Letters to the Editor

Calculations of electronegativity and hardness of $(CO)_5Mn$ and $(CO)_4Co$ groups

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The group electronegativity (GEN) and hardness[1] of organometallic groups L_nM are important quantitative parameters in the study of the polarity of the bonds formed by these groups and the reactivity of the corresponding compounds. The data published are mainly for organic groups,[2—4] while the data of quantum-chemical calculations and the results of the experimental determination of GEN and the hardness of organometallic groups, in particular, those containing transition metals, are scarce. Based on experimentally determined values of the ionization potentials and electron affinity, the Mulliken[1] GEN has been determined[5] for the $(CO)_5Mn$ moiety. The work of the German authors (Ref. 6) is devoted to calculations of the electronegativity and hardness of organometallic groups, including those containing transition metals. The conclusions about the comparative electronegativity of $(CO)_5Mn$ and $(CO)_4Co$ based on the study of the fluorine chemical shifts (FCS) in the compounds $(4\text{-}FC_6H_4)_3SnML_n$ have been described previously.[7]

The results of *ab initio* calculations of the electronegativity and hardness of the $(CO)_5Mn$ and $(CO)_4Co$ groups are presented in this work. The calculations were performed by the ΔSCF method,[1] in terms of which the ionization potential $I = E_0 - E_c$ and electron affinity $A = E_a - E_0$ (E_c, E_0, and E_a are the total energies of the cation, neutral radical, and anion of the group considered, respectively) were determined; then the GEN (χ) and hardness (η) were calculated by the Mulliken formulae: $\chi = (I + A)/2$ and $\eta = (I - A)/2$. As is known,[1] these equations are the first approximation of the differential representation of the χ and η values obtained in terms of electron density function theory.[8]

The total energies E_c, E_0, and E_a were calculated by the GAMESS program[9] in the MIDI basis. The geometric parameters of the groups were specified on the basis of the X-ray data[10] for compounds containing the fragments studied and remained unchanged as the number of electrons varied, as it is required by the ΔSCF method. In fact, although this choice of geometry does not correspond to the minimum of the energy of the isolated group, it is the choice that is the most correct for the calculations of χ and η, because the properties of the fragment in real systems are studied in this case.

For a more adequate description of the anion at the key atom of the group (Co and Mn), the diffuse d-function, whose exponent optimized for the anions of the corresponding atoms turned out to be equal to 0.143 for Co and 0.117 for Mn, was added to the standard basis. The calculations showed that the specification of the diffuse s- and p-functions decreases the energies of the cation, anion, and neutral radical by the same value, exerts no effect on the ionization potential and electron affinity, and is likely a simple extension of the basis. At the same time, the inclusion of the diffuse d-function substantially decreases the energy of the anion and

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Table 1. Calculation of ionization potentials (I), electron affinity (A), GEN (χ), and hardness (η) for $(CO)_5Mn$ and $(CO)_4Co$ groups

L_nM	Method	I	A	χ	η	FCS,*
		eV				ppm
$(CO)_5Mn$	*ab initio*	5.75	0.11	2.93	2.82	−1.46
	TO INDO[6]	7.67	1.42	4.55	3.13	
$(CO)_4Co$	*ab initio*	6.35	0.23	3.29	3.06	−3.00
	TO INDO[6]	7.92	0.93	4.43	3.49	

* FCS in the ^{19}F NMR spectra of compounds $(4\text{-}FC_6H_4)_3SnML_n$ (see Ref. 7).

exerts almost no effect on the energy of the cation. The calculations for various organic groups showed that on going from the anion to the cation, the biggest change in the charge occurs precisely at the key atom. Therefore the specification of the diffuse functions on the other atoms does not make a noticeable contribution to the values of I and A of these groups. In addition, the existence of the diffuse functions worsens substantially the convergence of the self-conformity process. Therefore, in this work, we restricted ourselves to specifying the diffuse function only on the key atom of the group.

The results of the calculation of I, A, χ, and η are presented in Table 1, where similar values obtained previously[6] by the semiempirical TO INDO method and the values of FCS for the compounds $(4\text{-}FC_6H_4)_3SnMn(CO)_5$ (**1**) and $(4\text{-}FC_6H_4)_3SnCo(CO)_4$ (**2**)[7] are presented for comparison. It can be seen from the data in Table 1 that the shielding of the F atom decreases substantially on going from compound **1** to compound **2**. This, in turn, indicates an increase in the GEN on going from the $(CO)_5Mn$ group to $(CO)_4Co$. Thus, it can be seen that, unlike the calculations by the TO INDO methods, the results of the *ab initio* calculations are consistent with the experimental data. It is noteworthy that the GEN value obtained for $(CO)_5Mn$ still differs from the value $\chi = 5.2$ eV calculated[5] from the experimental data on I and A, which indicates that the accuracy of the calculations performed is insufficient. Probably, the result would be better if the electron correlation (the use of a better basis, the method of configuration interactions,[11] *etc.*) were taken into account more rigorously, but this is not within our technical capabilities.

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