Organometallic Chemistry

Effect of aryl ligands on the chemical hardness of arylmercury cations

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^{19}F NMR spectroscopy was used to study the exchange reactions involving 4-fluorothiophenoxides, 4-nitrophenoxides, chlorides, and acetates of arylmercury and triphenylphosphinegold. The analysis of the data on equilibrium constants allows one to obtain information on the comparative chemical hardness of $ArHg^+$ and Ph_3PAu^+ cations. The increase in the electron-donating ability of aryl ligands enhances the chemical hardness of $ArHg^+$ cations, their influence being best described by σ^0 constants of substituted phenyl groups.

Key words: hardness, chemical hardness; mercury, gold, exchange equilibria; ^{19}F NMR spectra.

The prediction of the reactivity of metal—element σ-bonds is one of the main problems of organometallic chemistry. The principle of hard and soft acids and bases (HSAB) seems to be promising in this respect.[1] This principle was of a qualitative character for several decades, but the prerequisites apparently have appeared recently for its transformation into a quantitative theory.[2] For example, the concept of absolute hardness was developed, and the quantitative parameters of the absolute hardness of metal atoms and cations were suggested.[3,4] The quantum-chemical calculations of the hardness of metal atoms were performed.[5] Recently, works[6,7] on the calculation of the hardness of the simplest organic and organoelement groups containing C, N, O, S, Si, and P as key atoms have been published.

At the same time, there are no published calculated data on the hardness of organometallic groups or cations, and experimental results are very scarce.[8] Therefore, it seems urgent to study the possibility of the qualitative or quantitative prediction of the comparable hardness of organometallic cations on the basis of hardness parameters of central metal atoms or cations in organometallic fragments. In particular, the problem of prediction of the character of the distribution of competing organometallic groups between hard and soft anionoid ligands is of great significance. It is also of interest to elucidate the possibility of the existence of qualitative or quantitative regularities in the effect 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

$$QX + Q^*Y \rightleftharpoons Q^*X + QY,$$

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 toward the formation of pairs of fragments of the "hard—hard" (hh) and "soft—soft" (ss) types.[9]

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

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Many types of organometallic compounds of nontransition and, to a lesser extent, transition metals are convenient objects for studying these exchange reactions, because exchange processes involving metal—heteroatom bonds of these compounds are often faster in the preparative time scale and even in the NMR time scale.[10]

In the present work, the exchange equilibria in the systems

$$\underset{\mathbf{1a-g}}{ArHgSC_6H_4F\text{-}4} + \underset{\mathbf{2a-c}}{Ph_3PAuX} \rightleftharpoons ArHgX + \underset{\mathbf{2d}}{Ph_3PAuSC_6H_4F\text{-}4}$$

1: Ar = 4-$Me_2NC_6H_4$ (**a**), 4-MeC_6H_4 (**b**), Ph (**c**), 4-FC_6H_4 (**d**), 4-ClC_6H_4 (**e**), 3-$CF_3C_6H_4$ (**f**), 3,4-$Cl_2C_6H_3$ (**g**)

2: X = $OC_6H_4NO_2$-4 (**a**), Cl (**b**), OCOMe (**c**)

were studied by the ^{19}F NMR method in order to obtain the data on the comparative chemical hardness of the $ArHg^+$ and Ph_3PAu^+ cations.

These cations were chosen because they are isoelectronic, the corresponding elements are close in the Periodic system, and the exchange reactions on metal—heteroatom bonds in organylmercury and triorganylphosphinegold derivatives occur very readily.[11,12] The choice of the anionoid ligands is caused by the fact that the parameters of the chemical hardness are known[9] for the corresponding anions or their close analogs: 14, 19, 23, and 23 kcal mol^{-1} for PhS^-, Cl^-, PhO^-, and $MeCOO^-$, respectively. In addition, the pair of the SPh and $OC_6H_4NO_2$-4 ligands is characterized by the close steric requirements and acidities of the corresponding HX-acids,[13] which differ only by 0.5 pK_a units in DMSO. According to the data presented above, SC_6H_4F-4 is the softest and $OC_6H_4NO_2$-4 and OCOMe are the hardest of the ligands chosen, while Cl occupies an intermediate position. According to the HSAB principle, it should be expected that the distribution of the cations studied between harder and softer anions characterizes the comparative hardness of organometallic cations.

The use of ^{19}F NMR spectroscopy for the determination of equilibrium constants (K_{eq}) of the studied exchange reactions is based on the substantial difference between the fluorine chemical shifts (FCS) for compounds **1a—g** and **2d**. For example, for 0.02 *M* solutions of **1c** and **2d** in benzene, the FCS values are equal to 4.49 and 8.50 ppm, respectively. For a benzene solution of a mixture of the compounds mentioned of the same concentration of each component, only one signal at 6.50 ppm is observed, which attests to a fast (in the ^{19}F NMR time scale) exchange of 4-fluorothiophenolate ligands. A similar situation is observed in the ^{19}F NMR spectra of solutions of mixtures of compounds **1c** and **2a**, **2b**, and **2c**.

According to the dynamic method for the determination of K_{eq} on the basis of the NMR spectra in fast equilibrium systems

$$\mathbf{1a-g} + \mathbf{2a-c} \rightleftharpoons ArHgX + \mathbf{2}$$

FCS should depend on relative molar ratios of the ligand 4-FC_6H_4S bonded to the Hg or Au atom and on the FCS values for this ligand in two possible states. The FCS indicated is determined by the expression

$$\delta F = \alpha \cdot \delta F(Au) + \beta \cdot \delta F(Hg),$$

where $\delta F(Hg) = \delta F(\mathbf{1a-g})$ and $\delta F(Au) = \delta F(\mathbf{2d})$. When the equimolar concentrations of the initial reagents are used, the equation presented above transforms into the following expression

$$\delta F = \alpha \cdot \delta F(Au) + (1 - \alpha) \cdot \delta F(Hg),$$

according to which the coefficient α can be determined in the following way:

$$\alpha = [\delta F - \delta F(Hg)]/[\delta F(Au) - \delta F(Hg)].$$

In turn, according to the equation of the exchange reaction,

$$K_{eq} = \alpha^2/(1 - \alpha)^2.$$

This expression was used for the calculation of K_{eq} for the exchange equilibria studied.

At first let us consider the results obtained by the study of the exchange reactions

$$\mathbf{1a-g} + \mathbf{2a} \rightleftharpoons ArHgOC_6H_4NO_2\text{-}4 + \mathbf{2}\ .$$

The data on the FCS for compounds **1a—g** used in the calculations of K_{eq} for the exchange reactions are presented in Table 1. The values of FCS observed for the exchange systems and K_{eq} calculated on the basis of FCS are presented in Table 2. The study was carried out at the concentrations of 0.02 mol L^{-1} with respect to each component. At these concentrations, FCS for the exchange system become independent of the concentration. It was shown by an example of the exchange reaction of

Table 1. Chemical shifts in ^{19}F NMR spectra for solutions of compounds $ArHgSC_6H_4F$-4 (**1**) in benzene

Compound	Ar	FCS, ppm
1a	4-$Me_2NC_6H_4$	4.98
1b	4-MeC_6H_4	4.65
1c	Ph	4.49
1d	4-FC_6H_4	4.12
1e	4-ClC_6H_4	4.06
1f	3-$CF_3C_6H_4$	3.95
1g	3,4-$Cl_2C_6H_3$	3.87

Table 2. Chemical shifts in ^{19}F NMR spectra and equilibrium constants for the exchange systems

$$ArHgSC_6H_4F\text{-}4 + Ph_3PAuOC_6H_4NO_2\text{-}4 \rightleftharpoons Ph_3PAuSC_6H_4F\text{-}4 + ArHgOC_6H_4NO_2\text{-}4$$

Compound	Ar	FCS, ppm	K_{eq}
1a	4-$Me_2NC_6H_4$	6.58	0.69
1b	4-MeC_6H_4	6.10	0.37
1c	Ph	5.95	0.32
1d	4-FC_6H_4	5.55	0.24
1e	4-ClC_6H_4	5.53	0.24
1f	3-$CF_3C_6H_4$	5.25	0.16
1g	3,4-$Cl_2C_6H_3$	5.01	0.11

Table 3. Chemical shifts in ^{19}F NMR spectra and equilibrium constants for the exchange systems

$$ArHgSC_6H_4F\text{-}4 + Ph_3PAuCl \rightleftharpoons Ph_3PAuSC_6H_4F\text{-}4 + ArHgCl$$

Compound	Ar	FCS, ppm	K_{eq}
1a	4-$Me_2NC_6H_4$	6.71	0.93
1b	4-MeC_6H_4	6.29	0.55
1c	Ph	6.20	0.55
1d	4-FC_6H_4	5.79	0.39
1e	4-ClC_6H_4	5.76	0.38
1f	3-$CF_3C_6H_4$	5.60	0.32
1g	3,4-$Cl_2C_6H_3$	5.33	0.21

$PhHgOC_6H_4NO_2$-4 with **2d** that the FCS value is independent of the nature of the initial reagents.

It follows from the data of Table 2 that the equilibrium of the reaction of compound **1c** with **2a** is shifted toward the initial compounds. According to this, the $PhHg^+$ cation exhibits a somewhat higher trend to form a bond with the anion $^-SC_6H_4F$-4 softer 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 Au and Hg atoms, which are equal to 3.46 and 5.54 eV, respectively,[4] and the values of the absolute hardness of Au^+ and Hg^{2+} cations, which are equal to 5.6 and 7.7 eV, respectively.[4] It also contradicts the data of the quantum-chemical calculations of the hardness of Au and Hg atoms (3.55 and 5.02 eV, respectively, calculated in the X_α approximation, and 3.44 and 5.29 eV, respectively, calculated in the Gunnarson—Lindquist approximation[5]).

Thus, the results do not agree with the assertion[6] that the group hardness is mainly determined by the hardness of the central atom. Several reasons for this disagreement are possible. One of them is likely the fact that in the case of nonisostructural cations the predominant effect on their comparative hardness can be exerted by the differences in the effects of unlike ligands on the hardness of the corresponding atoms or atomic cations. The other reason is probably related to the potential inaccuracy of the existing parameters of absolute hardness. In the case of the absolute hardness parameters, this can be caused by the approximate character of the formula for their calculation,[14] and for the parameters obtained by the quantum-chemical calculations this can be a consequence of neglecting relativistic effects.[5]

Steric factors cannot affect the positions of the equilibria studied, because the consideration of the Stewart—Brigleb molecular models for compounds $PhHgOC_6H_4NO_2$-4, **1c**, **2a**, and **2d** excludes the possibility of steric interactions of the ligands SC_6H_4F-4 and $OC_6H_4NO_2$-4 with the phenyl groups at the Hg and P atoms. This also concerns the acetate ligand. Therefore, the ligands mentioned are characterized by the same steric requirements with respect to the organometallic groups PhHg and Ph_3Au. It is reasonable that this is valid for such a ligand as Cl as well.

At the same time, polar factors can exert a certain effect on the positions of the equilibria studied, namely: electronegativity of organometallic groups. It is likely that the HSAB principle is fulfilled rather strictly only in the case when the competing ligands or groups possess different hardnesses but the same electronegativities.[15] 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_4 group for compounds **1d** and 4-$FC_6H_4HgOC_6H_4NO_2$-4 in benzene solutions, which are equal to −1.66 and −2.59 ppm, respectively. Therefore, it is desirable to study exchange equilibria involving organometallic compounds containing OAr and SAr with equal electronegativities.

As follows from the data of Table 3, K_{eq} for the exchange reaction of compound **1c** with **2b** is equal to 0.55, which also testifies to a somewhat lower hardness of the $PhHg^+$ compared to that of Ph_3PAu^+. The value of K_{eq}, which is somewhat higher than that for the reaction of compound **1c** with **2a**, is caused by a lower hardness of the Cl^- anion compared to that of $^-OC_6H_4NO_2$-4.

On the contrary, unexpected results were obtained for the reaction of PhHgOCOMe (**3c**) with **2d**. It turned out that the equilibrium is shifted toward the initial reagents (Table 4), which likely indicates a higher hardness of the $PhHg^+$ cation compared to that of Ph_3PAu^+. These experimental data contradict the results obtained for the two previous systems. It is probable that the anomaly observed is caused by the existence of the intramolecular coordination in compound **3c**. According to the literature data,[16] crystals of this compound are characterized by a somewhat shortened intramolecular distance (2.85 Å) between the Hg atom and the O atom of the carbonyl group of the acetate ligand, which is by 0.05 Å shorter than the sum of the van der Waals radii of the corresponding atoms. The formation of the chelate cycle should result in the additional stabilization of compound **3c** and shift the equilibrium toward this compound. Unlike this, according to the

Table 4. Chemical shifts in ^{19}F NMR spectra and equilibrium constants for the exchange systems

$$\mathrm{ArHgOCOMe} + \mathrm{Ph_3PAuSC_6H_4F\text{-}4} \rightleftharpoons \mathrm{Ph_3PAuOCOMe} + \mathrm{ArHgSC_6H_4F\text{-}4}$$

Compound	Ar	FCS, ppm	K_{eq}
1a	4-$Me_2NC_6H_4$	8.05	0.032
1b	4-MeC_6H_4	7.44	0.140
1c	Ph	7.96	0.024
1e	4-ClC_6H_4	7.68	0.051
1f	3-$CF_3C_6H_4$	7.73	0.041
1g	3,4-$Cl_2C_6H_3$	7.16	0.170

X-ray diffraction analysis data,[17] no intramolecular coordination is observed in the crystals of $Ph_3PAuOCOMe$. It can be concluded in light of these results that the use of the acetate ligand for studying the comparative hardness of organometallic cations[18] seems unreasonable.

It was of interest to elucidate how the change in the electronic requirements on the aryl ligand affects the chemical hardness of the $ArHg^+$ cations. For this purpose, the effects of substituents in the phenyl group at the Hg atom on the K_{eq} values were studied for the exchange reactions

$$\mathbf{1a{-}g} + \mathbf{2a} \rightleftharpoons \mathrm{ArHgOC_6H_4NO_2\text{-}4} + \mathbf{2d}.$$

As follows from the data of Table 2, the presence of electron-donating substituents enhances the trend of the $ArHg^+$ cation toward binding with the $^-OC_6H_4NO_2$-4 anion compared to that with the $^-SC_6H_4F$-4 anion, while electron-accepting substituents exert the opposite effect. It can be shown that for this exchange reaction the dependences of K_{eq} on dissociation constants (K_d) of arylmercury derivatives are described by the following expression:

$$\log K_{eq} = \log K_d(\mathrm{ArHgSC_6H_4F\text{-}4}) - \log K_d(\mathrm{ArHgOC_6H_4NO_2\text{-}4}).$$

Unfortunately, we failed to find literature data on the character of the influence of aryl ligands at nontransition metal atoms on the heterolytic dissociation constants of M—O and M—S bonds. It should be expected from general concepts that an increase in the electron-donating ability of the aryl ligand should favor the heterolytic dissociation of the Hg—S and Hg—O bonds due to an increase in the stability of the $ArHg^+$ cation formed. According to these concepts and the data on the increase in K_{eq} as the electron-donating ability of the aryl ligand increases, it should be concluded that the substituents in the aryl ligand affect the dissociation of a less polar Hg—S bond to a higher extent than that of the more polar Hg—O bond.

The results make it possible to conclude that a decrease in the electronic requirements of the aryl ligand enhances the hardness of the $ArHg^+$ cation. There are no published calculated data on the character of the effect of electron-donating and electron-accepting substituents on the hardness of aryl ligands. It can be assumed on the basis of general considerations that it will decrease under the effect of electron-donating substituents, because an increase in the charge on the key atom of the ligand should enhance its hardness.[19] At the same time, it is known that the change of the hard ligand to the soft one can both decrease[20] and increase[21] the hardness of the metal atom. The first effect is called symbiotic,[20] and the second effect is antisymbiotic.[21] Thus, the antisymbiotic effect is characteristic of the influence of aryl ligands on the hardness of the $ArHg^+$ cations.

In order to establish quantitative regularities in the influence of polar effects of aryl ligands on the hardness of the $ArHg^+$ cations, the correlations of the logarithm of the equilibrium constant for the aforementioned exchange reaction with the Hammett[22] (σ) and Taft[23] (σ^0) constants were performed for aryl ligands, and the following linear dependences were obtained:

$$\log K_{eq} = -0.65\sigma - 0.54,\ r = 0.969,\ s = 0.07;$$

$$\log K_{eq} = -0.70\sigma^0 - 0.49,\ r = 0.978,\ s = 0.06.$$

These data are evidence that the polar effect of aryl ligands on $\log K_{eq}$ is best described by the σ^0 constants. It is noteworthy that, according to the correlation established and the expression of $\log K_{eq}$ by K_d considered above for compounds **1** and $ArHgOC_6H_4NO_2$-4, it can be assumed that the effect of aryl ligands on the dissociative ability of the Hg—S and Hg—O bonds is also reflected by the σ^0 constants.

It has been shown recently[24] that the equilibrium constant for the exchange reactions of the general type

$$\mathrm{QX} + \mathrm{Q^*Y} \rightleftharpoons \mathrm{Q^*X} + \mathrm{QY},$$

controlled by the hardness of the cations Q^+ and Q^{*+} and anions X^- and Y^- can be expressed as follows:

$$\log K_{eq} = B(\eta_Q - \eta_{Q^*})(\eta_Y - \eta_X),$$

where η is the hardness of the cations Q^+ and Q^{*+} or anions X^- and Y^-. If the changes in K_{eq} occur due to the variation of the nature of only one cationoid group, the following expression is valid

$$\log K_{eq} = a\eta_Q + c.$$

According to this expression, when $Q = L_nM$, the effect of the ligand L on K_{eq} reflects the character of its influence on the hardness of the cation L_nM^+. Therefore, the results allow one to conclude that the polar effect of aryl ligands on the hardness of the $ArHg^+$ cations is best described by the σ^0 constants.

Similar regularities were found for the exchange equilibria

$$\mathbf{1a,c,e{-}g} + \mathbf{2b} \rightleftharpoons \mathrm{ArHgCl} + \mathbf{2d}.$$

For these reactions, K_{eq} also increases monotonically as the electron-donating ability of the aryl ligand is enhanced. The extent of the change in K_{eq} is somewhat lower than that in the case of the exchange reactions of compounds **1a—g** with **2a**, which agrees with the smaller differences in the hardness of the $^{-}$SPh and Cl^{-} anions compared to those of $^{-}$SPh and $^{-}$OPh. The character of the change in K_{eq} also corresponds to the growth of the hardness of the $ArHg^{+}$ cations as the electron-donating ability of the aryl ligand increases. The good linear dependences of $\log K_{eq}$ on σ and σ^0 were obtained similarly:

$$\log K_{eq} = -0.51\sigma - 0.33,\ r = 0.975,\ s = 0.05;$$

$$\log K_{eq} = -0.54\sigma^0 - 0.29,\ r = 0.981,\ s = 0.04,$$

the latter of which is characterized by a somewhat better correlation coefficient.

A different situation was observed for the effect of the nature of the aryl ligand on the K_{eq} values for the exchange reactions

$$\underset{\mathbf{3a-f}}{ArHgOCOMe} + \mathbf{2d} \rightleftharpoons \mathbf{1a-c,e-g} + \mathbf{2c}$$

3: Ar = 4-$Me_2NC_6H_4$ (**a**), 4-MeC_6H_4 (**b**), Ph (**c**), 4-ClC_6H_4 (**d**), 3-$CF_3C_6H_4$ (**e**), 3,4-$Cl_2C_6H_3$ (**f**)

As follows from the data in Table 4, no monotonic change in K_{eq} is observed when the electron-accepting ability of the aryl ligand increases. This is likely caused by the effect of chelating of the acetate ligand discussed above. In fact, it can be shown that in the case of exchange reactions the dependence of K_{eq} on the dissociative ability of arylmercury derivatives is determined by the expression

$$\log K_{eq} = \log K_d(\mathbf{3}) - \log K_d(\mathbf{1}) + c.$$

When chelating is present in compounds **3**, the polar effect of substituents in the aryl ligand on the dissociative ability of the Hg—O bond is complicated. The electron-donating substituent should facilitate the dissociation of the Hg—O bond due to the stabilization of the $ArHg^{+}$ cation and weakening of the chelate cycle due to a decrease in the partial positive charge on the metal atom, but it should make the dissociation difficult due to the strengthening of the chelate cycle caused by an increase in the electron density on the acetate ligand. A similar situation will also take place in the case of electron-accepting substituents. The existence of chelating in compounds **3** can prevent the elucidation of the influence of polar effects of substituents on the hardness of the $ArHg^{+}$ cations due to the action of opposite factors. Therefore, to investigate similar problems, one should study exchange equilibria involving organometallic compounds that do not contain potential chelating ligands.

This circumstance will be taken into account in the further studies of the effects of ligands on the chemical hardness of other organometallic cations including nontransition or transition metals.

Experimental

^{19}F-{^{1}H} NMR spectra were recorded on a Bruker WP-200 SY spectrometer with the working frequency of 188.31 MHz at 25 °C for 0.02 *M* solutions in benzene. Resonance conditions were stabilized by the external standard D_2O. FCS values were measured by the substitution method relative to the external standard (fluorobenzene) in the same solvent and at the same concentration as the compound studied. The sign "+" corresponded to the upfield shift of the signal compared to the standard. The error in the determination of FCS was not greater than ±0.02 ppm. The error in the determination of K_{eq} by the dynamic method did not exceed ±10 %.

Compounds **1a**,[25] **1b**,[26] **1c**,[25] **1d**,[25] **1e**,[26] **1f**,[26] and **1g** [26] described previously, were obtained by the action of arylmercury hydroxides or acetates on 4-FC_6H_4SH. The known compounds **2a**,[27] **2b**,[28] **2c**,[29] and **2d** [30] were synthesized by the procedures published previously. Compounds **3a**,[31] **3b**,[32] **3c**,[33] **3d**,[34] **3e**,[35] and **3f** [35] were obtained by either the mercurization[30—32] or reaction of $Hg(OCOMe)_2$ with diarylmercury.[35] All compounds mentioned were identified by melting points.

Compound $PhHgOC_6H_4NO_2$-4 was synthesized by a procedure, described previously,[36] by the action of PhHgOH on $HOC_6H_4NO_2$-4. Compound 4-$FC_6H_4HgOC_6H_4NO_2$-4 was obtained similarly (yield 48 %) as a yellow finely crystalline powder with m.p. 171—172 °C. Found (%): C, 33.23; H, 1.67; N, 3.20. $C_{12}H_8FHgNO_3$. Calculated (%): C, 33.20; H, 1.84; N, 3.23.

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