Study of the effect of triarylphosphine ligands on chemical hardness of triarylphosphinegold cations

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Exchange reactions with the participation of triarylphosphinegold and phenylmercury 4-fluorothiophenoxides, 4-nitrophenoxides, and acetates were studied by ^{19}F NMR spectroscopy. The data on the comparative chemical hardness of Ar_3PAu^+ and $PhHg^+$ cations were obtained based on the data on the equilibrium constants. The chemical hardness of Ar_3PAu^+ cations increases as the electron-donating ability of triarylphosphine ligands increases. The effect of these ligands is described by the σ or σ^0 constants of substituted phenyl groups and by ionization potentials of their electron pairs or the pK_a values.

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

Recently, great interest has been expressed in the problems of chemical hardness.[1—10] In connection with the question of whether the principle of soft and hard acids and bases[5] is promising in the organometallic chemistry, it is worthwhile to study quantitatively the character of the effect of the nature of ligands on the hardness of organometallic groups or cations. One possible way of solving this problem is to study exchange equilibria with the participation of hard and soft anions X and Y:[7,8,10]

$$L_nM^1X + L_nM^2Y \rightleftharpoons L_nM^1Y + L_nM^2X.$$

Previously,[5] studies of the reactions

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

have yielded the quantitative data on the effect of aryl ligands on the hardness of $ArHg^+$ cations. It has been established that the value of the constant of an exchange equilibrium ($\log K_{eq}$) is linearly proportional to the hardness of the organometallic cation η[10] according to Eq. (1).

$$\log K_{eq} = a\eta + c \quad (1)$$

In this work, the exchange reactions were studied by ^{19}F NMR spectroscopy in the following systems:

$$\underset{\mathbf{1a—f}}{Ar_3PAuSC_6H_4F\text{-}4} + \underset{\mathbf{2a—b}}{PhHgX} \rightleftharpoons \underset{\mathbf{2c}}{PhHgSC_6H_4F\text{-}4} + Ar_3PAuX$$

1: Ar = $4\text{-}(CH_3)_2NC_6H_4$ (**a**); $4\text{-}CH_3OC_6H_4$ (**b**); $4\text{-}CH_3C_6H_4$ (**c**); Ph (**d**); $4\text{-}FC_6H_4$ (**e**); $4\text{-}ClC_6H_4$ (**f**);

2: X = $OC_6H_4NO_2\text{-}4$ (**a**); $OCOCH_3$ (**b**)

with the aim of elucidating the effect of triarylphosphine ligands on the hardness of Ar_3PAu^+ cations.

The choice of the phenylmercury derivatives as the reaction partners was determined by the known data[7] that the hardnesses of the $PhHg^+$ and Ph_3PAu^+ cations are similar. In addition, organomercury derivatives[11] and triorganylphosphinegold derivatives[12] are characterized by high reactivities of the metal—heteroatom bonds in exchange reactions. The choice of anionoid ligands was determined by the fact that the parameters of chemical hardness for the corresponding anions and their closest analogs are known.[5] These parameters are 14, 23, and 23 kcal mol^{-1} for PhS^-, PhO^-, and $MeCOO^-$, respectively. In addition, the $SC_6H_4F\text{-}4$ and $OC_6H_4NO_2\text{-}4$ ligands have similar structures, and the corresponding acids HX would be expected to have close values of dissociation constants.[13] Of the ligands studied, $SC_6H_4F\text{-}4$ is a soft ligand, and $OC_6H_4NO_2\text{-}4$ and $OCOCH_3$ are hard ligands. According to the principle of soft and hard acids and bases, the character of distribution of the organometallic fragments among hard and soft anionoid ligands would be expected to determine the comparative hardness of organometallic cations.

The use of the ^{19}F NMR spectroscopy for determining equilibrium constants (K_{eq}) of exchange reactions is based on a substantial difference in the fluorine chemical shifts, on the one hand, for compounds **1a—f** and, on the other hand, for compound **2c**. For example, the fluorine chemical shifts relative to PhF were 8.50 and

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4.49 ppm for benzene solutions of compounds **1d** and **2c** (at concentrations of 0.02 mol L^{-1}), respectively, whereas only one signal at 6.50 ppm was observed for a benzene solution of a mixture of these compounds at the same concentrations of both components. This indicates that rapid (within the ^{19}F NMR time scale) exchange of 4-fluorothiophenoxide ligands between organometallic groups occurs in a solution of a mixture of these compounds. An analogous situation was observed in the ^{19}F NMR spectra of solutions of mixtures of **2c** with **1a—c, e—f**.

The so-called dynamic method was used for determining equilibrium constants of exchange reactions. According to this method, in the rapid equilibrium systems:

$$\mathbf{1a{-}f} + \mathbf{2a{-}b} \rightleftharpoons \mathbf{2c} + Ar_3PAuX$$

the values of the fluorine chemical shifts should depend on mole fractions of the $4\text{-}FC_6H_4S$ ligand bonded to the mercury or gold atom and on the values of the fluorine chemical shift for this ligand in two possible states. Therefore, an average chemical shift is determined by Eq. (2):

$$\delta F = \alpha\delta F(Au) + \beta\delta F(Hg), \quad (2)$$

where $\delta F(Au)$ are the fluorine chemical shifts for compounds **1a—f**, $\delta F(Hg)$ is the chemical shift for compound **2c**, and α and β are mole fractions of the corresponding compounds. The following equation may be written for equimolar amounts of the initial reagents:

$$\delta F = \alpha\delta F(Au) + (1 - \alpha)\delta F(Hg). \quad (3)$$

Hence, it follows that the mole fraction α can be determined from the following formula:

$$\alpha = [\delta F - \delta F(Hg)]/[\delta F(Au) - \delta F(Hg)]. \quad (4)$$

According to the equation of the exchange reaction, $K_{eq} = (1 - \alpha)^2/\alpha^2$.

Table 1. ^{19}F chemical shifts and equilibrium constants (K_{eq}) for the benzene solutions of the compounds $Ar_3PAuSC_6H_4F$-4 (**1a—f**) and the systems $Ar_3PAuSC_6H_4F\text{-}4 + PhHgOC_6H_4NO_2\text{-}4 \rightleftharpoons Ar_3PAuOC_6H_4NO_2\text{-}4 + PhHgSC_6H_4F\text{-}4$ (I) and $Ar_3PAuSC_6H_4F\text{-}4 + PhHgOCOMe \rightleftharpoons Ar_3PAuOCOMe + PhHgSC_6H_4F\text{-}4$ (II)

Ar	δ ^{19}F			K_{eq}	
	1a—f	I	II	I	II
$4\text{-}Me_2NC_6H_4$	9.41	5.37	8.47	21	0.056
$4\text{-}MeOC_6H_4$	8.66	5.72	7.92	5.7	0.047
$4\text{-}MeC_6H_4$	8.63	5.89	7.99	3.83	0.033
Ph	8.50	5.95	7.96	3.05	0.024
$4\text{-}FC_6H_4$	7.86	5.99	7.31	1.55	0.035
$4\text{-}ClC_6H_4$	7.67	5.98	7.11	1.29	0.046

This formula was used for calculating the equilibrium constants of the exchange reactions studied.

Let us consider the results obtained in the studies of the following exchange reactions:

$$\mathbf{1a{-}f} + \mathbf{2a} \rightleftharpoons \mathbf{2c} + Ar_3PAuOC_6H_4NO_2\text{-}4.$$

The fluorine chemical shifts observed for compounds **1a—f** and for the exchange systems and the equilibrium constants calculated based on these shifts are given in Table 1. The exchange reactions were studied at concentrations of 0.02 mol L^{-1} of both reagents (at these concentrations, the fluorine chemical shift of the exchange reaction no longer depends on concentrations). It was demonstrated that the fluorine chemical shift for this exchange system is independent of the nature of initial reagents when **2c** and $Ph_3PAuOC_6H_4NO_2$-4 are used as the initial reagents.

From Table 1 it follows that for the reactions of **1a—f** with **2a**, the equilibrium constant depends substantially on the nature of the triarylphosphine ligand. This constant varies by more than an order of magnitude. In all the cases, the equilibrium is shifted to the reaction products. Correspondingly, the Ar_3PAu^+ cations exhibit a somewhat higher tendency to form bonds with a harder $^-OC_6H_4NO_2$-4 anion and are characterized by a higher hardness than that of the $PhHg^+$ cation. These results do not agree with the published data[14] on the absolute hardness of the Au (3.46 eV) and Hg (5.54 eV) atoms and of the Au^+ (5.6 eV) and Hg^{2+} (7.7 eV) cations. The hardness of Ar_3PAu^+ cations increases as the electron-donating ability of triarylphosphine ligands increases. An analogous situation was observed in the case of $ArHg^+$ cations, whose hardness also increases as the electron-donating ability of the aryl ligand increases.[7]

The relationship between K_{eq} for the exchange reactions studied and the nature of triarylphosphine ligands is determined by their effect on the dissociation constants of the derivatives of triarylphosphinegold and is described by the following equation:

$$\log K_{eq} = \log K_D(\mathbf{1a{-}f}) - \log K_D(Ar_3PAuOC_6H_4NO_2\text{-}4) + C. \quad (5)$$

Unfortunately, data on the character and the extent of the effect of triarylphosphine ligands at the transition-metal atoms on the constants of heterolytic dissociation of metal—sulfur and metal—oxygen bonds are unavailable in the literature. Based on general considerations, an increase in the electron-donating ability of a triarylphosphine ligand would be expected to favor heterolytic dissociation of the Au—S and Au—O bonds owing to stabilization of the Ar_3PAu^+ cation that formed. According to these concepts and based on the fact that the K_{eq} value increases as the electron-donating ability of Ar_3P increases, it may be concluded that substituents in the triphenylphosphine ligand affect the dissociating ability of the Au—S bond to a greater extent as compared to the Au—O bond.

The results of calculations of the effect of substituents on the hardness of substituted triphenylphosphine ligands are unavailable 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.[15] It is also known that the replacement of a hard ligand with a soft ligand can decrease[4] as well as increase[5] the hardness of the metal atom. The first effect is called symbiotic,[4] and the second effect is called antisymbiotic.[5] Therefore, the antisymbiotic effect manifests itself both in the influence of triarylphosphine ligands on the hardness of Ar_3PAu^+ cations and in the influence of aryl ligands on the hardness of Ar_3Hg^+ cations.

With the aim of establishing quantitative regularities of the effect of the nature of triarylphosphine ligands on the hardness of Ar_3PAu^+ cations, the correlations between the $\log K_{eq}$ values for the reactions of compounds **1a—f** with **2a** and the Hammett[16] (σ) and Taft[17] (σ^0) constants of substituted phenyl groups, the values of ionization potentials of the lone electron pair,[18] and the basicity constants[19] of triarylphosphines were studied. The following linear dependences were obtained:

$$\log K_{eq} = -1.48\sigma + 0.39 \quad r = 0.984 \quad s = 0.09$$

$$\log K_{eq} = -1.68\sigma^0 + 0.49 \quad r = 0.979 \quad s = 0.10$$

$$\log K_{eq} = -0.91IP + 7.60 \quad r = 0.985 \quad s = 0.08$$

$$\log K_{eq} = 0.16\mathrm{p}K_a - 3.26 \quad r = 0.994 \quad s = 0.05$$

These results demonstrate that the polar effect of triarylphosphine ligands on $\log K_{eq}$ are best described by the Hammett constants σ of substituted phenyl groups, whereas the $\mathrm{p}K_a$ values are the best characteristics of the effect of the donating ability of Ar_3P ligands. Hence, taking into account Eq. (1), it follows that the effect of triarylphosphine ligands on the chemical hardness of Ar_3PAu^+ cations is best described by either the σ constants of substituted phenyl groups or their $\mathrm{p}K_a$ values. According to Eq. (5), this conclusion is true also for the effect of triarylphosphine ligands on the dissociating ability of the Au—S and Au—O bonds.

A different situation was observed in the studies of the effect of triarylphosphine ligands on the equilibrium constants for the exchange reactions:

Table 2. Yields, melting points, the data of elemental analysis, and ^{31}P chemical shifts (in $CDCl_3$) for compounds **1a—c, e—f, 3a—c, e—f,** and **4a—d**

Compound	Yield (%)	M.p./°C	Found/Calculated (%) C	H	P	S	Molecular formula	$\delta^{31}P$
[4-$Me_2NC_6H_4$]$_3$PAuSC$_6$H$_4$F-4 (**1a**)	39	179—180	49.82 50.35	4.65 4.79	4.68 4.32	4.27 4.28	$C_{30}H_{34}AuFN_3PS$	34.29
(4-MeOC$_6$H$_4$)$_3$PAuSC$_6$H$_4$F-4 (**1b**)	52	140—141	48.16 47.93	3.68 3.72	4.76 4.58	4.63 4.80	$C_{27}H_{25}AuFO_3PS$	35.69
(4-MeC$_6$H$_4$)$_3$PAuSC$_6$H$_4$F-4 (**1c**)	64	135—136	51.37 51.60	4.08 4.00	5.27 4.93	5.04 5.10	$C_{27}H_{25}AuFPS$	37.49
(4-FC$_6$H$_4$)$_3$PAuSC$_6$H$_4$F-4 (**1e**)	68	155—156	45.02 45.01	2.39 2.51	4.94 4.83	4.96 5.00	$C_{24}H_{16}AuF_4PS$	36.99
(4-ClC$_6$H$_4$)$_3$PAuSC$_6$H$_4$F-4 (**1f**)	41	165—166	41.84 41.79	2.30 2.34	4.53 4.49	4.81 4.65	$C_{24}H_{16}AuCl_3FPS$	37.59
[4-(CH$_3$)$_2$NC$_6$H$_4$]$_3$PAuOCOMe (**3a**)	31	205—206	48.51 48.30	5.02 4.99	4.62 4.79	— —	$C_{26}H_{33}AuN_3O_2P$	22.00
(4-MeOC$_6$H$_4$)$_3$PAuOCOMe (**3b**)	40	130—132	45.52 45.41	3.98 3.98	5.16 5.09	— —	$C_{23}H_{24}AuO_2P$	24.23
(4-MeC$_6$H$_4$)$_3$PAuOCOMe (**3c**)	48	155—156	49.37 49.30	4.33 4.32	5.54 5.52	— —	$C_{23}H_{24}AuO_2P$	26.32
(4-FC$_6$H$_4$)$_3$PAuOCOMe (**3e**)	46	159—161	42.24 41.97	2.65 2.64	5.69 5.41	— —	$C_{20}H_{15}AuF_3O_2P$	26.00
(4-ClC$_6$H$_4$)$_3$PAuOCOMe (**3f**)	50	165—166	38.30 38.64	2.45 2.43	4.87 4.98	— —	$C_{20}H_{15}AuCl_3O_2P$	26.85
[4-Me$_2$NC$_6$H$_4$]$_3$PAuBr (**4a**)	34	246—248	43.64 43.13	4.72 4.52	4.24 4.63	— —	$C_{24}H_{30}AuBrN_3P$	30.81
(4-MeOC$_6$H$_4$)$_3$PAuBr (**4b**)	43	196—198	40.21 40.08	3.40 3.36	5.03 4.92	— —	$C_{21}H_{21}AuBrO_3P$	32.04
(4-MeC$_6$H$_4$)$_3$PAuBr (**4c**)	58	214—215	43.28 43.39	3.63 3.64	5.63 5.32	— —	$C_{21}H_{21}AuBrP$	34.18
(4-ClC$_6$H$_4$)$_3$PAuBr (**4d**)	53	200—201	33.76 33.65	1.92 1.88	4.67 4.82	— —	$C_{18}H_{12}AuBrCl_3P$	33.90

$$\mathbf{1a{-}f} + \mathbf{2b} \rightleftharpoons \underset{\mathbf{3a{-}f}}{\mathrm{Ar_3PAuOCOMe}} + \mathbf{2c}$$

3: Ar = 4-Me$_2$NC$_6$H$_4$ (**a**); 4-MeOC$_6$H$_4$ (**b**); 4-MeC$_6$H$_4$ (**c**); Ph (**d**); 4-FC$_6$H$_4$ (**e**), 4-ClC$_6$H$_4$ (**f**).

From Table 1 it follows that in this case there is no clear relationship between the equilibrium constants and the nature of the aryl group in the triarylphosphine ligand. This fact is analogous to that observed previously[7] in studies of the exchange reactions of **1d** with ArHgOCOMe and was attributed to chelation of the acetate ligand as a result of intramolecular coordination of the mercury atom to the carbonyl oxygen atom of the carboxylate ligand. In particular, this chelation manifests itself in the fact that for the reactions of **1a—f** with PhHgOCOMe, the equilibrium is shifted to the initial compounds, whereas for the reactions of **1a—f** with **2a** the equilibrium is shifted to the reaction products. However, in the case of compound **3d**, intramolecular coordination is absent[21] as opposed to compound **2b**, in which weak intramolecular coordination may occur as evidenced by the X-ray structural data.[20]

In this connection, it may be suggested that this phenomenon is caused by the effect of intramolecular dipole-dipole interactions in compounds **3a—f** on their stability. As mentioned above, the relationship between $\log K_{\mathrm{eq}}$ and the dissociating ability of derivatives of triarylphosphinegold can be described by the following equation:

$$\log K_{\mathrm{eq}} = \log K_{\mathrm{D}}(\mathbf{1a{-}f}) - \log K_{\mathrm{D}}(\mathbf{3a{-}f}) + C.$$

Dipole-dipole interactions between dipoles of the $\mathrm{Au^{\delta+}{-}O^{\delta-}}$ and $\mathrm{C^{\delta+}{=}O^{\delta-}}$ bonds should stabilize compounds **3a—f** with respect to heterolytic dissociation. However, the character of the effect of substituents in the triphenylphosphine ligand on the intensity of dipole-dipole interactions is dual: introduction of electron-donor substituents will decrease $\delta+$ on the Au atom but increase $\delta-$ on the carbonyl oxygen atom (the opposite situation occurs in the case of electron-withdrawing substituents). This results in the fact that the K_{eq} value for the reaction under consideration is virtually independent of the donating ability of the triarylphosphine ligand. These data demonstrate once again that the acetate ligand cannot be used in studies of comparative chemical hardness of organometallic cations.

Experimental

The ^{19}F and ^{31}P NMR spectra were recorded on a Bruker WP-200 SY spectrometer (the operating frequency was 188.3 MHz for ^{19}F and 81.03 MHz for ^{31}P). Resonance conditions were stabilized relative to external D$_2$O. The fluorine chemical shifts were recorded by the substitution method relative to external PhF in the solvent and at the concentration identical to those used for the compounds and the system studied (0.02 *M*). The plus sign corresponds to the upfield shift of the signal relative to the standard. The errors in determination of fluorine chemical shifts and K_{eq} were no more than ±0.02 ppm and ±10%, respectively. The values of δ^{31}P were measured by the substitution method relative to external 85% H$_3$PO$_4$ and are given without correction for the bulk magnetic susceptibility. The plus sign corresponds to the downfield shift of the signal. The error in determination of δ^{31}P was no more than ±0.1 ppm.

Compounds **1d**, **2a**, **2b**, **2c**, **3d**, and Ph$_3$PAuOC$_6$H$_4$NO$_2$-4 were prepared according to the known procedures (see Refs. 22—27, respectively) and identified from the melting points. Triarylphosphinegold bromides (**4a—d**) were prepared from AuBr$_3$ by the following reactions:

$$\mathrm{AuBr_3 + KBr + SO_2 \rightarrow KAuBr_2},$$

$$\mathrm{KAuBr_2 + Ar_3P \rightarrow \underset{\mathbf{4a{-}d}}{Ar_3PAuBr}}$$

4: Ar = 4-Me$_2$NC$_6$H$_4$ (**a**); 4-MeOC$_6$H$_4$ (**b**); 4-MeC$_6$H$_4$ (**c**); 4-ClC$_6$H$_4$ (**d**).

The above-mentioned compounds were used as the initial compounds in the synthesis of the corresponding 4-fluorothiophenoxides and acetates:

$$\mathbf{4a{-}d} + \mathrm{NaSC_6H_4F\text{-}4} \rightarrow \mathbf{1a{-}c,\ f},$$

$$\mathbf{4a{-}d} + \mathrm{MeCOOAg} \rightarrow \mathbf{3a{-}c,\ f}.$$

Compounds **1e** and **3e** were synthesized according to the same procedures starting from (4-FC$_6$H$_4$)$_3$PAuCl (**5**).[28]

Syntheses of triarylphosphinegold bromides (4a—d). KBr (0.54 g, 4.57 mmol) was added to a solution of AuBr$_3$ (2 g, 4.57 mmol) in ethanol (50 mL) and a stream of SO$_2$ was passed through with stirring until the color of the solution changed from dark red to pale yellow. The precipitate was filtered off. Then a solution of Ar$_3$P (4.5 mmol) in a minimum amount of benzene was added with stirring to the filtrate. After 30 min, the solvent was evaporated to dryness. The dry residue was dissolved in CHCl$_3$ and chromatographed on Al$_2$O$_3$. Then the resulting compound was reprecipitated from CHCl$_3$ with light petroleum.

Syntheses of triarylphosphinegold 4-fluorothiophenoxides (1a—c, e—f). Compounds **4a—d** or **5** (0.7 mmol) were added with stirring to a suspension of NaH (0.024 g, 1 mmol) in a solution of 4-FC$_6$H$_4$SH (0.1 g, 0.94 mmol) in anhydrous THF (a large excess of 4-FC$_6$H$_4$SH affords polynuclear compounds that do not contain Ar$_3$P). Once **4a—d** or **5** reacted completely (a control was carried out by chromatography on SiO$_2$ in C$_6$H$_6$), two drops of H$_2$O and K$_2$CO$_3$ were added to the reaction mixture. Then the mixture was filtered, and the solution was concentrated to ~15 mL. Light petroleum was added dropwise until the solution became turbid. Then the mixture was filtered once again, and the product was precipitated with an excess of light petroleum.

Syntheses of triarylphosphinegold acetates (3a—c, e—f). MeCOOAg (0.23 g, 1.4 mmol) was added to a solution of **4a—d** or **5** (0.7 mmol) in a 1 : 1 THF—benzene mixture (25 mL). The suspension was stirred until the initial **4a—d** or **5** were consumed completely (a control was carried out by chromatography on SiO$_2$ in C$_6$H$_6$). The reaction mixture was twice filtered through a thick filter and then through a tube packed tightly with cotton (careful filtration was necessary to remove completely silver salts, which hinder isolation of the final product). The solvent was removed under reduced pressure at −20 °C. The residue was dissolved in a minimum amount of C_6H_6 and filtered once again. The product was precipitated with light petroleum.

The yields and melting points of the resulting compounds and the results of elemental analysis are given in Table 2.

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