

A Role of Non-bonding Interactions in the Chemistry of Organometallic Compounds

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(Received October 3, 1988)

Abstract

The degree of space shielding of skeleton metal atoms by ligands (radicals) in molecules of organometallic compounds, comprising metal atom chains or plane metal cycles, is calculated. The calculations involved constructing the projection of the molecule onto the closed, continuous surface embracing metal skeleton, as well as calculation of the total (S) and shielded area (S_g) squares of this surface. The ratio $K = S_g/S$ was taken as a shielding degree. A role of non-bonding interactions in the formation of the molecule structure and the structure of a condensed state of organometallic compounds are discussed.

In the last years quantitative calculations of the size of ligands (radicals) in organometallic compounds (OMC) are used for investigation of non-bonding interactions ligand (radical)–ligand (radical) (R...R) influence on the structure and properties of OMC. The investigation of non-bonding interactions in molecules using calculation of solid angles of substituents (ligands) enables one to reveal characteristic properties of molecular structure dependent on those interactions, as well as to study the relation of the structure with various properties, in particular with reactivity [1–5], stability of OMC in various synthesis–decomposition processes [1, 3–5], volatility [6, 7], complex formation [8] etc. From our point of view such works are primarily useful for the proper quantitative understanding of various processes with participation of OMC.

Tolman's cone angles method is one of the approaches to the problem [9]. A limitation of this method is that the calculation of the cone angle of ligands (radicals) in various compounds has been carried out only for one metal–ligand distance. This limitation is cleared away in the works [1, 2] where it has been proposed to make use of the solid angle q (radian) formed by ligands (radicals) on metal atoms and the values of q relationship versus M–R distance were calculated, allowing evaluation of a coordination environment at a metal atom (atoms) or metal atom (atoms) shielding by ligands (radicals) for various compounds. A similar approach has been

developed in other works [4, 5, 10]. There are some other versions of such evaluations based on considering the nearest coordination environment at a central metal atom [11, 12], evaluation of a cone angle in analytical form [13, 14], using cone angles for metal clusters [15], as well as on evaluation of ligand profile [16]. For OMC molecules, comprising metal–metal (M–M) bonds similar evaluations based on the calculation of a cylindrical projection for the molecule with a M–M bond have been proposed [1, 2, 17].

The methods mentioned above can be used only for OMC molecules with one or two metal atoms and are not applicable in the general case for polynuclear OMC with more complex structure containing chains, cycles or polycycles formed of metal atoms connected by M–M bonds. The authors of this article worked out the computer program for calculation of the degree of space shielding of skeleton metal atoms by ligands (radicals) in OMC molecules, comprising metal atom chains with arbitrary length and geometry or plane metal cycles (in particular, M_3 fragments in metal clusters) [18]. The calculations involved constructing the OMC molecule projection onto the closed, continuous surface embracing metal skeleton, as well as calculation of the total (S) and shielded area (S_g) squares of this surface. In the case of the OMC comprising metal chains, the mentioned surface is formed by integrated portions of cylindrical (a cylinder axis coincides with a M–M bond) and spherical (sphere centers are located in the metal atoms) surfaces of the same radius, while for the OMC comprising the plane metal cycle it is formed by integrated portions of cylindrical and spherical surfaces as well as by two planes that are parallel to the metal cycle. Projection on the cylinder and the sphere has been constructed in cylinder and spheric coordinate systems correspondingly and that on the plane has been normal to the latter. The ratio $K = S_g/S$ was taken as a shielding degree. In all cases atoms were represented by balls with corresponding van der Waal's radii. Figures 1–3 illustrate the method of molecule projection constructing.

Modelling of the closed surface through integration of the necessary number of spheric and cylindric surface portions, as well as the planes seems quite

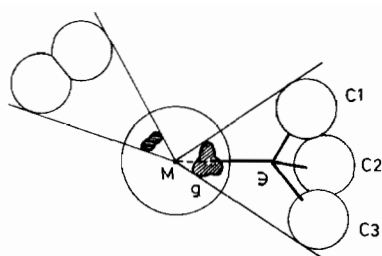


Fig. 1. Scheme illustrating calculation of a solid angle of a ligand (radical).

natural, by virtue of the fact that it takes into account the real geometry of the OMC molecules and allows calculations of the shielding degree for any OMC type to be carried out. For example one can use the projection on the sphere with the center in a metal atom for the mononuclear OMC and on the cylinder and two semispheres with the center in atoms M_1 and M_2 for a binuclear OMC with a M_1-M_2 bond, the cylinder axis coinciding with that bond.

In the molecule structure of OMC non-bonding interactions govern the coordination environment of the active center that is a metal atom (atoms).

Criterion $K \leq 1$ (or $Q \leq 4\pi$ that is equivalent to it, where $Q = \sum_i^n q_i$, n = number of ligands (radicals) in the case of OMC with one metal atom) enables one to estimate the abilities of various atoms and ligands (radicals) to form all kinds of OMC molecules as well as the absence of barriers to the molecule formation due to non-bonding interactions $R \dots R$. From our point of view this criterion supplements the reconstruction analysis of the OMC molecule structure by Hoffmann [19] based on electronic structure.

The criterion $Q \leq 4\pi$ can be used also for the OMC with several metal atoms, which may be considered as composed of separate metal atoms. For example it is known that the insertion of one PtL_2 fragment ($L = PPh_3$) into the $Hg-X$ bond in $R_3X-Hg-XR_3$ ($X = Ge, Sn$; $R = Ph, C_6F_5$) molecules causes formation of $R_3X-Hg-PtL_2-XR_3$ molecules with a four-membered metallo-chain, yet at the given R one could not succeed in inserting the second PtL_2 fragment into the other $Hg-X$ bond [20]. The solid angles sum Q (with the center in Hg) for $(C_6F_5)_3Ge-Hg-PtL_2-Sn(C_6F_5)_3$ is equal to 12.03 rad., whereas for the expected molecule $(C_6F_5)_3Ge-PtL_2-Hg-PtL_2-Ge(C_6F_5)_3$ it is equal to 16.36 rad. The second

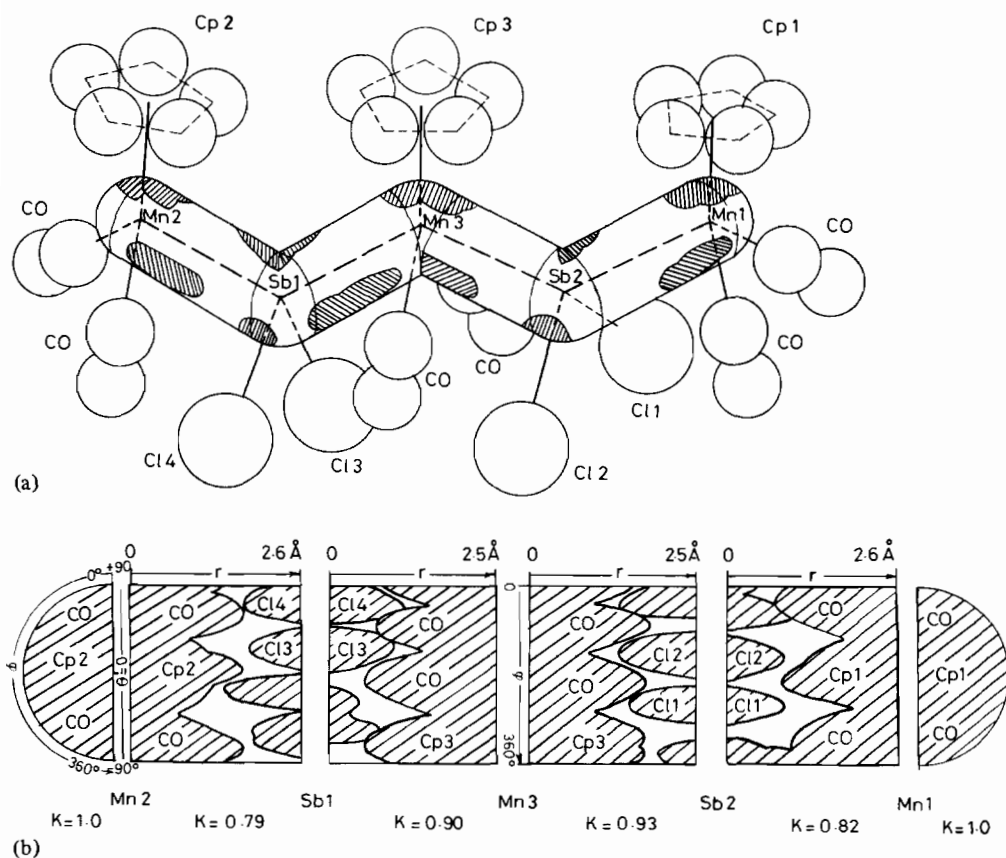
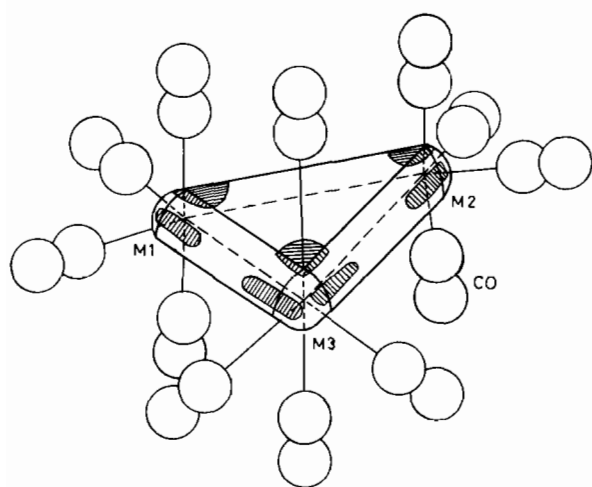
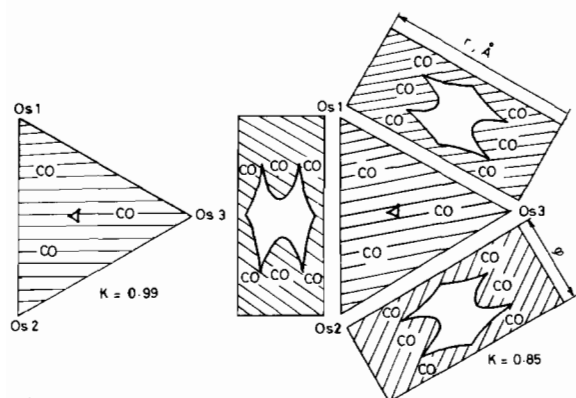


Fig. 2. Scheme illustrating a construction of molecular projection on the metal embracing surface (a) and surface projection developments for $[(C_5H_5)(CO)_2MnSbCl_2]_2Mn(CO)_2(C_5H_5)$ (b). The shielded area is cross-hatched.



(a)



(b)

Fig. 3. Scheme showing a construction of a molecular projection on the 3-nuclear metal cycle embracing surface (a) and surface projection development for $\text{Os}_3(\text{CO})_{12}$ molecule (b). Spherical parts of the surface are omitted for clarity. K values are given for different parts of the molecule.

value markedly exceeds 4π indicating drastic barriers due to the non-bonding interactions $\text{R}\dots\text{R}$ to form such a molecule. Conversely the $(\text{CF}_3)\text{Ge}-\text{PtL}_2-\text{Hg}-\text{PtL}_2-\text{Ge}(\text{CF}_3)_3$ molecule having a less bulky group $\text{R} = \text{CF}_3$ has $Q = 11.46$ rad. showing the potential to obtain it. In fact such a molecule was obtained and has been proved by X-ray analysis [21].

Using an analysis procedure similar to that described above, the possible existence of a new type lanthanide compound $\text{Cp}_3\text{Ln}(\text{NCMe})_2$, $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ [10] was predicted and then confirmed by synthesis.

In the structure of a condensed state non-bonding interactions governing the coordination environment of metal atom (atoms) affect both the molecular structure and molecule packing. Since the $\text{R}\dots\text{R}$ interactions in distinction to metal-ligand (radical)

($\text{M}-\text{R}$) and metal-metal ($\text{M}-\text{M}$) interactions are a necessary structure element of the OMC condensed state, the degree of space shielding of the metal atom by the ligands (radicals) features the degree of space hindering of the realization of intermolecular $\text{M}-\text{R}$ and $\text{M}-\text{M}$ interactions by intra- and intermolecular $\text{R}\dots\text{R}$ interaction in the structure.

The greater is the shielding degree, the more likely it is that the structure of a condensed state OMC will be only formed by $\text{R}\dots\text{R}$ interactions. On the other hand the realization of $\text{M}-\text{M}$ or $\text{M}-\text{R}$ interactions seems to be a natural stage on the path to the formation of a polynuclear OMC with the $\text{M}-\text{M}$ (metal clusters, OMC comprising metallochains, metallo-cycles) and $\text{M}-\text{R}$ (OMC comprising bridge $\text{R}\dots\text{M}-\text{R}'$ oligomer or polymer structures) bonds. Numerous examples can be brought about when OMC molecules having a little shielding of the metal atoms, as for example, ligands with unstable oxygen atoms, form in a solid state the oligomer or polymer structures with $\text{M}-\text{M}$ or $\text{M}-\text{O}$ bonds. By this means, the stability of the structure formed by molecules of organo-element compounds in relation to the realization of intermolecular $\text{M}-\text{M}$ and $\text{M}-\text{R}$ interactions as well as to the formation of polynuclear OMC classes mentioned above are also determined by the shielding of metal atom (atoms) by ligands (radicals) [3].

The above described distinguishing feature of the stability of the condensed state structure in relation to the formation of $\text{M}-\text{M}$ bonds is valid not only for polynuclear OMC of MR_nL_m type, but also for the polynuclear OMC, metal clusters, $\text{M}_k\text{R}_n\text{L}_m$, by virtue of the fact that their molecules have in principle a similar structure to that of the polynuclear OMC, the only difference being that they do not have a single but a group of metal atoms surrounded by ligands (radicals).

Shielding of metal atoms by ligands in the structure of a condensed state of the organometal compounds can be brought about not only due to the ligands surrounding in the molecular structure, but also because of the molecules in the packing. Therefore the character of the molecule arrangement in the packing, i.e. its symmetry, is of great importance. The influence of packing symmetry on the stability of the OMC structure in relation to the formation of $\text{M}-\text{M}$ bonds in it can be illustrated by the example of $(\text{Ph}_3\text{Ge})_2\text{Hg}$. This compound decomposes with Hg elimination on melting, as well as in the solid amorphous state, but is stable in a single crystal state, seemingly due to the fact that the crystal packing provides a shielding of the Hg atoms from each other [17, 22].

The conclusions mentioned above are supported, for example, by the calculations of K values for the OMC containing metal chains with $\text{M}-\text{M}$ bonds. Figures 2b and 4-7 illustrate the projection developments of molecules and K values for some OMC,

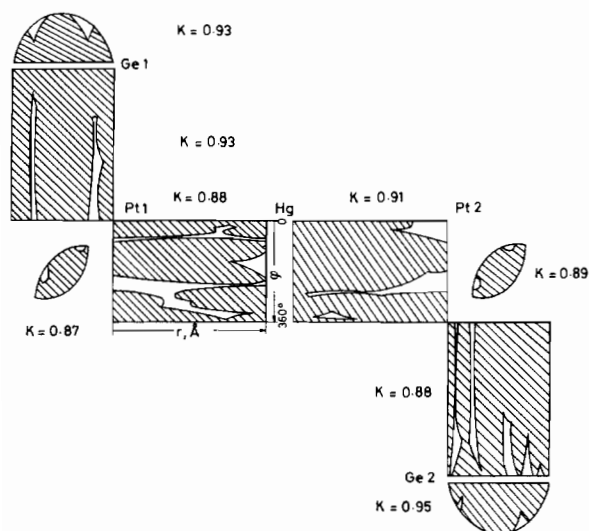
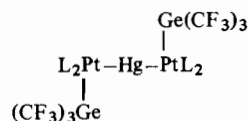


Fig. 4. The projection development of

(L = PPh₃) for various parts of the molecule.

comprising the skeleton composed of metal atoms in the form of ordinary or branched metal chains and metal cycles, indicating that the molecules of this type have higher values of the space shielding degree: $K = 0.93$ for $[\text{C}_5\text{H}_5(\text{CO})_2\text{MnSbCl}_2]_2\text{Mn}(\text{CO})_2\text{C}_5\text{H}_5$ [23] (Fig. 2b); $K = 0.91$ for $[(\text{CF}_3)_3\text{Ge}(\text{PPh}_3)_2\text{Pt}]_2\text{Hg}$ [24] (Fig. 4); $K = 0.74$ for $\text{Ph}_3\text{Ge}-\text{Hg}-\text{Ni}(\text{Cp})-\text{GePh}_3-\text{Hg}-\text{Ni}(\text{Cp})\text{GePh}_3-\text{Hg}-\text{GePh}_3$ [25] (Fig. 5); $K = 0.89$ for the anion $[(\text{C}_6\text{F}_5)_3\text{Ge}]_3\text{Hg}^-$ [26] (Fig. 6); $K = 0.76$ for the molecule $[\text{Fe}(\text{CO})_4\text{Cd}]_4 \cdot 2\text{C}_3\text{H}_6\text{O}$ with an eight-membered metalocycle [27] (Fig. 7).

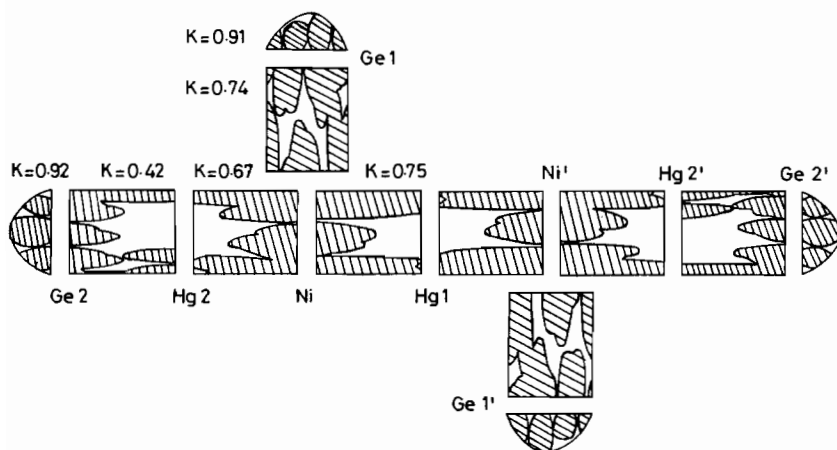
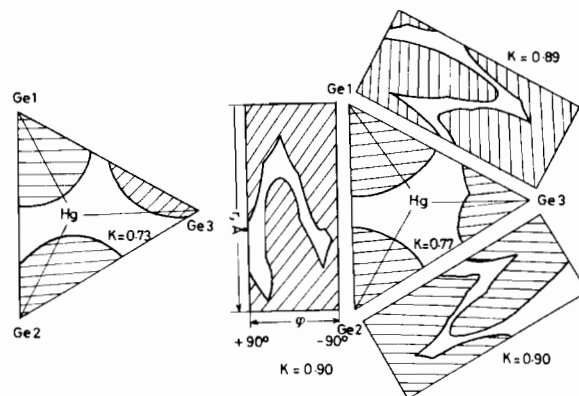
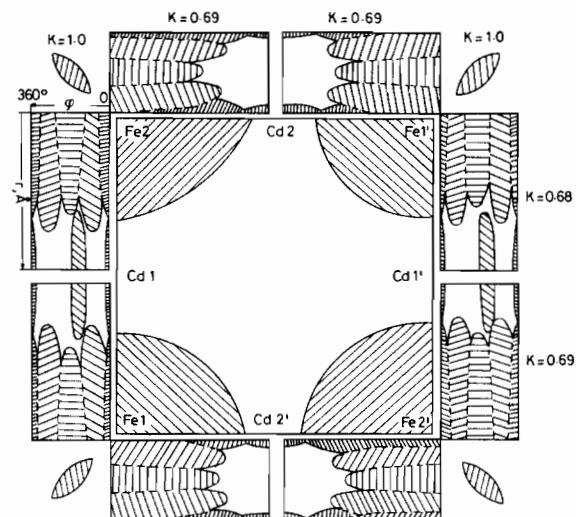
Fig. 5. Projection development of centrosymmetrical molecule $\text{Ph}_3\text{Ge}-\text{Hg}-\text{Ni}(\text{Cp})\text{GePh}_3-\text{Hg}-\text{Ni}(\text{Cp})\text{GePh}_3-\text{Hg}-\text{GePh}_3$ and shielding coefficient values for various parts.Fig. 6. The $[(\text{C}_6\text{F}_5)_3\text{Ge}]_3\text{Hg}^-$ anion projection development and shielding coefficient values K for various parts of the anion.Fig. 7. Projection development of centrosymmetrical molecule $[\text{Fe}(\text{CO})_4\text{Cd}]_4 \cdot 2\text{C}_3\text{H}_6\text{O}$ with an eight-membered metal cycle and shielding coefficient values for various parts of the molecule.

TABLE 1. Shielding degree (K, Q) of metal atoms in some mono- and polynuclear organo-element compounds

Compound	K	Q (rad.)	Compound	K	Q (rad.)
TiMe ₄	0.70	8.79	Cp ₂ Ti	0.64	8.04
TiPh ₄	0.74	9.29	Cp ₂ TiCl ₂	1.0	12.56
Ti(t-Bu) ₄	0.88	11.05	Cp ₂ TiCl	0.82	10.30
Ti(CH ₂ SiMe ₃) ₄	0.93	11.68	CpTiCl ₃	0.85	10.68
Ti(CH ₂ CMe ₃) ₄	1.0	12.56	Cp ₂ V	0.69	8.67
VMe ₄	0.79	9.92	Cp ₂ VCl ₂	1.0	12.56
VPh ₄	0.85	10.68	CpVCl ₃	0.93	11.68
V(CH ₂ SiMe ₃) ₄	1.0	12.56	Cp ₂ VCl	0.89	11.18
V(C ₆ H ₂ Me ₃) ₄	1.0	12.56	Cp ₂ Cr	0.74	9.29
(Me ₃ Ge) ₂ Hg	0.40	5.95 ^b	Cp ₂ CrCl	0.93	11.68
(Ph ₃ Ge) ₂ Hg	0.46	6.60 ^b	Cp ₂ Mn	0.80	10.05
[(C ₆ F ₅) ₃ Ge] ₂ Hg	0.59	7.70 ^b	Cp ₂ Fe	0.89	11.18
(C ₆ F ₅) ₃ GeHgPtL ₂ Sn(C ₆ F ₅) ₃ ^a	0.90	12.03 ^b	Cp ₂ Ni	0.78	9.80
[(CF ₃) ₃ GeL ₂ Pt] ₂ Hg ^a	0.91	11.46 ^b			
[(C ₆ F ₅)Ge] ₃ Hg ⁻	0.89	11.05 ^b			
[(C ₅ H ₅)(CO) ₂ MnSbCl ₂] ₂ ⁻					
Mn(CO) ₂ (C ₅ H ₅)	0.93				
Fe(CO) ₄ Cd·C ₃ H ₆ O	0.76				
Os ₃ (CO) ₁₂	0.92				
Mn(μ-NO) ₃ Cp ₃ (μ ₃ -NO)	0.95				
Cr ₂ Fe(μ-OR) ₂ (CO) ₄ Cp ₂	0.90				
Rh ₃ (CO) ₃ Cp ₃	0.91				

^aL = PPh₃. ^bSolid angles sum with the apex in the Hg atom.

By comparison, K values of such unstable compounds as (R₃Ge)₂Hg R = Me, Ph are less (0.67 and 0.70 correspondingly). Lower K values for these molecules are determined by the weak shielding of the central Hg atom (K values for the cylinder part of projections are only 0.18 (R = Me) and 0.27 (R = Ph)) whereas the shielding of Ge atoms by the Ph group is markedly higher (K values for the spherical parts of the projections equal to 0.91 (R = Me) and 0.93 (R = Ph)). In Table 1 K values for these and some other OMC are given. As can be seen from Table 1, K values for the thermally stable molecules for such a type are close to 0.9, i.e. the metallo-chain in them is substantially shielded by ligands (radicals). In refs. 1–3 we already pointed out the relationship between the K value and the thermal stability of transition metal alkyl derivatives. It was demonstrated in ref. 4, that the average K value for about 400 organic compounds of actinides is approximately 0.8 and the relationship of K with the stability of these compounds was also pointed out.

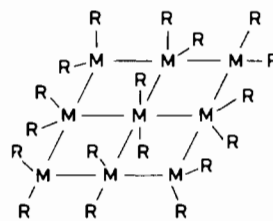
Compounds with a three-nuclear metal cycle also have a substantial shielding. This is illustrated by the projection (Fig. 3b) of Os₃(CO)₁₂ ($K = 0.92$) as well as by K values for some other similar metal clusters (see Table 1).

From our point of view the data presented suggest a stabilizing role of non-bonding R...R interactions. It seems that by selecting the proper metal atoms

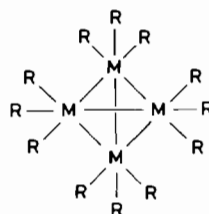
surrounding by ligands (radicals) one can achieve structure stabilization of mononuclear OMC – MR_nL_m, as well as OMC with one dimensional –M–M– chains,



a two-dimensional metal net

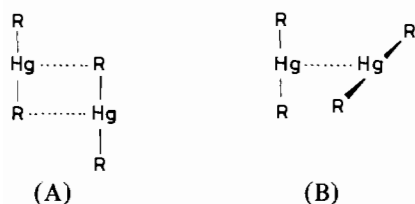


or a three-dimensional framework



constructed of metal atoms.

It proved to be useful to consider the influence of non-bonding R...R interactions on the reactivity and in particular on the geometry of the transition state in some OMC reactions. Thus inclusion of non-bonding interactions in the semiempirical calculations of the OMC molecule potential energy surface enabled one to reveal that they determine the activation barrier in the reaction of direct synthesis of bisarenechromium compounds [28] and in ligand interchange for R_2Hg compounds [29]. In the latter case with consideration of R...R interactions, the most probable is not a plane (A), but a 'cross-type' (B) transition state where ligand interchange occurs [29].



Acknowledgement

The authors wish to acknowledge their gratitude to the late Academician G. A. Razuvaev (deceased February 12, 1989) for his constant interest in this work and discussion of the results.

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