EFFECT OF VICINAL TERT-BUTYL GROUPS ON THE CRYSTAL STRUCTURE OF THE UNSUBSTITUTED $Cp_2Mo_2(CO)_6$ DIMER COMPLEX OF MOLYBDENUM

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Abstract: *Comparison of the structural parameters of the monosubstituted complex (^{t}BuCp)$_2$Mo$_2$(CO)$_6$ (**1**) with the corresponding structural parameters of the disubstituted (1,2-^{t}Bu$_2$Cp)$_2$Mo$_2$(CO)$_6$ (**3**) and unsubstituted Cp$_2$Mo$_2$(CO)$_6$ (**2**) complexes allowed us to identify the features of the crystal structure (**3**) caused by the presence of two tert-butyl substituents in the 1,2- (vicinal) position in the cyclopentadienyl (Cp) ring. These features are manifested primarily in the change in the length of the Mo–Mo bond, the magnitude of the rotation angle of both the ^{t}Bu$_2$Cp ring around the Ct–Mo axis and the tert-butyl groups around the C(ring)–C(^{t}Bu) bond, the length of the C–C bonds in both in the cyclopentadienyl C$_5$-ring and the tert-butyl substituent, and the values of the internal and external C–C–C angles of the cyclopentadienyl C$_5$-ring. Most of these features are due to steric interactions observed in the crystal structure (3) between different groups and fragments of the molecule.*

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. [1-6]. 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 [7-10].

Our interest in the crystal structure of the molybdenum complex (^{t}Bu$_2$Cp)$_2$Mo$_2$(CO)$_6$ (**3**) [11] is related to the idea that we used in interpreting the crystal structure of the monosubstituted tert-butyl complex (^{t}BuCp)$_2$Mo$_2$(CO)$_6$ (**1**) [12]. The interpretation of the changes in the structural parameters of complex (**1**) compared to (**2**) [13] was based on the idea of the presence of steric interaction between the tert-butyl substituent in the Cp ring and the trans-carbonyl ligand (C12O3). Indeed, this interaction in (**1**) is quite clearly manifested in the valence angles Ct–Mo–C12, Mo^i–Mo–C12, C11–Mo–C12, as well as in the rotation of the ^{t}BuCp ring around the Ct–Mo axis, away from the trans-carbonyl group. However, with distance from this region of steric interaction, the changes in the structural parameters decrease and become close to the experimental error, which does not allow us to confidently interpret the causes of these changes in the structure of (**1**). Therefore, a comparative analysis of the structural parameters of the monosubstituted complex (**1**) and the sterically more strained complex (**3**) with two bulky tert-butyl groups in the vicinal position can give us additional information that allows us to confirm

or refute some of the assumptions made during the interpretation of the crystal structure of (**1**). At the same time, this analysis will allow us to clarify the features of the crystal structure (**3**) caused by the appearance of the second tert-butyl group in the vicinal position of the Cp ring.

In accordance with the above, *the aim of this work* is to identify the features of the crystal structure of (^{t}Bu$_2$Cp)$_2$Mo$_2$(CO)$_6$ (**3**) [11] known in the literature by means of a comparative analysis of its structural parameters with the corresponding parameters of the monosubstituted derivative (^{t}BuCp)$_2$Mo$_2$(CO)$_6$ (**1**) and the partially unsubstituted complex (Cp)$_2$Mo$_2$(CO)$_6$ (**2**) [13].

Experimental part

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

Crystallographic data for (**1**) have been collected in the Cambridge Crystallographic Data Center, CCDC: 2243119.

The synthesis of complex (**3**) and the X-ray structural study of its single crystal are described in [11]. Since the crystal structure of the monosubstituted complex (**1**) was not known at that time, a comparative analysis of these two structures was not carried out.

Results and discussion

Both complexes (**1**) [12] and (**3**) [11] are in the trans-conformation in the crystalline state. This allows us to make a well-founded comparison of the corresponding parameters and, on this basis, draw certain conclusions about the features of their structure. Thus, a comparative analysis of the structural parameters of (**1**) [12] with the corresponding parameters of (**3**) [11] and, partially, (**2**) [13] showed that the introduction of a second tert-butyl group in the 1,2-position into the ^{t}BuCp ring of complex (**1**) is generally accompanied by a significant increase in steric tension in molecule (**3**).

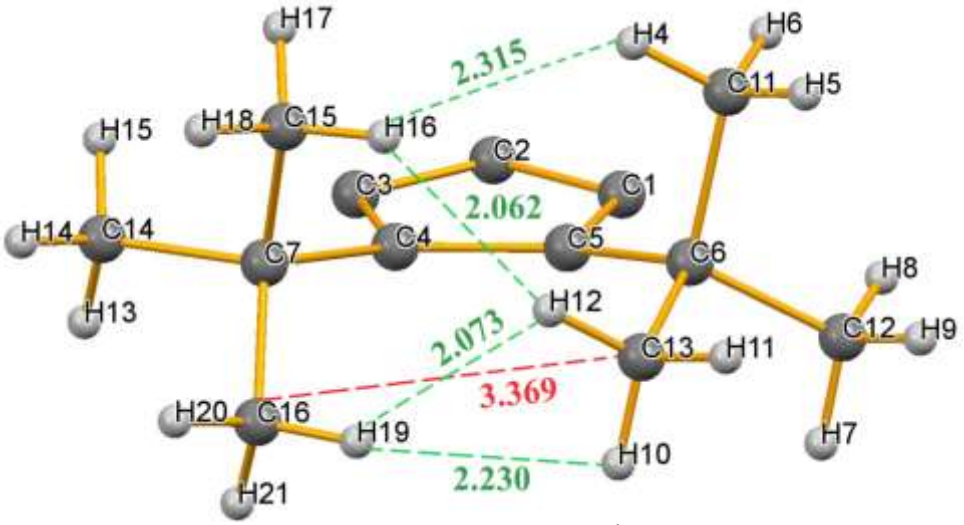


Fig. 1. Shortened non-valent contacts H…H (less than 2.4 Å) and C…C (less than 3.4 Å) between vicinal tert-butyl groups

It was established that steric interactions between the following fragments and groups were observed in the crystal structure of (3):

1. *Vicinal tert-butyl substituents of the ^{t}Bu$_2$Cp ligand;*

2. *Tert-butyl substituents and the trans-CO group;*

3. *Cis-CO groups bonded to the "neighboring" Mo atoms;*

4. *The C$_5$H$_3$-ring and the "neighboring"*

cis-CO groups;

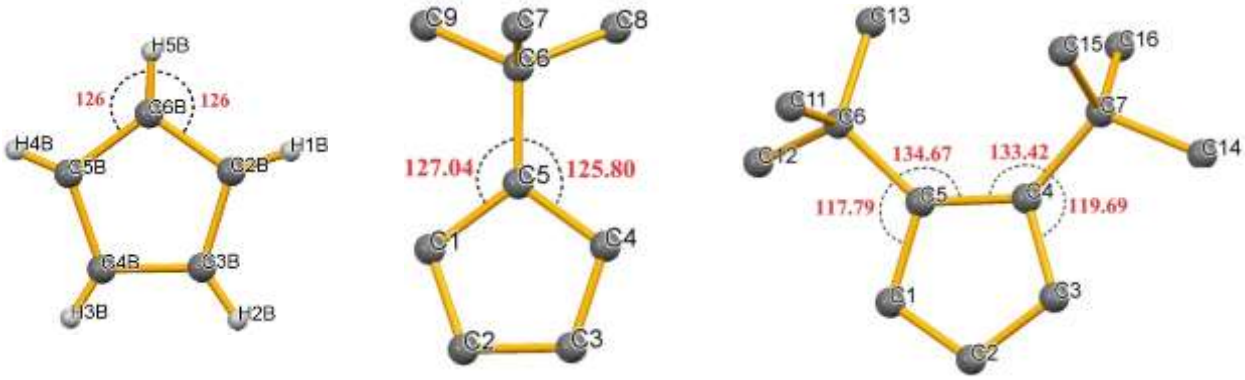
5. *The tert-butyl substituent and the closest CH fragment of the C_5H_3-ring.*

Let us briefly consider what structural data confirm the presence of each of the above types of steric interaction in (**3**).

1. *The steric interaction between the vicinal tert-butyl substituents of the $^tBu_2Cp$ ligand is confirmed by the following features of the crystal structure (**3**):*

a – The presence of short non-valent contacts between the vicinal tert-butyl substituents of the ring (Fig. 1).

b – Deviation of the values of the external angles of the $^tBu_2C_5H_3$ ligand (C1–C5–C6 (117.79°), (C4–C5–C6 (134.67°), C5–C4–C7 (133.42°) and C3–C4–C7 (119.69°)) by 6–8° from the ideal value (126°) of this angle in the undistorted Cp ligand (Fig. 2). The values of these angles in (**3**) differ by approximately the same amount from the values of the angles (125.80° and 127.04°) observed in the tert-butylcyclopentadienyl ($^tBuC_5H_4$) ligand of complex (**1**) (Fig. 2).



undistorted Cp ligand $^tBuC_5H_4$ ligand in (**1**) $^tBu_2C_5H_3$ ligand in (**3**)

Fig. 2. Differences in the values of external C–C–C angles in $^tBuC_5H_4$ and $^tBu_2C_5H_3$ ligands of complexes (**1**) and (**3**).

c – Rotation of the tert-butyl substituents around the C4–C7 (≈26°) and C5–C6 (≈11°) bonds counterclockwise (if viewed above the Mo–Mo bond). The values of the rotation angles (26° and 11°) are given relative to the position of the tert-butyl substituent in (**1**).

d – Elongation of the C4–C5 bond (1.465 Å) and the accompanying changes in the internal angles of the ring.

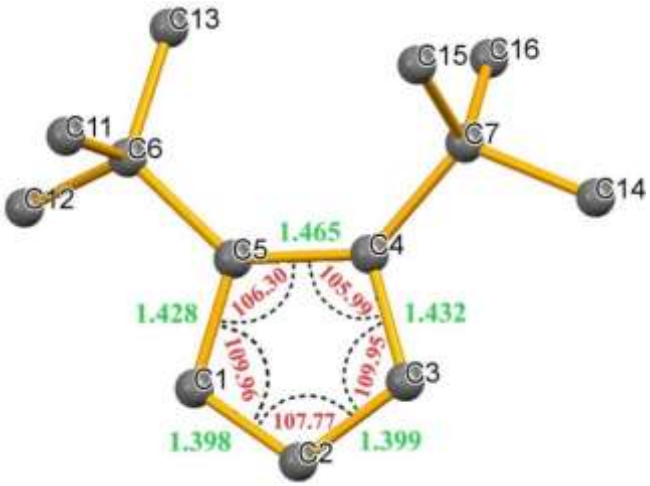


Fig. 3. Elongation of the C4–C5 bond and the accompanying changes in the internal angles of the C_5-ring in (**3**)

In (**3**), the bond between the substituted carbon atoms of the ring, i.e. the C4–C5 bond (1.465 Å) is noticeably longer than both the neighboring C–C bonds (1.432, 1.428, 1.399, and 1.398 Å) (Fig. 3) and the C–C bonds in the ^{t}BuCp (1.437–1.398 Å) and Cp (1.408–1.399 Å) rings of complexes (**1**) [12] and (**2**) [13].

The elongation of the C4–C5 bond in (**3**) is accompanied by a decrease in the internal angles C1–C5–C4 and C3–C4–C5 (by 1.7–2°) and an increase in the angles C2–C1–C5 and C2–C3–C4 (by 2°) (Fig. 3) relative to the ideal value of the internal angle of a regular pentagon (108°). In this case, the angle C1–C2–C3 (107.77°) remains virtually unchanged and retains a value close to the ideal value (108°).

e – Deviation of vicinal tert-butyl substituents from the mean plane of the ^{t}Bu$_2$C$_5$H$_3$ ring away from the Mo atom. Thus, in complex (**3**), the tert-butyl substituent at C5 deviates by 13.12° from the mean plane of the ^{t}Bu$_2$C$_5$H$_3$ ring away from the Mo atom, and the tert-butyl substituent at C4 – by 11.34°, which is noticeably larger than in the case of the methyl substituent [15-19].

2. *Steric interaction between tert-butyl substituents and the trans-CO group*

The presence of the above-mentioned steric interaction in (**3**) (Fig. 4) is indicated, first of all, by changes in the values of the valence angles Ct–Mo–C$_{trans\text{-}CO}$, Mo^i–Mo–C$_{trans\text{-}CO}$ and Ct–Mo–Mo^i in the series of complexes (**2**)→(**1**)→(**3**) (Table 1). Moreover, the changes in these valence angles in (**3**) are greater than in the monosubstituted tert-butyl complex (**1**).

Table 1. Values of the bond angles Ct–Mo–C$_{trans\text{-}CO}$, Mo^i–Mo–C$_{trans\text{-}CO}$ and Ct–Mo–Mo^i in (**2**), (**1**) and (**3**).

Bond Angle	Complex (**2**) [13]	Complex (**1**) [12]	Complex (**3**) [11]
Ct–Mo–C$_{trans\text{-}CO}$, (°)	113.89	116.27	118.49
Mo^i–Mo–C$_{trans\text{-}CO}$, (°)	128.27	126.27	124.46
Ct–Mo–Mo^i, (°)	117.75	117.54	117.04

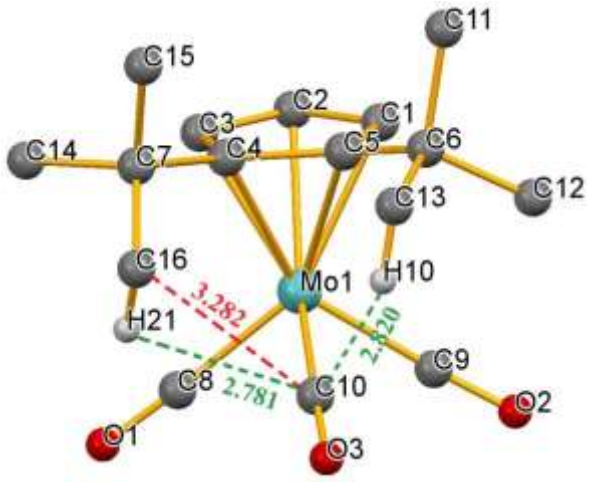


Fig. 4. Shortened non-valent contacts between tert-butyl substituents and trans-CO group in molecule (**3**)

It should be noted that in (**3**) the steric interaction between the trans-carbonyl group and the tert-butyl substituent at C4 is also reflected in a slight shortening of the Csp^3(16)–Csp^3(7) bond (1.525(8) Å) relative to the length of 1.54 Å usually accepted for the Csp^3–Csp^3 bond [20] and in the rotation of the ^{t}Bu$_2$C$_5$H$_3$ ring around the Ct–Mo axis, away from the trans-carbonyl group by approximately 2.12°, compared to the position of the Cp ring in (**2**).

3. *Steric interaction between cis-CO groups bound to "neighboring" Mo atoms (contacts C9…C8A and C8…C9A)*

In molecule (**3**), the lengths of non-valent contacts between the carbon atoms of the cis-carbonyl groups bound to the "neighboring" Mo

atoms (C9…C8A and C8…C9A) are less than the sum of the van der Waals radii of two carbon atoms (3.4 Å) (Fig. 5). Therefore, there are steric interactions of a repulsive nature between the indicated cis-CO groups. Moreover, in (**3**), the steric interaction between the cis-CO ligands bound to the "neighboring" Mo atoms is enhanced compared to the corresponding interactions in (**2**) and (**1**). This is evident from the monotonic nature of the reducing the length of non-valent contacts cis-CO…cis-C^iO^i in the sequence (**2**) → (**1**) → (**3**) – 2.810 Å in (**2**) [13] → 2.771 Å in (**1**) [12] → 2.765 Å in (**3**) [11]. In our opinion, one of the reasons for the stretching of the Mo–Mo bond (3.253 Å) in (**3**) are the aforementioned short C9…C8A and C8…C9A contacts (2.765 Å) between the two halves of the molecule.

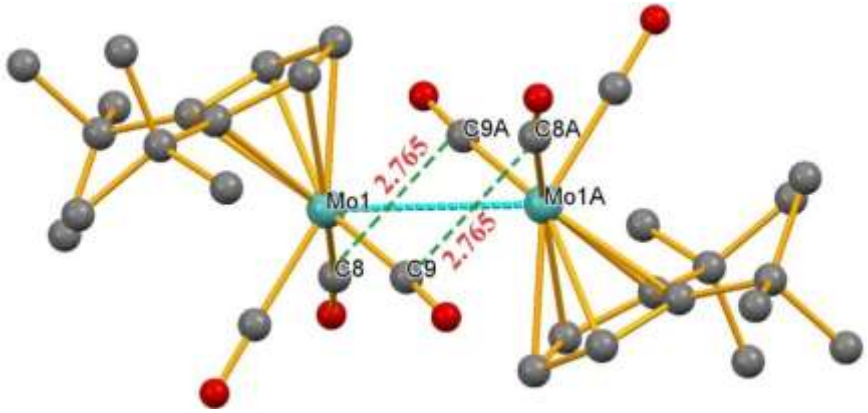


Fig. 5. Shortened non-bonded contacts between cis-CO groups bound to the "adjacent" Mo atoms (C9…C8A and C8…C9A) in (**3**)

4. *Steric interaction between the C_5H_3-ring and the "adjacent" cis-CO (C9AO2A, C8AO1A) groups.*

The values of non-bonded contacts between the hydrogen and carbon atoms of the ring and the C and O atoms of the "adjacent" cis-CO groups in (**2**), (**1**) and (**3**) are given in Table 2. In principle, in the series of complexes (2)→(**1**)→(**3**), the monotonic nature of the primary structural changes caused by the steric interaction between the substituent and the trans-carbonyl group (Table 1) should lead to a consistent reducing the length of non-valent contacts between the two halves of the molecules. In Section **3** we demonstrated this using the example of the reducing of cis-CO…cis-C^iO^i contacts. However, from Table 2 it follows that when transition from (**1**) to (**3**), the lengths of contacts between the ring atoms and the atoms of the "neighboring" cis-CO groups (with the exception of C2…C9A (3.315 Å)) not only do not reduce, but on the contrary, increase.

Table 2. The lengths of non-valent contacts between the ring atoms and the atoms of the "neighboring" cis-CO groups in (**2**), (**1**) and (**3**) are less than 3.4 Å(C…C), 2.9 Å(C…H), 2.72 Å(O…H) and 3.22 Å(C…O).

Non-valent contact in (**2**), Å)*	Non-valent contact in (**1**), (Å)	Non-valent contact in (**3**)*, (Å)
–**	H4...$O2^i$ – 2.596	H3…O2A – 2.675
–**	C4...$O2^i$ –3.212	C3…O2A – –**
C2…C1B – 3.346	C4…$C11^i$ – 3.268	C3…C9A – 3.289
C3…C1B – 3.291	C3…$C11^i$ –3.354	C2…C9A – 3.315
H2…C8B – 2.856	H3...$C10^i$ – 2.766	H2…C8A – 2.867
C3…C8B –3.227	C3...$C10^i$ – 3.154	C2…C8A – 3.188

* – For (**1**), (**2**) and (**3**) the atomic designations provided by the Mercury program for their crystal structures are given [13, 12, 11]
** – The lengths of these contacts are greater than the sum of the van der Waals radii of the corresponding atoms.

Obviously, the elongation of the Mo–Mo bond (3.253 Å) in (**3**) cannot explain the observed changes in the lengths of contacts between the ring atoms and the atoms of the "neighboring" cis-CO in the series (**2**), (**1**) and (**3**) in Table 2. Because in (**3**) the contact C2…C9A (3.315 Å), unlike the other four contacts, is shortened. Therefore, the reasons for the observed tendency of changing the degree of steric interaction between the ring atoms and the atoms of the "neighboring" cis-CO groups in (**3**) should most likely be associated with changes in the structural parameters of the ring upon transition from (**1**) to (**3**).

5. *Steric interaction between the tert-butyl substituent and the nearest CH fragment of the C_5H_3-ring.*

The lengths of the non-valent contacts (C…C, C…H and H…H) between the ^{t}Bu substituent at the C4 atom and the C3H3 fragment of the ring, as well as between the ^{t}Bu substituent at C5 and the C1H1 fragment (Fig. 6) indicate that significant steric interactions exist between them. However, it should be noted that the degree of steric interaction of the ^{t}Bu substituents with the corresponding CH fragments does not correspond to the value of the external C–C–C angle between the interacting fragments. In particular, the lengths of non-valent contacts between the ^{t}Bu substituent and the C3H3 fragment are shorter than the contacts between the second ^{t}Bu substituent and the C1H1 fragment, while the external angle at the C3H3 fragment (C3–C4–C7(119.69°)) is larger than the external angle C1–C5–C6(117.79°) at the C1H1 fragment.

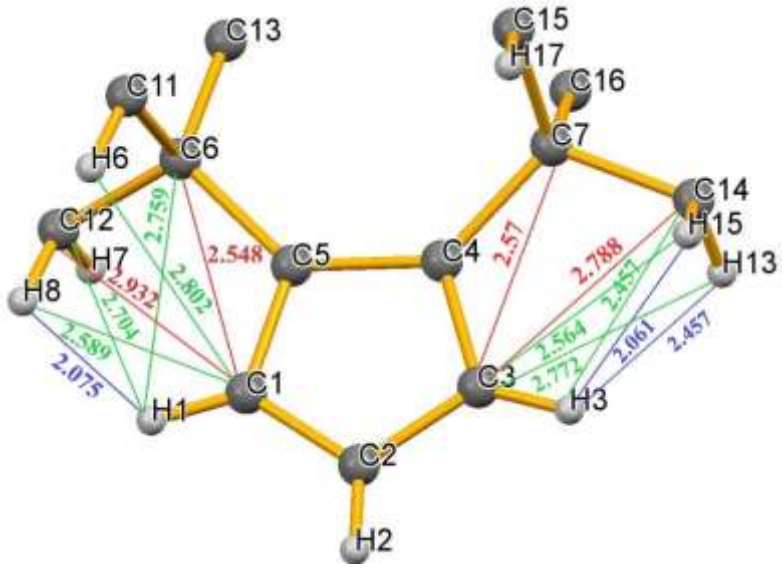


Fig. 6. Steric interactions of ^{t}Bu substituents with C3H3 and C1H1 fragments of the C_5H_3-ring in (**3**)

Steric interactions of ^{t}Bu substituents with C1H1 and C3H3 fragments of the ring very likely also cause the elongation of the C3–C4 and C1–C5 bonds of the ring (Fig. 4), since the positive inductive effect of two tert-butyl substituents should, in principle, lead to a shortening of these bonds. We hope that a more detailed examination of both the mutual influence of tert-butyl substituents and their interaction with the trans-carbonyl group will allow us to more clearly present the reasons not only for the above-mentioned discrepancies, but also for a number of features of the crystal structure (**3**), noted in sections 1–4 of this article.

Conclusion

Understanding the reasons for the change in the structural parameters of the monosubstituted complex (^{t}BuCp)$_2$Mo$_2$(CO)$_6$ (**1**), compared to the corresponding parameters of the unsubstituted complex Cp$_2$Mo$_2$(CO)$_6$ (**2**) allowed us to identify a number of features of the crystal structure of a sterically more complex molecular system – (1,2-^{t}Bu$_2$Cp)$_2$Mo$_2$(CO)$_6$ (**3**). These features are due to several types of steric interactions that act between the tert-butyl substituents themselves and between the tert-butyl substituent and the trans-carbonyl group, as well as between the substituent and the nearest CH ring fragment. In addition, steric interactions of cis-carbonyl groups with cis-CO groups and the C_5H_3-ring at the "neighboring" Mo atom also contribute to the formation of structural features (**3**). The essence of these structural features allows us to conclude that in changes in the structural parameters of such sterically highly strained binuclear complexes; the steric factor of the alkyl substituent plays a decisive role, rather than its electronic factor.

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