Organometallic Chemistry

On the inductive effects of the organometallic groups $M(CO)_mCp_n$ and $HgM(CO)_mCp_n$ (M = Co, Mo, Mn, Fe, Re)

M. I. Sykhrannova, S. Ya. Khorshev, A. N. Tatarnikov, and E. N. Gladyshev*

Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603600 N. Novgorod Russian Federation
Fax: +7 (8312) 35 6480

Based on the dependences $\nu(CO) = a + b\sigma^*$ for IR spectra of carbonyl complexes of transition metals, the inductive constants of the organometallic fragments $M(CO)_mCp_n$ and $HgM(CO)_mCp_n$ (M = Co, Mo, Mn, Fe, Re) have been determined. The acceptor properties of the organometallic fragments have been shown to change according to the order of the nucleophilicity of the anions: $Fe(CO)_2Cp$ > $Re(CO)_5$ > $Mn(CO)_5$ > $Mo(CO)_3Cp$ > $Co(CO)_4$.

Key words: carbonyl complexes of cobalt, molybdenum, manganese, iron rhenium; inductive effect.

In our work on the thermal instability of $Cp_n(CO)_mMHgER_3$ (M = Mn, Fe, Co, Mo, Re), we have only considered the steric and electron factors of the ER_3 fragment (E = Si, Ge).[1] Due to the absence of data concerning the steric, resonance, and inductive constants of the $Cp_n(CO)_mM$ fragment, it proved impossible to estimate the effect of the organometallic group on the stability of compounds of this type. On the basis of the data concerning reactivity, it was suggested that the $Co(CO)_4$ group has electron-withdrawing properties, unlike the other carbonylmetal groups, which are considered to be donor substituents.[2] The inductive constant was only determined for the $Cp(CO)_2Fe$ fragment,[3] which is electron-releasing *via* both inductive ($\sigma_I = -0.25$) and resonance ($\sigma^0_R = -0.29$) mechanisms. Since no data about σ^* for the other substituents have been reported, the purpose of the present work was to determine the inductive constants of organometallic substituents for the carbonyl and cyclopentadienylcarbonyl complexes of transition metals.

As a basis for determining the constants, we used the principle of the separate transmission (through the metal atom) of the inductive and mesomeric effects of the R substituents in complexes on the CO groups that are in the *cys*- and *trans*-positions relative to R (see Ref. 4). Proceeding from the available experimental and theoretical data, the authors of Refs. 4, 5 concluded that in the $RMn(CO)_5$ complexes only the inductive effect of R should be transferred to the equatorial CO groups, while the mesomeric effect should not notably manifest itself with respect to these groups. Therefore, in the IR spectra of these compounds, the position of the E type band should only depend on the σ^* Taft inductive parameter. The dependences between the E type $\nu(CO)$ frequencies and σ^* have been studied for eight manganese complexes:[4]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1482—1484, August, 1994.

1066-5285/94/4308-1405 $12.50

$$\nu(\mathrm{CO}) = 2011 + 15.5\sigma^* \ (r = 0.997)$$

and for twenty-three rhenium compounds:[5]

$$\nu(\mathrm{CO}) = 2017 + 13.1\sigma^*.$$

The equations obtained were used to calculate the σ^* values of the R substituents, for which the above-mentioned characteristics had not been determined.

We used this principle to obtain the correlation equations for the carbonyl and cyclopentadienylcarbonyl complexes of cobalt, molybdenum, and iron. In the cases of the complexes of molybdenum and iron, the high-field ν(CO) bands for the CO-group symmetric vibrations were used as the indicative bands. For comparison, the ν(CO) frequencies of the carbonyl complexes of manganese and rhenium are included to Table 1. In order to estimate correctly the inclination of the metal atom to transfer the inductive effect of the R substituent to the equatorial CO groups, Table 1 shows the frequencies only for compounds that have the same R bonded with the transition metal M atom. It should be pointed out that the IR spectra of the manganese complexes were obtained in cyclohexane solutions, and those of Fe, Co, Mo, and Re complexes were recorded in various solvents (cyclohexane, benzene, toluene, CCl_4, $CHCl_3$) due to their low solubility in cyclohexane. The ν(CO) frequencies that were obtained for solutions of complexes in THF, dioxane, and acetonitryl were not included in Table 1.

The mathematical processing of the experimental data revealed that the valence vibration frequencies of the equatorial CO groups in the carbonyl complexes of Co, Mo, and Fe, similar to the Mn and Re complexes, depend lineary on the inductive constant σ^* of the R substituent (Table 2). However, the slopes of the straight correlation lines are not the same. The value of *b* falls within the 14.75—17.06 interval. Two possible reasons for the difference in *b* are the following: 1) the sensitivity of the inductive transmission to the nature of the metal atom is, though not much, different; 2) different solvents were used for obtaining the spectra.

Taking into account the fact that the vibration of the carbonyl groups bonded with the different metal atoms is not accompanied by their interaction,[5] we measured the ν(CO) frequency in the IR spectra of the dimeric carbonyl complexes and put its value into the corresponding equation, which enabled us to calculate the inductive constant for the organometallic fragment (Table 3). This method for evaluating the σ^*-constants is not applicable only to $[Cp(CO)_2Fe]_2$, since in the solutions of this complex there are two isomers in equilibrium, *i.e.*, the isomer with bridge CO-groups $Fe(CO)_2Fe$ (99.4 %) and the isomer containing the Fe—Fe bond (0.6 %).[6] The inductive constant of $Fe(CO)_2Cp$, that was determined by the ^{19}F NMR spectra is −1.5 according to the Taft scale.[3] We calculated this constant using the frequency of the Si—H valence vibration (2103 cm^{-1}) for complex $Cp(CO)_2FeSiH_3$ (see Ref. 7) and obtained a similar σ^* value of −1.4. Therefore, according the inductive mechanism, the $Cp(CO)_2Fe$ fragment is even more electron-releasing than the Et_3Ge-group ($\sigma^* = -1.1$). All of the other organometallic fragments are moderate acceptors (Table 3).

Table 1. Valence vibration frequencies for the equatorial CO groups in the IR spectra of transition metal complexes[4,5,7—10] (cm^{-1}).

R	M					σ^*
	Mn	Fe	Co	Mo	Re	
$SnMe_3$	1991	—	—	1990	1990	−1.29
$SiMe_3$	2000	1996	—	2004	1997	−0.72
$SiPh_3$	2003	2004	2003	—	2012	−0.52
$SnPh_3$	2004	2000	2006	2005	2012	−0.45
SiH_3	2010	2008	2007	2005	—	−0.1
Me	2011	2010	—	2015	2012	0
p-MeO—C_6H_4	2017	—	—	—	2018	0.36
p-Me—C_6H_4	2018	—	—	—	2018	0.46
H	2016	2014	—	—	2015	0.49
Ph	2021	2021	—	—	2020	0.6
$Sn(C_6F_5)_3$	2034	2034	—	—	—	1.48
$SiCl_3$	2035	2035	2037	2038	2037	1.55
CF_3	2042	2053	2055	2054	—	2.0
C_6F_5	2042	—	—	—	2046	2.0
$SnBr_3$	2043	2039	2043	—	2046	2.06
$SnCl_3$	2046	2050	2048	—	2047	2.26
$GeBr_3$	2046	2043	2048	2040	—	2.26
$GeCl_3$	2047	2050	2050	2047	—	2.32
Br	2052	—	—	2045	2050	2.8
Cl	2054	—	—	2055	2055	2.9

Table 2. Parameters of the correlation equations $\nu = a + b\sigma^*$ for carbonyl complexes of transition metals

Compound	*a*	*b*	*n*	*r*
$(CO)_5Mn—R$	2011	15.25±0.16	20	0.999
$(CO)_2MCpFe—R$	2009	17.10±0.94	14	0.982
$(CO)_5Co—R$	2011	16.90±1.20	9	0.982
$(CO)_4CpMo—R$	2012	14.75±1.22	11	0.971
$(CO)_3Re—R$	2012	14.90±0.77	15	0.983

Table 3. Inductive constants σ^* of organometallic fragments

R	ν(CO)**	σ^*	R	ν(CO)**	σ^*
$Co(CO)_4$	2025	0.83	$HgCo(C)_4$	2005	−0.35
$Mo(CO)_3Cp$	2018	0.41	$HgMo(CO)_3Cp$	2000	−0.81
$Mn(CO)_5$	2015	0.26	$HgMn(CO)_5$	1995	−1.05
$Re(CO)_5$	2015	0.20	$HgRe(CO)_5$	2000	−0.81
$Fe(CO)_2Cp$*	—	−1.4	$HgFe(CO)_2Cp$	1963	−2.69
$GeEt_3$		−1.12	$HgGeEt_3$		−2.37

*According to Ref. 3, this value is −1.5. ** ν(CO) are shown only for the one band in complexes $[Cp_n(CO)_mM]_2$ and $[Cp_n(CO)_m]_2Hg$ that was used in the calculation of σ^*.

The acceptor ability of the organometallic fragments increases in good agreement with the order in which the nucleophilicity of the anions changes:[8] $Fe(CO)_2Cp$ > $Re(CO)_5$ > $Mo(CO)_3Cp$ > $Co(CO)_4$, and with the order of decreasing stability[9] of the M—E bond:
Fe—E > Re—E > Mn—E > Mo—E (E = Ge, Sn).

The valence vibration frequencies for the CO group in $Cp_n(CO)_mMHgGeEt_3$ were always lower than those for compounds $Cp_n(CO)_mMGeEt_3$. We attributed this fact to the greater electron-releasing ability of the $HgGeEt_3$ fragment compared with that of the $GeEt_3$ fragment. In fact, the inductive constant σ^*_{HgGeEt} that was calculated by the above-mentioned equations (Table 3) was −2.37. Thus, the electron-releasing ability of the triethylgermylmercury group appeared to be 1.3 higher (according to the Taft scale) than that of the triethylgermyl group. It was of interest to calculate the inductive constants of the $Hg(CO)_mCp_n$ fragments. We determined the σ* values of $HgM(CO)_mCp_n$ from the ν(CO) frequencies for the equatorial groups in the IR spectra of the mercury salts of transition metal complexes (Table 3). It is clear that all of the $HgM(CO)_mCp_n$ groups are electron-releasing according to the inductive mechanism. In addition, one can see that the higher the acceptor ability of the carbonylmetal fragment, the lower the electron-releasing ability of the carbonylmetal mercury group.

The investigation of the structure, IR, mass, and Moessbauer spectra of compounds $M[Co(CO)_4]_2$, $M[Fe(CO)_2Cp]_2$, and $M[Mn(CO)_5]_2$ (M = Zn, Cd, Hg) showed[10] that, when the central atom is varied, the shortening of the metal—metal bond and the insignificant change in the charge of the Co, Fe, and Mn atoms are caused by reverse donation from the occupied d_{xy}- and d_{yz}-orbitals of the cobalt, iron, and manganese to the free p_x- and p_y-orbitals of Zn, Cd, and Hg. Taking into account the relative dimensions and the symmetry of the interacting orbitals, the authors of Ref. 10 concluded that π-bonding should be of more importance in the zinc derivatives than in the mercury derivatives.

We believe that the d_π—p_π-interaction also makes a considerable contribution to the M—Hg bond. Table 3 shows that the acceptor abilities of the $Mn(CO)_5$ and $Re(CO)_5$ fragments are about the same, while the $HgMn(CO)_5$ fragment is more electron-releasing than $HgRe(CO)_5$. The donation of the d-electrons of the manganese atom to the vacant p-orbitals of the mercury atom results in a greater electron-releasing ability of the $HgMn(CO)_5$ group than that expected for the purely inductive interaction *via* the Hg—Mn bond.

References

1. G. A. Abakumov, A. N. Tatarnikov, M. I. Sykhrannova, S. Ya. Khoroshev, and E. H. Gladyshev, *Metalloorgan. Khim.*, 1992, **5**, 941 [*Organomet. Chem., USSR*, 1992, **5** (Engl. Transl.)].
2. A. N. Karasyov, N. E. Kolobova, A. S. Polak, V. S. Shpinel', and K. N. Anisimov, *Teoret. i Exper. Khim.*, 1966, **2**, 126 (in Russian).
3. A. N. Nesmeyanov, L. G. Makarova, and I. V. Polovyanyuk, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 607 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1972, **21**, 567 (Engl. Transl.)].
4. A. A. Ioganson, A. B. Antonova, B. V. Lokshin, N. E. Kolobova, K. N. Anisimov, and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 1957 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1969, **18** (Engl. Transl.)].
5. A. A. Ioganson, Dr. Sci. (Chemistry) Thesis, Institute of Chemistry and Chemical Technology, Russian Academy of Sciences, Krasnoyarsk, 1989 (In Russian).
6. K. Noack, *J. Organometal. Chem.*, 1967, **7**, 151.
7. E. Amberder and E. Muhuhofer, H. Sterr, *J. Organometal. Chem.*, 1969, **17**, 5.
8. A. N. Nesmeyanov, N. E. Kolobova, V. N. Khandozhko, and K. N. Anisimov, *Zh. Organ. Khim.*, 1974, **44**, 313 [*J. Org. Chem. USSR*, 1974, **44** (Engl. Transl.)].
9. H. E. Kolobova, A. B. Antonova, and K. N. Anisimov, *Usp. Khim.*, 1969, **38**, 1802 [*Russ. Chem. Rev.*, 1969, **38** (Engl. Transl.)].
10. M. L. Kafcher and C. L. Simon, *Inorg. Chem.*, 1972, **11**, 1651.

Received November 29, 1993;
in revised form May 26, 1994