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STERIC FACTOR DEPENDENCE OF THE STRUCTURES OF CERTAIN Cp-CONTAINING COMPOUNDS

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Summary

A simple procedure for quantitative estimation of steric hindrance is proposed. The method suggested enables one to solve a priori the problem related to steric hindrance in any hypothetical mononuclear complex. The possibilities of the system offered are demonstrated for compounds of the type MCp_n. If the sum of normalized solid angles $\sum_{i=1}^{n} (S_i/r_i^2)$ exceeds unity or is appreciably less than unity, then structural rearrangements take place in such a molecule.

Non-valent interactions in a molecule are known to affect its structure significantly, particularly if the molecule is sterically overloaded. In the majority of cases, researchers restrict themselves only to a qualitative description of the distortions that occur in the geometry of a molecule. Nonetheless, there are several ways of estimating steric factors quantitatively; for every ligand, a certain parameter depending on the ligand form is introduced which is proportional to its dimensions. As the steric characteristic of a ligand, Tolman [1] suggests the use of the value of the apex angle of a cone enclosing the given ligand. The atoms of the ligand in this case form the edges with the corresponding intermolecular radii and the vertex of the cone coincides with the complexing atom. The Tolman technique enables the variation in some geometric, energy and kinetic parameters to be explained satisfactorily for a number of transition metal complexes with tertiary phosphines.

For quantitative estimation of the spatial screening of the metal atom in compounds of the type MR_n, Soviet researchers, for instance Titova et al. [2], have made use of the solid angle with its vertex at atom M which is filled with ligand R whose atoms are also defined by the rigid spheres of Van der Waals radii. The sum of solid angles for all n ligands of a molecule characterizes the extent to which the central atom is screened and correlates well with the thermal stability data of these compounds.

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The extension of Tolmans's concept of cone angles to cluster compounds is discussed in ref. 3.

Extensive use of "steric calculations" is restricted by the non-availability of a simple and universal procedure similar to the idea of covalent radii. However, the interest in this problem is not subsiding. This is demonstrated by the number of publications dedicated to the topic, for example refs. 4 and 5, in which the idea of using solid angles of ligands has been elaborated and, in our opinion, unjustifiably made complex.

The author has proposed a procedure for quantitative estimation of steric hindrance; it is free of certain disadvantages inherent in the methods described earlier [6]. In particular, it is not necessary to make use of Van der Waals radii, which are known to be unsuitable in calculating intermolecular non-valent distances. Besides, the proposed method enables one to solve a priori the problem related to steric hindrance in any arbitrary hypothetical mononuclear complex.

The method suggested in ref. 6 consists in the fact that the solid angle of a ligand is computed not from its model, but is determined in the following manner from the experimental data. Obviously, non-valent contacts between ligands are established in a mononuclear complex at some distance r from its centre. The line of contact divides the surface of the sphere of radius r into regions with areas S_i. By definition, the solid angle taken over by one ligand equals S_i/r_i^2. The sum of solid angles of all ligands of the complex containing n ligands is equal to 4π radian, i.e. $\sum_{i=1}^{n} (S_i/r_i^2) = 4\pi$. Dividing both sides of this equality by 4π gives

$$\sum_{i=1}^{n} (S_i'/r_i^2) = 1 \tag{1}$$

where $S_i' = S_i/4\pi$.

Having carried out calculations for any ligand in each of the structurally studied compounds of type ML_n (for these compounds, S' is readily determined because eq. 1 becomes the product $nS'/r^2 = 1$; hence, $S' = r^2/n$), we obtain in general a set of different values of S' for ligand L. The minimum value, i.e. $(S')_{\min}$, depends, apparently, only on the dimensions of the ligand, its form and its ability to deform. As this value is determined by the steric requirements of the ligand, we shall use it as the steric characteristic of the ligand and denote it by $\mathcal{S}$.

In a similar manner, one can find $\mathcal{S}$ for most common ligands. Taking into account the fact that a minimun value of constants is used, it can be ascertained that the inequality

$$\sum_{i=1}^{n} (\mathcal{S}_i/r_1^2) \leqslant 1 \tag{2}$$

holds for any mononuclear complex with a large probability. The value r_i appearing in this inequality is, as a rule, the distance between the central atom of the complex and that atom of the ligand with which the metal–ligand chemical bond is accomplished. Indeed, in a mononuclear complex molecule a closer interligand contact exists, as a rule, between the ligand atoms next to its centre, because the more remote parts of the ligand molecule have for their location a sufficiently large volume of the coordination space, which increases in proportion to the cube of the distance measured from the centre of the complex. Besides, a molecule gets rid of possible stresses between remote parts of the ligands because the ligands are able to turn near the M–L direction.

The calculations made by assuming cone or solid angle computed from a model of a molecule framed by balls of Van der Waals radii [1–5] to be the steric characteristic of a ligand help in the comparison of any molecular parameter for several related compounds. The method proposed in ref. 6 enables a definite forecast to be made for an arbitrary, separately taken, molecule. It is sufficient to have tabulated values of $\mathcal{S}$ and to compute r as the M–L distance using covalent radii of elements. The obtained sum of normalized solid angles $\sum_{i=1}^{n} (\mathcal{S}_i/r_i^2)$, denoted in further discussion by Σ, is the characteristic density of filling the coordination space of the central atom of the complex. If $\Sigma > 1$, then the corresponding molecule will probably be very unstable due to overloading. And what is more, if Σ proves to be much less than unity, then the molecule will most probably be labile; in this case, this will be due to coordination underloading. Here, it must be stressed that these prognoses are a necessary, but not sufficient, condition of the existence of a molecule.

The prognostic possibilities of the proposed method show up more completely in those cases when the interligand contacts in a molecule are attained in a comparatively thin spherical layer and the ligands are not too branched, because otherwise intramolecular packing of ligands will start to play a major role. These conditions are fulfilled by MCp_n-type compounds, which are the subject of study of this report.

For subsequent computations, we have to know the characteristic areas $\mathcal{S}$ for η^5- and η^1-cyclopentadienyl ligands. According to ref. 6, $\mathcal{S}(\eta^5\text{-Cp})$ 2.05 and $\mathcal{S}(\eta^1\text{-Cp})$ 0.65 Å^2.

Table 1 contains the computed values only for the most typcial compounds, but not for all the structurally studied compounds of type MCp_n, their number being

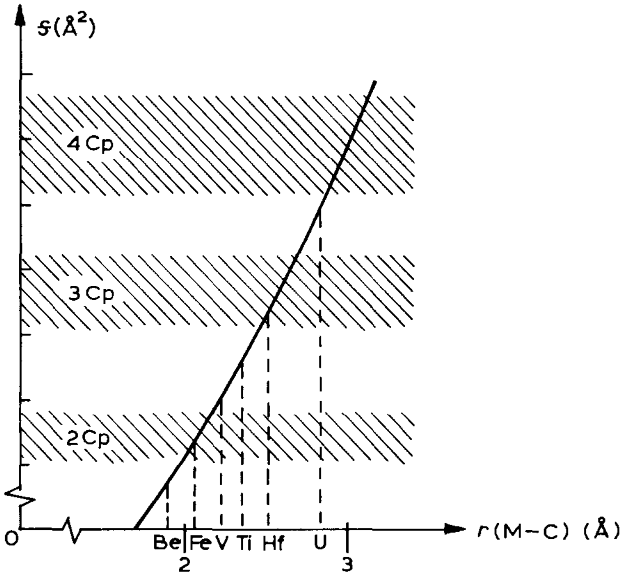

Fig. 1. Graphic solution of the equation $n\mathcal{S}(\text{Cp})/K$, $I \geqslant K \geqslant 0$ 85.

very large. From this, one can conveniently follow the general laws.

The second column of Table 1 contains the sum of normalized solid angles Σ_c; it has been computed on the assumption that all n cyclopentadienyl ligands of molecule MCp_n are connected to the metal atom through a π-bond. If this sum exceeds unity or is appreciably less than unity, then rearrangements take place in the molecule. As a result of these arrangements, the coordination sphere of the metal atom (given in column 3) is so filled that the filling density of the coordination space in an actual molecule Σ_a attains a standard value.

If in a molecule of the compound $BeCp_2$ both Cp rings are bonded with the Be atom through π-bonds, then $\Sigma_c = 1.09$. Obviously, this molecule would be overloaded. The hindrance is removed by shifting one of the rings into the sandwich plane; at the expense of this, Σ_a in the actual molecule decreases to 0.92. In classical dicyclopentadienyl metals of the ferroceno type, the metal atom is located between two parallel η^5-Cp rings. Such a molecular structure is realized for metals with covalent radius varying between 0.98 and 1.28. The sum of normalized solid angles is in the range from 0.98 to 0.85. Vanadocene occupies a special place; its Σ_a is very low and equals 0.81, i.e. two η^5-Cp rings do not saturate the metal coordination space. As a result, the labile molecule of vanadocene acts as a catalyst for D–H exchange in benzene. Besides, it is known that vanadocene can bond to an additional ligand, for instance chlorine, with the formation of a wedge-type sandwich.

The decrease of Σ_c in the hypothetical sandwich titanocene $Ti(\eta^5\text{-}Cp)_2$ to 0.74 results in the non-existence of such a molecular structure. According to indirect data, the titanium atom in $TiCp_2$ attains steric saturation due to the formation of dimers with a Ti–Ti bond and bifunctional Cp rings [20].

In $TiCp_3$, $TiCp_4$, $ScCp_3$, $HfCp_4$ and $ZrCp_4$, the molecules with a stoichiometric amount of (η^5-Cp) groups are unstable due to overloading ($\Sigma_c > 1$). Steric hindrance is removed because one or two rings happen to be bonded with the metal through a σ-bond. Such a ring requires, of course, much less space ($\mathcal{S} = 0.65$) and, as a result, Σ_a decreases to acceptable values. In a molecule of $TiCp_3$, two η^5-Cp rings form a wedge-shaped sandwich in the fissure of which enters the third ring bonded to the Ti atom only by two carbon atoms. For $TiCp_4$, a molecular structure with two η^5-Cp and two σ-Cp rings is realized. Here, it may be noted that for bicyclopentadienyl compounds of transition metals with covalent radii exceeding 1.30, the formation of molecules with a wedge-shaped sandwich conformation is generally typical.

In tricyclopentadienyl scandium, the steric hindrance is removed by polymerization [12]. Wedge-like sandwich fragments of $ScCp_2$ are bonded with bridge-type σ-Cp rings, which in the case given prove to be bidentate. As a result, every scandium atom coordinates two η^5-Cp and two η^1-Cp rings. A similar composition of the coordination sphere of the metal atom is found in the monomer $HfCp_4$. The $ZrCp_4$ molecule is significantly different from its hafnium analogue. In it, the Zr atom is coordinated by three η^5-Cp rings and one η^1-Cp ring. The spatial load increases (compared to $HfCp_4$) and, as a consequence, the molecule expands appreciably: the interatomic Zr–C distances are greater than the corresponding Hf–C distances (by 0.08 Å [17]).

$NdCp_3$, $SmCp_3$ and $ThCp_3$ compound containing metal atoms with large covalent radii would be sterically underloaded even if all three rings in the monomer molecule were bonded through π-bonds (Σ_c less than 0.80). As a consequence, association takes place in all of these compounds and, by virtue of this, the Cp rings of neighbouring molecules become unfixed in the metal coordination sphere. These bridge-type rings prove to be bifunctional: with one metal atom they are bonded through a π-type bond and with the other through a σ-type bond. The most diverse structures are possible in this case: the $\mathrm{NdCp_3}$ molecule is tetrameric, $\mathrm{SmCp_3}$ is polymeric, and $\mathrm{ThCp_3}$ is dimeric. The filling density of the metal coordination space increases in all cases up to reasonable values.

Uranium tetracyclopentadienyl is made up of monomeric molecules. All the rings are of the η^5-Cp type. Σ_a is very large; the molecule is overloaded and that is why the U–C bond length increases to 2.83 Å [19]; this is 0.1 Å more than the corresponding distances in unstressed molecules of uranium.

Let us now represent graphically the results obtained. As shown above, the value of Σ for actually existing molecules lies between 1 and 0.85. For compounds of the type $\mathrm{M}(\eta^5\text{-Cp})_n$, formula (2) may be written as: $n\mathcal{S}(\mathrm{Cp})/r^2 = K$, where $K = 1 \div 0.85$. Hence

$$n\mathcal{S}(\mathrm{Cp})/K = r^2 \tag{3}$$

The left-hand side of this equality is the area required to accommodate n ligands of the η^5-Cp type. Precisely, this is the range of minimum (for $K = 1$) and maximum (for $K = 0.85$) areas. The right-hand side is proportional to the area of a sphere of radius r, i.e. it characterizes the coordination capacity of a metal atom. In Fig. 1 we have plotted r in Å on the ordinate and $n\mathcal{S}(\mathrm{Cp})/K$ on the abscissa. The horizontal shaded bands conform to the ranges of the values of $n\mathcal{S}(\mathrm{Cp})/K$ for different n, K varying between 1 and 0.85. The lower boundary of each band corresponds to $K = 1$, i.e. it is indicative of the minimum space required to accommodate n η^5-Cp groups. The upper boundary conforms to maximum free filling of the metal coordination sphere ($K = 0.85$). It should be borne in mind that our arguments are probably. They can be formulated in the following manner: the central part of the band

TABLE 1

SUM OF NORMALIZED SOLID ANGLES $\sum_{i=1}^{n} (\mathcal{S}_i/r_i^2)$ FOR SOME MOLECULES OF TYPE MCp_n

Compound	Σ_c	Actual composition of the metal atom coordination sphere	Σ_a	Reference
$\mathrm{BeCp_2}$	1.09	$1(\eta^5\text{-Cp}), 1(\eta^1\text{-Cp})$	0.92	12
$\mathrm{FeCp_2}$	0.98	$2(\eta^5\text{-Cp})$	0.98	8
$\mathrm{CrCp_2}$	0.85	$2(\eta^5\text{-Cp})$	0.85	9
$\mathrm{VCp_2}$	0.81	$2(\eta^5\text{-Cp})$	0.81	10
$\mathrm{TiCp_2}$	0.74			
$\mathrm{TiCp_3}$	1.10	$2(\eta^5\text{-Cp}), 1(\eta^2\text{-Cp})$	0.93	11
$\mathrm{ScCp_3}$	1.00	$2(\eta^5\text{-Cp}), 2(\eta^1\text{-Cp})$	0.86	12
$\mathrm{NdCp_3}$	0.79	$3(\eta^5\text{-Cp}), 1(\eta^1\text{-Cp})$	0.86	13
$\mathrm{SmCp_3}$	0.79	$3(\eta^5\text{-Cp}), 1(\eta^2\text{-Cp})$	0.92	14
$\mathrm{ThCp_3}$	0.77	$3(\eta^5\text{-Cp}), 1(\eta^1\text{-Cp})$	0.87	15
$\mathrm{TiCp_4}$	1.42	$2(\eta^5\text{-Cp}), 2(\eta^1\text{-Cp})$	0.96	16
$\mathrm{ZrCp_4}$	1.14	$3(\eta^5\text{-Cp}), 1(\eta^1\text{-Cp})$	0.96	17
$\mathrm{HfCp_4}$	1.14	$2(\eta^5\text{-Cp}), 2(\eta^1\text{-Cp})$	0.88	18
$\mathrm{UCp_4}$	1.02	$4(\eta^5\text{-Cp})$	1.02	19

conforms to most favourable spatial conditions and on approaching the edges of this band these conditions deteriorate in the direction of over- or underloading. The solid line is a quadratic function of r^2. Obviously, the interaction of this curve with the horizontal bands gives a solution to eq. 3 and the coordinates of the points of intersection of the r^2 curve with the band boundaries yields, for a definite n, a range of M–C bond lengths. Thus, one obtains a list of metals that can coordinate n η^5-Cp groups. Therefore, knowing the interatomic distance M–C, one can determine, using the curve, how many η^5-Cp groups saturate the coordination space of the given metal atom, and can also find the possibility of combining additional ligand. For instance, it is seen from Fig. 1 that a beryllium atom cannot coordinate two η^5-Cp groups; for a titanium atom, two η^5-Cp groups are not enough to saturate the coordinate space, but three would be too much. Neodymium atom, in addition to three η^5-Cp groups, can take up an additional ligand with steric constant S less than that of cyclopentadienyl. Using the graph, similar information can be obtained for any transition metal.

In conclusion, we shall consider another application of our technique. The molecules of monochlorides of dicyclopentadienyl compounds of metals, Cp_2MCl, are known to be both monomeric and dimeric. In a series of compounds, for example Cp_2VCl, Cp_2ScCl and Cp_2YCl, due to an increase in the size of the metal atom, and, hence, its coordination capacity, the space filling density Σ_c in a monomeric molecule decreases from 0.95 for V to 0.81 for Sc and 0.72 for Y. Therefore, there is no (dimensional) hindrance to the formation of a monomeric Cp_2VCl molecule; scandium and, particularly, yttrium analogues should be unstable due to underloading. According to ref. 20, the Cp_2VCl molecule is indeed monomeric. The scandium compound yields dimers with chlorine cross-links [21]. In the $(Cp_2ScCl)_2$ molecule, an additional atom of chlorine enters into the metal atom coordination sphere and, as a result, Σ_a increases up to a satisfactory value of 0.94. Note that the vanadium dimer, in which Σ_c is much greater than unity, i.e. $\Sigma_c = 1.10$, is not formed. In the dimer molecule $(Cp_2YCl)_2$ [22], there is obviously coordination underloading ($\Sigma_a = 0.84$). Combination of an additional ligand is therefore possible with the formation of compounds $(Cp_2YCl)_2AlH_3OEt_2$ [23] and $(Cp_2YCl\ AlH_3NEt_3)_2$ [24], in which, besides two η^5-Cp groups and two chlorine atoms, one hydrogen atom belonging to the alan molecule enters into the coordination sphere of the yttrium atom.

Thus, the proposed technique makes it possible to obtain easily and readily a priori useful information about the degree of filling of the coordination sphere of the central atom of a complex and to infer the stability of various molecular configurations.

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