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Electronegativity and chemical hardness of organoelement groups†

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The experimental approaches to estimation of comparative electronegativity and chemical hardness of organometallic groups have been proposed. Qualitative data on the electronegativity of L_nM groups were obtained from ^{19}F NMR study of model systems 4-$FC_6H_4QML_n$ (Q = C≡C, N(R), O, C(O)O, S), (4-$FC_6H_4)_3SnML_n$ and (4-$FC_6H_4)_3SnQML_n$ (Q = O, S), containing a great variety of different organometallic groups containing transition or heavy main-group metals. The data on chemical hardness of L_nM groups were obtained from NMR study of distribution of different L_nM groups between hard and soft anions. The following basic results have been obtained. (1) The relative electronegativity and chemical hardness of L_nM groups can change in parallel or not with the electronegativity and hardness of the central metal atom. (2) The substituents in Ar can substantially modify electronegativity and hardness of Ar_nM groups; the influence of Ar groups has an inductive nature; the increase in electron-donating ability of aryl ligands enhances the hardness of Ar_nM cations. (3) The relative electronegativity and hardness of L_nM groups in L_nMX are invariant and do not depend on X.

Keywords: bond polarity; electronegativity; group electronegativity; hardness; chemical hardness; exchange equilibria; ^{19}F NMR spectra

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INTRODUCTION

The prediction of the reactivity of metal–element σ-bonds L_nM—E is one of the main problems of organometallic chemistry. These bonds are of great importance in catalysis, e.g. in addition of these bonds to acetylenes [1][1] and in migration processes such as tautomerism [2],[2] as well as exchange reactions [3], where M—E bonds are broken and formed:[3]

$$L_nM{-}X + RC{\equiv}C{-}H \xrightarrow{Cat} \begin{matrix} R & & L_nM \\ & C{=}C & \\ X & & H \end{matrix} \quad (1)$$

$$L_nM{-}X{-}Z{=}Y \rightleftharpoons X{=}Z{-}Y{-}ML_n \quad (2)$$

$$L_nM{-}X + L_nM^*{-}Y \rightleftharpoons L_nM{-}Y + L_nM^*{-}X \quad (3)$$

The main factors that influence the reactivity of these bonds are their polarity and polarizability, as well as ability for heterolytic dissociation. The polarity of σ-bonds has a substantial effect on their energy.[4] At the same time, the problems of energetics of these bonds attract attention because the thermochemistry of organometallic compounds has been intensively developed in recent years.[5]

It is obvious that the above properties should depend on such fundamental characteristics of L_nM groups as electronegativity and hardness. Recently the main attention has been concentrated on the problems and quantum-chemical calculations of the polarity of σ-bonds and group electronegativity (GEN).[6-15] Novel atomic electronegativity (AEN) scales have been proposed[16–18] and quantum-chemical calculations of GEN have been carried out for a number of the simplest organic and organoelement groups L_nE containing elements of II and III Periods (E = C, N, O, P, S).[13,14,19] In contrast, the data on GEN of organometallic groups (E = M) containing transition or heavy main-group metal atoms are rather scarce,[17,20] apparently, since

Table 1 The electronegativities of elements of IV B Group obtained in the framework of different scales of electronegativity

Scale	C	Si	Ge	Sn	Pb
Pauling	2.55	1.90	2.01	1.96	2.33
Allred–Rochov	2.50	1.74	2.02	1.72	2.45
Mulliken	6.27	4.77	4.60	4.30	3.90
Allen	2.54	1.99	1.92	1.82	—

the calculation of multielectronic systems with *d*- and *f*-orbitals presents difficulties and for compounds of elements of IV–VI Periods it is necessary to take into account relativistic effects.[18,21]

In this connection, it seemed to be of current interest to compare experimentally the GEN of groups containing transition and heavy main-group metals and the polarity of bonds formed by these groups. These investigations would answer the question, as whether it is possible to evaluate the comparative polarity of bonds in using the data on AEN of the central metal atoms. Such a possibility cannot be excluded without experimental confirmation, in particular for related groups containing central metal atoms from the same group. In this connection, it should be noted that the values of AEN proposed by different scales are rather ambiguous and the sequence of their changes may be different even for metals from the same group (Table 1 and series [4]–[7] for elements of Group IV).

$$\text{Pauling:} \quad \text{Si} < \text{Sn} < \text{Ge} < \text{Pb} < \text{C} \qquad (4)$$

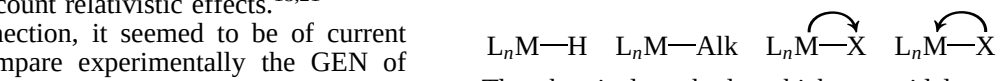
$$\text{Allred–Rochov:} \quad \text{Sn} < \text{Si} < \text{Ge} < \text{Pb} < \text{C} \qquad (5)$$

$$\text{Mulliken:} \quad \text{Pb} < \text{Sn} < \text{Ge} < \text{Si} < \text{C} \qquad (6)$$

$$\text{Allen:} \quad \text{Sn} < \text{Si} < \text{Ge} < \text{C} \qquad (7)$$

To estimate the influence of the difference in the polarity of H—X and M—X bonds in HX-acids and their organometallic derivatives L_nMX on the comparative energy of these bonds the values of the central metal AEN have usually been used,[22,23] ignoring the influence of ligands. Additional interest in comparative GEN of L_nM groups is connected with prediction of the effect of GEN on the position of σ-metallotropic equilibria [2].[24] Finally, it has recently been found that the use of the Pearson principle of hard and soft acids and bases (HSAB) requires taking into account GEN of corresponding groups.[25,26] This gives rise to the question, as whether the comparative GEN of two L_nM group remains invariant in passing from bonds with hard ligands to bonds with soft ligands.

The prediction of comparative polarity of M—E bonds is complicated by the fact that in many cases the electronic interactions in these bonds are not simple. The problem is that the true σ-bonds are formed only in the case when M is bonded to an atom without electronic pairs and low-lying unoccupied orbitals. In other cases there is a probability of existence of donor-accepting interactions, whose contribution can depend on M as well as on X. It may be that this contribution will dominate the polarization of intrinsic σ-bonds and will produce variable GEN.



The chemical methods, which are widely used for the study of electronic effects of substituents, are not suitable for investigation of interactions across M—X bonds owing to the high reactivity of these bonds. Different sparing physical methods are used for this purpose, as well as quantum chemistry. In these investigations the empirical relations between the character of electron density distribution and the corresponding parameters in the framework of different physical methods, as well as DM, have usually been used. The discussion of the possibilities of the above methods and their limitations for investigation of the polarity of M—X bonds is beyond the scope of the present work. Table 2 gives some literature examples of the estimation of GEN of L_nM groups.

In the series of our papers we have developed novel experimental approaches to estimation of the relative electronegativity and chemical hardness of organometallic groups. The review of corresponding results is presented in this paper.

THE RELATIVE ELECTRONEGATIVITY OF L_nM GROUPS

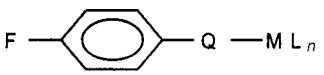
Two experimental approaches to estimation of comparative electronegativity of L_nM groups have been proposed. The first approach was based on the study of fluorine chemical shifts (FCS). It has been shown that qualitative data on the comparative polarities of the metal–element bonds and, respectively, on comparative GEN of L_nM groups can be obtained from ^{19}F NMR studies of model

Table 2 Some literature data on the electronegativities of L_nM groups

L_nM	χ (eV) (Pauling)	Estimation[a] method	L_nM	χ (eV) Pauling	χ (eV) Mulliken	Estimation method
Me_3Ge	2.19	A	Ph_2Sb	1.96		B
	1.94	B		1.82		C
	1.77	C	Ph_2Bi	1.97		B
Me_3Sn	2.30	A		1.82		C
	1.79	B	$(CO)_5Mn$	2.47		E
	1.61	C			5.2	F
				1.31	4.55	G
Me_3Pb	1.75	B	$(CO)_4MnPPh_3$	1.98		E
	1.56	C	$(CO)_2CpFe$	2.10		E
				2.1	5.0	H
MeHg	1.75	D				
	2.24	B	$(CO)_4Co$	2.3	5.4	H
	1.12	C		1.27	4.43	G
PhHg	1.85	D				

[a] A: Calculation by Huheey.[27] B: Calculation by Imamoto–Masuda.[28] C: Calculation by Gordy.[29] D: From solubility product of L_nMX in water.[30] E: From fluorine chemical shifts of 3-$FC_6H_4CH_2ML_n$.[31] F: From experimental data on ionization potential and electron affinity.[17] G: Quantum-chemical calculation.[32] H: From ^{119}Sn Mössbauer spectra.[33]

systems **1**:



1

Q═C≡C, N(R), O, C(O)O, S

involving Q—M bonds and *p*-FC_6H_4 indicator group.[34] It was suggested that the main factor influencing the fluorine shielding for related systems is the electronic density on the Q fragment. It was supposed that this density is intermediate between electron density in symmetrical compounds 4-FC_6H_4Q—QC_6H_4F-4 (nonpolar bond) and electronic density in ionic compounds 4-FC_6H_4Q-M^+. Thus for system **1** involving the fixed fragment Q the fluorine shielding must depend on M—X bond polarity. This approach was applied to study the polarity of M—C, M—N, M—O or M—S bonds involving a great variety of different organometallic groups containing transition or heavy main-group metals.

From the systematic point of view it was important to support the data obtained in the framework of the above approach by results obtained in the framework of some other independent method. Another approach was based on the study of the influence of polar substituent effects on the position of the exchange equilibria [8]:

$$L_nM—X_1 + H—X_2 \rightleftharpoons L_nM—X_2 + H—X_1 \quad (8)$$

in the systems involving HX-acids and their L_nM derivatives, where X_1 and X_2 have the same key atoms.[24,35] The equilibrium constant can be expressed as:

$$\log K_{eq}[8] = \log K_D(L_nMX_1) - \log K_D(L_nMX_2) + \log K_D(HX_2) - \log K_D(HX_1)$$

where K_D is the dissociation constant of the corresponding bond. If a linear dependence of [9]:

$$\log K_D(L_nMX) = A_{MX} \log K_D(HX) + C_{MX} \quad (9)$$

exists between the dissociation constants of the HX acids and their L_nM derivatives, the equilibrium constant is given by the following expression:

$$\log K_{eq}[8] = (A_{MX} - 1)[pK_a(HX_2) - pK_a(HX_1)] \quad (10)$$

It should be noted that the existence of a linear dependence of [9] in organic solvents may be expected on the basis of polarographic data.[36] Previous to our investigations the experimental support was obtained for methylmercury derivatives in water.[37,38]

The study of the influence of substituents in the X fragment on the equilibrium position of reactions [8] in the same solvent, in which the acidities of HX acids were measured, usually in DMSO,[39] allows one to determine the coefficient A_{MX}, which characterizes quantitatively the relative polarity of H—X and M—X bonds. If the polarity of the M—X bond is higher than the polarity of the H—X

bond, then AMX < 1. If the polarity of the M—X bond is lower than that of the H—X bond then A_{MX} > 1. For a pure ionic bond A_{MX} should be equal to zero. It should be taken into account that in the case of strongly solvating DMSO we have to deal with GEN of L_nM groups modified by strong solvation rather than with intrinsic GEN. In those cases, in which values of pK_a of the corresponding series of acids have not been determined, the observation of relation [11]:

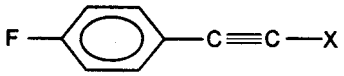
$$\log K_{eq}[8] = a\sigma + b \qquad (11)$$

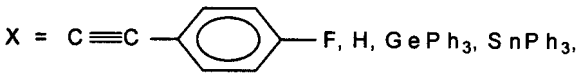
between $\log K_{eq}[8]$ and the polar constant σ for substituents in the X fragment serves as an indirect indication that the relation [9] exists.

These principles were used in the study of equilibria [8] by the NMR technique, which allows one to study fast and slow reactions on the NMR time scale. It should be emphasized that the second approach is based not on the logical considerations as the first one, but on the pure mathematics.

The relative polarity of M—C bonds

For the investigation of the relative polarity of the M—C bonds the derivatives of 4-fluorophenylacetylene have been chosen.[40]



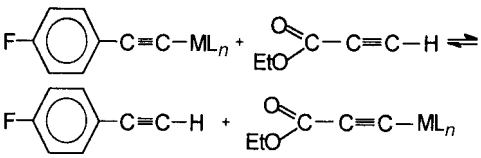


X = C≡CC6H4F-4, H, GePh3, SnPh3, PbPh3, HgPh, AuPPh3, Mn(CO)5, Re(CO)5, W(CO)3Cp, Mo(CO)3Cp, Cr(CO)3Cp, Fe(CO)2Cp

It can be seen from Table 3 that the fluorine shielding increases in going from symmetrical 1,4-di-*p*-fluorophenylbutadiine containing a nonpolar C—C bond to organometallic derivatives of 4-fluorophenylacetylene. In the case of the groups with the same electronic configuration of the highest occupied orbitals (Hg—Au, W—Pb and so on) the metal–carbon bonds involving transition metals have a higher polarity than those involving heavy main-group metals. The above data indicate that the polarity of heavy main group metal–carbon bonds increases in the series:

$$Ph_3Ge < Ph_3Sn < Ph_3Pb < Ph_2Bi < PhHg$$

The same results follow from the exchange equilibria in systems involving 4-fluorophenylacetylene, ethyl propiolate and their derivatives in toluene:[41]



[12]

ML_n = $SnPh_3$, $PbPh_3$, HgPh

K_{eq}[12] = 1.0, 5.3, 8.9

The equilibrium [12] is shifted to the right in the case of $L_nM = Ph_3Pb$ and to a greater degree in the case of L_nM = PhHg. In the case of $L_nM = Ph_3Sn$, $K_{eq} = 1$. This fact means that the polarities of the C—Sn and C—H bonds are practically the same.

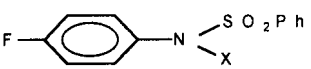
Table 3 The FCS[a] for 4−$FC_6H_4C{\equiv}CX$ in toluene[40]

X	FCS	X	FCS
$C{\equiv}CC_6H_4F{-}4$	−4.08	$AuPPh_3$	1.64
$GePh_3$	−2.82	$Mn(CO)_5$	1.29
$SnPh_3$	−2.59	$Re(CO)_5$	1.46
H	−2.51	$W(CO)_3Cp$	1.49
$PbPh_3$	−1.74	$Mo(CO)_3Cp$	1.53
$BiPh_2$	−1.57	$Cr(CO)_3Cp$	1.62
CPh_3	−1.47	$Fe(CO)_2Cp$	3.10
HgPh	−1.52		

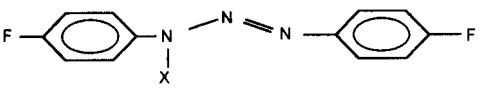
[a] In ppm from external PhF. Sign '+' corresponds to upfield shift.

The relative polarity of M—N bonds

In the case of M—N bonds the organometallic derivatives of NH-acids of three different types were used: (4′-fluorophenyl)benzenesulfonamide (FPBSA)[42,43] and the two tautomeric systems di-(4-fluorophenyl)triazene (DFPT)[44–48] and 2-(4′-fluorophenyl)benzimidazol (FPBI).[49]



X = H, HgPh, $AuPPh_3$, K



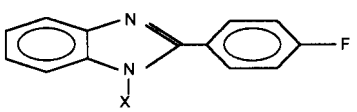
X = H, HgPh, $AuPPh_3$, $(o\text{-Tol})M(PEt_3)_2$

M = Ni, Pd, Pt

Table 4 The FCS[a] derivatives of (4′-fluorophenyl)benzensulfonamide (FPBSA) and di-(4-fluorophenyl)triazene (DFPT) in toluene as well as for derivatives of 2-(4′-fluorophenyl)benzimidazol (FPBI) in DMSO[42–49]

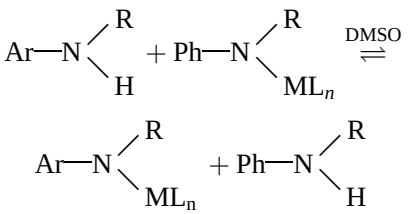
	System		
X	FPBSA	DFPT	FPBI
H	3.80	5.60	−1.32
HgPh	4.89	7.01	−0.96
$AuPPh_3$	7.97	8.91	0.38
K	14.17 (in DMSO)	—	—
Ni(*o*-Tol)$(PEt_3)_2$	—	8.44; 10.49	—
Pd(*o*-Tol)(PEt3)$_2$	—	8.63; 11.28	—
Pt(*o*-Tol)(PEt3)$_2$	—	8.36; 11.22	—

[a] In ppm from external PhF. Sign '+' corresponds to upfield shift.



X = H, HgPh, $AuPPh_3$

It follows from FCS values for FPBSA (Table 4) that the polarity of M—N bonds increases in going from the Hg—N bond to the Au—N bond; however, these bonds are to a large degree covalent, because corresponding FCS values are substantially lower than 14 ppm for the potassium derivative of FPBSA. For model substituted benzenesulfonamides and their PhHg- and Ph_3PAu-derivatives the linear dependences between p*K*a and log K_{eq} [13] have been found.[43,50]



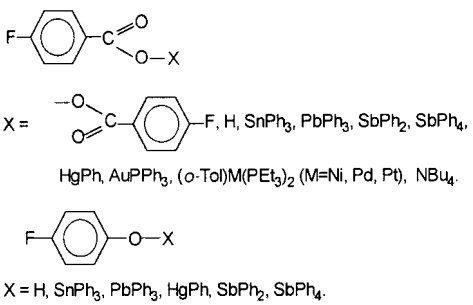
[13]

$$\log K_{eq}[13] = -0.26pK_a + 3.30$$
$$(ML_n = AuPPH_3); A_{Au-N} = 0.74$$
$$\log K_{eq}[13] = -0.27pK_a + 3.53$$
$$(ML_n = HgPh); A_{Hg-N} = 0.73$$

From the values of the A_{M-N} coefficients it follows that the polarities of the Au—N and Hg—N bonds are nearly the same. At the same time, the FCS values indicate a greater polarity for the Au—N bond than for the Hg—N bond. Thus the method based on the FCS allows one to reveal finer differences between bond polarities.

The relative polarity of M—O bonds

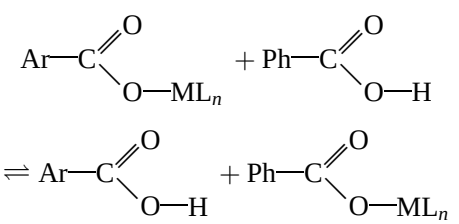
In the case of M—O bonds the derivatives of two types of HO-acid have been investigated, which involving 4-fluorobenzoic acid[51,52] and 4-fluorophenol.[52,53]



From the FCS of derivatives of benzoic acids (Table 5) it can be seen that the polarity of the M—O bonds increases in the series:

$$H-O < Ph_3Sn-O < Ph_2Sb-O < PhHg-O < Ph_3Pb-O < Ph_4Sb-O < Ph_3PAu-O < (o-Tol)M(PEt_3)_2-O$$

For three organometallic groups [PhHg, Ph_4Sb and (*o*-Tol)Ni$(PEt_3)_2$] data on the relative polarity of M—O bonds were supported by exchange equilibrium method.[54,55]



[14]

Table 5 The FCS[a] for 4−$FC_6H_4C(O)OX$ in toluene[51,52]

X	FCS	X	FCS
H	−8.42	$AuPPh_3$	−2.11
CPh_3	−6.63	$Ni(o\text{-Tol})(PEt_3)_2$	−1.38
$SnPh_3$	−6.35	$Pd(o\text{-Tol})(PEt_3)_2$	−0.45
$SbPh_2$	−6.11	$Pt(o\text{-Tol})(PEt_3)_2$	−1.11
HgPh	−4.79	NBu4 [b]	2.41
$PbPh_3$	−4.36		

[a] In ppm from external PhF. Sign '−' corresponds to downfield shift.
[b] In DMSO.

$$\log K_{eq}[14] = (A_{M-O} - 1)pK_a + B$$
$$A_{M-O} = 0.80(Hg—O) < 0.63(Sb—O) < 0.35(Ni—O)$$

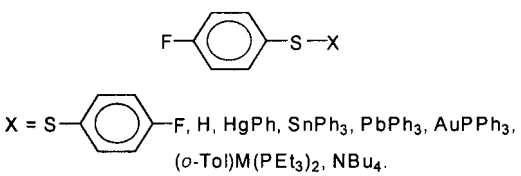
It follows from the values of $A_{M—O}$ that the M—O bond polarity increases in the order:

$$Hg—O < Sb(V)—O < Ni—O$$

Similar results have been obtained for organometallic derivatives of 4-fluorophenol.[56,57]

The relative polarity of M—S bonds

For investigation of the relative polarity of M—S bonds the derivatives of 4-fluorothiophenol have been studied:[52,56]



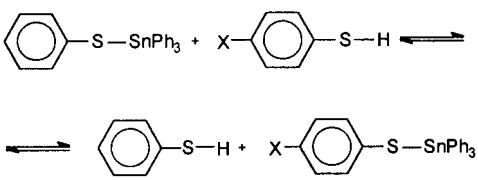
It was found that the polarities of M—S bonds involving main-group metals are rather close due to the fact that the corresponding values of FCS (Table 6) fall within a narrow range around 0.6 ppm, whereas the whole range from disulfide to tetrabutylammonium 4-fluorothiophenoxide is equal to 17 ppm.

The method of exchange equilibria also confirmed this conclusion. In DMSO the position of exchange equilibrium [15]:

Table 6 The FCS[a] for 4-FC_6H_4SX in toluene[52,56]

X	FCS	X	FCS
SC_6H_4F-4	0.59	$AuPPh_3$	8.74
H	3.88	$Ni(o\text{-Tol})(PEt_3)_2$	10.83
$PbPh_3$	3.81	$Pd(o\text{-Tol})(PEt_3)_2$	11.46
$SnPh_3$	3.21	$Pt(o\text{-Tol})(PEt_3)_2$	11.25
HgPh	4.47	NBu4[b]	16.91

[a] In ppm from external PhF. Sign '+' corresponds to upfield shift.
[b] In DMSO.



[15]

$$K_{eq} = 2.2(X = NO_2); K_{eq} = 1.7(X = NMe_2)$$

does not depend practically on substituent,[35] in spite of the fact that the difference in pK_a values of corresponding thiols is very large (nine units of pK_a). At the same time the polarity of transition metal–sulfur bonds is very similar for nickel, palladium and platinum and close to that of the ionic bond.[52]

The ligand influence on the polarity of metal–element bonds

It has been shown for a variety of L_nMX compounds[57–61] that GEN of L_nM and polarity of M—X bond varies significantly with the nature of σ- or n-ligands L. Thus, polarity decreases with increase in electron-accepting ability of σ-aryl ligands and the influence of these ligands is inductive owing to the fact that the correlation of the FCS values with σ^0 constants of substituted phenyl groups is better than that with the σ constant of Hammett (Table 7).

The increase in electron-accepting ability of Ar groups may give rise to inversion of polarity of the M—X bond. Such an effect was found in the case of Ar_3Sn—S bonds. The increase in electron-accepting ability of Ar in going from the Ph_3Sn group to the $(3,4,5\text{-}Cl_3C_6H_2)_3Sn$ group causes the inversion

Table 7 The correlations of the FCS for $Ar_nMQC_6H_4F{-}4$ with σ or σ^0 constants of Ar groups[57–61]

$Ar_nMQC_6H_4F{-}4$	
$ArHgC{\equiv}C_6H_4F{-}4$	FCS = $(-0.72 \pm 0.02)\sigma - 1.57$; $r = 0.978$; $S = 0.11$
	FCS = $(-0.85 \pm 0.01)\sigma^0 - 1.53$; $r = 0.994$; $S = 0.05$
$ArHgN(SO_2Ph)C_6H_4F{-}4$	FCS = $(-0.72 \pm 0.05)\sigma + 4.25$; $_r = 0.939$; $_S = 0.11$
	FCS = $(-1.09 \pm 0.02)\sigma^0 + 1.31$; $r = 0.985$; $S = 0.06$
$Ar_3SnOC_6H_4F{-}4$	FCS = $(-2.54 \pm 0.12)\sigma + 12.83$; $r = 0.949$; $S = 0.21$
	FCS = $(-2.83 \pm 0.04)\sigma^0 + 12.95$; $r = 0.986$; $S = 0.11$
$Ar_3SnSC_6H_4F{-}4$	FCS = $(-4.25 \pm 1.35)\sigma + 1.35$; $r = 0.933$; $S = 0.33$
	FCS = $(-4.00 \pm 0.22)\sigma^0 + 2.91$; $r = 0.987$; $S = 0.15$
$ArHgSC_6H_4F{-}4$	FCS = $(-0.66 \pm 0.40\sigma + 4.30$; $r = 0.883$; $S = 1.44$
	FCS = $(-1.11 \pm 0.02)\sigma^0 + 4.30$; $r = 0.964$; $S = 0.09$
$ArPt(PPh_3)_2SC_6H_4F{-}4$	FCS = $(-0.76 \pm 0.11)\ \sigma + 11.62$; $r = 0.913$; $S = 0.17$
	FCS = $(-0.86 \pm 0.07)\ \sigma^0 + 11.67$; $r = 0.954$; $S = 0.13$
$Ar_3PAuSC_6H_4F{-}4$	FCS = $(-1.61 \pm 0.10)\ \sigma + 8.19$; $_r = 0.944$; $_S = 0.23$
	FCS = $(-2.42 \pm 0.03)\ \sigma^0 + 8.33$; $r = 0.990$; $S = 0.10$

of the polarity of the Sn—S bond:[35]

$$(3,4,5-Cl_3C_6H_2)_3Sn^{\delta-}{-}S^{\delta+}C_6H_4F-4,\quad FCS = -0.35\,ppm$$

$$4\text{-}FC_6H_4S{-}SC_6H_4F-4, FCS = 0.59\,ppm$$

$$Ph_3Sn^{\delta+}{-}S^{\delta-}C_6H_4F-4, FCS = 2.94\,ppm$$

In regard to *n*-ligands, it was found that in the case of compounds (*o*-Tol)$M(PR_3)_2SC_6H_4F$-4 and (*o*-Tol)$M(PR_3)_2OC(O)C_6H_4F$-4 (M = Ni, Pt) the relative polarity of the M—S or M—O bonds increases with increase in the donor ability of R_3P ligands only on condition that steric requirements are not changed. The influence of *n*-ligands, which have different steric requirements, is determined by two opposite effects: the donor ability and the steric factor.[61–67]

Comparison of calculated and empirical GEN of some L_nM groups

The *ab initio* calculations for the GEN of Ar_3Si and Ar_3Sn groups containing meta-, para- and poly-substituted phenyl groups were performed (Table 8).[68] From these calculations it follows that GEN increases with increase of electronegativity of Ar. It is interesting to note that the difference in GEN of Ar_3Si and Ar_3Sn groups, which equals 0.23 eV for the most electron-accepting Ar i.e. 3,4,5-$Cl_3C_6H_2$, decreases significantly (0.05 eV) for the most electron-donating Ar group, i.e. *p*-$Me_2NC_6H_4$. At the same time, the difference between the AEN of silicon and tin atoms is larger: 0.47 eV. These results show once again that the substituents in L can modify the difference in GEN between related groups. The better correlation of GEN values with the σ^0 Taft constants than with the σ Hammett constants suggests the conclusion obtained above on the basis of FCS, that the influence of Ar ligands on GEN of Ar3E groups has an inductive nature.

Good correlations have been found for corresponding values of FCS for compounds (**2**)–(**5**) and calculated values of GEN:

$Ar_3SiC_6H_4F$-4 **2**; $Ar_3SnC_6H_4F$-4 **3**;
$Ar_3SnCH_2C_6H_4F$-4 **4**; $Ar_3SnSeC_6H_4F$-4 **5**

in which the *p*-FC_6H_4 indicator is bonded to the L_nM group directly or through carbon or sulfur.

$$FCS(\mathbf{2}) = (2.186 \pm 0.012)\chi + 5.426;\quad r = 0.989; S = 0.26.$$

$$FCS(\mathbf{3}) = (2.151 \pm 0.010)\chi + 5.852;\quad r = 0.990; S = 0.24.$$

$$FCS(\mathbf{4}) = -(1.58 \pm 0.01)\chi + 12.0;\quad r = 0.984; S = 0.17.$$

$$FCS(\mathbf{5}) = -(2.00 \pm 0.01)\chi + 9.87;\quad r = 0.993; S = 0.16.$$

Thus, it should be expected that in the general case of compounds $Ar_nE{-}QC_6H_4F$-4 the change in FCS can represent the quantitative measure of GEN modification under the effect of substituent. Moreover, it is possible to estimate with a high degree of certainty the relative polarity of E—Q bonds on the basis of the study of the regularities of FCS changes.

Table 8 The *ab initio* calculated electronegativities of Ar_3Si and Ar_3Sn groups and FCS for compounds $Ar_3SiC_6H_4F$-4 (**2**), $Ar_3SnC_6H_4F$-4 (**3**), $Ar_3SnCH_2C_6H_4F$-4 (**4**) and $Ar_3SnSC_6H_4F$-4 (**5**)[68]

	χ(eV)		FCS[a]			
Ar	Ar_3Si	Ar_3Sn	**2**	**3**	**4**	**5**
4-$Me_2NC_6H_4$	2.97	2.92	−0.8	−0.16		
4-$MeOC_6H_4$	3.10	3.04	−1.8	−1.13	6.93	
4-MeC_6H_4	3.33	3.25	−1.7	−1.13	6.91	3.41
3-MeC_6H_4	3.37	3.29	−1.8	−1.15	7.04	3.41
Ph	3.48	3.39	−2.3	−1.52	6.71	2.94
4-FC_6H_4	3.97	3.84	−3.1	−2.31	6.05	2.18
3-FC_6H_4	4.03	3.90	−3.7		5.74	1.90
4-ClC_6H_4	4.23	4.09	−3.5	−2.63	5.64	1.81
3-ClC_6H_4	4.23	4.18	−4.0	−3.07	5.59	1.68
3-$CF_3C_6H_4$	4.41	4.23		−3.43		
3,4-$Cl_2C_6H_3$	4.81	4.63	−5.0	−3.91	4.77	0.73
3,5-$Cl_2C_6H_3$	4.88	4.69		−4.53	4.39	0.20
3,4,5-$Cl_3C_6H_2$	5.38	5.15	−6.4	−5.25		−0.35

[a] In ppm from external PhF. Sign '+' corresponds to upfield shift.

The relative polarities of tin–transition metal bonds

In order to investigate the comparative GEN of groups involving transition metals, the relative polarity of tin–metal bonds in the compounds (4-$FC_6H_4)_3Sn—ML_n$ (**6**) has been studied (Table 9).[69] The conclusions on direction and degree of polarization of Sn—M bonds were made on the basis of comparison of FCS for compounds **6** with the FCS of symmetrical distannane with the nonpolar Sn—Sn bond. In the case of the cobalt compound the Sn—Co bond is polarized in the sense $Sn^{\delta+}—Co^{\delta-}$. In all other cases the Sn—M bonds are polarized in the sense $Sn^{\delta-}—M^{\delta+}$. From the data obtained, it follows that in the interaction with the tin atom the decrease of GEN of L_nM groups takes place in the order:

$$(CO)_4Co > (CO)_5Mn > Cp(CO)_3Cr > Cp(CO)_3Mo > Cp(CO)_3W > (CO)_5Re > Cp(CO)_2Fe$$

This sequence corresponds satisfactorily to literature data on the dissociative ability of tin–metal bonds in Ph_3SnML_n compounds,[70] as well as to the data on their Mössbauer spectra.[71]

A comparison of the above series with the order of change of AEN calculated according to Mulliken (Co, 4.26; W, 4.19; Fe, 4.03; Re, 4.01; Mo, 3.92; Cr, 3.76; Mn, 3.72) as well as of limited data on spectral AEN (Co, 1.82; Fe, 1.79; Mn, 1.74; Cr, 1.57), indicates that in the general case there is no agreement of GEN with AEN. Moreover, even in the case of related L_nM, the GEN of L_nM does not run parallel to AEN of M:

$$\text{GEN: } (CO)_5Mn > (CO)_5Re;$$
$$\text{AEN: } Mn > Re;$$
$$Cp(CO)_3Cr > Cp(CO)_3Mo > Cp(CO)_3W$$
$$Cr < Mo < W$$

These results show that the interaction of ligands with the metal atom may cause the inversion of GEN with respect to AEN. These data support the validity of Pearson's opinion that the AEN are not a reliable measure of bond polarity. Moreover, these

Table 9 The FCS[a] for (4-$FC_6H_4)_3SnML_n$ in benzene[69]

Compound	FCS	Compound	FCS
(4-$FC_6H_4)_3SnSn(C_6H_4F-4)_3$	−2.45	(4−$FC_6H_4)_3SnRe(CO)_5$	−0.54
(4−$FC_6H_4)_3SnFe(CO)_2Cp$	−0.40	(4−$FC_6H_4)_3SnCr(CO)_3Cp$	−1.32
(4−$FC_6H_4)_3SnCo(CO)_4$	−3.00	(4−$FC_6H_4)_3SnMo(CO)_3Cp$	−1.00
(4−$FC_6H_4)_3SnMn(CO)_5$	−1.46	(4−$FC_6H_4)_3SnW(CO)_3Cp$	−0.87

[a] In ppm from external PhF. Sign '−' corresponds to downfield shift.

Table 10 The results of *ab initio*[72] and TO INDO calculations[20] of electronegativities of the $(CO)_5Mn$ and $(CO)_4Co$ groups and the values of FCS for the compounds $(4\text{-}FC_6H_4)_3SnMn(CO)_5$ (**7**) and $(4\text{-}FC_6H_4)_3SnCo(CO)_4$ (**8**)

L_nM	The method of calculation	χ (eV)	FCS[a] for **7** or **8**
$Mn(CO)_5$	*ab initio*	2.93	−1.46
	TO INDO	4.55	
$Co(CO)_4$	*ab initio*	3.29	−3.00
	TO INDO	3.49	

[a] In ppm from external PhF. Sign '−' corresponds to downfield shift.

data show that the use of AEN of the central metal atom for estimation of the relative polarity of bonds formed by organometallic groups containing transition metals may, in the general case, lead to wrong conclusions.

Our results[72] of the *ab initio* calculation of GEN of the $(CO)_5Mn$ and $(CO)_4Co$ groups performed by the ΔSCF methods are presented in Table 10, where similar values obtained previously in literature by the semiempirical TO INDO method[20] and the values of FCS for the compounds $(4\text{-}FC_6H_4)_3SnMn(CO)_5$ (**7**) and $(4\text{-}FC_6H_4)_3SnCo(CO)_4$ (**8**) are also presented for comparison. It can be seen from the data of Table 10, that the shielding of fluorine decreases substantially on going from compound **7** to compound **8**. This, in turn, indicates an increase in GEN in going from the $(CO)_5Mn$ to $(CO)_4Co$. Thus, in contrast to the calculations by the TO INDO method, the results of the *ab initio* calculations are consistent with the experimental data.

The analysis of the above sequences of change in M—Q bond polarity in model systems **1** involving different Q shows that these sequences are very similar. The following general conclusions could be deduced from the results obtained:

(1) The L_nM groups involving transition metals in all cases form more polar M—X bonds than L_nM groups involving heavy main-group metals.
(2) The comparison of the above sequences with the Mulliken AEN of the central atom shows that GEN of L_nM does not run parallel to AEN of M. For some L_nM the inversion of GEN in comparison with AEN takes place due to the ligand influence.

The relative GEN of Ar_3E groups in systems $Ar_3E—X—E'Ar_3$

According to Pauling, AEN is the ability of an atom in a molecule to attract electrons. An analogous determination should also be true for GEN of organic or organometallic groups. Therefore, the following model systems are promising in studies of comparative GEN of L_nM:

$$L_nM—X—M^*L_m \quad (X = S \text{ or } O).$$

In these hinge systems, organometallic groups L_nM and L_mM^* compete with each other for the electron density distribution in the triad system MXM^* according to their ability to withdraw the electron density. We have chosen the systems involving derivatives of Group IVB elements ($n = m = 3$). In order to answer the question, as to whether the comparative GEN remains invariant in passing from bonds with hard ligands to bonds with soft ligands, hard oxygen and soft sulfur were taken as heteroatoms. The tris(4-fluorophenyl)stannyl group was chosen as an indicator of change in electron density on X. Thus, we have studied the Ph_3M derivatives of tris(4-fluorophenyl)stannanol (**9**) and of tris(4-fluorophenyl)stannanethiol (**10**).[73,74] Prior to these investigations, such systems as the tris-(4-fluorophenyl)stannyl halides have been studied (Table 11). The minus sign corresponds to a downfield shift of the signal relative to PhF (decrease in the shielding). The data of Table 11 demonstrate that in going from $(4\text{-}FC_6H_4)_3Sn—Sn(C_6H_4F—4)_3$, which has a nonpolarized Sn—Sn bond, to compounds $(4\text{-}FC_6H_4)_3Sn—X$ (X = Hal) with $Sn^{\delta+}—X^{\delta-}$ bonds, which are polarized according to the values of absolute electronegativities (eV) of tin and halogen atoms (Sn, 4.30; Cl, 8.30; Br, 7.59; I, 6.76) a decrease in the fluorine shielding takes place. The extent of shielding decreases as the electronegativity of the halogen atom increases according to the following equation:

$$FCS = -0.31\chi(Hal) - 1.88; r = 0.983, S = 0.06.$$

Therefore, the FCS in compounds $(4\text{-}FC_6H_4)_3SnX$ adequately reflects the comparative electronegativity of the moiety X. According to the FCS the polarization of M—E bonds increases in the sequences:

$$Si < Ge < Sn < Pb \ (X = 0) \text{ and}$$
$$Si < C < Ge < Sn < Pb \ (X = S)$$

Thus GEN of the Ph_3E groups decreases in the series:

Table 11 The FCS[a] for systems $(4\text{-}FC_6H_4)3SnXEPh_3$ as well as for $(4\text{-}FC_6H_4)_3SnHal$ in benzene[73,74]

Compound	FCS	Compound	FCS
$(4\text{-}FC_6H_4)_3SnOSiPh_3$	−3.84	$(4\text{-}FC_6H_4)_3SnSn(C_6H_4F{-}_4)_3$	−2.45
$(4\text{-}FC_6H_4)_3SnOGePh_3$	−3.11	$(4\text{-}FC_6H_4)_3SnCl$	−4.41
$(4\text{-}FC_6H_4)_3SnOSnPh_3$	−2.78	$(4\text{-}FC_6H_4)_3SnBr$	−4.27
$(4\text{-}FC_6H_4)_3SnOPbPh_3$	−2.14	$(4\text{-}FC_6H_4)_3SnI$	−3.94
$(4\text{-}FC_6H_4)_3SnSCPh_3$	−2.63		
$(4\text{-}FC_6H_4)_3SnSSiPh_3$	−2.74		
$(4\text{-}FC_6H_4)_3SnSGePh_3$	−2.60		
$(4\text{-}FC_6H_4)_3SnSSnPh_3$	−2.55		
$(4\text{-}FC_6H_4)_3SnSPbPh_3$	−2.13		

[a] In ppm from external PhF. Sign '−' corresponds to downfield shift.

$$Si < C < Ge < Sn < Pb$$

A good correlation between FCS and AEN of the central atoms of the Ph_3E group was established:

$$FCS = -0.66\chi + 0.40; r = 0.961(X = O)$$
$$FCS = -1.80\chi + 4.93; r = 0.967(X = S) \text{ (except for the } Ph_3C \text{ group)}$$

These data indicate that the dependence of GEN of the Ph_3M groups on the AEN of the central metal atoms firstly is not only qualitative, but also quantitative, and secondly, remains unchanged in the case of the metal bonded to the hard oxygen or soft sulfur anion.

This dependence does not hold for the Ph_3C group, which may be caused by two factors. Firstly, when passing from Ph_3C to Ph_3Si, an additional transfer of electron density from the sulfur atom to the E atom can occur due to interaction between unoccupied 3*d* orbitals of the silicon atom and 3*p* orbitals of the sulfur atom, which contain lone electron pairs. Secondly, direct interaction of the π-electron systems of the aromatic rings of the $(4\text{-}FC_6H_4)_3Sn$ and Ph_3C groups can occur. Thus, analysis of the Stewart–Briegleb structural models demonstrates that the distance between the planes of the aromatic rings of the $(4\text{-}FC_6H_4)_3Sn$ and Ph_3E groups sharply decreases in going from $(4\text{-}FC_6H_4)_3SnSSiPh_3$ to $(4\text{-}FC_6H_4)_3SnSCPh_3$. As a result, a direct interaction between the π-electron systems and partial transfer of electron density to the antibonding orbitals of the 4-fluorophenyl ligand become possible. This may cause an increase in the shielding of fluorine and an apparent decrease in the group electronegativity of the Ph_3C group.

To answer this question we have studied the derivatives of 4-fluorothiophenol of the type $Ph_3ESC_6H_4F\text{-}4$ (E = C, Si, Ge, Sn, Pb),[75] because analysis of the molecular models demonstrates that there are no contacts between the π-electron systems of the phenyl and 4-fluorothiophenoxide ligands. It follows from the FCS values that GEN of Ph_3E groups decreases in the order:

$$Ph_3C(-0.24\,ppm) < Ph_3Si(1.91) < Ph_3Ge(2.32) < Ph_3Sn(3.08) < Ph_3Pb(3.71)$$

A good linear dependence exists between FCS and AEN:

$$FCS = -1.65\chi + 10.03\ (r = 0.994, S = 0.19)$$

Hence, despite the fact that the question of the correctness of using the difference between AEN as a measure of the polarity of a bond is still an open question,[76,77] in the present case, this parameter reflects rather adequately the variation of the polarity of the M—O and M—S bonds.

In view of the series found by us in which the GEN of the Ph_3M groups decreases in order $Ph_3Si > Ph_3Ge > Ph_3Sn > Ph_3Pb$, the results[78] obtained in the ^{119}Sn and ^{207}Pb NMR study of the polarity of the Pb—M and Sn—M bonds in compounds $Ph_3Pb—MPh_3$ or $Ph_3Sn—MPh_3$ seem to be surprising. Based on the increase in the shielding of ^{207}Pb in going from $Ph_3PbPbPh_3$ to $Ph_3PbSnPh_3$ and then to $Ph_3PbGePh_3$, it was concluded that the M—M bonds in these compounds are polarized as $Pb^{\delta-}—Sn^{\delta+}$ and $Pb^{\delta-}—Ge^{\delta+}$, which implies that the GEN of the Ph_3Pb group is greater than those of Ph_3Sn and Ph_3Ge. The shielding of ^{119}Sn in Ph_3SnMPh_3 compounds increases in the series $Ph_3Pb < Ph_3Sn < Ph_3Ge$, which, by analogy, should also point to a decrease in GEN in the series $Ph_3Pb > Ph_3Sn > Ph_3Ge$.

In this connection we have studied the ^{119}Sn and ^{207}Pb chemical shifts in compounds $Ph_3SnOMPh_3$ and $Ph_3PbOMPh_3$ (Table 12).[73] As follows from

Table 12 The ^{119}Sn and ^{207}Pb chemical shifts in benzene[73]

Compound	^{119}Sn[a] (ppm)	Compound	^{207}Pb[b] (ppm)
$Ph_3SnOSiPh_3$	−98.4	$Ph_3PbOSiPh_3$	−107.3
$Ph_3SnOGePh_3$	−89.1	$Ph_3PbOGePh_3$	−98.6
$Ph_3SnOSnPh_3$	−81.8	$Ph_3PbOSnPh_3$	−76.2
$Ph_3SnOPbPh_3$	−77.2	$Ph_3PbOPbPh_3$	−63.6

Sign '−' corresponds to upfield shift.
[a] From external Me_4Sn.
[b] From external Me_4Pb.

the data presented in Table 12, the regularities of the effect of the nature of the metal on ^{119}Sn and ^{207}Pb chemical shifts in the compounds studied by us are the same as those in Ph_3SnMPh_3 and Ph_3PbMPh_3 compounds. In all cases, the shielding of the ^{119}Sn and ^{207}Pb nuclei increases in the order $Ph_3Pb < Ph_3Sn < Ph_3Ge < Ph_3Si$, which should indicate, from the viewpoint of Koglin *et al.*,[78] that the GEN of the Ph_3M groups decreases in the order $Ph_3Pb > Ph_3Sn > Ph_3Ge > Ph_3Si$.

This conclusion is in contradiction with our results obtained by ^{19}F NMR for compounds **9** and **10**. Since, in the case of $L_nMQC_6H_4F$-4 compounds, the ^{19}F NMR data on the comparative polarity of the M—Q bonds are consistent with the results obtained in the study of exchange equilibria, we believe that our results are more reliable.

THE RELATIVE HARDNESS OF L_nM GROUPS

For the prediction of the reactivity of metal–element σ-bonds the principle of hard and soft acids and bases (HSAB)[79] seems to be promising. This principle was of a qualitative character for several decades, but the prerequisites have appeared recently for its transformation into a quantitative theory.[80] For example, the concept of absolute hardness was developed, and quantitative parameters for the absolute hardness of metal atoms and cations were suggested.[81,82] The quantum-chemical calculations of the hardness of metal atoms were performed.[83] Recently, the calculations of the hardness of the simplest organic and organoelement groups containing carbon, nitrogen, oxygen, sulfur, silicon and phosphorus as key atoms have been published.[14,15] At the same time, there are no published calculated data on the hardness of organometallic groups or cations, and experimental results are very scarce.[84] Therefore, it seemed appropriate to study the possibility of the qualitative or quantitative prediction of the comparable hardness of organometallic cations on the basis of hardness parameters of the central metal atoms or cations in organometallic groups. In particular, the problem of prediction of the character of distribution of competing organometallic groups between hard and soft anionoid ligands is of great significance. It was also of interest to elucidate the possibility of the existence of qualitative or quantative regularities in the influence of the nature of ligands on the hardness of organometallic cations.

A convenient approach to the solution of these problems is the study of the exchange equilibria of the type [16]:[25]

$$Q—X + Q^*—Y \rightleftharpoons Q^*—X + Q—Y \qquad (16)$$

where Q and Q* are cationoid fragments and X and Y are the anionoid fragments of molecules. These fragments can be differentiated to relatively harder and softer ones, and, according to the HSAB principle, the exchange reaction should occur with the formation of pairs of fragments of the 'hard–hard' (hh) and 'soft–soft' (ss) types:

$$hs^* + sh^* \rightleftharpoons hh^* + ss^*$$

Many types of organometallic compound of heavy main-group metals and, to a lesser extent, transition metals are convenient objects for the study of these exchange reactions, because exchange processes involving metal–heteroatom bonds of these compounds (see reaction [3]) often proceed on the preparative time scale and even on the NMR time scale.[3]

The relative hardness of two different L_nM cations has been determined by studying equilibrium constants in systems [17] involving soft

Table 13 The equilibrium constants for reactions [17][85–87]

L_nM	L_mM^*	K_{eq}[17]
Ph_3Pb	Ph_3Sn	>1600
PhHg	Ph_3Sn	>1600
PhHg	Ph_3Pb	>1600
PhHg	Ph_3PAu	2.9
Ph_3Sn	(*o*-Tol)Ni(PEt_3)$_2$	12
(*o*-Tol)Pd(PEt_3)$_2$	(*o*-Tol)Ni(PEt_3)$_2$	>400
(*o*-Tol)Pd(PEt_3)$_2$	Ph_3Pb	0.036

4-FC_6H_4S- and hard 4-$NO_2C_6H_4O$- anions:[85–87]

$$L_nM{-}OC_6H_4NO_2-4 + L_mM{-}SC_6H_4F-4 \rightleftharpoons L_nM{-}SC_6H_4F-4 + L_mM^*{-}OC_6H_4NO_2-4 \quad (17)$$

The choice of these anionoid ligands is caused by the fact, that the parameters of the chemical hardness of their close analogue (PhS and PhO) are known: 14 and 23 kcal mol^{-1}.[25] In addition, this pair is characterized by the close steric requirements and acidities of corresponding HX acids, which differ only by 0.5 pK_a units in DMSO.[39]

We have studied by ^{19}F NMR the reactions [17] involving various possible combinations of different pairs of organometallic cations. Some data are presented in Table 13.

The following data on comparative hardness of L_nM cations have been obtained for the chemical hardness of related L_nM groups from K_{eq}[17]:

$$PhHg < Ph_3PAu; Ph_3Pb < Ph_3Sn; (o\text{-Tol})Pd(PEt_3)_2 < (o\text{-Tol})Ni(PEt_3)_2$$

These sequences are in the completely opposite direction to increasing absolute hardness values η for the metal atoms. Absolute hardness $\eta = (I-A)/2$: Au (3.46) < Hg(5.54); Sn (3.05) < Pb (3.53); Ni (3.25) < Pd (3.89). For example, according to Table 13 the equilibrium of reaction [17] is shifted to the right. Thus the $PhHg^+$ cation exhibits a somewhat higher trend to form a bond with the softer anion $^-SC_6H_4F$-4 than the Ph_3PAu^+ cation and is characterized by lower chemical hardness. This conclusion contradicts the data on the values of the absolute hardness of gold and mercury atoms (3.46 eV and 5.54 eV respectively) and Au^+ and Hg^{2+} cations (5.6 eV and 7.7 eV, respectively).[17] It also contradicts the data of the quantum-chemical calculations of the hardness of Au and Hg atoms (3.55 eV and 5.02 eV), calculated in the X_α approximation, and in the Gunnarson–Lindquist approximation (3.44 eV and 5.29 eV).[83]

The above results do not agree with the assertion that the hardness of the group is mainly determined by the hardness of the central atom.[14] Several reasons for this disagreement are possible. One of them is probably the fact that in the case of nonisostructural cations the predominant effect on their comparative hardness can be determined by differences in the effects of unlike ligands on the hardness of the corresponding atoms or cations. The other reason is probably related to the possible inaccurancy of existing parameters of absolute hardness. This can be caused by the approximate character of the formula $(\eta\ (I-A)/2$ used for their calculations,[88] whereas for the parameters obtained by the quantum-chemical calculations this can be a consequence of neglecting relativistic effects.[83] The last reason is supported by the fact that even in the case of related L_nM groups (tin–lead, nickel–palladium) their chemical hardness does not run parallel to absolute hardness of M. Thus, in the general case, parameters of absolute hardness cannot be used for the prediction of relative group hardness (GH).

At the same time, polar factors can exert a certain effect on the position of equilibria studied, namely, the electronegativity of L_nM groups.[25] It is likely that the HSAB principle is obeyed strictly only in the case when the competing ligands or groups have different hardness but the same electronegativities.[26] This is consistent with the earlier conclusion,[24] that for the exchange reactions [3] the position of equilibrium depends not only on the nature of the central metal atom and the R groups, but also on the difference in polarities of M—X and M—X*, as well as of M—Y and M*—Y bonds. In our case, the ligands SC_6H_4F-4 and $OC_6H_4NO_2$-4 are characterized by different electronegativities. This is evidenced by the FCS values for the 4-FC_6H_4Hg group for compounds 4-$FC_6H_4HgSC_6H_4F$-4 and 4-$FC_6H_4HgOC_6H_4NO_2$-4 in benzene solutions, which are equal to -1.66 ppm and -2.59 ppm, respectively.[87] Therefore, it is desirable to study exchange equilibria involving organometallic compounds containing OAr and SAr with equal electronegativities.

The comparison of FCS for the compounds $Ar_3SnSC_6H_4F$-4 and $Ar_3PbSC_6H_4F$-4 has shown that the influence of Ar ligands on GEN of Ar_3M groups prevails over that of AEN of central atoms. This fact has allowed us to find a pair of isoelectronegative groups—(4-$FC_6H_4)_3Sn$ and (3-$ClC_6H_4)_3Pb$ (FCS in benzene for both compounds

is equal to 2.16 ppm). The equilibrium constant of reaction involving these groups:

$$\begin{aligned}&(3-ClC_6H_4)_3Pb—SC_6H_4F-4\\&\quad+(4-FC_6H_4)_3Sn—OC_6H_4NO_2-4\\&\rightleftharpoons(3-ClC_6H_4)_3Pb—OC_6H_4NO_2-4\\&\quad+(4-C_6H_4)_3Sn—SC_6H_4-4\end{aligned}\qquad(18)$$

is equal to 1.7×10^{-3}.[87] This fact suggests that from isoelectronegative Ar_3Sn and Ar_3Pb groups the tin-containing groups are much harder than lead-containing ones.

We have also studied reactions in systems involving the softer Ph_3Pb and the harder Ph_3Sn groups. One anion (soft 4-fluorothiophenoxide) was fixed, and others were anions with known absolute hardness (OH, Cl, Br, I)[89]

$$\begin{aligned}&Ph_3Sn—SC_6H_4F\text{-}4+Ph_3Pb—X\\&\quad\rightleftharpoons Ph_3Sn—X+Ph_3Pb—SC_6H_4F\text{-}4\end{aligned}\qquad(19)$$

It was found that K_{eq} [19] increases with decrease in hardness of X in the order:

X =	OH <	Cl <	Br <	I
$K_{eq}[19]$ =	1.4×10^{-3}	0.51	3.5	45
η(eV) =	5.67	4.7	4.2	3.7

and a good correlation of equilibrium constant logarithm with absolute hardness η of anions exists:

$$\log K_{eq}[19]=-2.27\eta+10.14,\ r=0.996$$

It may be shown that for exchange reactions of the general type [16] the dependence of equilibrium constant on the hardness of cation and anion is given by the equation:

$$\log K_{eq}[16]=B(\eta_Q-\eta_{Q*})(\eta_Y-\eta_X)$$

This equation can be considered as a quantitative formulation of the HSAB principle. If Q^*, X and Y are constants and Q equals L_nM, we obtain the final expression:

$$\log K_{eq}=a\eta_{L_nM}+c$$

Thus we can formulate the general conclusion that the influence of the ligand L on $\log K_{eq}$ will reflect its influence on the chemical hardness of the L_nM^+ cation. This fact is the basis for study of quantitative regularities in the influence of σ- or *n*-ligands on the hardness of ArHg, Ar_3Sn and Ar_3PAu cations in the reactions [20]–[22]:[85,86,90]

$$\begin{aligned}&ArHg—SC_6H_4F+Ph_3PAu—OC_6H_4NO_2\text{-}4\\&\quad\rightleftharpoons ArHg—OC_6H_4NO_2\text{-}4\\&\quad+Ph_3PAu—SC_6H_4F\text{-}4\end{aligned}\qquad(20)$$

$$\begin{aligned}&Ar_3PAu—SC_6H_4F-4+PhHg—OC_6H_4NO_2\text{-}4\\&\quad\rightleftharpoons Ar_3PAu—OC_6H_4NO_2\text{-}4\\&\quad+PhHg—SC_6H_4F\text{-}4\end{aligned}\qquad(21)$$

$$\begin{aligned}&Ar_3Sn—C_6H_4F\text{-}4+Ph_3Pb—Cl\\&\quad\rightleftharpoons Ar_3Sn—Cl+Ph_3Pb—SC_6H_4F\text{-}4\end{aligned}\qquad(22)$$

It follows from Table 14 that the electron-withdrawing substituents in aryl ligands at metal atoms or in triarylphosphine leads to an increase in ability of the L_nM cations to form a bond with the softer $^-SC_6H_4F$-4 anion. In accordance with the HSAB principle, this should mean that the chemical hardness of L_nM cations decreases with increase in electron-withdrawing ability of the aryl ligands. Unfortunately, the data on the influence of substituents on hardness of Ar are not available in the literature. It is believed that the hardness will decrease under the effect of electron-donor substituents because an increase in the charge on the key atom of the ligand increases its hardness.[80] It is also known that the replacement of a hard ligand with a soft ligand can decrease[91] as well as increase[92] the hardness of the metal atom. The first effect is called symbiotic and the second effect is called antisymbiotic. Therefore, the antisymbiotic effect manifests itself both in the influence of σ-Ar ligands on the hardness of the $ArHg^+$ and Ar_3Sn^+ cations and *n*-Ar_3P ligands on the hardness of the Ar_3PAu^+ cation.

With the aim of establishing quantitative regularities of the effects of ligands on hardness of L_nM cations, the correlations between $\log K_{eq}$ and Hammett[93] or Taft[94] constants of substituted phenyl groups, the values of ionization potentials of the lone electron pair[95] and the basicity constants[96] of triarylphosphines were studied. It has been found that the influence of σ-Ar ligands on chemical hardness of $ArHg^+$ and Ar_3Sn^+ cations is better described by σ^0 constants of substituted phenyl groups:

$$\begin{aligned}&\log K_{eq}[20]=-0.65\sigma-0.54,\\&\quad r=0.969, S=0.07\\&\log K_{eq}[20]=-0.70\sigma^0-0.49,\\&\quad r=0.978, S=0.06,\end{aligned}$$

Table 14 Equilibrium constants for the exchange systems [20]–[22][85,86,90]

Ar	K_{eq}[20]	K_{eq}[21]	K_{eq}[22]
4-$Me_2NC_6H_4$	0.69	21	
4-$MeOC_6H_4$		5.7	
4-MeC_6H_4	0.37	3.83	1.1
Ph	0.32	3.05	1
4-FC_6H_4	0.24	1.55	0.65
4-ClC_6H_4	0.24	1.29	0.57
3-$CF_3C_6H_4$	0.16		
3,4-$Cl_2C_6H_3$	0.11		0.24
3,4,5-$Cl_3C_6H_2$			0.15

$$\log K_{eq}[22] = -0.81\sigma - 0.08,\quad r = 0.988, S = 0.06$$
$$\log K_{eq}[22] = -0.796\sigma^0 - 0.05,\quad r = 0.994, S = 0.04$$

In the case of *n*-Ar_3P ligands the effects of these ligands are better described by the σ constants of the substituted phenyl groups or their pK_a values than by the σ^0 constants or lone pair ionization potentials (IP):

$$\log K_{eq}[21] = -1.48\sigma + 0.39,\quad r = 0.984, S = 0.09$$
$$\log K_{eq}[21] = -1.68\sigma^0 + 0.49,\quad r = 0.979, S = 0.10$$
$$\log K_{eq}[21] = -0.91\mathrm{IP} + 7.60,\quad r = 0.985, S = 0.08$$
$$\log K_{eq}[21] = 0.16\mathrm{p}K_a - 3.26,\quad r = 0.994, S = 0.05$$

At the same time, it should be taken into account that according to the FCS (4-$FC_6H_4)_3Sn$ group for compounds (4-$FC_6H_4)_3SnCl$ (−4.41 ppm) and (4-$FC_6H_4)_3SnSC_6H_4F$-4 (−3,61 ppm) the SC_6H_4F-4 ligand possess the lower electronegativity compared with that of the chlorine ligand.[97] It has been mentioned above that the electronegativities of Ar_3Sn groups were calculated.[68] In addition, it has been shown that these values correlate closely with σ^0 constants of substituted phenyl groups. In this connection, the above data suggest the existence of correlation between log K_{eq} values and the electronegativity values for Ar_3Sn groups, which is expressed by the equation:

$$\log K_{eq}[22] = -0.46\chi + 1.58; r = 0.993, S = 0.04$$

This result affords strong evidence that the influence of Ar ligands on the chemical hardness of Ar_3Sn^+ cations, which decreases with increase in electron-accepting ability of Ar ligands, represents a consequence of the electronegativity variation for Ar_3Sn groups, which favours bond formation between the more electronegative Ar_3Sn group and the less electronegative 4-FC_6H_4S ligand.

Conclusion

The following basic results have been obtained.

(1) The relative electronegativity and chemical hardness of L_nM groups can change in parallel or not with the electronegativity and hardness of the central metal atom.

(2) The substituents in Ar can substantially modify electronegativity and hardness of Ar_nM groups; the influence of Ar groups has an inductive nature; the increase in electron-donating ability of aryl ligands enhances the hardness of Ar_nM cations.

(3) The relative electronegativity and hardness of L_nM groups in L_nMX are invariant and do not depend on X.

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