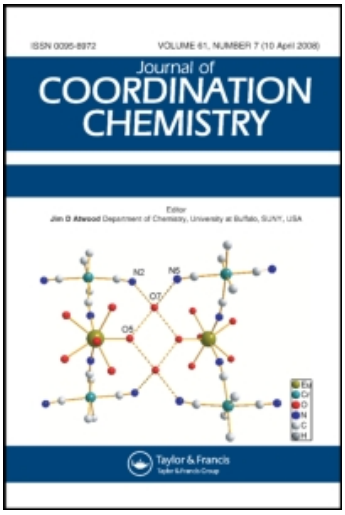

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GOLD(I) COMPLEXATION WITH TRIALKYL/TRIARYL PHOSPHINE SELENIDE LIGANDS

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A number of phosphine selenide ligands and their gold(I) complexes of general formula $R_3P{=}Se{-}Au{-}X$ (where X is Cl^-, Br^- and CN^- and R = phenyl, cyclohexyl and tolyl) were prepared. The complexes were characterized by elemental analysis, IR and ^{31}P NMR spectroscopic methods. In the IR spectra of all complexes a decrease in frequency of P=Se bond upon coordination was observed, indicating a decrease in P=Se bond order. ^{31}P NMR showed that the electronegativity of the substituents is the most important factor determining the ^{31}P NMR chemical shift. It was observed that phosphorus resonance is more downfield in alkyl substituted phosphine selenides, as compared to the aryl substituted ones. Ligand disproportionation in the complex $Cy_3P{=}SeAuCN$ in solution to form $[Au(CN)_2]^-$ and $[(Cy_3P{=}Se)_2Au]^+$ was investigated by ^{13}C and ^{15}N NMR spectroscopy.

Keywords: Gold(I); phosphine; selenide; NMR; disproportionation

INTRODUCTION

The importance of gold(I) compounds in the treatment of rheumatoid arthritis[1–3] has recently increased interest in gold(I) coordination chemistry. Myocrisin (gold(I) thiomalate), Solganol (gold(I) thioglucose) and Auranofin [(2,3,4,6-tetra-*o*-acetyl-1-thio-*β*-*D*-glucopyranosato-*S*) triethylphosphine gold(I)] have been successfully used over many years for the treatment of rheumatoid arthritis.[1–4]

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Gold(I) has a strong tendency to form linear two coordinate complexes of the type L–Au–X, where L is a neutral Lewis base (*e.g.*, phosphines, thioethers, *etc.*) and X is a halide or pseudohalide.[5–7] Au(I) is a soft Lewis acid and forms very stable complexes with softer sulfur, phosphorus or selenium containing ligands.[8] Examples of ligands containing sulfur bonded to gold(I) are thiolates,[5] thiones[9,10] and thiourea.[11] Phosphines are the common phosphorus containing ligands and several Au(I) complexes with different phosphines have been reported.[12,13] The more common examples of selenium containing ligands are selenides and selenolates.[14,15] Some phosphine selenide gold(I) complexes have already been reported.[16,17] In the present study, we report new trialkyl/triaryl phosphine selenide Au(I) complexes and ligand disproportionation in the complex $Cy_3P{=}SeAuCN$. This disproportionation is observed for the first time and the biological significance of such reactions is that they may alter the solution chemistry of gold(I) complexes used in the treatment of rheumatoid arthritis.[6]

EXPERIMENTAL SECTION

Chemicals

$AuBr \cdot 2H_2O$ and $HAuCl_4 \cdot 3H_2O$ were obtained from ICN Chemicals Co. All phosphines were obtained from the Strem Chemical Co. $K^{13}C^{15}N$ was obtained from Isotec Co., USA.

Synthesis of Ligands

All phosphine selenide ligands were prepared by the reaction of KSeCN with phosphines in an inert atmosphere (in some cases under reflux) according to the following equation.[18]

$$R_3P + KSeCN \rightarrow R_3P{=}Se + KCN$$

The following ligands were prepared: $Ph_3P{=}Se$, $Cy_3P{=}Se$, $(Cy \cdot Ph_2)P{=}Se$, $(p\text{-}Tol)_3P{=}Se$, $(m\text{-}Tol)_3P{=}Se$, and $(p\text{-}Tol \cdot Ph_2)P{=}Se$ (where Ph = phenyl, Cy = cyclohexyl and Tol = tolyl).

Synthesis of Complexes

$R_3P{=}Se{-}Au{-}Br$

To $AuBr \cdot 2H_2O$ (0.2000 g, 0.639 mmol) in 10 cm^3 of water, an equimolar amount of $R_3P{=}Se$ in 20 cm^3 of acetone was added. The mixture was

stirred for half an hour, after which the color of the solution changed to yellow, brown or red. After evaporation of acetone and filtration of aqueous solution, the product was recrystallized from acetone or ethanol.

$Cy_3P{=}Se{-}AuCl$ and $(m\text{-}Tol)_3P{=}Se{-}AuCl$

$HAuCl_4 \cdot 3H_2O$ (0.3233 g, 0.821 mmol) was dissolved in 20 cm^3 of ethanol. The flask was wrapped in aluminum foil. Dimethyl sulfide was added in excess, until a white precipitate was formed. Dimethyl sulfide was added with continuous stirring under N_2 and in the dark. A white precipitate was filtered and washed with cold ethanol and then with anhydrous ether. The product, $Me_2S{-}AuCl$ was then dried under vacuum.

$Me_2S{-}AuCl$ (0.1842 g, 0.625 mmol) was slurried in 20 cm^3 of acetone and then an equimolar amount of $Cy_3P{=}Se$ or $(m\text{-tol})_3P{=}Se$ dissolved in 15 cm^3 of acetone was added. The solution was stirred for 1 h in the fume hood, after which the solution was filtered and the filtrate was cooled in the refrigerator for recrystallization.

$Cy_3P{=}Se{-}AuCN$

$Cy_3P{=}Se$ (0.0920 g, 0.256 mmol) was dissolved in methanol in a 250 cm^3 quickfit flask. An equimolar amount of AuCN was added to this solution. The solution was then refluxed for 7–8 days. After this period the solution was changed to colorless. The solvent was evaporated to a volume of 15–20 cm^3. The solution was then filtered and the filtrate was left in refrigerator for recrystallization.

Elemental analyses and physical properties of all complexes are given in Table I. An attempt to prepare the cyano- and chlorogold(I) complexes of the other phosphine selenide ligands was unsuccessful.

IR Studies

The solid state IR spectra of the ligands and complexes were recorded on a Perkin Elmer IR 180 spectrophotometer using KBr pellets. The frequencies of P=Se bands are given in the Table II.

^{31}P NMR Studies

^{31}P NMR Spectra were measured at 80.9 MHz on a Varian XL-200 NMR spectrometer at a probe temperature of 297 K. ^{31}P NMR chemical shifts were measured relative to the internal reference 85% H_3PO_4. Solutions were

TABLE I Analyses of the R_3P=SeAuX complexes

R_3P=SeAuX	*C* (%)	*H* (%)	*N* (%)	*Color*	*Yield* (%)	*m.p.* (°C)
Cy_3P=Se–AuBr	35.13 (34.00)	5.33 (5.19)	0.00	Yellow	62.82	155–156
Cy_3P=Se–AuCl	37.36 (36.53)	5.58 (5.99)	0.00	White	17.02	173–175
Cy_3P=Se–AuCN	39.64 (39.18)	5.66 (5.67)	2.27 (2.41)	White	38.19	153–154
$(Cy \cdot Ph_2)P$=Se–AuBr	35.48 (34.62)	3.53 (3.37)	0.00	White	50.65	126–127
$(p\text{-Tol})_3P$=Se–AuBr	39.31 (38.17)	3.34 (3.18)	0.00	White	54.07	174–176
$(m\text{-Tol})_3P$=Se–AuCl	40.86 (40.90)	3.44 (3.41)	0.00	Light green	56.92	155–156
$(m\text{-Tol})_3P$=Se–AuBr	39.00 (38.17)	3.26 (3.18)	0.00	White	55.97	128–130
$(p\text{-Tol} \cdot Ph_2)P$=Se–AuBr	35.07 (36.08)	2.61 (2.69)	0.00	White	49.86	118–120
Ph_3P=Se–AuBr	33.74 (34.96)	2.28 (2.43)	0.00	White	45.57	175 (decomposed)

TABLE II Values of ν(CO) of R_3P, $^1J_{Se-P}$ of phosphine selenide ligands and IR frequencies, ν (cm^{-1}), of the P=Se band of ligands and complexes

R_3P=Se (L)	*ν(CO)** (cm^{-1})	*$^1J_{Se-P}$** (Hz)	*ν of the ligand (L)*	*ν of the L–AuBr*	*$\Delta\nu$ between L–AuBr and ligand*
Cy_3P=Se	2056.4	683	548	517	31
				520[a]	28
				519[b]	29
$(Cy \cdot Ph_2)P$=Se	2064.8	—	537	522	15
$(p\text{-Tol})_3P$=Se	2066.7	724	543	531	12
$(m\text{-Tol})_3P$=Se	2067.9	726	548	537	11
				530[c]	18
$(p\text{-Tol} \cdot Ph_2)P$=Se	2068.2	—	555	540	15
Ph_3P=Se	2068.9	735	561	536	25

*Values taken from Ref. 22. [a] ν for Cy_3P=Se–AuCl; [b] ν for Cy_3P=Se–AuCN; [c] ν for $(m\text{-Tol})_3P$=Se–AuCl.

prepared using deuterated acetone-d_6. In each case a sharp singlet was observed and no splitting due to ^{77}Se was observed. The chemical shifts of all compounds are given in Table III.

Ligand Disproportionation in [Cy_3P=Se–$Au^{13}C^{15}N$]

The ligand disproportionation of the complex, [Cy_3P=Se–AuCN] (with labelled ^{13}C and ^{15}N) has been studied by ^{13}C and ^{15}N NMR spectroscopy using a 0.025 M solution in methanol-d_4. ^{13}C spectra were recorded on Varian XL-200 NMR spectrometer at a frequency of 50.30 MHz with

TABLE III ^{31}P NMR chemical shifts (δ in ppm relative to H_3PO_4) of the ligands and complexes in d_6-acetone

$R_3P{=}Se$ (L)	(δ) of the ligand (L)	(δ) of the L–Au–Br	$\Delta\delta$ between L–Au–Br and ligand
$Cy_3P{=}Se$	56.33	58.51	+2.18
		59.35[a]	+3.02
		58.64[b]	+2.31
$(Cy \cdot Ph_2)P{=}Se$	44.03	39.40	−4.63
$(p\text{-Tol})_3P{=}Se$	31.37	26.42	−4.95
$(m\text{-Tol})_3P{=}Se$	33.08	27.72	−5.36
		26.21[c]	−6.87
$(p\text{-Tol} \cdot Ph_2)P{=}Se$	32.50	27.25	−5.25
$Ph_3P{=}Se$	32.84	27.79	−5.01

[a] δ for $Cy_3P{=}Se{-}AuCl$; [b] δ for $Cy_3P{=}Se{-}AuCN$; [c] δ for $(m\text{-Tol})_3P{=}Se{-}AuCl$.

broadband ^1H decoupling at 297 K. The chemical shifts were measured relative to internal reference dioxane at 67.4 ppm from TMS. ^{15}N spectra were recorded on Jeol JNM-LA 500 NMR spectrometer at a frequency of 50.55 MHz. $NH_4{}^{15}NO_3$ was used as external reference, which is at 375.11 ppm relative to pure CH_3NO_2, 380.2 ppm.[11]

RESULTS AND DISCUSSION

The reaction of AuBr with trialkyl and triaryl phosphine selenide resulted as an addition product as follows:

$$AuBr + R_3PSe \rightarrow R_3PSe{-}AuBr$$

In the IR spectra of phosphine selenides the P=Se stretching bands (depending on the substituents at the phosphorus) nearly follow the same pattern as given in the literature,[19] which is: 421–543 (R, alkyl groups attached to phosphorus), 525–532 (R, alkyl and R_1, R_2 aryl), and 544–574 (R, aryl groups).

Upon complexation with Lewis acids *e.g.*, AuBr, AuCN a decrease in the frequency of the P=Se is observed. This decrease is indicative of reduction in P=Se bond order on selenium coordination to gold(I). Similar observations were made when AuCN was bonded to the thione group of imidazolidine-2-thione and its derivatives.[10] There was a similar decrease in ν(P=Se) band after complexing with Cu(I).[20]

Generally it is assumed that the P=Se bond in $R_3P{=}Se$ is a coordination bond, on which $p\pi{-}d\pi$ bonds are superimposed, due to back bonding

from selenium p electrons ($3p_x^2$ and $3p_y^2$) to empty d orbitals of phosphorus ($3d_{xz}$ and $3d_{yz}$).[21] The amount of additional π bonding involving d orbitals of phosphorus also depends on the nature of substituents on phosphorus.

Electronic effects of the substituents are measured in terms of ν(CO) for $R_3PNi(CO)_3$ and $^1J_{Se-P}$ values defined by Tolman.[22] Electronic parameters, ν(CO) and $^1J_{Se-P}$ compare the electronegativities or basicities of the phosphine ligands. A decrease in ν(CO) or $^1J_{Se-P}$ is associated with a decrease in electronegativity of phosphine. The ν(CO) of the phosphines and IR frequencies and $^1J_{Se-P}$ values of the phosphine selenides are given in Table II.

A relation between the electronegativity of the phosphines in phosphine selenides and the shift in IR frequency upon complexation is observed with some exceptions. It is observed that as the electronegativity decreases, the shift in IR frequency is also decreased. This shows that the P=Se bond becomes stronger, while the Au–Se bond weakens as the electronegativity of the phosphines is decreased. The stronger P=Se bond may be due to more pronounced $p\pi$–$d\pi$ bonding. A large decrease in IR frequency of Cy_3P=Se after complexation represents the highly basic character of the ligand. This basicity is expected to increase the stability of the Au–Se bond.

The CN stretch in the cyanoethyl group in the IR occurs at 2246 cm^{-1} while in the cyano complex [$Cy_3PSeAuCN$], cyanide is found at 2140 cm^{-1}. This decrease in frequency is due to the donation of $d\pi$ electron density from gold to CN^- antibonding orbitals, thus weakening the C–N bond.[23]

In the ^{31}P NMR spectra of all ligands and complexes a sharp singlet was observed. As shown in Table III, in each case there was an upfield shift upon complexation except for Cy_3P=Se. The upfield shift indicates that the selenium accepts π electron density from the metal, which in turn enhances $p\pi$–$d\pi$ bonding in P=Se bond. Thus Cy_3P=Se has the least capacity for back bonding among these ligands.

The electronegativity of substituents is the most important variable in determining the ^{31}P chemical shift. With increasing electronegativity of the R groups the phosphorus atom becomes more positively charged and back bonding from π electrons of ligands to the empty d orbitals of phosphorus increases.[24] The presence of $p\pi$–$d\pi$ bonds leads to an increase of electron density around the phosphorus atom, thus augmenting its shielding. Thus in the case where alkyl substituents (instead of aryl) are attached to phosphorus, back donation of electrons from selenium is less, causing less shielding and hence an increase in chemical shift.

In (m-Tol)$_3$P=Se the phosphorus is observed more downfield than in Ph_3P=Se because of the larger C–P–C angle (106.6°[25] and 106°,[26] respectively) since angle opening on coordination is consistent with a downfield

shift.[22] The greater upfield shift upon complexation for $(m\text{-Tol})_3P{=}Se$ than for $Ph_3P{=}Se$ represents a more basic character for this ligand. In $(p\text{-Tol})_3P{=}Se$ a small downfield shift is assumed to be due to the electron releasing capacity of the methyl groups at the *para* position. This could hinder shielding at the phosphorus by reducing the $p\pi{-}d\pi$ character in the P=Se bond. In $(Cy \cdot Ph_2)P{=}Se{-}AuBr$, the smallest upfield shift is due to the presence of the less electronegative cyclohexyl group.

In cyano and chloro complexes of $Cy_3P{=}Se$, $Cy_3P{=}Se{-}AuCN$ and $Cy_3P{=}Se{-}AuCl$ a slightly greater downfield shift was observed as compared to the corresponding bromo complexes (Table III). The change is because of the π acceptor nature of CN^- and poor electron donating ability of Cl^- as compared to Br^-.[27] In $(m\text{-Tol})_3P{=}Se{-}AuCl$ a greater upfield shift and also a larger shift in the IR frequency indicates a stronger Au–Se bond as compared to the bromo complex. This shows that the electron accepting or donating ability of the X ligands also affects the ^{31}P chemical shift of the $R_3P{=}SeAuX$ complexes.

Labile ligand exchange is characteristic of cyano gold(I) complexes because of the very large formation constant of $[Au(CN)_2]^-$ ($\log\beta = 36$),[28] which drives the ligand exchange in the forward direction, generating $[Au(CN)_2]^-$. Ligand exchange reactions have been reported for a variety of cyano phosphine gold(I) complexes.[7,13,29] These complexes are usually monomers and two coordinate in the solid state. Since gold(I) is generally labile, there exists the possibility of ligand scrambling to form the symmetrically substituted complexes according to the equilibrium[6] below:

$$2R_3P{-}AuCN \Leftrightarrow [(R_3P)_2Au]^+ + [Au(CN)_2]^-$$

This equilibrium generally exists in solution. However, it has been reported that Tris(2-cyanoethylethyl)phosphine (CEP) forms an ionic complex, $[(CEP)_2Au]^+$ $[Au(CN)_2]^-$, both in solution as well as in the solid state.[30] Ligand disproportionation is also known for thiolato cyano gold(I) complexes.[31] To our knowledge, this is the first report which describes $R_3P{=}Se{-}AuCN$ complexes undergoing similar ligand scrambling reactions.

Ligand disproportionation in $[Cy_3P{=}Se{-}AuCN]$ was studied by ^{13}C and ^{15}N NMR spectroscopy. ^{31}P NMR at 297 K showed only one resonance at 63.02 ppm indicating that $[Cy_3P{=}Se{-}AuCN]$ is in a rapid equilibrium with $[Au(CN)_2]^-$ and $[(Cy_3P{=}Se)_2Au]^+$. However, two distinct resonances were observed in the ^{13}C NMR of $[Cy_3P{=}Se{-}Au^{13}C^{15}N]$ (Figure 1). One resonance at 151.40 ppm is characteristic of $[Au(^{13}C^{15}N)_2]^-$,[6] while the other at 146.44 ppm can be assigned to ^{13}C of $[Cy_3P{=}Se{-}Au^{13}C^{15}N]$. This is

explained by the equilibrium below:

$$2[Cy_3P{=}Se{-}AuCN] \Leftrightarrow [Au(CN)_2]^- + [(Cy_3P = Se)_2Au]^+$$

In an expansion of downfield region of the spectrum (Figure 1(a)), it was observed that the resonance due to ^{13}C of $[Cy_3P{=}Se{-}AuCN]$ is a doublet with $^1J(^{13}C{-}^{15}N) = 8.9$ Hz, while the $[Au(CN)_2]^-$ resonance appears as a triplet with an average coupling constant of 6.4 Hz. The $^{13}C{-}^{15}N$ coupling in $[Au(CN)_2]^-$ follows the simple AA'XX' spin system rather than A_2X_2 system. The simple triplet appearance of the ^{13}C spectrum arises due to the

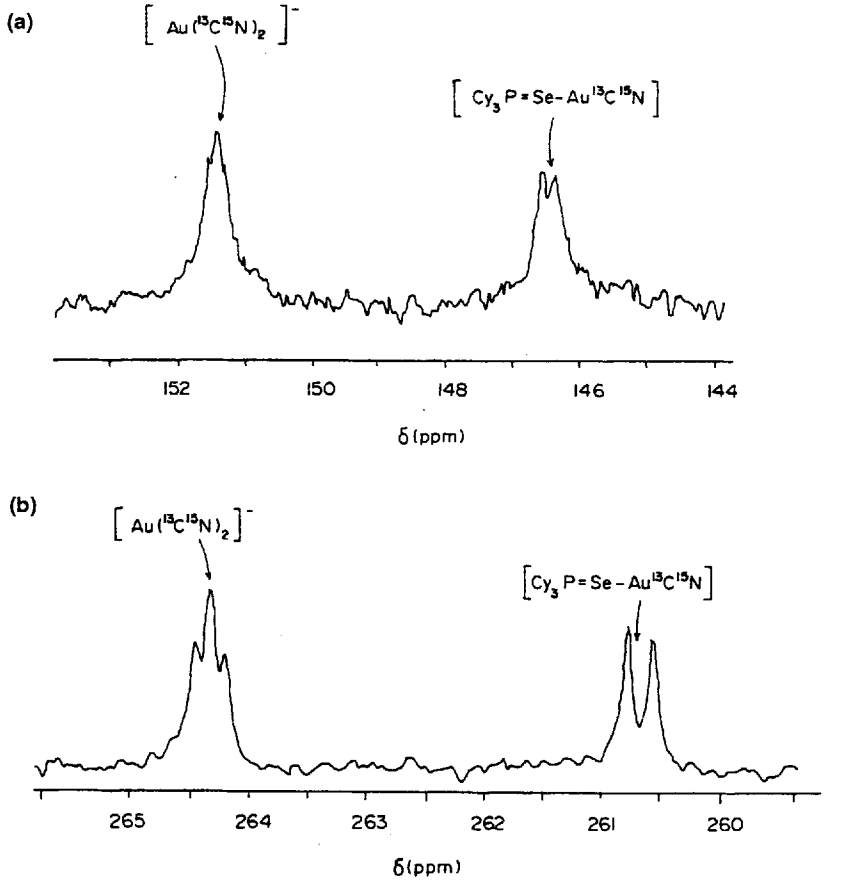

FIGURE 1 The (a) 50.30 MHz ^{13}C NMR spectrum and (b) 50.55 MHz ^{15}N NMR spectrum of 0.025 M $[Cy_3P{=}Se{-}Au^{13}C^{15}N]$ in CD_3OD.

TABLE IV Comparison of the ^{13}C, ^{15}N and ^{31}P chemical shifts (in ppm) of Cy_3P–Au–CN and Cy_3P=Se–Au–CN complexes in CD_3OD

Complex	$\delta(^{13}C)$	$\delta(^{15}N)$	$\delta(^{31}P)^a$	$\delta(^{13}C)$ *of* $[Au(CN)_2]^-$	$\delta(^{13}P)$ *of* $[(Cy_3P)_2Au]^{+a}$	*Ref.*
Cy_3P–Au–CN	160.29	264.35	56.27	151.70	64.86	29
Cy_3P=Se–Au–CN	146.44	260.65	63.02	151.40		This work

[a] ^{31}P chemical shifts are relative to H_3PO_4.

fact that $^2J(^{13}C-^{13}C) \gg {}^4J(^{15}N-^{15}N)$ and the inner lines of the AB subspectrum are so close together that they cannot be resolved (the outer lines lie below the limit of detection). Thus, only the sum of the coupling constants $[^1J(^{13}C-^{15}N) + {}^3J(^{13}C-^{15}N)]$ is extracted from the separation of the outer lines of the triplet and they lie in the range 10.4–13.2 Hz.[29]

^{15}N spectrum also showed two resonances corresponding to the above equilibrium (Figure 1(b)). One resonance at 260.65 ppm appeared as a doublet due to $^{13}C-^{15}N$ coupling in the complex with $^1J(^{13}C-^{15}N)$ of 10.1 Hz. The other resonance at 264.33 ppm is a triplet of $[Au(CN)_2]^-$ with an average coupling constant of 6.5 Hz. The ^{13}C and ^{15}N regions are identical in appearance as expected from AA'XX' system.

Comparison of the ^{13}C, ^{15}N and ^{31}P chemical shifts of Cy_3P–Au–CN and Cy_3P=Se–Au–CN is made in Table IV.[29] The ^{31}P chemical shift of Cy_3P–Au–CN in methanol-d_4 is 53.53 ppm relative to TMP (which is 2.74 ppm from H_3PO_4).[32] The ^{13}C chemical shift of Cy_3P–Au–CN is almost 14 ppm downfield as compared to Cy_3P=Se–AuCN. This indicates that Cy_3P=Se is a weaker σ donor as compared to Cy_3P. When it binds to the electron rich d^{10} center, the second lone pair on the donor atom may produce significant π repulsion.[33] Due to less electron density on gold(I), back bonding by C–N is reduced and an upfield shift is observed.

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