fragment C5-C6-C7-C8-N2. Both metallacycles, in structures **3** and **4**, have the same behavior; the WBIs are from 1.2 to 1.6.

Additionally, we have calculated the complexes when the beryllium atom is tetracoordinated forming the correspondig metallacycles (η^2 -C₅H₇)₂Be (**5**), (C₄H₅NH)₂Be (**6**), (η^2 -C₄H₅O)₂Be (**7**), (η^2 -C₄H₅S)₂Be (**8**), Fig. 4. We have compared their energies with complexes 1–4 and the tetracoordinated complexes are higher in energy, ranging from 2.91 to 11.26 kcal mol⁻¹. The structure with the lowest energy difference belongs to the complex formed with ligands with oxygen **7**, while the structure with higher energy is formed with ligands when X=CH₂. The explanation is easy if we think about how each heteroatom donates electron density to the beryllium atom. The oxygen atom donates more electron density in comparison with the carbon atom. In other words, for tetracoordinated complexes, ligands with oxygen stabilize more with the

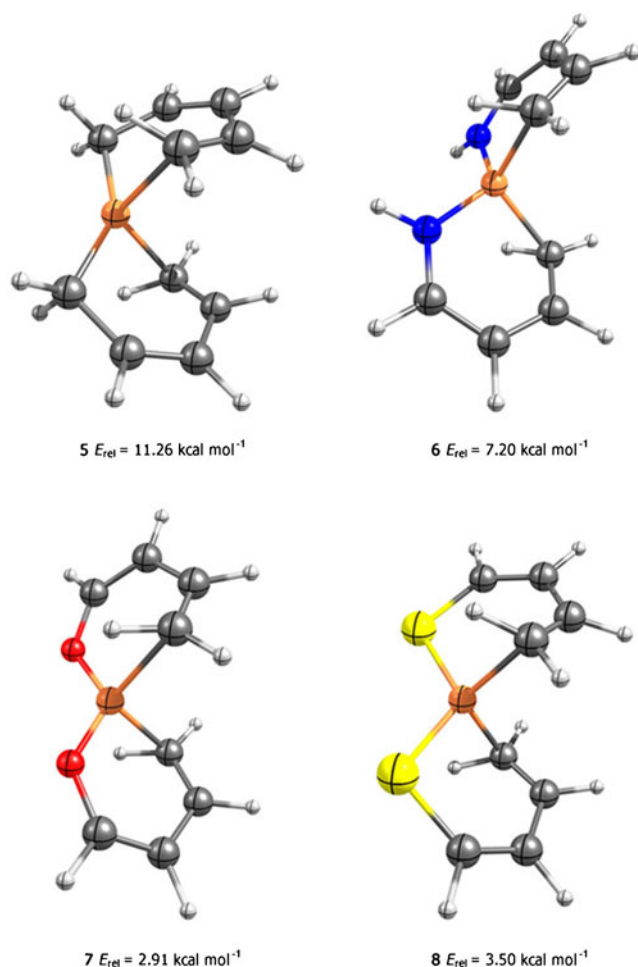


Fig. 4 Complexes **5–8** η^2 coordinated and their relative energies compared with the most stable structures shown in Figs. 2 and 3

beryllium atom than ligands with carbon (see complexes **7** and **5**, respectively). Structures **5–8** were characterized as true minima and belong to the C_2 point group.

Conclusions

Studies with the PBE/6-311++G(3d,2p) method have shown that beryllium atom prefers a coordination number of three when the ligands contain in their structures oxygen, nitrogen and sulfur, molecules **2**, **3** and **4**. Moreover, with the pentadienyl ligand, the preferred coordination number of beryllium atom is six, η^5 with the first ligand and η^1 with the second ligand, as half sandwich **1**. The WBIs analysis show that the bond orders in structures **1–4**, are in good agreement with their respective bond lengths. Finally, the most stable forms that the ligands adopt when they are coordinated to the beryllium atom are: U and W shapes. The U-shaped ligand is the most prevalent in all our calculated complexes.

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