STERIC EFFECT OF THE TERT-BUTYL SUBSTITUENT IN THE CRYSTAL STRUCTURE OF THE BINUCLEAR COMPLEX $(^tBuCp)_2Mo_2(CO)_6$ (^tBuCp = tert-$C_4H_9C_5H_4$)

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Abstract: *The features of the crystal structure of bis(tert-butylcyclopentadienyltricarbonyl)molybdenum(I)) $(^tBuCp)_2Mo_2(CO)_6$ (**1**) have been established. Molecule (**1**), like the molecule of the unsubstituted complex $Cp_2Mo_2(CO)_6$ (**2**)($Cp – C_5H_5$), is in the trans-form. Both complexes (**1**) and (**2**) are sterically strained. However, the steric strain of molecule (**1**) is more pronounced, which is due to the steric interaction of the tert-butyl substituent with the trans-carbonyl (C12O3) group. Comparative analysis of structural parameters of complexes (**1**) and (**2**) made it possible to show that this interaction is reflected in changes in most structural parameters of complex (**1**). First of all, it is reflected in an increase in the Ct–Mo–C12 angle (Ct – is the centroid of the C_5-ring), in a decrease in the Mo^i–Mo–C12 and C12–Mo–C11 angles, as well as in the rotation of the ^tBuCp ring around the Ct–Mo axis, away from the trans-C12O3 group. The rise of the cis-C11O2 group relative to the middle plane of the C_5-ring is also accompanied by a reduction in non-valent contacts between cis-carbonyl ligands bonded to different Mo atoms ((C11O2)C…C($C10^iO1^i$), ((C10O1)C…C($C11^iO2^i$) (2.771 Å). The appearance of shorter non-valent contacts between the two halves ($^tBuCpMo(CO)_3$) of molecule (**1**) is not reflected in the length of the Mo–Mo bond (CIF file CCDC № 2243119).*

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

Introduction

One of the directions for studying the electronic and steric influence of alkyl substituents in the cyclopentadienyl ring on the structure and chemical transformations of cyclopentadienyl complexes of transition metals is the study of the crystal and molecular structure of binuclear cyclopentadienyl and alkylcyclopentadienyl tricarbonyl complexes of molybdenum [1–9]. In this aspect, more suitable systems are monosubstituted molybdenum complexes of the composition $(RCp)_2Mo_2(CO)_6$, in which the separation of the role of the electronic and steric effects of the substituent in the observed crystal structure [4] should be relatively easier. To date, the crystal structures of $(RCp)_2Mo_2(CO)_6$ complexes have been studied, where the R substituent is n-propyl, isopropyl, n-butyl, secondary (sec-)butyl, 1-ethylpropyl, cyclohexyl, etc. [4]. The results of these studies showed that all the above-mentioned complexes $(RCp)_2Mo_2(CO)_6$, like the unsubstituted complex (**2**), have a trans-conformation in the crystal [4]. A comparative analysis of the structural parameters of the $(RCp)_2Mo_2(CO)_6$ complexes, carried out by us, shows that despite the differences in the volumes of the hydrocarbon substituent in the Cp ring, the values of the bond angles Ct–Mo–$C_{trans\text{-}CO}$, Mo^i–Mo–$C_{trans\text{-}CO}$ and Mo^i–Mo–Ct are approximately the same as the value of the corresponding angle in the unsubstituted complex (**2**) [3]. In fact, this means that in the crystalline state in the listed complexes, there is no steric interaction between the substituent (R) in the ring and the trans-carbonyl group. Most likely, this is due to the fact that in these complexes hydrocarbon radicals bonded to the carbon atom Cp of the ring through "their own" primary or secondary carbon atom. Therefore, during crystallization of the complex, as a result of rotation of the substituted RCp ring around the Mo–Ct axis and the radical R around the R(C)–$C_{subst.}$(ring) bond ($C_{substituted}$ – substituted carbon atom of the RCp ring), from the side of the ring towards "its" Mo atom, either two hydrogen atoms or one hydrogen atom and one alkyl (methyl,

ethyl, etc.) group of the R substituent will be directed. As a consequence, the steric interaction of the R substituent with “its” CO groups (especially with the trans-CO group) turns out to be insignificant, and it does not manifest itself in the values of the above-mentioned valence angles. However, if we use an alkyl radical that binds to the Cp ring via “its” tertiary carbon atom, in particular the tert-butyl radical, then in the crystal two methyl groups will be directed towards “its” Mo atom [10, 11] and therefore it will be impossible to avoid steric interaction of the R substituent with “its” CO groups (especially with the trans-CO group).

In order to find out whether this is so, and if so, how this steric interaction is reflected in the structural parameters of (**1**), in this article a comparative analysis of the structural parameters of (**1**), which was previously synthesized and studied by us [12], is carried out with the corresponding parameters of the unsubstituted (**2**), monosubstituted sec-butyl $({}^{s}\text{BuCp})_2\text{Mo}_2(\text{CO})_6$ [4], and 1,2-disubstituted tert-butyl $(1,2\text{-}{}^{t}\text{Bu}_2\text{Cp})_2\text{Mo}_2(\text{CO})_6$ [13] complexes.

Experimental Part

The conditions of synthesis (**1**) and X-ray structural study of its single crystal were given in the works [12, 14]. Deep-red crystals of the title complex suitable for single crystal X-ray analysis were grown in toluene at a temperature of −10 °C.

The values of some bond lengths and bond angles in complex (**1**) are given in Table 1.

Table 1. The values of some bond distances and bond angles in complex (**1**)

Bond	***d*, Å**	**Angle**	**ω, degree**
Mo–C(1)	2.318(3)	Ct–Mo–Mo^{i}	117.54
Mo–C(2)	2.357(3)	Ct–Mo–C10	127.22
Mo–C(3)	2.381(3)	Ct–Mo–C11	125.89
Mo–C(4)	2.360(3)	Ct–Mo–C12	116.27
Mo–C(5)	2.356(3)	C12–Mo–C11	76.04
Mo–Ct	2.021	C12–Mo–C10	79.65
Mo–Mo^{i}	3.232	C11–Mo–C10	106.46
C(1)–C(5)	1.437(4)	Mo^{i}–Mo–C11	70.61
C(5)–C(4)	1.419(4)	Mo^{i}–Mo–C12	126.09
C(4)–C(3)	1.419(4)	Mo^{i}–Mo–C10	71.04
C(3)–C(2)	1.406(4)	C(9)–C(6)–C(5)	112.4(2)
C(2)–C(1)	1.418(4)	C(8)–C(6)–C(5)	110.9(2)
C(5)–C(6)	1.525(4)	C(7)–C(6)–C(5)	106.1(2)
C(6)–C(7)	1.536(4)	C(9)–C(6)–C(7) C(9)–C(6)–C(8)	109.3(3) 109.6(3)
C(6)–C(8)	1.522(4)	C(8)–C(6)–C(7)	108.5(3)
C(6)–C(9)	1.505(4)	C(2)–C(3)–C(4)	108.2(3)
Mo–C(12)	1.960(3)	C(3)–C(4)–C(5)	108.9(2)
Mo–C(10)	1.990(3)	C(2)–C(1)–C(5)	108.7(2)
Mo–C(11)	1.992(3)	C(3)–C(2)–C(1)	107.8(2)
O(1)–C(10)	1.158(3)	C(1)–C(5)–C(4)	106.2(2)
O(2)–C(11)	1.151(3)	C(4)–C(5)–C(6)	125.8(2)
O(3)–C(12)	1.154(3)	C(1)–C(5)–C(6)	127.1(3)
		Ct–C(5)–C(6)	170.92
		O(1)–C(10)–Mo	174.6(2)
		O(2)–C(11)–Mo O(3)–C(12)–Mo	173.1(2) 178.2(2)

Intermolecular non-valent contacts in the crystal cell are within normal limits. The shortest intermolecular contact, in which hydrogen atoms do not participate, is between oxygen atoms at a distance of 3.177 Å.

Results and Discussion

The crystal structure of (**1**) is shown in Fig. 1. Like complex (**2**) [3], complex (**1**) is in the trans-form – the torsion angle Ct–Mo–Mo^i–Ct^i is 180°. The molecule of (**1**) is sterically highly strained. The steric strain is caused by short non-valent contacts both between the carbon atoms of the "neighboring" cis-CO groups (cis-CO)C...C^i(cis-C^iO^i)(2.771(4) Å), and between the cis-CO groups and the "neighboring" substituted ring (Table 2), as well as between the tert-butyl and trans-C12O3 groups (C12…H9A(2.651 Å) and O3…H9A(2.684 Å), section ***b***).

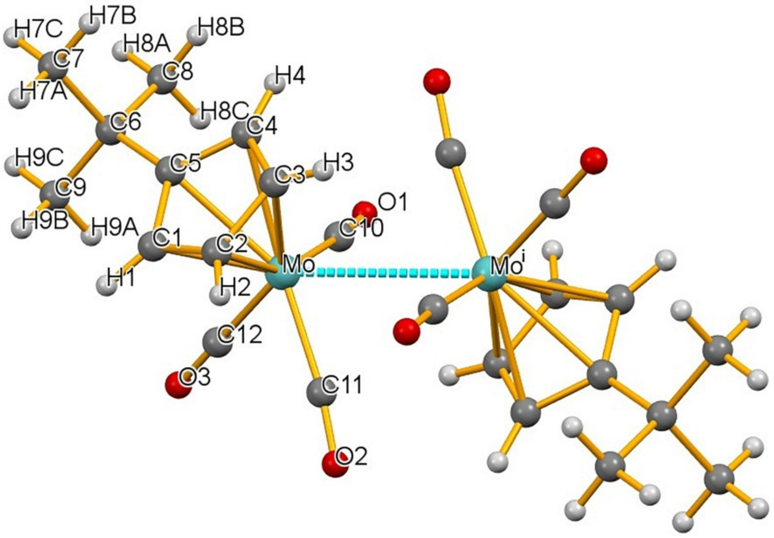


Fig. 1. Crystal structure of the complex (^{t}BuCp)$_2$Mo$_2$(CO)$_6$ (**1**)

a – Orientation of the ^{t}BuCp ring. It is known [3,15] that in unsubstituted binuclear complexes $Cp_2M_2(CO)_6$ (M – Cr, Mo, W) strong steric strain is observed above and below the M–M bond. Therefore, in the crystalline state (**1**), the ^{t}Bu substituent in the ring tends to be located opposite the Mo–Mo bond, approximately above the trans-carbonyl group (C12O3). In this case, the tert-butyl group is located relative to the trans-carbonyl group above the angle $C_{trans\text{-}CO}$–Mo–$C_{cis\text{-}CO}$, which in the unsubstituted complex (**2**) [3] has a larger value: C_2–Mo–C_3 = 79.2° > C_2–Mo–C_1 = 77.9° (Table VIII and Fig. 1 in [3]). Consequently, in complex (**1**), the ^{t}BuCp ring will take a position in which the tert-butyl group will be directed above the angle C12–Mo–C10 (79.65(1)°), since, for steric reasons, such a location of the substituent is energetically more favorable than over the C12–Mo–C11 angle (76.04(1)°).

b – Angle Ct–Mo–$C_{trans\text{-}CO}$. The steric interaction between the tert-butyl (mainly methyl $C9H_3$) and trans-carbonyl (C12O3) groups is primarily manifested in a change in the value of the Ct–Mo–$C_{trans\text{-}CO}$ (Ct–Mo–C12) angle. Thus, in the ^{t}BuCpMo(CO)$_3$ fragment, the Ct–Mo–C12 angle (116.27°) is approximately 2.4° greater than the corresponding angle in the unsubstituted complex (**2**) (113.89°) [3]. The presence of this interaction is indicated by short non-valent contacts C12…H9A(2.651 Å) and O3…H9A(2.684 Å), as well as a shortening of the length of the C6(sp^3)–C9(sp^3) bond (1.505 Å), relative to the length (1.54 Å), accepted for the C(sp^3)–C(sp^3) bond [16]. Additional confirmation of this assumption is the fact that in the molecule of the isomer of complex (**1**) – the sec(s)-butyl complex (^{s}BuCp)$_2$Mo$_2$(CO)$_6$ [4], in which the steric interaction between the sec-butyl and trans-carbonyl groups is practically absent, the value of the Ct–Mo–$C_{trans\text{-}CO}$ angle is 114.2° and is very close to the value of the corresponding angle (113.89°) in the unsubstituted complex (**2**).

It should be noted that the increase in the Ct–Mo–C12 angle in (**1**) by 2.4° is practically not accompanied by a decrease in the Ct–Mo–Mo^i angle (117.54°) compared to the same angle (117.74°) in (**2**) [3]. The observed decrease (0.2°) is within the experimental error. It is very likely that the constancy of the Ct–Mo–Mo^i angle in (**1**) (relative to the corresponding angle in the $(RCp)_2Mo_2(CO)_6$ complexes) is due, on the one hand, to the strong steric congestion above and below the Mo–Mo bond (Table 2), and on the other hand, to the expenditure of part of the energy of the steric interaction between the substituent in the ring and the trans-carbonyl group on the rotation of the ^{t}BuCp ring around the Ct–Mo axis (section ***e***).

Table 2. Lengths of non-valent contacts between atoms of the cyclopentadienyl ring and "neighboring" cis-C^{i}O^i groups in molecules (**1**) and (**2**)

Non-valent contact in (1)	**Distance (Å)**	**Non-valent contact in (2)***	**Distance (Å)**
H4...O2^i	2.596	H1B...O1	2.807
C3… C10^i	3.154	C3B…C8	3.227
C4…C11^i	3.268	C3B…C1	3.291

* – for complex (**2**), atomic designations provided by the Mercury program for its crystal structure are given [3].

c* – *Distance Ct–Mo. In complex (**1**), the distance from the center of the tert-butylcyclopentadienyl ring (Ct) to the Mo atom (Ct–Mo) (2.021 Å) is slightly longer than the corresponding distance (2.009 Å) in the unsubstituted complex (**2**) [3]. The bond elongation (0.012 Å) is within the experimental error and does not reflect an increase in the nucleophilicity of the ^{t}BuCp ring due to the electron-donating characteristic of the tert-butyl substituent. In principle, in the crystal structures of such sterically highly strained molecules as $(RCp)_2M_2(CO)_6$ (M=Cr, Mo, W), it is unlikely that the electronic effects of alkyl substituents will be detected (with the possible exception of the frequencies of the stretching vibrations of the C≡O bond and the bond lengths in the M–C≡O fragment, if the studies are carried out under appropriate conditions [2, 17]). Moreover, the presence of π-acceptor CO groups associated with the metal atom in the molecule suppresses the increased nucleophilicity of the ^{t}BuCp ligand. The appearance of short contacts between the ^{t}BuCp ring and "its own" (C12…H9A (2.651 Å), O3…H9A (2.684 Å), C10…H8C (2.879 Å), C11…C2 (ring) (3.219(3) Å)), as well as "neighboring" CO groups (Table 2) should also prevent the reduction of the Ct–Mo distance in (**1**).

***d* – *Asymmetry of the Mo–cyclopentadienyl Ring Bonding (Mo–C_5-ring)*.** The values of the Mo–C(C_5-ring) bond distances in complex (**1**) (Table 1) indicate that the bonding between the Mo atom and the ^{t}BuCp ring, i.e., the Mo–C_5-ring bonding, is as asymmetric as in the complexes $(C_5H_5)_2M_2(CO)_6$, M=Cr, Mo, W [3, 15]. The asymmetry of the Mo–C_5-ring bonding is that the distances from M to the ring carbon atoms located above the M–M bond are greater than to the carbon atoms on the opposite side of the ring. In complex (**1**), the Mo–C_5-ring bonding is less asymmetric than in the unsubstituted complex (**2**), despite the fact that the Cp ligand is more symmetric than the ^{t}BuCp ligand. One of the reasons for the lower asymmetry of the Mo–C_5 ring binding in complex (**1**) can be associated with the location of the tert-butyl group in the ring approximately above the trans-carbonyl group, as a result of which the steric interaction between the tert-butyl and trans-C12O3 groups tends to raise the opposite side of the Cp ring. This assumption is also confirmed by the fact that in the disubstituted $(1,2\text{-}^tBu_2Cp)_2Mo_2(CO)_6$ [13, 18, 19] complex, in which the trans-carbonyl group (C10O3) sterically interacts with both vicinal tert-butyl substituents, the degree of asymmetry of the Mo–C_5 ring binding continues to decrease.

e* – *Substituted Cyclopentadienyl (^{t}BuCp) Ring. As noted in section ***b***, the steric interaction of the tert-butyl radical with the trans-C12O3 group in (**1**) is accompanied by a slight rotation of the ^{t}BuCp ring around the Ct–Mo axis (away from the trans-C12O3 group). The rotation angle is 6.15° (8.18°–2.03°) relative to the position of the Cp ring in complex (**2**) (Fig. 2). In this case, the short contact (C4H4)H4…O2^i(C11^{i}O2^i)(2.596 Å) that appears between the two halves of the molecule (**1**) as a result of rotation of the ^{t}BuCp ring and a slight rise of the cis-C11O2 group toward the plane of the ring (section ***g-1***) probably prevents both further rotation of the ring and a decrease in the Ct–Mo–Mo^i angle (section ***b***).

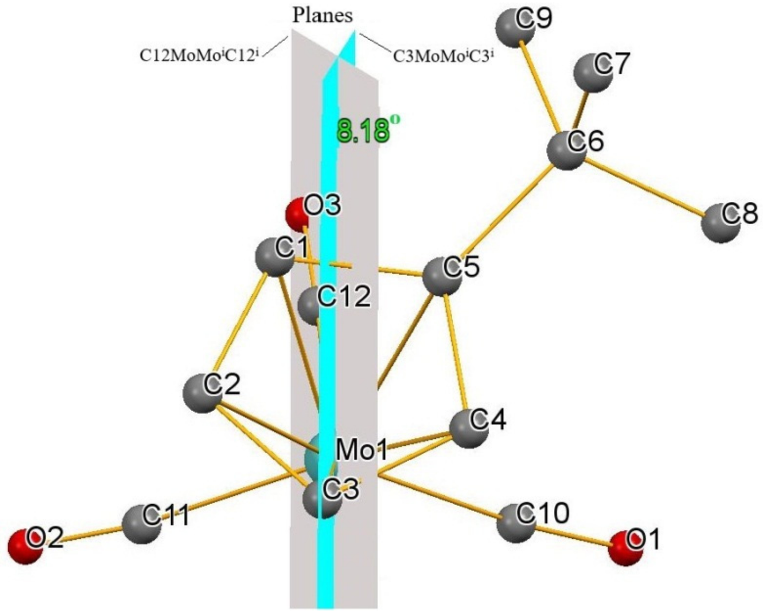


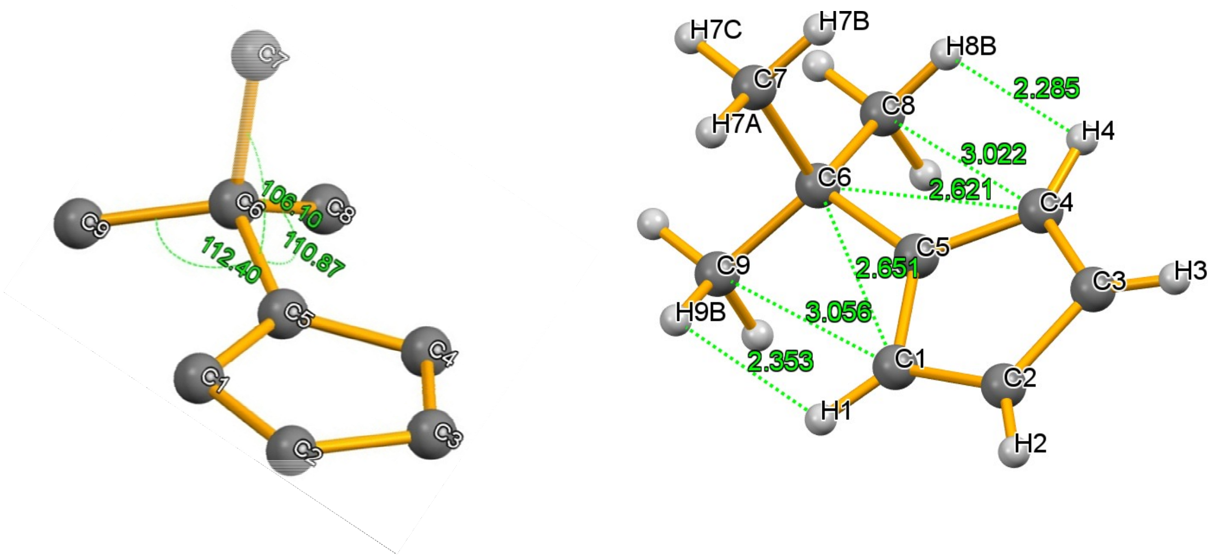
Fig. 2. The angle between planes C12MoMo^{i}C12 and C3MoMo^{i}C3^i in (**1**). (In (**2**) the corresponding angle is 2.03°). (*For clarity, hydrogen atoms are not shown*)

In (**1**), the internal angles of the cyclopentadienyl ring (except for the C1C5C4 angle) are within the experimental error equal to 108° (Table 1). Only the C1C5C4 angle, where the carbon atom C5 is connected to the tert-butyl group, is 106.2°. The reasons for the decrease in this angle are probably related to the presence of short contacts between the methyl group ($C9H_3$, $C8H_3$) and the corresponding fragment (C1H1, C4H4) of the ring – (C9…C1(3.056(5) Å), H1...H9B(2.353 Å); and C8…C4(3.022(5) Å), H4...H8B(2.285 Å)) (Fig. 3***b***) (see also [10, 11]).

For the carbon atoms of the C_5-ring, the greatest deviation from the middle plane of the ring is observed for the substituted C5 atom (0.01 Å, away from the Mo atom), and the smallest for the C2 atom (0.002 Å, towards the Mo atom). Deviation of the tert-butyl group from the Cp ring plane away from the Mo atom is approximately 9.1° (see also [10,11,20-22]).

The distances of the C–C bonds in the substituted ring range from 1.406 Å to 1.437(4) Å (Table 1). According to [23], the C1–C5 bond, located above the trans-C12O3 group, is the longest bond (1.437 Å) in the ring. The molecular mirror plane C12MoMo^{i}C12^i passing through the carbon atoms of the trans-carbonyl groups intersects the C3–C4 bond.

f – Tert-Butyl Group. The values of the external angles ^{t}BuCp of the ring (C1–C5–C6(127.1°) and C4–C5–C6(125.8°)) indicate that the tert-butyl group is slightly deviated from the straight line Ct–C5 towards the C4H4 fragment of the ring. A joint consideration of the values of these angles with the values of the angles at the quaternary carbon atom (C6) of the ^{t}Bu group (C5–C6–C9(112.4°) and C5–C6–C8(110.9°) (Fig. 3***a***)) allow us to assume that a repulsive force acts on the tert-butyl group (more precisely on the methyl group $C9H_3$) from the left side.



a *b*

Fig. 3. ***a*** – Values of angles C5–C6–C9, C5–C6–C8, and C5–C6–C7 (*hydrogen atoms are not shown for clarity*); ***b*** – non-valent contacts between the methyl group ($C9H_3$, $C8H_3$) and the corresponding fragment (C1H1, C4H4) of the ring

The values of the shortened non-valent contacts of the methyl group $C9H_3$ with the ring fragment C1H1 (C9…C1(3.056(5) Å), (H1…H9B(2.353 Å)) and the methyl group $C8H_3$ with the fragment C4H4 (C8…C4(3.022(5) Å), (H4…H8B(2.285 Å)) (Fig. 3***b***) within the experimental error are the same. Therefore, the deviation of the tert-butyl group from the straight line Ct–C5 towards the C4H4 fragment should be associated with the steric influence of the trans-carbonyl (C12O3) ligand on the methyl group $C9H_3$ (section ***b***).

The above steric influence affects the position of all three methyl groups of the tert-butyl substituent. Thus, under the action of the trans-carbonyl group, the C9 atom of the methyl group $C9H_3$ is slightly raised and becomes closer to the middle plane 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). The influence on the position of the methyl group $C7H_3$ is confirmed by the larger value of the torsion angle C1–C5–C6–C7 (87.0(3)°) compared to the torsion angle C4–C5–C6–C7 (–80.5(3)°). In fact, the tert-butyl group under the action of the trans-carbonyl ligand rotates slightly around the C5–C6 bond in a clockwise direction (if looking above the Mo–Mo bond). If the above-mentioned steric interaction of the methyl group $C9H_3$ did not exist, then the C9 and C8 atoms of both methyl groups, directed toward the metal atom (Mo), would be at the same distance from the plane of the ring, and the indicated torsion angles would be numerically equal [11].

Of the six C–C–C angles at the quaternary carbon atom of the ^{t}Bu group, three angles have values close to tetrahedral (109.5°), two angles – discussed above – (C5–C6–C9(112.4°) and C5–C6–C8(110.9°) are larger, one angle – C5–C6–C7(106.1°) is smaller than tetrahedral (Fig. 3***a***). The decrease in the C5–C6–C7 angle is logically associated with the increase in the C5–C6–C9 and C5–C6–C8 angles from tetrahedral, respectively, to 112.4° and 110.9°, since with these displacements of the methyl groups $C9H_3$ and $C8H_3$, the methyl group $C7H_3$ should deviate towards the Cp ring in order to reduce steric interaction with them.

***g* – *Mo(CO)$_3$ fragment*.** The values of the valence angles between the carbonyl groups of the $Mo(CO)_3$ fragment, as well as between the carbonyl groups and the Mo–Mo^{i} bond, are given in Tables 3 and 4, respectively. For comparison, the values of the corresponding valence angles in complex (**2**) are also given.

1. *Angles between carbonyl groups – C12–Mo–C11, C12–Mo–C10, C10–Mo–C11*

A comparative analysis of the nature and magnitude of the change in angles both between the carbonyl groups and the Ct–Mo–C(CO) angle in complexes (**1**), (**2**) [3] (Tables 3 and 4) and

(^{s}BuCp)$_2$Mo$_2$(CO)$_6$ [4] allows us to reveal that in complex (**1**), under the steric influence of the tert-butyl substituent, the trans-C12O3 group shifts toward the cis-C11O2 group, as a result of which the C12–Mo–C11 angle (76.04°) is approximately 1.8° smaller than the corresponding angle (77.88°) in complex (**2**). In this case, the carbonyl group of cis-C11O2 is raised towards the plane of the ring by approximately 1.06° relative to the position of the corresponding cis-CO group in (**2**). The changes in the other two valence angles C12–Mo–C10(0.4°) and C10–Mo–C11(0.6°) (Table 3), although within the experimental error, however, the nature of this change (increase) correctly reflects the directions of displacement of the trans-C12O3 and cis-C11O2 groups, under the influence of the ^{t}Bu substituent in the ring.

Table 3. Bond angles between CO groups of the Mo(CO)$_3$ fragment in (**1**) and (**2**)

Angles in (1)	(°)	**Angles in (2)***	(°)
C12–Mo–C11	76.04	C7B–Mo1B–C1B	77.88
C12–Mo–C10	79.65	C7B–Mo1B–C8B	79.21
C11–Mo–C10	106.46	C1B–Mo1B–C8B	105.95

* – For complex (**2**), atom designations provided by the Mercury program for its crystal structure are given [3]

1. Angles between carbonyl groups and the Mo–Mo^{i} bond – Mo^{i}–Mo–C12, Mo^{i}–Mo–C11, Mo^{i}–Mo–C10

From the data in Table 4 it follows that in complex (**1**) the nature and magnitude of the change in the above three angles are consistent with the presence of the steric influence of the tert-butyl substituent on the trans-C12O3 group. Thus, in accordance with the indicated interaction, the value of the angle Mo^{i}–Mo–C12 (126.09°) becomes approximately 2.3° less than the corresponding angle (128.36°) in (**2**). This explanation is also confirmed by the value of the angle Mo^{i}–Mo–C$_{\text{trans-CO}}$ in the sec-butyl complex (^{s}BuCp)$_2$Mo$_2$(CO)$_6$ [4], in which the steric influence of the alkyl substituent on the trans-CO group is practically absent. As a consequence, the angle Mo^{i}–Mo–C$_{\text{trans-CO}}$ (128.26°) in the sec-butyl complex, in contrast to the corresponding angle in (**1**) (126.09°), remains virtually unchanged and remains approximately the same (128.36°) as in (**2**) [3].

Table 4. Bond angles between CO groups and the Mo–Mo^{i} bond in (**1**) and (**2**)

Angles in (1)	(°)	**Angles in (2)***	(°)
Mo^{i}–Mo–C11	70.61	Mo1–Mo1B–C1B	71.43
Mo^{i}–Mo–C12	126.09	Mo1–Mo1B–C7B	128.36
Mo^{i}–Mo–C10	71.04	Mo1–Mo1B–C8B	70.96

* – For complex (**2**), atom designations provided by the Mercury program for its crystalline structure are given [3]

The shift of the trans-C12O3 group towards the cis-C11O2 group is accompanied (section ***f-1***) by a slight rise of the latter, as a result of which the cis-C11O2 group comes closer to both the Mo–Mo^{i} bond (Mo^{i}–Mo–C11=70.61(8)° in (**1**) instead of 71.43° in (**2**)), and to the average plane of the ^{t}BuCp ring (Ct–Mo–C11=125.89° in (**1**) instead of 126.95° in (**2**)). An indirect confirmation of a slight lift of the cis-C11O2 group can also be the reduction of non-valent contacts between the cis-CO groups (C11…C10^{i} and C10…C11^{i}) bonded to different Mo atoms (2.771(4) Å in (**1**) compared to 2.810 Å in (**2**) [3]).

The cis-C10O1 group, with the exception of a very weak interaction with the methyl group (C8H$_3$) of the ^{t}Bu substituent (C10…H8C(2.879 Å)), is practically not involved in additional steric interactions, compared to the corresponding cis-CO group of complex (**2**). For this reason, the value of the Mo^{i}–Mo–C10 angle (71.04°) is practically equal to the value of the corresponding angle (70.96°) in complex (**2**) (Table 4).

Conclusions

Thus, in contrast to the binuclear molybdenum complexes of the composition $(RCp)_2Mo_2(CO)_6$ (R = n-propyl, isopropyl, n-butyl, secondary (sec-)butyl, etc.), in which the hydrocarbon radical R is linked to the Cp ring by “its” primary or secondary carbon atom, in the crystal structure of the binuclear complex $(^tBuCp)_2Mo_2(CO)_6$, in the molecule of which the tert-butyl substituent is linked to the Cp ring by “its” tertiary carbon atom, steric interaction between the hydrocarbon radical and the trans-carbonyl (C12O3) group is clearly evident. This interaction is primarily manifested in the values of the Ct–Mo–C12, Mo^i–Mo–C12, C12–Mo–C11 valence angles, in the rotation of the ^{t}BuCp ring around the Ct–Mo axis, away from the trans-carbonyl group, as well as in the structural parameters of the tert-butyl substituent itself. Against this background, the practical invariance of the Ct–Mo–Mo^i angle in (**1**) is considered to be the result of strong steric strain above and below the Mo–Mo bond and rotation of the ^{t}BuCp ring around the Ct–Mo axis, which partially weakens the steric interaction between the tert-butyl and trans-carbonyl groups. Changes in the above-mentioned angles and rotation of the ^{t}BuCp ring, in turn, cause changes in virtually all structural parameters of complex (**1**), including non-valent contacts both between “adjacent” cis-CO groups (C11…C10^i and C10…C11^i) and between cis-CO groups and the “adjacent” substituted ring.

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