FEATURES OF THE CRYSTALLINE STRUCTURE OF (1,2-^{t}Bu$_2$Cp)$_2$Mo$_2$(CO)$_6$ AND THEIR POSSIBLE CAUSES

N.Z. Ibrahimova, D.B. Tagiyev, G.M. Jafarov, I.U. Lyatifov

Acad. M. Nagiyev Institute of Catalysis and Inorganic Chemistry Ministry of Science and Education of the Republic of Azerbaijan, H.Javid ave., 113, AZ 1143 Baku, Azerbaijan
e-mail: nigar-ibrahimova93@mail.ru

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Abstract: *Comparative analysis of the structural parameters of the substituted cyclopentadienyl moieties (^{t}BuC$_5$H$_4$ and ^{t}Bu$_2$C$_5$H$_3$) of two binuclear molybdenum complexes ((^{t}BuCp)$_2$Mo$_2$(CO)$_6$ (**1**) and (1,2-^{t}Bu$_2$Cp)$_2$Mo$_2$(CO)$_6$ (**3**)) and two sandwich complexes of iron (the cation of 1,1′-di-tert-butylferrocenium (^{t}BuCp)$_2$Fe$^+$ (**4**) and 1,2,1′,2′-tetra-tert-butylferrocene (1,2-^{t}Bu$_2$Cp)$_2$Fe (**5**)) allowed us to identify the structural features of the ^{t}Bu$_2$C$_5$H$_3$ fragment in (**3**) and to establish the reasons that account for them. It is shown that the main changes in the structural parameters (valence and torsion angles, bond lengths) of the fragment 1,2-^{t}Bu$_2$C$_5$H$_3$ are due to steric interactions of vicinal ^{t}Bu-substituents between themselves, as well as with the corresponding nearest CH fragment of the ring. Differences in the degree of steric interaction of vicinal ^{t}Bu-substituents with CH ring fragments in (**3**) are interpreted by the steric influence of the trans-carbonyl (C10O3) group on the ^{t}Bu-substituent at C4. The latter interaction is also reflected in the larger value (≈26°) of the rotation angle of the ^{t}Bu-substituent at C4, compared to the rotation angle (≈15°) of the corresponding ^{t}Bu-substituent in (**5**), caused only by the steric interaction of vicinal ^{t}Bu-substituents among themselves. In (**3**), the steric influence of the trans-carbonyl group on the ^{t}Bu-substituent at C4 is also accompanied by a change in the direction of rotation of the ^{t}Bu-substituent at C5, as a result of which the conformations of the ^{t}Bu-substituents with respect to each other and to the ring plane differ markedly from the conformations of the ^{t}Bu-substituents in (**5**). In the binuclear complexes of molybdenum (**3**) and (**1**), the degree of steric interaction between the trans-carbonyl group and ^{t}Bu-substituents does not correspond to the rotation angle of the substituted cyclopentadienyl ring ((6.15°) ^{t}BuC$_5$H$_4$ and (2.12°) 1,2-^{t}Bu$_2$C$_5$H$_3$) around the Ct–Mo axis, which was interpreted by the inhibition of rotation of the 1,2-^{t}Bu$_2$C$_5$H$_3$ ring due to increased repulsion forces between the ^{t}Bu-substituent at C5 and the trans-C10O3 group in (**3**). The analysis of the lengths of shortened nonvalent C$_5$-ring...cis-C^{i}O^i and cis-CO...cis-C^{i}O^i contacts between the two halves of molecules (**1**), (**3**) and unsubstituted complex Cp$_2$Mo$_2$(CO)$_6$ (**2**), and the reasons causing them allowed us to conclude that the shortening of the lengths of cis-CO...cis-C^{i}O^i contacts in the series (**2**)→(**1**)→(**3**) is the most probable reason for the elongation of the Mo–Mo bond in (**3**).*

Keywords: *cyclopentadienyl ligand, tert-butyl group, carbonyl group, binuclear molybdenum complex, steric effect, crystal structure*
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Introduction

The introduction of alkyl substituents into the cyclopentadienyl ring of cyclopentadienyl- and cyclopentadienylcarbonyl complexes of transition metals changes the electronic and steric characteristics of these complexes, which in turn affects such characteristics of the complex as redox potential, rate of the electron exchange reaction, stability in solution or in the presence of oxygen, stability to heating, catalytic activity, etc. [1-4]. Therefore, the study of the role of electronic and steric interactions of substituents on the structure and transformation of cyclopentadienyl complexes is an important direction in the development of organometallic chemistry. In recent years, significant information on the crystal structures of binuclear molybdenum complexes with Mo–Mo bonds has been obtained in this direction in [5-7]. In particular, in [7], as a result of a comparison of structural parameters of three binuclear

complexes of molybdenum – unsubstituted (**2**) [8], monosubstituted (**1**) [9], and 1,2-disubstituted tert-butyl (**3**) [10] complexes - the types of steric interactions observed in the crystalline state (**3**) were revealed. Most of these interactions were confirmed by the lengths of the corresponding intramolecular nonvalent contacts, changes in the valence angles between chemical bonds, and rotation angles of the corresponding groups. However, in a number of cases, the lengths of these contacts did not fully correspond to the observed structural changes [7]. In addition, the reasons causing changes in the lengths of nonvalent contacts and rotation angles of both tert-butyl substituents and the substituted cyclopentadienyl ring were not discussed in this work. Therefore, in order to fully interpret the features of the crystal structure of (**3**), as well as to establish the reasons causing them, a comparative analysis of the structural parameters of (**3**) with the corresponding parameters of two sandwich-type complexes – the cation of 1,1′-di-tert-butylferrocenium (**4**) [11] and 1,2,1′,2′-tetra-tert-butylferrocene (**5**) [12] – was additionally carried out in this work. The inclusion of these two complexes is due to the fact that in the crystal of the above complexes, the tert-butyl substituent is practically not involved in steric interaction with the second ring [11, 12]. As a consequence, we here observe structural features due to steric interactions only within the substituted cyclopentadienyl ligand, i.e., interactions between the vicinal substituents themselves and between the substituent and atoms of the nearest CH fragments of the ring. In our opinion, this comparison will allow us to identify structural features (**3**) caused by steric interaction of vicinal tert-butyl groups with "their" CO groups, which in turn will allow us to correctly interpret the causes of structural features (**3**).

Thus, *the purpose of this work* is to determine the reasons for the structural features of complex (**3**) [7] by comparative analysis of the structural parameters of (**3**) with the corresponding parameters of two sandwich tert-butyl complexes (**4**) and (**5**) and one binuclear molybdenum complex (**1**).

Experimental part

The conditions of synthesis and X-ray structural studies of single crystals (**1**) and (**3**) were given in detail in [9, 10]. All structural parameters for complexes (**1**) and (**3**) were obtained by us using the Mercury program.

Result and discussions

1. ***Structural features of the substituted 1,2-^{t}Bu$_2$C$_5$H$_3$ fragment.*** Structural features of the substituted 1,2-^{t}Bu$_2$C$_5$H$_3$ fragment are observed in the structural parameters of the ring, in the arrangement of vicinal ^{t}Bu-substituents both in relation to each other and to the ring plane.

The indicated features of the 1,2-^{t}Bu$_2$C$_5$H$_3$ fragment are mainly due to the shortened nonvalent H...H and C...C contacts between vicinal ^{t}Bu-substituents (Table 1). The values of these contacts indicate that even though the ^{t}Bu-substituents are significantly deviated from each other (by about 15°, Fig. 1), these contacts are quite short. This means that there are still significant steric interactions between the ^{t}Bu-substituents, as noted in [7, 10]. The H...H and C...C repulsive interactions tend to weaken the steric tension between the ^{t}Bu-substituents and therefore lead to such primary structural changes as the deviation of the substituents from each other (in the plane of the ring), their rotation around the C4–C7 and C5–C6 bonds, and the stretching of the C4–C5 bond (Fig. 1).

Table 1. Shortened nonvalent H...H (less than 2.4 Å) and C...C (less than 3.4 Å) contacts between vicinal tert-butyl groups in (**3**)

Nonvalent contacts	H16...H12	H16...H4	H19...H12	H19...H10	C16…C13
Contact length, Å	2.062	2.315	2.073	2.230	3.369

1*a*. *Structural features of the substituted C_5H_3 ring.* Deviation of vicinal ^{t}Bu-groups from each other, first of all, is reflected in the change of external angles of C_5-ring – increase of C6–C5–C4 and C7–C4–C5 and decrease of C6–C5–C1 and C7–C4–C3, relative to the ideal value (126°) of this angle in the unsubstituted cyclopentadienyl ligand. The mutual repulsion of ^{t}Bu groups is also accompanied by the stretching of the C5–C4 bond (1.465 Å) (Fig. 1), relative to the C–C bond (≈1.40 Å) in the unsubstituted complex (**2**) [8].

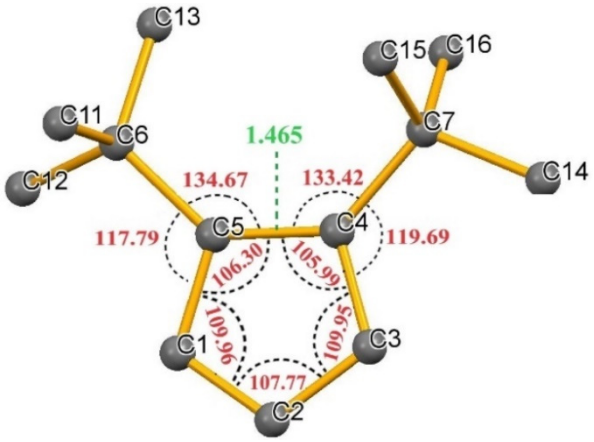

Fig. 1. Internal angles and some of the external angles (°) of the 1,2-^{t}Bu$_2$C$_5$H$_3$ ring in (**3**)

Changes in the external angles of the C_5-ring and the C5–C4 bond length are in turn accompanied by changes in the values of the internal angles of the cyclopentadienyl C_5-ring, compared to its ideal value (108°) [7]. Thus, we consider the decrease in the internal angles of C1–C5–C4 (106.30°) and C3–C4–C5 (105.99°) from 108° as a geometric consequence of the stretching of the C5–C4 bond. The increase of the internal angles C2–C1–C5 (109.96°) and C2–C3–C4 (109.95°) is considered as a result of steric interaction of the corresponding methyl groups ($C12H_3$, $C14H_3$) with the nearest CH fragments (C1H1, C3H3) of the ring (Section **1*b***) and stretching of the C5–C4 bond. The internal angle C1–C2–C3 (107.77°), which is not sterically affected by ^{t}Bu-substituents, practically does not change and remains the same in magnitude as in the unsubstituted complex (**2**) [8].

1*b*. *Peculiarities of steric interaction of tert-butyl substituents with the nearest CH fragments of the C_5H_3-ring in (**3**).* The joint consideration of the angles – C7–C4–C5, C6–C5–C4, C3–C4–C7, C1–C5–C6, C4–C7–C14, and C5–C6–C12 (Fig. 1), as well as the distance of atoms C12 and C14 from the midplane of the ring (Fig. 3), conducted in this work allows us to conclude that it is the short nonvalent contacts between $C14H_3$ and C3H3 (Tab. 2) [7] and determine both the larger value of the C3–C4–C7 (119.69°) angle (compared to C1–C5–C6 (117.79°)) and the smaller values of the C5–C4–C7 (133.42°) and C4–C7–C16 (115.4°) angles (compared to C4–C5–C6 (134.67°) and C5–C6–C13 (117.0°), respectively).

Table 2. Shortened H...H (less than 2.4 Å), C...H (less than 2.9 Å), and C...C (less than 3.4 Å) contacts between the ^{t}Bu-substituent and the corresponding CH fragment of the ring in (**3**)

Contacts between the C12H3 and C1H1		Contacts between the $C14H_3$ and C3H3	
C1…C6	2.548	C3…C7	2.576
C1…C12	2.932	C3…C14	2.788
C1…H6	2.802	C3…H15	2.564
C1…H8	2.589	C3…H13	2.772
H1…C6	2.759	H3…C14	2.457
H1…C12	2.704	H3…H15	2.061
H1…H8	2.075	H3…H13	2.349

The presence of more shortened contacts between C14H3 and C3H3 (in comparison with the corresponding contacts between C12H3 and C1H1) (Table 2) is due, on the one hand, to the smaller value of the angle C14–C7–C4 (109.6°) (in comparison with C12–C6–C5 (110.6°)) and to the proximity of the methyl group of C14H3 to the midplane of the ^{t}Bu$_2$Cp ring (in comparison with the methyl group of C12H3). Thus, the C14 atom is located at a distance of 0.256 Å from the midplane, while the C12 atom is located at a distance of 0.539 Å. Moreover, the C14 atom is located above the midplane of the ring, while the C12 atom is located below the plane (Fig. 3).

To understand the reasons for these structural differences in (**3**), in particular, the non-standard location of the methyl group C14H3 relative to the plane of the 1,2-disubstituted ring, it is useful to consider the features of crystal structures of 1,2-disubstituted tert-butyl complexes of transition metals in which there are no additional ligands, such as CO, with which ^{t}Bu-substituents could sterically interact. Such systems include, for example, 1,1′,2,2′-tetra-tret-butylferrocene (1,2-^{t}Bu$_2$Cp)$_2$Fe (**5**), in the crystal of which vicinal ^{t}Bu-substituents sterically interact only with each other and with the nearest CH ring fragments [12]. Analysis of the structural parameters of (**5**) shows that in it the mutual arrangement of vicinal ^{t}Bu-groups is symmetrical both with respect to each other and to the midplane of the ring. And as a consequence, the steric interaction of each ^{t}Bu-substituent (more precisely, their methyl groups C7H3 and C7BH3) with the corresponding nearest CH fragment of the ring is the same. Therefore, in the sandwich complex, the lengths of the nonvalent contacts corresponding to the contacts discussed in Table 2 are equal to each other [12]. Consequently, the difference in the interactions of the vicinal ^{t}Bu-substituents with the corresponding CH fragments of the ring observed in (**3**) should be attributed to an additional steric interaction between the trans-carbonyl group and the ^{t}Bu-substituent at C4 [7]. This interaction, together with the steric interaction between the vicinal ^{t}Bu-substituents, causes more significant structural changes of the ^{t}Bu-substituent at C4 (compared to the substituent at C5) (Section **1*c***). The mentioned additional steric interaction (C10...C16 (3.282 Å), (C10...H21(C16) (2.781 Å)) manifests itself in the fact that the methyl group of C14H3 is located above the ring plane, and the C14–C7–C4 (109.6°) angle is smaller than the C12–C6–C5 (110.6°) angle. As a result, the nonvalent contacts between C14H3 and C3H3 become shorter than those between C12H3 and the C1H1 fragment.

Thus, the differences in the degree of steric interaction of vicinal tert-butyl substituents with CH ring fragments in (**3**) are due to the steric influence of the trans-carbonyl group on the tert-butyl substituent at C4.

However, in (**3**) steric interactions between vicinal ^{t}Bu-substituents, as well as between the trans-carbonyl group and vicinal substituents, are reflected not only in the change in the spatial arrangement of these two methyl groups (C14H3 and C12H3) but also in all other methyl groups of both ^{t}Bu-substituents. Let us consider these conformational changes and the reasons for them in more detail.

1*c*. *Conformational features of the vicinal tert-butyl substituents in (3)*. In order to determine the conformational features of the vicinal ^{t}Bu-substituents in (**3**), it is necessary to consider the conformational features of the ^{t}Bu-substituent in (**1**) and in the two corresponding tert-butyl complexes where there is no steric interaction of the ^{t}Bu-substituent with other ligands bound to the metal atom. As noted in the previous section, sandwich-type complexes such as the 1,1′-di-tert-butylferrocenium cation (^{t}BuCp)$_2$Fe$^+$ (**4**) and 1,1′,2,2′-tetra-tert-butyl-ferrocene (1,2-^{t}Bu$_2$Cp)$_2$Fe (**5**) can be taken as such complexes. In this aspect, the common feature of complexes (**1**), (**4**), and (**5**) is that in them each ^{t}Bu group has two methyl groups directed away from the ring plane towards the metal atom (Mo, Fe) and one away from the metal atom (Fig. 2***a***). Moreover, in (**4**) all three Me groups are symmetrically located relative to the plane of the substituted cyclopentadienyl (^{t}BuCp) ring. Thus, the carbon atoms of two Me groups directed to the Fe atom are located at the same distance from the ring plane, equal to 0.445 Å (Table 3); the third Me group directed away from the Fe atom is characterized by the same torsional angles (C2C1C4C6) equal to 85.94° [11]. In (**5**), the steric repulsion arising between 1,2-^{t}Bu-substituents is accompanied by the rotation of each substituent by approximately 15° relative to the position of the ^{t}Bu-substituent in

(**4**). If viewed from above the plane of the ring, the right substituent rotates counterclockwise, and the left substituent rotates clockwise. Thus, in (**5**) for the ^{t}Bu-substituent located on the right, the torsional angles of the Me group directed away from the metal atom are –99.88° (C2BC1BC4BC6B) on the right and 71.06° (C1C1BC4BC6B) on the left, while in (**4**) the torsional angles of the corresponding Me group are the same and equal to 85.94°.

In ^{t}Bu$_2$Cp ring of (**5**) both ^{t}Bu-substituents are located symmetrically relative to each other: their corresponding Me groups directed towards the Fe atom are characterized by the same torsional angles (C1C1BC4BC5B (–52.09) and C1BC1C4C5 (52.09); C2BC1BC4BC7B (16.60) and C2C1C4C7 (–16.60)). The distances from the ring plane to the carbon atoms (C5, C5B) of the nearest to each other Me groups (C5H$_3$ and C5BH$_3$) are the same and are 0.724 Å, and for the atoms (C7, C7B) of the distant Me groups (C7H$_3$ and C7BH$_3$), they are 0.107 Å (Table 3).

Table 3. Torsional angles (φ) and distances (*d*) of carbon atoms of Me groups of tert-butyl substituents from the ring plane in complexes (**1**), (**3**), (**4**), and (**5**).

(^{t}BuCp)$_2$Fe$^+$ (4)		**(^{t}BuCp)$_2$Mo$_2$(CO)$_6$ (1)**	
φ, °	*d,* Å	**φ**, °	*d,* Å
C2C1C4C6 = 85.94 C2C1C4C6 = 85.94		C4C5C6C7 = –80.54 C1C5C6C7 = 87.01	
C2C1C4C5 = 33.06 C2C1C4C5 = –33.06	*d*(C5) = 0.445 *d*(C5) = 0.445		*d*(C7) = 0.242 *d*(C8) = 0.371
(1,2-^{t}Bu$_2$Cp)$_2$Fe (5)		**(1,2-^{t}Bu$_2$Cp)$_2$Mo$_2$(CO)$_6$ (3)**	
φ, °	*d,* Å	**φ**, °	*d,* Å
C2BC1BC4BC6B = –99.88 C1C1BC4BC6B = 71.06		C3C4C7C15 = –106.80 C5C4C7C15 = 60.67	
C1C1BC4BC5B = –52.09 C1BC1C4C5 = 52.09	*d*(C5B) = 0.724 *d*(C5) = 0.724	C5C4C7C16 = –64.45 C4C5C6C13 = 29.82	*d*(C16) = 0.785 *d*(C13) = 0.091
C2BC1BC4BC7B = 16.60 C2C1C4C7 = –16.60	*d*(C7B) = 0.107 *d*(C7) = 0.107	C3C4C7C14 = 8.0 C1C5C6C12 = –43.27	*d*(C14) = 0.256* *d*(C12) = 0.539

- The C14H$_3$ methyl group is located above the plane of the substituted ring in (3**).*

However, in the monosubstituted binuclear molybdenum complex (**1**), unlike the two sandwich complexes (**4**) and (**5**) considered, the ^{t}Bu-substituent sterically additionally interacts with the trans-carbonyl group [9]. In particular, the C9 atom of the methyl group C9H$_3$ is raised and becomes closer to the midplane of the ring (0.242 Å), while the C8 atom of the methyl group C8H$_3$ is slightly removed (0.371 Å) (relative to their symmetrical arrangement). For the methyl group C7H$_3$, the additional steric interaction is reflected in the different value of torsional angles – C4C5C6C7 (–80.54°) and C1C5C6C7 (87.01°) (Table 3). Because of the different degree of deviation of the ring carbon atoms (C1, C4, C5) from the midplane of the ring in (**1**), the deviation of the values of the given torsional angles from the value of 85.94° (observed in (**4**)) does not occur to the same degree. Therefore, it is not reasonable to use them to characterize the rotation angle of the ^{t}Bu-substituent around the C5–C6 bond in (**1**). More accurately, the rotation angle can be characterized using the torsional angles MoC5C6C9 (62.95°) and MoC5C6C8 (–60.17°). Since in (**4**) the corresponding torsional angles of FeC1C4C5 (–61.00°) and FeC1C4C5 (61.00°) are the same and numerically equal to 61.00°, the maximum rotation angle of the ^{t}Bu-substituent in (**1**) will be of the order of 2°, in the clockwise rotation direction.

Thus, in the monosubstituted tert-butyl molybdenum complex (**1**), the steric interaction of the trans-carbonyl group with the ^{t}Bu-substituent along with the rotation of the ^{t}BuCp ring around the Ct–Mo axis [9] (see also section

2) also causes the rotation of the ^{t}Bu-substituent itself around the C5–C6 bond by a small (≈2°) angle in the clockwise direction. In this case, both Me groups ($C9H_3$ and $C8H_3$) of the ^{t}Bu-substituent, as well as in the considered sandwich complexes (**4**) and (**5**), remain directed away from the ring plane towards the metal atom.

The analysis of the corresponding structural parameters in the disubstituted molybdenum complex (**3**) (Table 3) allows us to conclude that the joint steric influence of the vicinal ^{t}Bu-substituent at C5 and the trans-carbonyl group (C10O3) on the ^{t}Bu-substituent at C4 is accompanied by rotation of the latter around the C4–C7 bond (counterclockwise) by an angle approximately equal to 26° relative to the position of the ^{t}Bu-group in (**1**) (or by 24° relative to the position of the ^{t}Bu-group in the monosubstituted complex (**4**)). In other words, the rotation angle of the ^{t}Bu-substituent at C4 is about 9° greater than the rotation angle of the corresponding ^{t}Bu-substituent in (**5**). At the same time, in (**3**), the C16($C16H_3$) atom moves 0.543 Å downward, and the C14($C14H_3$) atom moves 0.607 Å upward, relative to the position of the atoms (C9 and C8) of the corresponding methyl groups ($C9H_3$ and $C8H_3$) in the monosubstituted (**1**). As a result, the C14H_3 methyl group appears not under the plane but above the ^{t}Bu$_2$C$_5$H$_3$ plane of the ring: the distance from the C14 atom to the ring plane is 0.256 Å (Fig. 3). Probably, the larger rotation angle of the ^{t}Bu-substituent at C4 is also promoted by the fact that in (**3**) both ^{t}Bu-substituents rotate in the same direction – counterclockwise. However, this rotation is not synchronous, since the ^{t}Bu-substituent at C5 is rotated by 11° less than the ^{t}Bu-substituent at C4 (Fig. 2b). In (**5**), on the other hand, the vicinal ^{t}Bu-substituents rotate (turn) in opposite directions (Fig. 2a). As a result of the difference in the rotation directions of the ^{t}Bu-substituents, the methyl groups of $C6H_3$ and $C6BH_3$ in (**5**) are closer together (C6...C6B (3.588 Å)) compared to the distance between the $C11H_3$ and $C15H_3$ groups in (**3**) (C11...C15 (3.796 Å)).

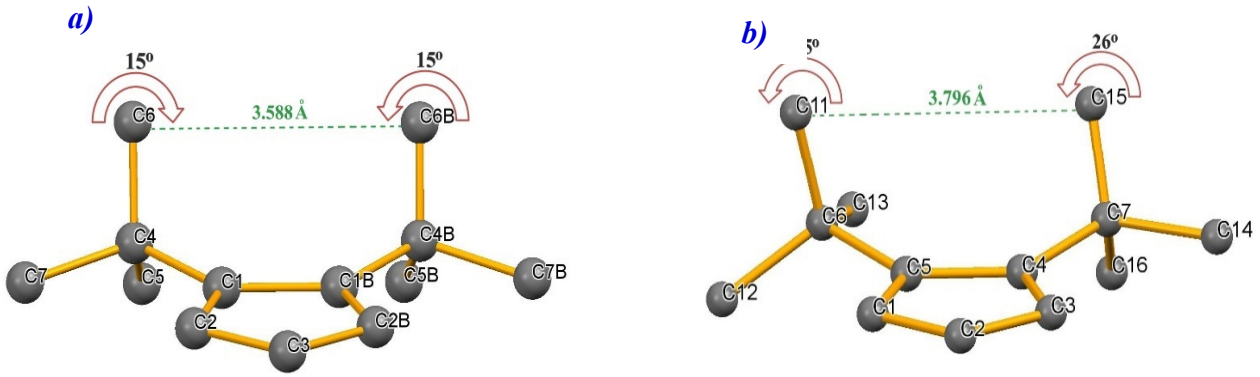

Fig. 2. Rotation angles of vicinal ^{t}Bu-substituents in (**5**) – ***a*** and (**3**) – ***b***

Thus, in (**3**) the steric influence of the trans-carbonyl group (C10O3) on the ^{t}Bu-substituent at C4 is accompanied not only by the rotation of the latter around the C4–C7 bond [7] (see also section 2), but also by a change in the direction of rotation of the ^{t}Bu-substituent at C5, as a result of which the conformations of the ^{t}Bu-substituents and their methyl groups change markedly both relative to each other and relative to the ring plane, as compared to the same in (**5**).

It should be noted that in the above conformation of the ^{t}Bu-substituent at C4, steric forces act on it from the C3H3 side of the fragment (C3...C14 (2.788 Å), C3...H15(C14) (2.564 Å), H3...C14 (2.457 Å), H3...H15(C14) (2.061 Å)), the trans-carbonyl group (C10...C16 (3.282 Å), C10...H21(C16) (2.781 Å)), and the neighboring ^{t}Bu-substituent ((C13)H12...H16(C15) (2.062 Å), (C13)H10...H19(C16) (2.230 Å)), which tend to further deflect it away from the ring plane, away from the Mo atom. However, despite this, its deflection angle (γ=11.34°) is smaller than for the ^{t}Bu-substituent at C5 (γ=13.12°) (Figure 3). It is possible that the non-standard conformation of the ^{t}Bu-substituent at C4 (when there are not two but one methyl group under the ring and therefore only one nonvalent contact with the metal atom – C16...Mo (3.863 Å)), as well as the shortened contacts C16...C13 (3.369 Å), (C11)H4...H16(C15) (2.315 Å), and (C13)H12...H19(C16) (2.073 Å), play a more

important role in the actually observed angle of deviation of the ^{t}Bu-substituent at C4 from the ring plane, i.e., in the reduction of this angle.

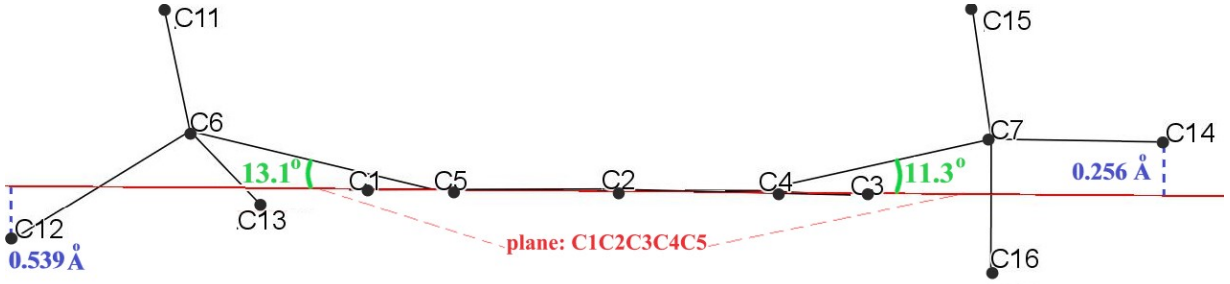

Fig. 3. Deviation of the ^{t}Bu-groups away from the ring plane away from the Mo atom in (**3**)

The additional steric interaction of the trans-carbonyl group with the methyl groups of $C16H_3$ and $C13H_3$ in (**3**) – (C16)H21...C10 (2.781 Å), C16...C10 (3.282 Å), and (C13)H10...C10 (2.820 Å) is also manifested in the larger distance between these Me groups than the corresponding distance in (**5**). Thus, the C16...C13 (3.369 Å) contact in (**3**) is 0.090 Å longer than the C5...C5B (3.279 Å) contact in (**5**), despite the fact that the bond lengths of C5–C4 (1.465 Å) and C1–C1B (1.468 Å), to whose atoms the vicinal ^{t}Bu-substituents are attached, are almost equal. In principle, because of the rotation of the ^{t}Bu-groups in (**5**) in opposite directions (Fig. 2a), one would expect the C5...C5B contact in (**5**) to be longer than the C16...C13 contact in (**3**).

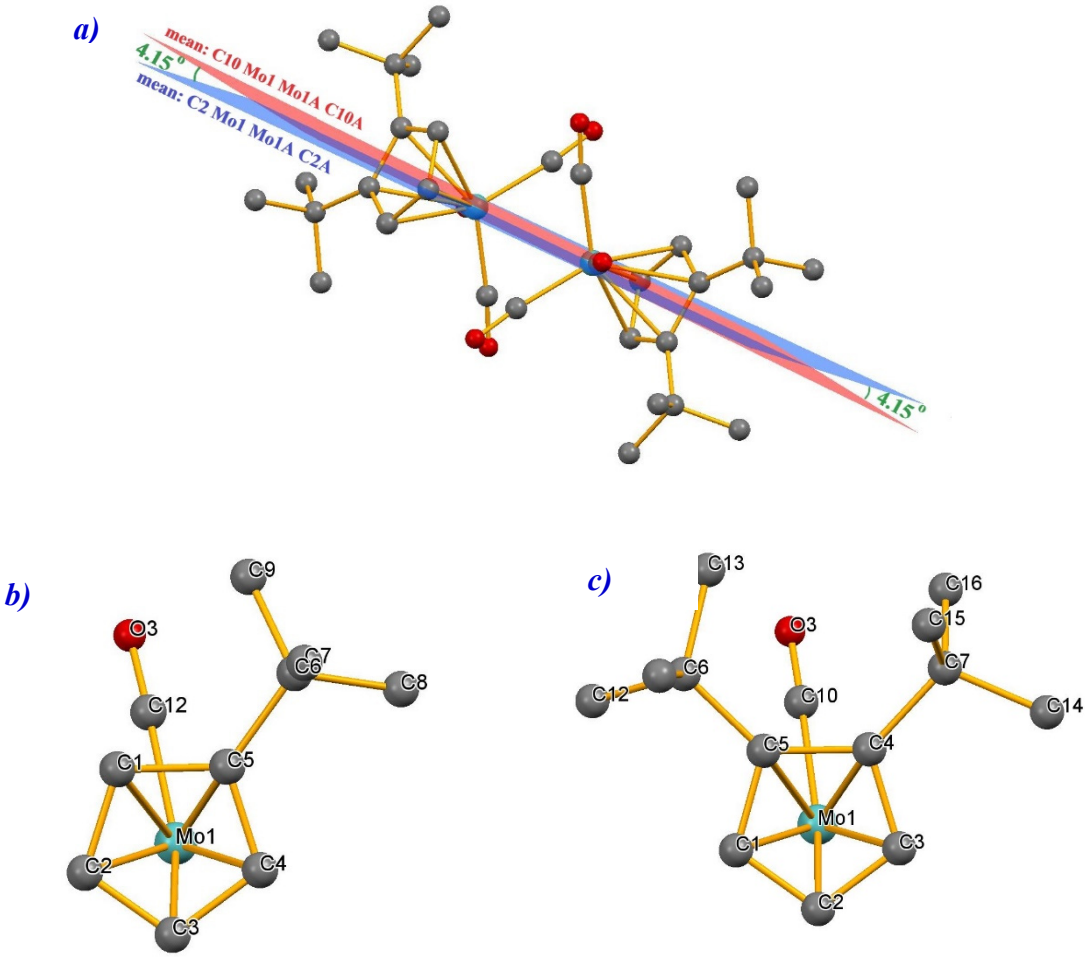

Fig. 4. ***a*** - Angle between the C10MoMo^{i}C10^i and C2MoMo^{i}C2^i planes in (**3**), characterizing the rotation of the ^{t}Bu$_2$C$_5$H$_3$ ring around the Ct–Mo axis (Mo=Mo1, Mo′=Mo1A); ***b***- and ***c*** - Projection of Mo–C12–O3 and Mo–C10–O3 fragments on the plane of the substituted ring in (**1**) and (**3**)

2. ***Rotation of the ^{t}Bu$_2$C$_5$H$_3$ ring around the Ct–Mo axis in (3)***. In (**3**), the steric influence of the trans-carbonyl group on the ^{t}Bu-substituent at C4 is also reflected in the slight rotation of the ^{t}Bu$_2$C$_5$H$_3$ ring around the Ct–Mo axis, away from the trans-carbonyl group by about 2.12°, compared to the position of the Cp ring in (**2**). In the monosubstituted complex (**1**), a similar steric interaction led to a rotation of the ^{t}BuC$_5$H$_4$ ring by about 6.15° [9].

Considering that the steric interaction between the trans-carbonyl group and the ^{t}Bu-substituent at C4 in (**3**) is larger than the corresponding interaction in (**1**) [7], one would expect in (**3**) a larger rotation angle than 6.15°. In our opinion, the most likely reason that prevents further rotation of the ^{t}Bu$_2$C$_5$H$_3$ ring is related to the fact that during the ring rotation the ^{t}Bu-group at C5 gets closer to the trans-C10O3 ligand. As a result of their convergence, the steric repulsion between them increases, and the trans-C10O3 ligand prevents further rotation of the ring (since the projection of the Mo–C10–O3 fragment on the ring plane is located between the vicinal ^{t}Bu-substituents (Fig. 4 ***b*** and ***c***)).

Taking into account the rotation angle of the substituted ring in (**3**) and (**1**) allows us to explain the reasons for the non-monotonic change in the lengths of shortened contacts between ring atoms and atoms of "neighboring" cis-CO groups in (**3**), compared to (**1**) (Fig. 5) [7]. From the general picture of changes in the lengths of the above five contacts in (**3**) falls out the change in the length of the contact involving the carbon atom located directly above the Mo–Mo bond, i.e., atom C3 in (**2**) and (**1**) and C2 in (**3**): in contrast to the other four contacts, the contact (C2...C9A (3.315 Å) is shortened, the reasons for which can be understood on the basis of Figure 5. Fig. 5b shows that at a large rotation angle of the ^{t}BuC$_5$H$_4$ ring (6.15°) in (**1**), the C3 atom moves away from the "neighboring" CO groups, and therefore the length of the contact C3...C11^i (3.354 Å) in (**1**) becomes longer than the length of the corresponding contact C3...C8B(3.227 Å) in the unsubstituted complex (**2**) (Fig. 5a).

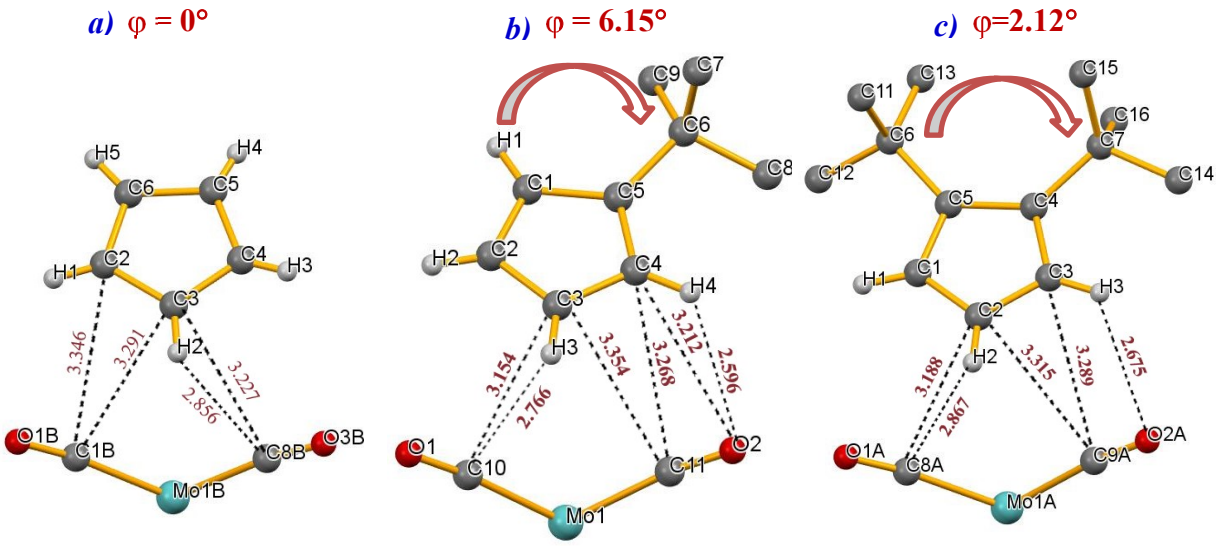

Fig. 5. Shortened nonvalent C$_5$-ring...cis-C^{i}O^i contacts between the two halves of molecules (**2**) (***a***), (**1**) (***b***) and (**3**) (***c***)

In (**3**), due to the smaller rotation angle of the ^{t}Bu$_2$C$_5$H$_3$ ring (2.12°), the C2 atom still remains close to the "neighboring" CO groups, and therefore the contact (C2...C9A (3.315 Å) in (**3**) turns out to be shorter (Fig. 5c) than C3...C11^i (3.354 Å) in (**1**).

The elongation of the other four contacts in (**3**), compared to those in (**1**), also corresponds to a smaller rotation angle of the ^{t}Bu$_2$C$_5$H$_3$ ring (2.12°) compared to the rotation angle of the ^{t}BuC$_5$H$_4$ ring (6.15°) in (**1**). It should be noted that although the discussed differences in contact lengths are within the experimental error, what is important is that the trend in the lengths of the five non-valent contacts is completely consistent

with the value of rotation of the substituted ring around the Ct–Mo axis in (**1**) and (**3**).

3. Steric interaction of cis-CO groups bonded to different Mo atoms (cis-CO...cis-C^{i}O^{i} interactions). It was noted in [7] that in the series of complexes (**2**)→(1)→(**3**) the lengths of cis-CO...cis-C^{i}O^{i} nonvalent contacts monotonically decrease: 2.810 Å→2.771 Å→2.765 Å, even though the Mo–Mo bond is stretched in (**3**) (from 3.232 Å in (**1**) to 3.253 Å) [8-10]. Analysis of the structural parameters of complexes (**2**), (**1**), and (**3**) allows us to conclude that the main reason for the shortening of these contacts is the steric influence of the tert-butyl substituent on the trans-carbonyl group. The displacement of the trans-carbonyl group toward the cis-CO groups, in turn, causes a subsequent displacement of the corresponding cis-CO group, bringing it closer to the middle plane of the ring, which leads to a shortening of contacts between the cis-CO groups located at the "neighboring" Mo atoms, i.e., the cis-CO...cis-C^{i}O^{i} contact. A distinctive feature of the "transfer" by the trans-carbonyl group of the steric influence of the tert-butyl substituents is that in (**1**) this influence is transferred to the cis-C11O2 group, which is located on one side of the C$_{trans\text{-}CO}$MoMo^{i}C$_{trans\text{-}C^{i}O^{i}}$ plane [9], while in (**3**) it is transferred to the cis-C8O1 group, which is located on the other side of the C$_{trans\text{-}CO}$MoMo^{i}C$_{trans\text{-}C^{i}O^{i}}$ plane [10]. In both complexes, the position of the second cis-CO group relative to the plane of the substituted cyclopentadienyl ring is practically unchanged. The displacement of one or the other cis-CO group is determined by the direction of displacement of the trans-carbonyl group under the action of substituents in the ring. The above features of the steric influence of the ^{t}Bu-substituent on the trans-CO group in (**1**) and (**3**) are confirmed by the data in Table 4.

Table 4. Changes in the values of the Ct–Mo–C$_{cis\text{-}CO}$ angle in complexes (**2**), (**1**) and (**3**)

(**2**)	Ct–Mo–C8B= 126.82°	Ct–Mo–C1B= 126.95°
(**1**)	Ct–Mo–C11= 125.89°	Ct–Mo–C10=127.22°
(**3**)	Ct–Mo–C9=125.80°	Ct–Mo–C8=125.98°

Table 4 shows that in (**3**) both angles Ct–Mo–C9 and Ct–Mo–C8 have the smallest value among the given values. It is for this reason that the lengths of the cis-CO...cis-C^{i}O^{i} contacts in (**3**) are the shortest (2.765 Å) even though the Mo–Mo bond is stretched (3.253 Å). Therefore, in our view, these repulsive forces are responsible for the observed elongation of the Mo–Mo bond. It should also be noted that although the differences in the values of the Ct–Mo–CO angles discussed in this section are within the experimental error, it is important that the trend in the values of these angles reflects the degree of enhancement of the steric interaction ^{t}Bu...trans-CO in (**3**), compared to (**1**).

Conclusıon

Thus, the comparative analysis of the structural parameters of (**3**) with the corresponding parameters of (**1**), (**4**), and (**5**) has allowed us to establish the structural features of the ^{t}Bu$_2$C$_5$H$_3$ fragment in (**3**) due to steric interactions both between the vicinal ^{t}Bu substituents in the ring and between each ^{t}Bu substituent and the nearest CH fragment of the ring. Differences in the structural parameters of the substituted ring, due to the complex belonging to the binuclear ones, were interpreted by the effect in these complexes of an additional steric interaction between the substituent in the ring and the trans-carbonyl group in (**3**) and (**1**). The absence of such steric interaction in the sandwich complexes and taking into account the difference in the degree of steric influence of the trans-carbonyl group on the ring substituents in complexes (**3**) and (**1**) allowed us to explain the magnitudes and directions of rotation of the ^{t}Bu substituents in (**3**), (**1**), (**4**), and (**5**). This in turn allowed us to interpret the conformational differences of the ^{t}Bu-substituents both with respect to each other and to the ring plane. A comparative analysis of the structural parameters of the binuclear complexes (**2**), (**1**), and (**3**) allowed us to propose the most probable reasons for (a) the discrepancy between the degree of steric interaction between the trans-carbonyl group and ^{t}Bu-substituents and the angle of

rotation of the 1,2-^{t}Bu$_2$C$_5$H$_3$ ring around the Ct–Mo axis and (b) the elongation of the Mo–Mo bond in (**3**) as compared to (**1**) and (**2**).

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