Role of steric factors in formation of O—H...M hydrogen bonds with metallocenes

T. V. Timofeeva,* E. S. Shubina, A. N. Krylov, and L. M. Epshtein

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

Molecular mechanics calculations of geometric parameters and energies of molecular complexes with a O—H...M hydrogen bond have been performed for osmocene and decamethylosmocene with three proton donors. The results of calculations demonstrated that when rings are methylated, steric hindrances to formation of this hydrogen bond increase. This is the reason for anomalously low formation constants of H-bonded Cp_2^*M molecular associates compared to Cp_2M associates.

Key words: metallocenes, M...H—X hydrogen bond, IR spectroscopy, molecular mechanics.

Previously, we discovered and studied hydrogen bonds between proton donors and transition metals using metallocenes and decamethylmetallocenes of the iron subgroup as examples.[1,2] Spectral characteristics and thermodynamic characteristics obtained from the spectral data reveal a discrepancy between the changes in the bond strength and the formation constants (K_{form}) on methylation of Cp rings. The strength of H-associates is enhanced owing to the donor properties of methyl groups ($Cp_2M < Cp_2^*M$), whereas the values of K_{form} decrease in the reverse order ($Cp_2M > Cp_2^*M$, see Refs. 1, 2). Formation constants for proton donor—metallocene complexes are two orders of magnitude smaller[2] than hydrogen-bonded complexes of organic bases, which have close factors of basicity of an H-bond (E_j). This suggests that steric hindrances are of considerable importance in the formation of an H-bond with the metal atom in metallocenes.

In this work, geometric parameters and energies of these complexes have been calculated by the molecular mechanics method (MM) for the purpose of elucidating the effect of steric factors on the formation of molecular complexes with M...H—X hydrogen bonds. The Cp_2Os—proton donor and Cp_2^*Os—proton donor systems were chosen for calculations. Phenol (1), fluoroacetylene (2), and hexafluoroisopropanol (3) were used as proton donors. The energy of a molecular complex was defined as the sum of conformational energies of molecules and an intermolecular interaction term.

Calculation Procedure

Calculations of the complexes were performed on a MicroVAX computer using the MM3 program (see Ref. 3) with the use of a parameter set included in the version developed in

1993. Because the program contains no characteristics of potentials, which allow the description of metallocenes with an Os atom and complexes with an M...H—X hydrogen bond, we chose parameters, that are needed for describing the geometry and energy of the molecules both of unsubstituted and substituted osmocenes and compounds with an Os...H hydrogen bond. For osmocene, we used the model identical to that for other metallocenes,[4] i.e., cyclopentadienyl ligands were fixed in a soft way in the coordination sphere of the metal atom with the use of a potential similar to that proposed by Hill. Ideal bond lengths r_0, which characterize this potential are average values of bond lengths taken from X-ray structural studies of substituted and unsubstituted osmocenes;[5] according to the data reported previously,[6] ε is 1/5 of energy of the cleavage of the M—Cp bond.

For the Os...H—X hydrogen bond, we used the potential, which is used for O...H—O hydrogen bonds in the MM3 program, i.e., the potential that depends both on the distance and the angle. We estimated the energy characteristics of Os...H—X hydrogen bonds based on the results of IR spectral studies.[1,2] Values of enthalpies of hydrogen bonds (ΔH), which were obtained from the known correlation between frequency shifts ($\Delta v(OH)$) and ΔH for different proton donors and metallocenes, are given in Table 1. As is evident from Table 1,

Table 1. Enthalpies of OH...M hydrogen bonds based on IR spectral data

Com-	ΔH/kcal mol^{-1}		
pound	phenol	n-fluorophenol	n-nitrophenol
Cp_2Ru	3.6	3.8	4.4
Cp_2Os	4.2	4.5	5.2
Cp_2^*Ru	4.5	4.7	5.8
Cp_2^*Os	5.6	5.8	7.1

Note. For the unmethylated complexes, the data were taken from data reported previously.[1]

the strengths of H-bonds for Cp_2Os and Cp_2^*Os are within the range 4.2—7.1 kcal mol^{-1}. Therefore, in the used model, energies of hydrogen bonds for all complexes were taken to be equal to 5.0 kcal mol^{-1}.

Data on lengths of hydrogen bonds with metal atoms are scarce. For example, it is known that the intramolecular Fe...H—O hydrogen bond in 4-(ferrocenylhydroxyphenyl)-4-butanediol has the following parameters: Fe...H is 3.03 Å and Fe...H—O is 123° (see Ref. 7). Analogous values for the Rh...H—O hydrogen bond in ψ-endo[2-(1-hydroxyethyl)nor-bornadiene]cyclopentadienylrhodium are 2.94 Å and 131°, respectively (see Ref. 8).

Note that an intramolecular hydrogen bond is, apparently, slightly longer than analogous bonds in intermolecular hydro-gen-bonded complexes; however, data on geometry of these uncharged complexes are unavailable. Only neutron diffraction studies of salts are known; in these works, structural character-istics of hydrogen bonds of the ionic type were determined. Thus, for the N—H...Co hydrogen bond in the $Et_3NH^+Co(CO)_4^-$ salt, the parameters have the following values: 2.613 Å (H...Co) and 180° (Co...N—H) (see Ref. 9); the parameters of the N—H...Pt bond in $[NPr^n_4]_2[PtCl_4]$ cis-$[PtCl_2(NH_2Me)_2]$ have the following values: 2.262 Å and 167° (see Ref. 10).

The above-mentioned data allow us to choose 2.5 Å as the equilibrium distance for the M...H—O hydrogen bonds. Parameters of potentials, which were added to those contained in the above-mentioned version of the MM3 program and which are necessary for calculations of the mentioned molecular complexes, are given in Table 2.

Results and Discussion

Calculations of molecular complexes were performed using two alternative procedures: with and without taking into account the formation of a hydrogen bond with the metal atom. For complexes without a hydrogen bond, the initial geometry was given in several ways by varying the arrangement of the proton-donor molecule with respect to the metallocene. Figure 1 shows the structures of 1a—3a that correspond to the lowest energy minima.

When minimizing energies of complexes with hydro-gen bonds, we also started from several structural forms, in which the metal atom is at a distance of 2.0—2.5 Å from the active hydrogen atom. The results of calcula-tions for these complexes (1b—3b) are also shown in Fig. 1. Because parameters of potentials were chosen rather roughly, there is no point in discussing geometric parameters of complexes with hydrogen bonds in detail;

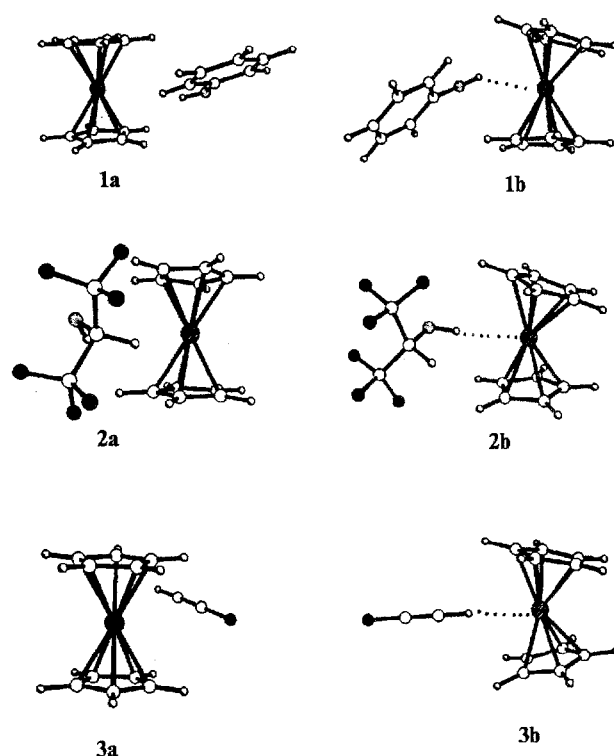**Fig. 1.** Mutual arrangement of molecules in Cp_2^*Os complexes with 1—3: *a*, without a hydrogen bond; *b*, with a hydrogen bond.

however, it should be mentioned that in osmocene and its molecular complexes without a hydrogen bond, the cycles are parallel to each other, while in calculated complexes with a M...H—O hydrogen bond, the angle between the planes of Cp rings is 15—17°.

We analyzed energies (ΔE/kcal mol^{-1}) of bimolecular complexes of osmocene or decamethylosmocene with and without a hydrogen bond:

	1	2	3
Cp_2Os	2.53	1.76	3.27
Cp_2^*Os	1.35	0.83	0.58

It is evident that with rather rough values of the parameters of a hydrogen bond, which we used, formation of this hydrogen bond is energetically favorable for both

Table 2. Parameters of the potentials for calculations of conformations of osmocene and its molecular complexes with a hydrogen bond

Bond	ε/kcal mol^{-1}	r_0/Å
M—C(Cp) π interaction		
Os—C(Cp)	20.0	2.195
Os—C(Cp*)	20.0	2.244
M...H hydrogen bond		
Os...H	5.0	2.5

Table 3. Calculated energies and geometric parameters of hydrogen bonds in bimolecular complexes

Complex	Os...H /Å	Os...X /Å	Os...H—X /deg	ΔE /kcal mol^{-1}
$Cp_2Os \cdot 1$	2.62	3.59	167	−3.3
$Cp_2Os \cdot 2$	2.54	3.62	179	−3.5
$Cp_2Os \cdot 3$	2.55	3.51	176	−3.6
$Cp_2^*Os \cdot 1$	2.78	3.73	162	−2.6
$Cp_2^*Os \cdot 2$	2.71	3.79	177	−2.9
$Cp_2^*Os \cdot 3$	3.27	4.09	147	−1.1

osmocenes. However, in all cases, a gain in energy (ΔE) for unmethylated osmocene is larger than that for methylated osmocene. It is interesting that for Cp_2M the value of E increases as proton-donor properties enhance in the series $2 < 1 < 3$, while for decamethylosmocene, this order changes: $3 < 2 < 1$.

The effect of the shape of proton-donor molecules and hence, of all intermolecular interactions, is clearly seen by the example of fluoroacetylene. In the complex without a hydrogen bond, the axis of the acetylene molecule is nearly parallel to one of the C—C bonds in the Cp ring, while, in the structure with an H-bond, the orientation of molecule **3b** is such that the C—H...M angle is 180°. Because the initial parameters for Cp_2Os and $Cp_2{}^*Os$ are taken to be equal, a smaller gain in ΔE for $Cp_2{}^*Os$ is determined by an increase in steric hindrances to approach of a proton donor. This is also evident from the Os...H and Os...O distances given in Table 3; these distances for unmethylated osmocene (2.55—2.62 Å) are smaller than those for methylated osmocene (2.78—3.27 Å).

Therefore, the results of calculations by the MM method confirm the proposal, which was made based on IR spectral studies of hydrogen bonds of a new type with transition metals in metallocenes.

Formation constants for H-complexes of decamethylmetallocenes are smaller than those for metallocenes because of steric hindrances.

References

1. E. S. Shubina, A. N. Krylov, A. Z. Kreindlin, M. I. Rybinskaya, and L. M. Epstein, *J. Mol. Struct.*, 1993, **301**, 1.
2. L. M. Epstein, A. N. Krylov, and E. M. Shubina, *J. Mol. Struct.*, 1994, **322**, 345.
3. N. L. Allinger, Y. H. Yuh, and J.-H. Lii, *J. Am. Chem. Soc.*, 1989, **111**, 8551.
4. T. V. Timofeeva, J.-H. Lii, and N. L. Allinger, *J. Am. Chem. Soc.*, 1994, in press.
5. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc. Perkin Trans. 2*, 1987, S1.
6. M. F. Ryan, J. R. Eyler, and D. E. Richardson, *J. Am. Chem. Soc.*, 1992, **114**, 8611.
7. Yu. T. Struchkov, A. S. Batsanov, S. Toma, and M. Salisova, *J. Organomet. Chem.*, 1987, **329**, 373.
8. L. E. Vinogradova, L. A. Leites, I. T. Chizhevskii, N. V. Rastova, N. E. Kolobova, A. I. Yanovskii, and Yu. T. Struchkov, *Metalloorg. Khim.*, 1989, **2**, 769 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
9. L. Brammer, M. C. McCann, R. M. Bullock, R. K. McMullan, and P. Sherwood, *Organomet.*, 1992, **11**, 2339.
10. L. Brammer, J. M. Charonck, P. L. Goggin, R. J. Goodfellow, A. G. Orpen, and T. F. Koetzle, *J. Chem. Soc., Dalton Trans.*, 1991, 1789.