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NMR Spectroscopy on Heavy Nuclei of Transition Metal Complexes. The Role of Polarization Effect

A. N. Egorochkin, O. V. Kuznetsova, N. M. Khamaletdinova, and Yu. A. Kurskii

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
ul. Tropinina, 49, Nizhnii Novgorod, 603950 Russia
e-mail: egor@iomc.ras.ru

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Abstract—Chemical shifts (δ) and spin–spin coupling constants (*J*) in the NMR spectra on heavy nuclei M (^{51}V, ^{55}Mn, ^{57}Fe, ^{95}Mo, ^{103}Rh, ^{187}Os, ^{195}Pt) for 27 series of transition metal complexes have been analyzed. In general case in the absence of steric factors the values of δ and *J* depend on three effects of substituents X: inductive, resonance, and polarization. The latter effect increases with the decrease in the distance between M and X and with growing charge on atom M. The contribution of the polarization effect varies from 0 to 80% depending on the type of the series.

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Chemical shifts δ in the NMR spectra on the heavy nuclei of central metals M and the spin–spin coupling constants *J* with participation of these nuclei contain important but not sufficiently analyzed information about the electronic structure of the transition metal complexes. The molecules containing the best studied nuclei ^{51}V, ^{55}Mn, ^{57}Fe, ^{95}Mo, ^{103}Rh, ^{187}Os, ^{195}Pt of atoms M [1–23] can be combined in narrow series L_mMBX_n and L_mMX_n. In these series, ligands L (η^5-C_5H_5, η^6-C_6H_6, CO) are linked directly to atom M as an indicator center, whereas substituents X (Alk, $NAlk_2$, OAlk, Hlg) can be separated from atom M by a bridge B (C_6H_4, η^5-C_5H_4, P). In each narrow series, the ligands L, center M, and bridge B are fixed, so the values of δ and *J* depend only on the properties of the varied substituents X.

Up to now one of the factors determining intramolecular interaction of substituents X with the indicator center M, namely, the polarization effect, was unreasonably omitted. This fact did not allow the full comprehension of the relationship between both the values of δ and *J* and the donor–acceptor properties of substituents X. At the same time, the existence of such relationship follows from general theoretical concepts.

Indeed, the shielding constant σ of nucleus A by electrons determining its chemical shift δ can be written [13, 21, 22] as Eq. (1).

$$\sigma = \sigma_d + \sigma_p + \sigma_n. \qquad (1)$$

Diamagnetic shielding σ_d determined first of all by internal electrons of atom A, has a large contribution to the value of σ, but its magnitude varies within narrow limits. The paramagnetic shielding σ_p, comparable in value with σ_d, varies within a wide range and can be approximately expresses by Eq. (2).

$$\sigma_p = \mathrm{const} < r_V^{-3} > \Delta E^{-1} c^2. \qquad (2)$$

Here, r_V is the radius of the valence electrons of atom A, Δ*E* is the mean excitation energy (the difference between the energies of HOMO and LUMO), c is the coefficient of the atomic orbital of A in the molecular orbital. A small in value nonlocal contribution σ_n is due to effects of magnetic anisotropy and intermolecular interactions.

The relationship between the three contributions into the shielding depends on the nature of nucleus, A. Thus, the shielding of ^{1}H nuclei is due to σ_d and σ_n contributions, whereas the shielding of ^{13}C and ^{19}F is mainly determined by paramagnetic contribution σ_p and to a lesser extent by diamagnetic contribution σ_d. In the shielding of heavy nuclei of transition metals the paramagnetic contribution σ_p predominates [1–23].

The traditional theory of intramolecular interaction of substituents X with reaction center R_C in compounds R_CX and R_CBX (where B is the linker)

Table 1. Chemical shifts δ (ppm) in the NMR spectra of compounds of series **I–IV**

X	**I**, δ_V[a]	**II**, δ_V[b]	**III**, δ_{Mn}[c]	**IV**, δ_{Mn}[c]
H	–	–1027	–1820	–1677
Me	305	–1037	–1833	–1680
CF_3	182	–	–1777	–1660
NMe_2	–	–1082	–	–
OMe	403	–1052	–1839	–1682
F	258	–1019	–1821	–1676
Cl	253	–1009	–1804	–1670
Br	251	–	–	–

[a] According to [10]; $VOCl_3$, $CDCl_3$. [b] According to [4, 23]; $VOCl_3$, THF. [c] According to [15]; $KMnO_4$, $CDCl_3$.

operates with the concepts of inductive effect (characterized by universal constant σ_I of substituent X) and resonance effect (characterized by constants σ_R, σ_R^+ and σ_R^- of substituent X applied when small positive, large positive, or large negative charge, respectively, is located on R_C) [25]. As the basis of the secondary scale of the σ_I and σ_R constants of substituent X the chemical shifts δ_F of the benzene derivatives FC_6H_4X and δ_C of C_6H_5X are used [25].

As mentioned, chemical shifts δ_M of heavy nuclei of transition metals are determined by paramagnetic shielding. This allows an assumption that the inductive and resonance effects of the substituents influence not only the chemical shifts δ_C and δ_F but also the δ_M values. In some works it was proved by the method of conformational analysis [19, 21]. However, in general, the chemical shifts δ_M in narrow series L_mMBX_n and L_mMX_n are affected by three effects: inductive, resonance, and polarization [23], as follows from Eq. (2). Indeed, the HOMO and LUMO in the molecules from these series are localized mainly on atoms M, and the energies of these orbitals depend on the above three substituent effects [26, 27]. At the same time, the investigation of the influence of polarization effect on the NMR spectral parameters is at a very early stage.

The goal of the present work was to elucidate the principal factors determining the influence of the polarization effect on the chemical shifts of heavy nuclei in the NMR spectra of transition metal complexes.

Table 2. Chemical shifts δ (ppm) and spin–spin coupling constants *J* (Hz) in the NMR spectra of compounds of series **V–VIII**

X	**V**, δ_{Mo}[a]	**VI**, δ_{Mo}[b]	**VII**, δ_{Rh}[c]	**VIII**, δ_V ($^1J_{VP}$)[d]
H	–1577	–787	–102	–
Me	–1583	–793	–106	–1875 (214)
t-Bu	–	–	–	–1833
Ph	–	–	–	–1813 (204)
CF_3	–1551	–774	–	–
CN	–	–	–127	–
NEt_2	–	–	–	–1806 (293)
NO_2	–	–	–134	–
OH	–	–	–121	–
OMe	–1587	–798	–	–1928 (366)
F	–1577	–	–	–1961 (488)
Cl	–1566	–785	–122	–

[a] According to [8, 23]; MoO_4^{2-}, $CHCl_3$. [b] According to [5]; MoO_4^{2-}, THF. [c] According to [17]; 3.16 MHz frequency standard, $CDCl_3$. [d] According to [22]; $VOCl_3$, THF.

Twenty seven narrow series of transition metal complexes (Tables 1–7, series **I–XXVII**): $4\text{-}XC_6H_4N\cdot VCl_3$ (**I**), $4\text{-}XC_6H_4OCV(CO)_3(Ph_2PCH_2CH_2PPh_2)$ (**II**), $4\text{-}XC_6H_4CH_2Mn(CO)_4PPh_3$ (**III**), $4\text{-}XC_6H_4CH_2COMn\cdot(CO)_4PPh_3$ (**IV**), $(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_4X$ (**V**), *trans*-$Mo(N_2)_2[(4\text{-}C_6H_4X)_2PCH_2CH_2P(4\text{-}C_6H_4X)_2]_2$ (**VI**), $(\eta^5\text{-}C_5H_5)(CO)(I)RhC_6H_4X$ (**VII**), $(CO)_5VPX_3$ (**VIII**), $(CO)_4(PhCH_2)MnPX_3$ (**IX**), $(CO)_4(PhCH_2CO)MnPX_3$ (**X**), $(\eta^5\text{-}C_5H_5)(CO)(COMe)FePX_3$ (**XI**), $(\eta^5\text{-}C_5H_5)\cdot Fe(\eta^5\text{-}C_5H_4X)$ (**XII**), *cis*-$(CO)_4Mo(PX_3)_2$ (**XIII**), $(CO)_5Mo(PPh_2X)$ (**XIV**), $Mo_2(O_2CX)_4$ (**XV**), $LMo(NO)X_2$ (**XVI**), $[(bpy)Mo(CNX)_5](PF_6)_2$ (**XVII**), $(COD)(Cl)RhPX_3$ (**XVIII**), $(Me_3P)Cl_2Os(\eta^6\text{-}C_6H_5X)$ (**XIX**), $(\eta^5\text{-}C_5H_5)(Br)Os(PX_3)_2$ (**XX**), $(\eta^6\text{-}1,4\text{-}MeC_6H_4Pr\text{-}i)(Cl)(H)OsPX_3$ (**XXI**), $[PtX_6]^{2-}$ (**XXII**), *trans*-$[(Et_3P)_2(Cl)PtSiX_3]$ (**XXIII**), $(CO)_4V(\eta^5\text{-}C_5H_{5-n}X_n)$ (**XXIV**), $(Ph_3P)(CO)(Me)Fe(\eta^5\text{-}C_5H_4X)$ (**XXV**), $(CO)_5MoPX_3$ (**XXVI**), $(COD)(Me)RhPX_3$ (**XXVII**), allow the analysis of the effect of substituent X, and, in particular, the polarization effect, on the chemical shifts of heavy nuclei δ_M and direct spin–spin coupling constants $^1J_{MP}$. Whenever possible when choosing the series we standardized the solvent since the contribution of σ_n in Eq. (1) has some influence on δ_M (**XV**,

Table 3. Chemical shifts δ (ppm) in the NMR spectra of compounds of series **IX–XII**

X_3	**IX**, δ_{Mn}[a]	**X**, δ_{Mn}[a]	X_3	**XI**, δ_{Fe}[b]	X	**XII**, δ_{Fe}[c]
Bu_3	–2060	–1933	Me_3	1374	H	0
$(C_6H_{11})_3$	–1924	–1778	*i*-Pr_3	1683	Et	35.5
Me_2Ph	–2011	–1873	Me_2Ph	1414	Ph	188.2
$MePh_2$	–1876	–1759	$MePh_2$	1424	$CH=CH_2$	165.7
Ph_3	–1819	–1677	Ph_3	1531	COH	232.5
			$(OMe)_3$	1159	COMe	234.2
					COOMe	194.7

[a] According to [15]; $KMnO_4$, $CDCl_3$. [b] According to [19, 23]; $Fe(CO)_5$, C_6D_6. [c] According to [24]; $(\eta^5\text{-}C_5H_5)_2Fe$, $CDCl_3$.

Table 4. Chemical shifts δ (ppm) and spin–spin coupling constants *J* (Hz) in the NMR spectra of compounds of series **XIII–XVI**

X_6	**XIII**, δ_{Mo}[a]	X	**XIV**, δ_{Mo}[b] ($^1J_{MoP}$)	X	**XV**$_d$, δ_{Mo}[c, d]	**XV**$_t$, δ_{Mo}[c, e]	X_2	**XVI**, δ_{Mo}[f]
Et_6	–1764	NH_2	–1767 (148)	Me	3768	3702	$(OEt)_2$	464
Bu_6	–1742	NHMe	–1765 (146)	Pr	3730	3682	$(OPh)_2$	624
Me_2Ph_4	–1637	OMe	–1791 (156)	*i*-Pr	3719	3670	$(SPh)_2$	990
Et_2Ph_4	–1657	OEt	–1788 (159)	Bu	3746	3661	(OPh)Cl	1050
Bu_4Ph_2	–1688	OPr	–1788 (159)	*t*-Bu	3696	3656	(SPh)Cl	1200
Ph_6	–1556	OBu	–1788	CF_3	4144	4021	F_2	1274
$(OEt)_6$	–1807	OPh	–1775				Cl_2	1811
$(OPh)_6$	–1752	Cl	–1702 (165)					

[a] According to [3]; MoO_4^{2-}, CH_2Cl_2. [b] According to [6, 7]; MoO_4^{2-}, $CDCl_3$. [c] According to [9]; MoO_4^{2-}. [d] DMF. [e] THF. [f] According to [8]; MoO_4^{2-}, CH_2Cl_2.

Table 4) and did not consider series with bulky substituents to avoid strong steric effects, which may affect the value of δ_M [13, 21, 22].

To prove the existence of polarization effect we have used a correlation analysis. For this, it was convenient to introduce the concept of classical and nonclassical reaction series [23, 26, 27]. Classical series are the benzene derivatives $1,4\text{-}R_CC_6H_4X$ where the reaction center and the substituent X are separated by a linker $–C_6H_4–$ of large size and there is no direct polar conjugation between the atoms X and R_C. The effect of X on the chemical and physical properties *P* in these series (for example, on the value of δ_F in the NMR spectra of $1,4\text{-}FC_6H_4X$) is described by two-parameter equations of the type (3).

$$P = P_H + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-). \quad (3)$$

Here, P_H denotes the value of *P* for X =, H.

Principal difference of nonclassical series R_CBX and R_CX from the classical ones is a small length of linker B (–C≡C–, –CH=CH–, $–CH_2–$, etc.) or its absence. In other words, the distance between the reaction center and substituent X in nonclassical series is shorter than in classical series. Series R_C^qBX and R_C^qX bearing positive or negative charge *q* on atom R_C are of special interest, where the interaction between the atoms R_C^q and X is realized by three mechanisms. Two of them (inductive and resonance) were classical, whereas the third one (polarization) came into use only recently. This effect will be considered in detail below; now it suffices to note that the characteristics of the

Table 5. Chemical shifts δ (ppm) and spin–spin coupling constants *J* (Hz) in the NMR spectra of compounds of series **XVII–XX**

X	**XVII**, δ_{Mo}[a]	X_3	**XVIII**, δ_{Rh} ($^1J_{RhP}$)[b]	X	**XIX**, δ_{Os}, ($^1J_{OsP}$)[c]	X_6	**XX**, δ_{Os}[f]
Me	–19	Et_3	385 (148)	H	–2431 (266)	Me_6	–3506
i-Pr	–64	Pr_3	401 (147)	Me	–2364 (269)	Me_4Ph_2	–3418
t-Bu	–57	Bu_3	402 (146)	Et	–2352 (270)	Me_3Ph_3	–3324
C_6H_{11}	–98	Me_2Ph	358 (148)	*i*-Pr	–2348 (270)	Me_2Ph_4	–3393
CH_2Ph	–115	$MePh_2$	348 (151)	*t*-Bu	–2268 (267)	Ph_6	–3008
		Ph_3	393 (152)	Me, *i*-Pr	–2226 (272)[d]	$(OMe)_6$	–3816
		$(CH_2Ph)_3$	417 (151)	Me_6	–1829 (290)[e]	$(OPh)_6$	–3904
		$(NMe_2)_3$	557 (199)				
		$(OMe)_3$	253 (249)				

[a] According to [8]; MoO_4^{2-}, acetone; bpy = 2,2'-bipyridyl. [b] According to [18, 23]; 3.16 MHz frequency standard. cod = η^4-cyclooctadiene. [c] According to [20]; OsO_4, CD_2Cl_2. [d] For $(Me_3P)Cl_2Os(\eta^6\text{-}C_6H_4MePr\text{-}i)$ compound. [e] For $(Me_3P)Cl_2Os(\eta^6\text{-}C_6Me_6)$ compound. [f] According to [16]; OsO_4, acetone-d_6, toluene-d_8, THF-d_8.

Table 6. Chemical shifts δ (ppm) and spin–spin coupling constants *J* (Hz) in the NMR spectra of compounds of series **XXI–XXIII**

X_3	**XXI**, $^1J_{OsP}$[a]	X	**XXII**, δ_{Pt}[b]	X_3	**XXIII**, δ_{Pt}[c]
Me_3	260	Me	–314	H_3	–5067
i-Pr_3	265	CN	0	$H_2(C{\equiv}CH)$	–5049
Bu_3	263	OH	7150	H_2F	–4935
$(C_6H_{11})_3$	264	F	11180	H_2Cl	–4992
Me_2Ph	264	Cl	3850	HCl_2	–4853
$MePh_2$	270	Br	1980		
Ph_3	277				

[a] According to [20]; OsO_4, C_6D_6, acetone-d_6, toluene-d_8, THF-d_8. [b] According to [14]; $[Pt(CN)_6]^{2-}$, THF–CH_3OH. [c] According to [1]; $PtCl_6^{2-}$, CH_2Cl_2.

polarization effect in correlation analysis are universal constants σ_α calculated for different substituents X by nonempirical methods of quantum chemistry [28]. Therefore, for charged nonclassical series the three-parameter Eq. (4) is fulfilled.

$$P = P_H + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-) + c\sigma_\alpha. \qquad (4)$$

From the aforesaid, a simple criterion of the presence of polarization effect follows: an improvement of statistical parameters on going from the two-parameteric Eq. (3) to the three-parameteric Eq. (4). The use of this criterion allowed to prove the influence of polarization effect on such properties *P* of the molecules and their complexes as ionization potentials [29], electron affinities [30], binding energies of inner electrons [31, 32], energies of electron transfer [33], electrochemical redox potentials [26, 27], spectroscopic and thermodynamic characteristics of H-complexes [34], charge transfer complexes [35], silatranes [36, 37], and other donor–acceptor complexes [38].

Table 7. Chemical shifts δ (ppm) and spin–spin coupling constants *J* (Hz) in the NMR spectra of compounds of series **XXIV–XXVII**

X_n	**XXIV**, δ_V[a]	X	**XXV**, δ_{Fe}[b]	X_3	**XXVII**, $^1J_{MoP}$[c]	X	**XXVII**, δ_{Rh}[d]
H	–1534	H	1392	*t*-Bu_3	127	Me	23
Me	–1525	Me	1367	Et_2Ph	132	Et	57
Me_4	–1496	Ph	1500	Bu_2Ph	133	Pr	73
Me_5	–1492	COOMe	1576	Ph_3	144	Bu	73
COMe	–1406	NEt_2	1437	$Ph(NEt_2)_2$	159	NMe_2	165
Cl_5	–1010			$(NMe_2)_3$	173	OMe	–129
Br_5	–1029						

[a] According to [11, 12]; $VOCl_3$, THF. [b] According to [19], $Fe(CO)_5$, C_6D_6. [c] According to [2, 3]; MoO_4^{2-}, CH_2Cl_2. [d] According to [18]; 3.16 MHz frequency standard, C_6D_6.

Correlation equations of the type (3) and (4) for the series **I–XXVII** are given in Table 8. They were calculated using the Statgraphics 3.0 program. Regression analysis by the least-squares method was performed at the 95% level of confidence.

Equations (3) and (4) can be represented in the form (5) and (6), respectively.

$$P = P_H + Ind + Res. \tag{5}$$

$$P = P_H + Ind + Res + Pol. \tag{6}$$

From the three-parameteric equations (6) the inductive ($Ind = a\Sigma\sigma_I$), resonance [$Res = b\Sigma\sigma_R$ ($Res = b\Sigma\sigma_R^+$ or $Res = b\Sigma\sigma_R^-$)], as well as polarization ($Pol = c\Sigma\sigma_\alpha$) contributions into the total variation of the properties *P* (δ, *J*) caused by substituent X have been calculated (Table 8). As seen from Table 8, in series **I–XXVII** contributions *Ind* and *Res* vary from 0 to 100 and from 0 to 83%, respectively. Contribution *Pol* is observed not in all series, being varied from 0 to 80%.

Let us consider the reasons for the polarization effect to occur in the transition metal complexes L_mMX_n. The interaction of the central atom M with ligands L and substituents X is realized by a complex mechanism, which is traditionally divided in three components [39]:

(1) formation of two-electron covalent bond of the σ-, π- or δ-type by atom M with L and X;

(2) formation of a dative σ- or π-bond between the orbitals of L and X occupied by two electrons and the vacant orbital of atom M;

(3) formation of the σ- or π-bond between the orbital of atom M occupied by two electrons and the vacant orbitals of L and, X.

As a result of complex formation, charge *q* is developed on atom, M. Its value and sign strongly depend on the nature of L and, X. For example, with increasing n in complexes $M(CO)_n$ and $M(PR_3)_n$, the positive and negative charges on atom M, respectively, increase. Atom Mo in $Mo(CO)_6$ has a positive, and in $Mo(\eta^6\text{-}C_6H_6)_2$, a negative charge, so, in complex $Mo(\eta^6\text{-}C_6H_6)(CO)_3$ the charge on central atom is close to zero [39].

Therefore, narrow series L_mMX_n and L_mMBX_n **I–XXVII** can be considered as the aforementioned charged nonclassical series $R_C{}^qX$ and $R_C{}^qBX$ where the polarization effect can be characterized by constants σ_α of substituent, X. There is an alternative assessment of polarization effect. The positive or negative charge *q* on the indicator center M polarizes substituents X by inducing dipoles in them. The energy of electrostatic attraction E_{es} between the charge *q* and the induced dipole (polarization effect) stabilizes the charge and can be expressed by Eq. (7).

$$E_{es} = -q^2\alpha/(2r^4). \tag{7}$$

Here, α denotes the polarizability of substituent X, *r* is the distance between the charge and the induced dipole [30–38]. The energy E_{es} sharply decreases with the distance *r* and therefore it is absent (or negligibly small) in classical charged systems 1,4-$R_C{}^qC_6H_4X$.

Table 8. The coefficients and their standard deviations ($P_H \pm S_P$, $a \pm S_a$, $b \pm S_b$, $c \pm S_c$) of equations $P = P_H + a\Sigma\sigma_I + b\Sigma\sigma_R + c\Sigma\sigma_\alpha$, $P = P_H + a\Sigma\sigma_I + b\Sigma\sigma_R^+ + c\Sigma\sigma_\alpha$ or $P = P_H + a\Sigma\sigma_I + b\Sigma\sigma_R^- + c\Sigma\sigma_\alpha$, standard error of the approximation S_Y, correlation coefficients R, and sample size *n* for series **I–XXVII**[a], and inductive (*Ind*), resonance (*Res*), and polarization (*Pol*) contributions (%) in the change in the properties of *P* under the influence of substituents X

P	$P_H \pm S_P$	$a \pm S_a$	$b \pm S_b$	σ	$c \pm S_c$	S_Y[b]	*R*[b]	*n*	*Ind*	*Res*	*Pol*
δ_{V}, **I**	250±20	–137±38	–164±18	σ_R^+	–33±31	16(17)	0.975(0.974)	6	22±6	70±8	8±7
δ_{V}, **II**	–1027±2	61±7	38±2	σ_R^+	–9±6	3(4)	0.993(0.991)	6	29±3	66±4	5±3
δ_{Mn}, **III**	–1821±1	71±4	67±3	σ_R^-	0	2	0.996	6	40±2	60±3	0
δ_{Mn}, **IV**	–1677±1	26±1	23±1	σ_R^-	–2±1	0.5(0.7)	0.998(0.996)	6	40±2	57±2	3±2
δ_{Mo}, **V**	–1577±1	42±3	38±2	σ_R^-	–4±3	1(2)	0.995(0.993)	6	39±3	57±3	4±3
δ_{Mo}, **VI**	–787	2.9±0.1	3.9±0.1	σ_R	0.5±0.2	0.5(1.0)	0.999(0.995)	5	39±1	64±2	5±2
δ_{Rh}, **VII**	–105±2	43±4	0	–	0	2	0.984	6	100	0	0
δ_{V}, **VIII**	–1957±15	0	–7±4	σ_R^+	–57±8	19(46)	0.957(0.694)	6	0	20±11	80±11
$^1J_{VP}$, **VIII**	276±49	112±40	–15±8	σ_R^+	53±23	35(61)	0.956(0.855)	5	47±17	23±12	30±13
δ_{Mn}, **IX**	–3011±187	0	–962±255	σ_R^+	–142±40	27(72)	0.961(0.683)	5	0	52±14	48±13
δ_{Mn}, **X**	–2135±39	331±42	–336±106	σ_R	–83±28	13(28)	0.992(0.959)	5	52±7	25±8	23±8
δ_{Fe}, **XI**	408±151	–1043±157	–844±151	σ_R	–472±60	31(144)	0.984(0.562)	6	35±5	36±6	29±4
δ_{Fe}, **XII**	0	568±114	–187±137	σ_R	–118±54	23(32)	0.970(0.940)	7	58±12	17±12	25±11
δ_{Mo}, **XIII**	–2120±55	0	–55±14	σ_R	–105±12	19(54)	0.972(0.755)	8	0	27±7	73±8
δ_{Mo}, **XIV**	–1549±38	–382±52	150±20	σ_R^+	–119±36	7(12)	0.969(0.906)	8	40±6	52±7	8±2
$^1J_{MoP}$, **XIV**	139±4	34±6	–9±6	σ_R^-	–22±10	1.5(2.5)	0.975(0.945)	6	62±11	13±8	25±11
δ_{Mo}, **XV**$_d$	3948±69	118±70	76±56	σ_R^+	53±16	15(30)	0.996(0.984)	6	45±27	32±24	23±7
δ_{Mo}, **XV**$_t$	3864±39	78±40	86±32	σ_R^+	40±9	8(22)	0.998(0.988)	6	36±18	43±16	21±5
δ_{Mo}, **XVI**	4576±1180	–1169±890	3129±594	σ_R	840±233	118(235)	0.964(0.848)	7	11±8	47±9	42±12
δ_{Mo}, **XVII**	96±29	0	45±13	σ_R^+	32±7	12(40)	0.944(0.000)	5	0	47±14	53±12
δ_{Rh}, **XVIII**	178±18	–197±17	–117±7	σ_R	–94±10	12(49)	0.989(0.790)	9	29±2	45±3	26±3
$^1J_{RhP}$, **XVIII**	164±11	46±7	–34±7	σ_R^-	16±5	5(8)	0.992(0.977)	9	38±6	37±8	25±8
δ_{Os}, **XIX**	–2454±13	–1197±278	0	–	–125±41	18(29)	0.996(0.990)	7	58±13	0	42±14
$^1J_{OsP}$, **XIX**	266±1	0	–19±3	σ_R^+	3±2	0.9(1.1)	0.994(0.991)	7	0	83±13	17±12
δ_{Os}, **XX**	–4484±334	–355±133	–295±157	σ_R	–290±72	102(224)	0.942(0.674)	7	32±12	28±15	40±10
$^1J_{OsP}$, **XXI**	262±2	21±3	14±7	σ_R	–5±1	1(2)	0.986(0.935)	7	51±7	16±8	33±6
δ_{Pt}, **XXII**	2831±1741	1473±495	–731±333	σ_R^-	1664±477	1341(2914)	0.954(0.759)	6	29±10	30±14	41±12
δ_{Pt}, **XXIII**	–5081±15	314±37	0	–	55±28	19(20)	0.976(0.975)	5	83±10	0	17±9
δ_{V}, **XXIV**	–1511±22	187±18	0	–	–33±18	32(37)	0.990(0.987)	7	83±8	0	17±9
δ_{Fe}, **XXV**	1391±9	691±69	–107±35	σ_R^-	0	13	0.998	5	75±7	25±8	0
$^1J_{MoP}$, **XXVI**	121±2	26±2	–6±0.2	σ_R^+	–3±1	0.7(1.2)	0.999(0.998)	6	34±3	60±2	6±2
δ_{Rh}, **XXVII**	–141±9	–236±11	–55±2	σ_R^+	–83±7	4(24)	0.999(0.968)	6	40±2	44±2	16±1

[a] Constants σ_I, σ_R, σ_R^+, σ_R^-, and σ_α, applied in [30–38] are used. [b] The values calculated without considering the polarization effect on the properties of *P* are in parentheses.

Hence, for investigation of the polarization effect either contributions *Pol* (Table 8) or Eq. (7) can be used. Their combined use allows the consideration of the dependence of polarization effect on the distance *r* and charge *q* on atom M in more detail. For this, let us divide series **I–XXVII** into three groups.

The first group includes series **I–VII**. As follows from Tables 1 and 2, the distance *r* between the reaction (indicator) center (V, Mn, Mo, and Rh atoms) and substituent X is equal to or larger than value *r* in classical series 1,4-$R_CC_6H_4X$. Therefore, at first glance, it seems reasonable to assume the absence of polarization effect in series **I–VII**. However, as a matter of fact, the *Pol* contribution is equal to zero only in series **III** and **VII**. In series **I, II, IV–VI** the chemical shifts δ_M obey three-parameteric equations of the type (4). The statistical characteristics of the two-parameteric equations (3) are somewhat worse, that is, on going from the two-parameteric to the three-parameteric equations the standard error S_Y decreases and the correlation coefficient R increases (Table 8). Contribution *Pol* in series **I, II, IV–VI** is small (3–8%, Table 8) and it is due to direct polar conjugation, that is, the interaction of the indicator center M (V, Mn, Mo) with the substituent X via the π-electron system. As said above, in classical reaction series 1,4-$R_C{}^qC_6H_4X$ such an interaction is absent by definition. Formally, the direct polar conjugation can be considered as a rapprochement between the indicator center and substituent, resulting in appearance of a slight polarization effect.

The second group includes series **VIII–XXIII**. In these series, which are typically nonclassical, firstly, the distance *r* between the indicator center M (V, Mn, Fe, Mo, Rh, Os, Pt) and the substituent X (Tables 2–6) is smaller and the difference between the statistical characteristics S_Y and R of the three- and two-parameteric equations larger than in series **I–VII**, and, secondly, the polarization effect plays an important role (contribution *Pol* amounts 8 to 80%, Table 8).

The third group covers series **XXIV–XXVII**. There the distance *r* from substituents X to the indicator center M (V, Fe, Mo, Rh) is short, which is typical for nonclassical series. In spite of that, the polarization effect is relatively small (in series **XXIV, XXVI, XXVII**) or even absent (in series **XXV**). Apparently, this is due to the dependence of the polarization effect (and, hence, contribution *Pol*, Table 8) on the charge *q* on atom M, which cannot be determined experimentally.

As follows from Eq. (7), the polarization effect grows with the increase in the positive or negative charge on atom, M. It was already mentioned that the value and the sign of the charge *q* on atom M in complexes L_mMX_n is determined by a combination of donor–acceptor interactions of atom M with ligand L and substituent, X. The linker B in L_mMBX_n also contributes to these interactions. Besides, an additional factor can be mentioned, which complicates the relationship between contribution *Pol* and charge *q*, namely, the dependence of the ratio of contributions *Ind*, *Res*, and *Pol* on the array n in the series. The set n, that is, the number and the type of substituents X, determines the range of variation of constants σ_I, σ_R (σ_R^+, σ_R^-), and σ_α, and, hence, the contributions *Ind*, *Res,* and *Pol* in the given series. That is why the charges on atoms M, estimated by the use of values of *Pol* are at best no more than a rough approximation.

Let us consider in this approximation the series **XXIV–XXVII**. On going from $(CO)_5VPX_3$ (**VIII**) to $(CO)_4V(\eta^5\text{-}C_5H_{5-n}X_n)$ (**XXIV**) the contribution *Pol* decreases from 80 to 17% (Table 8). Apparently, this is not only due to the increased distance *r* between atom V and substituent X, but also due to a decrease in the positive charge on atom V with decrease in the number of ligands CO. From $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4X)$ (**XII**) to $(Ph_3P)(CO)(Me)Fe(\eta^5\text{-}C_5H_4X)$ (**XXV**) the contribution *Pol* decreases from 25 to 0%. Most probably, due to the effect of four ligands different in donor–acceptor properties, the charge on atom Fe in the molecules of series (**XXV**) becomes close to zero.

On going from $(cod)(Cl)RhPX_3$ (**XVIII**) to $(cod)(Me)RhPX_3$ (**XXVII**) the contribution *Pol* decreases from 26 to 16% (Table 8) in accordance with the oppositely directed effect of the acceptor (Cl) and donor (CH_3) substituents.

In conclusion, let us briefly discuss the spin–spin coupling constants ${}^1J_{MP}$ (Tables 2, 4–7, **VIII, XIV, XVIII, XIX, XXI,** and **XXVI**). In all series the polarization effect affects constants ${}^1J_{MP}$ (Table 8). The contribution *Pol* reaches 33%, with the minimal value (6%) in series **XXVI**, which belongs to the third group (see above). The spin–spin coupling constants are approximately expressed [13, 22] by Eq. (8).

$$ {}^1J_{MP} = \mathrm{const}({}^3\Delta E^{-1})S^2_M(0)S^2_P(0)P^2. \quad (8) $$

Here, ${}^3\Delta E$ is the mean energy of the triplet excitement, $S^2_M(0)$ and $S^2_P(0)$ is the density of the *s*-electrons on nuclei M and *P*, *P* is the contribution of the *s*-electrons to the formation of the M–P bond. The influence of the polarization effect on the value of $^{1}J_{\mathrm{MP}}$ in general is consistent with Eq. (8). Indeed, the polarization effect is known to affect the energy of the singlet–triplet transitions [33].

Therefore, the chemical shifts δ of heavy nuclei M and the spin–spin coupling constants J with their participation are determined by a combined action of the inductive, resonance, and polarization effects of substituents X. The polarization effect grows with the increase in the charge on atom M and with the shortening of the distance between atom M and atom (fragment) X. For the most of narrow series it is impossible to adequately describe the influence of substituents X on the values of δ and J without taking into account the polarization effect.

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