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Cooperative Electronic Ligand Effects in Pseudohalide Complexes of Rhodium(I), Iridium(I), Gold(I), and Gold(III)[1]

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The syntheses of the complexes *trans*-$M(P(C_6H_5)_3)_2(CO)X$ (M = Rh(I), Ir(I); X^- = NCO^-, NCS^-, $NCSe^-$; the Ir(I) selenocyanate complex also contains a coordinated acetone molecule), by metathesis reactions with the corresponding chloro complexes, LAuX, and diphosAu_2X_2 (L = $(C_6H_5)_3P$, $(C_6H_5)_3As$; diphos = 1,2-bis(diphenylphosphino)ethane; X^- = NCO^-, SCN^-, $SeCN^-$), either by metathesis with the corresponding chloro complex or (for the $(C_6H_5)_3P$ and diphos–SCN complexes) by reduction of $Au(SCN)_4^-$ in ethanol, are described. Bromine can be oxidatively added to the Au(I) complexes, producing complexes of the types $LAuBr_2X$ and diphos$Au_2Br_4X_2$. Simple addition takes place when X^- = Cl^- or NCO^- (and SCN^-, for the diphos complex). When X^- = SCN^- or $SeCN^-$, it is also oxidized and is replaced by Br^-. Thiocyanogen can be oxidatively added to $(C_6H_5)_3PAuCl$, producing a dithiocyanato complex. The synthesis of *trans*-$Pd(CH_3P(C_6H_5)_2)_2$-$(C_6F_5)NCS$ is also described. The observed pseudohalide bonding modes, which were determined on the basis of infrared spectral data (electronic spectra are also recorded), graphically illustrate the importance of charge and d-electron configuration to the functioning of cooperative electronic ligand effects in pseudohalide complexes. Attention is drawn to the disparate class a (symbiotic)–class b (antisymbiotic) bonding trends which have now been established for both thiocyanate and selenocyanate complexes.

Introduction

Since the first discovery[3] of cooperative ligand control of the bonding mode of the thiocyanate ion in square-planar palladium(II) and platinum(II) complexes, several papers[4–8] dealing with the effects of potential π-acceptor ligands on the bonding mode of the cyanate, thiocyanate, and selenocyanate ions in square-planar complexes have appeared in the literature. The results of these studies have shown that only the bonding mode of the thiocyanate ion can be influenced by the electronic nature of the other ligands present in the complex. The selenocyanate[5] and cyanate[7,8] ions, unlike their thiocyanate homolog, were found to be insensitive to changes in the electronic nature of other ligands in the coordination sphere.

The preceding investigations, save for one,[6] have involved d^8 complexes in which the metal occupies (at least formally) the 2+ oxidation state. Therefore, it was of considerable interest to assess the importance, if any, of cooperative electronic ligand effects on the bonding mode of the pseudohalides in d^8 square-planar complexes of both lower and higher oxidation states than palladium(II),[4,5,7] platinum(II),[4,7] and nickel(II).[8] If Turco and Pecile's π-bonding hypothesis[3] is correct, it would be expected that π-acceptor ligands would influence the bonding mode of the pseudohalide ions to a greater extent in complexes of lower oxidation state than those of higher oxidation state.

Experimental Section

Preparation of Compounds. ***trans*-$M(P(C_6H_5)_3)_2(CO)NCX$ Complexes (M = Ir(I), Rh(I); X = O, S).**—These complexes were prepared according to a modified procedure based on the method given by Jennings and Wojcicki[6] for the preparation of the rhodium(I) thiocyanate complex. The corresponding *trans*-chlorocarbonylbis(triphenylphosphine) complex (0.25 mmol, purchased from Strem Chemicals Inc., Danvers, Mass.) and 1.0 mmol of potassium thiocyanate (0.097 g) (for the preparation of the isothiocyanato complexes) or 1.0 mmol of tetraphenylarsonium cyanate dihydrate (0.46 g), prepared according to the method of Norbury and Sinha[7] (for the preparation of the isocyanato complexes) in Spectrograde acetone (125–200 ml), were refluxed for 3 hr. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness under reduced pressure, and the product was extracted into chloroform (25–50 ml). The extract was filtered, and then poured into 300 ml of 95% ethanol. After the ethanol solution was stirred for a few minutes, a yellow solid precipitated. The mixture was stirred an additional 0.5 hr, whereupon the product was isolated by filtration, washed with small amounts of ethanol and ethyl ether, and dried *in vacuo* over calcium sulfate.

***trans*-$Rh(P(C_6H_5)_3)_2(CO)NCSe$.**—A solution of 0.25 mmol of sodium selenocyanate (0.032 g) in 5 ml of Spectrograde acetone was added to 0.25 mmol of *trans*-$Rh(P(C_6H_5)_3)_2(CO)Cl$ (0.17 g) in 200 ml of Spectrograde acetone. After stirring for 15 min at room temperature, the reaction mixture was filtered to remove the precipitated sodium chloride. The filtrate was evaporated to dryness in the cold under reduced pressure. The residue was extracted into 25 ml of chloroform, and the product was precipitated by pouring the filtered extract into 200 ml of 95% ethanol. After stirring the mixture for 1 hr, the product was isolated by filtration, washed with ethyl ether, and dried *in vacuo* over calcium sulfate.

$Ir(P(C_6H_5)_3)_2(CO)(OC(CH_3)_2)NCSe$.—A solution of 0.25 mmol of sodium selenocyanate (0.032 g) in 10 ml of Spectrograde acetone was added to 0.25 mmol of *trans*-$Ir(P(C_6H_5)_3)_2(CO)Cl$ (0.20 g) in 300 ml of Spectrograde acetone. After stirring for 10 min at room temperature, the reaction mixture was filtered to remove the precipitated sodium chloride. The yellow filtrate was evaporated to *ca.* 25 ml in the cold under reduced pressure. The yellow product was isolated by filtration and dried *in vacuo* over calcium sulfate.

LAuCl Complexes (L = $(C_6H_5)_3P$, $(C_6H_5)_3As$).—A solution of 2.0 mmol of L in 20 ml of ethanol was added, with stirring, to 1.0 mmol of tetrachloroauric acid trihydrate (0.394 g) in 10 ml of ethanol. A white precipitate formed immediately, and, after stirring for 15 min, the product was isolated by filtration. It was washed with ethanol and ethyl ether and dried *in vacuo* over calcium sulfate.

diphosAu_2Cl_2 (diphos = 1,2-bis(diphenylphosphino)ethane).—A solution of 5.0 mmol of tetrachloroauric acid trihydrate (1.97 g) in 10 ml of ethanol was added to a slurry of 5.0 mmol of diphos (1.99 g) in 300 ml of ethanol. A yellow precipitate formed, whereupon the mixture was heated until the color disappeared. The mixture was cooled to room temperature, and the white product was isolated by filtration, washed with ethanol and ethyl ether, and dried *in vacuo* over calcium sulfate.

LAuNCO and diphos$Au_2(NCO)_2$ Complexes.—To a solution of 1.0 mmol of the corresponding chlorogold(I) complex (0.5 mmol

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[1] Abstracted from the Ph.D. Dissertation of N. J. D., University of Delaware, June 1971.

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for the diphos complex) in 25 ml of dichloromethane was added 2.0 mmol of silver cyanate (0.30 g). After stirring for 1 hr, the mixture was filtered, and the volume of the filtrate was reduced to *ca.* 5 ml. The product was precipitated by the addition of petroleum ether (bp 38–56°) (50–100 ml), isolated by filtration, washed with petroleum ether, and air-dried. After drying, the complexes were redissolved in 10 ml of dichloromethane, filtered, and reprecipitated by the addition of petroleum ether. The product was removed by filtration and dried *in vacuo* over calcium sulfate.

LAuSeCN and diphosAu$_2$(SeCN)$_2$ Complexes.—A solution of 1.1 mmol of sodium selenocyanate (0.14 g) in 10 ml of acetone was added, with stirring, to 1.0 mmol of the corresponding chlorogold(I) complex (0.5 mmol for the diphos complex) in acetone (10–75 ml). After stirring the mixture for 0.5 hr, the sodium chloride precipitate was removed by filtration. The volume of the filtrate was reduced until the product started to precipitate, whereupon it was isolated by filtration, washed with ethanol and ethyl ether, and dried *in vacuo* over calcium sulfate. The diphos–SeCN complex was redissolved in 25 ml of dichloromethane, filtered, and reprecipitated by the addition of 100 ml of petroleum ether. After stirring the mixture for 15 min, the product was removed by filtration and dried as described above.

$(C_6H_5)_3$PAuSCN.—A solution of 4.0 mmol of sodium thiocyanate (0.32 g) in 20 ml of ethanol was added to 1.0 mmol of sodium tetrachloroaurate(III) dihydrate (0.40 g) in 10 ml of ethanol. After stirring the mixture for 10 min, the sodium chloride precipitate was removed by filtration. A solution of 2.0 mmol of triphenylphosphine (0.53 g) in 30 ml of ethanol was added to the blood red filtrate, whereupon the solution lost its color. After stirring the mixture for 15 min, the solvent was removed under reduced pressure until the product started to precipitate. The product was isolated by filtration, washed with ethanol and ethyl ether, and dried *in vacuo* over calcium sulfate.

diphosAu$_2$(SCN)$_2$.—This complex was synthesized as described in the preceding preparation except that, upon the addition of 1.0 mmol of diphos (0.40 g) in 50 ml of ethanol, the product precipitated immediately. After stirring 1 additional hr, the product was isolated as described above.

$(C_6H_5)_3$AsAuSCN.—To a solution of 1.0 mmol of $(C_6H_5)_3$AsAuCl (0.54 g) in 25 ml of dichloromethane was added 2.0 mmol of silver thiocyanate (0.33 g). After stirring for 1 hr, the mixture was filtered, and the volume of the filtrate reduced to *ca.* 5 ml. The product was precipitated by the addition of 100 ml of petroleum ether. The white solid was isolated by filtration and air-dried. After drying, it was redissolved in 10 ml of dichloromethane, filtered, and reprecipitated by the addition of 100 ml of petroleum ether. The product was isolated by filtration and dried *in vacuo* over calcium sulfate.

LAuBr$_2$X ($X^- = Cl^-, Br^-, NCO^-$) and diphosAu$_2$Br$_4$X$_2$ ($X^- = Cl^-, Br^-, NCO^-, SCN^-$) Complexes.—These complexes were prepared by the same general procedure. The details of each reaction are shown in Table I.

To a slurry of the chloro- or pseudohalogenogold(I) complex in 25 ml of carbon tetrachloride was added a solution of bromine in carbon tetrachloride (1 ml of Br_2 diluted to 10 ml with CCl_4). After stirring the mixture for 2 hr at room temperature, the product was isolated by filtration, washed with carbon tetrachloride to remove excess bromine, and dried *in vacuo* over calcium sulfate.

$(C_6H_5)_3$PAu(SCN)$_2$Cl.—A freshly prepared −78° solution of 6.2 mmol of thiocyanogen (0.72 g) in carbon disulfide was added in three portions to a −78° slurry of 1.0 mmol of $(C_6H_5)_3$PAuCl (0.50 g) in 10 ml of carbon disulfide. After stirring the mixture for 2 hr at −78°, the orange product was isolated on a precooled funnel and washed with cold carbon disulfide. The product was air-dried and then dried *in vacuo* over calcium sulfate; yield 33%; dec pt 97–100°. *Anal.* Calcd for $C_{20}H_{15}AuClN_2PS_2$: C, 39.32; H, 2.48; N, 4.59. Found: C, 39.21; H, 2.55; N, 4.28.

***trans*-Pd(P(CH$_3$)(C$_6$H$_5$)$_2$)$_2$(C$_6$F$_5$)NCS.**—To a solution of 0.114 mmol of *trans*-Pd(P(CH$_3$)(C$_6$H$_5$)$_2$)$_2$(C$_6$F$_5$)Cl[9] (0.08 g) in 25 ml of acetone was added 1.0 mmol of sodium thiocyanate (0.08 g). After refluxing the mixture for 3 hr, the sodium chloride precipitate was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. Ethanol (15 ml) was added to the residue, and the resulting mixture was placed in the refrigerator for several hours. The white product was isolated by filtration and dried *in vacuo* over calcium sulfate; yield 48%. *Anal.* Calcd for $C_{33}H_{26}F_5NP_2PdS$: C, 54.90; H, 3.63; N, 1.94. Found: C, 54.72; H, 3.72; N, 1.93.

TABLE I

OXIDATIVE ADDITION REACTIONS OF LAuX AND diphosAu$_2$X$_2$ COMPLEXES WITH BROMINE

L	X	Amt of substrate used, mmol	Amt of Br_2–CCl_4 soln used, ml	Product
		LAuX Substrates		
$(C_6H_5)_3P$	Cl	2.0	3.0	LAuBr$_2$Cl
$(C_6H_5)_3P$	NCO	0.49	2.0	LAuBr$_2$NCO
$(C_6H_5)_3P$	SCN	0.09	2.0	LAuBr$_3$
$(C_6H_5)_3P$	SeCN	0.09	2.0	LAuBr$_3$
$(C_6H_5)_3As$	Cl	0.64	2.0	LAuBr$_2$Cl
$(C_6H_5)_3As$	NCO	0.82	2.0	LAuBr$_2$NCO
$(C_6H_5)_3As$	SCN	0.34	2.0	LAuBr$_3$
		LAu$_2$X$_2$ Substrates		
diphos	Cl	0.50	5.0[a]	LAu$_2$Br$_4$Cl$_2$
diphos	NCO	0.24	2.0	LAu$_2$Br$_4$(NCO)$_2$
diphos	SCN	0.17	2.0	LAu$_2$Br$_4$(SCN)$_2$
diphos	SeCN	0.25	2.0	LAu$_2$Br$_6$

[a] A bromine–carbon tetrachloride solution containing 2 ml of bromine diluted to 10 ml with CCl_4 was used in this preparation. The reaction time was lengthened to 6 hr.

Thiocyanogen.—A solution of 6.2 mmol of bromine (1.0 g) in 5 ml of carbon disulfide was added to a slurry of 12.8 mmol of silver thiocyanate (2.1 g) in 15 ml of carbon disulfide. The mixture was stirred until the color of bromine disappeared. The mixture was filtered and the filtrate was cooled to −78°. The cooled thiocyanogen solutions were used immediately after preparation.

Physical Measurements.—Carbon, hydrogen, and nitrogen microanalyses and molecular weight determinations were performed by the Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, West Germany, and Micro-Analysis, Inc., Wilmington, Del. The per cent yields, decomposition temperatures, and analytical results for the rhodium(I), iridium(I), gold(I), and gold(III) complexes prepared in this study are shown in Table II.

Measurements of molar conductivities, solid-state and solution infrared spectra, and visible–ultraviolet spectra were carried out as described previously.[10] All of the gold(I) complexes function as nonelectrolytes in nitrobenzene solution at 25°, the $(C_6H_5)_3$AsAuSeCN complex exhibiting the largest Λ_m value (1.1 ohm^{-1} cm^2 mol^{-1}). The infrared and visible–ultraviolet spectral data are shown in Tables III and IV.

Proton nmr spectra were recorded with a Varian A-60A nuclear magnetic resonance spectrometer. Tetramethylsilane was used as the internal standard. Decomposition temperatures were determined on a Fisher-Johns melting point apparatus and are uncorrected. All of the pseudohalide complexes described herein were found to be stable with respect to linkage isomerization, both in the solid state and in the solutions used for the spectral measurements.

Discussion

Rhodium(I) and Iridium(I) Complexes.—Although the complexes of the type *trans*-M(P(C$_6$H$_5$)$_3$)$_2$(CO)NCX (M = Rh(I), Ir(I); X = O, S) have been previously reported,[6,11–15] the data concerning them, except for the isothiocyanatorhodium(I) complex,[6] have been limited mainly to preparative details. All of the rhodium(I) and iridium(I) complexes prepared in this study were

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TABLE II

YIELDS, DECOMPOSITION TEMPERATURES, AND ANALYSES OF Rh(I), Ir(I), Au(I), AND Au(III) COMPLEXES

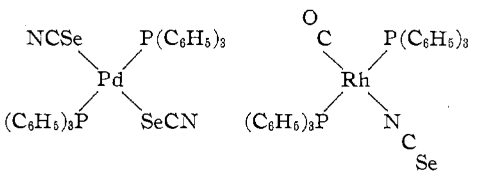
				Analyses, %					
				C		H		N	
M or L	X	% yield	Dec pt, °C	Calcd	Found	Calcd	Found	Calcd	Found
trans-$M(P(C_6H_5)_3)_2(CO)X$ Complexes									
Rh	NCO	45	194–197	65.43	65.70	4.34	4.17	2.01	2.21
Rh	NCS	55	174–178	63.96	63.66	4.24	4.32	1.96	2.65
Rh	NCSe	58	125–127	60.02	60.01	3.98	4.15	1.84	1.88
Ir	NCO	78	237–240	58.01	58.07	3.84	3.84	1.78	2.08
Ir	NCS	78	190–193	56.85	56.92	3.77	3.73	1.74	2.00
Ir[a]	NCSe[a]	40	123–126	54.24	53.87	4.00	3.70	1.54	1.81
LAuX Complexes									
$(C_6H_5)_3P$	Cl	84	241–243	43.70	43.86	3.06	3.08	. . .	. . .
$(C_6H_5)_3P$	NCO	89	202–204	45.52	45.37	3.02	3.05	2.79	2.95
$(C_6H_5)_3P$[b]	SCN[b]	41	165–166	44.30	44.25	2.92	2.75	2.71	2.61
$(C_6H_5)_3P$	SeCN	25	112–115	40.44	40.82	2.68	2.72	2.48	1.80
$(C_6H_5)_3As$	Cl	84	184–188	40.13	40.09	2.82	2.62	. . .	. . .
$(C_6H_5)_3As$	NCO	77	159–163	41.91	41.66	2.78	2.59	2.57	2.40
$(C_6H_5)_3As$[c]	SCN[c]	55	134–138	40.66	40.80	2.69	2.77	2.49	2.04
$(C_6H_5)_3As$	SeCN	30	115–117	37.52	37.81	2.49	2.81	2.30	1.83
LAu_2X_2 Complexes									
diphos	Cl	64	230–234	36.17	36.60	2.80	2.92	. . .	. . .
diphos	NCO	80	227–230	38.37	38.81	2.76	2.75	3.20	3.44
diphos[d]	SCN[d]	78	228–230	37.01	37.19	2.66	3.21	3.08	3.25
diphos	SeCN	40	126–129	33.55	34.44	2.41	2.65	2.80	2.75
$LAuBr_2X$ Complexes									
$(C_6H_5)_3P$	Cl	97	157–159	33.03	32.78	2.31	2.64	. . .	. . .
$(C_6H_5)_3P$	NCO	86	107–110	34.52	34.33	2.29	2.36	2.12	2.24
$(C_6H_5)_3P$	Br	97	146–150	30.93	30.83	2.16	2.13	. . .	. . .
$(C_6H_5)_3As$	Cl	96	75–78	30.95	30.76	2.16	2.26	. . .	. . .
$(C_6H_5)_3As$[e]	NCO[e]	97	. . .	32.37	. . .	2.14	. . .	1.87	. . .
$(C_6H_5)_3As$	Br	93	95–98	29.10	29.00	2.04	2.06	. . .	. . .
$LAu_2Br_4X_2$ Complexes									
diphos	Cl	99	139–142	26.40	26.60	2.04	2.06	. . .	. . .
diphos	NCO	82	123–127	28.12	27.92	2.02	2.47	2.34	2.19
diphos	SCN	87	114–117	27.38	27.31	1.97	2.03	2.28	2.05
diphos	Br	99	135–138	24.55	24.40	1.90	1.98	. . .	. . .

[a] Complex contains 1 mol of coordinated acetone (*vide infra*). [b] Molecular weight: theoret, 507; found, 494. [c] Molecular weight: theoret, 561; found, 559. [d] Molecular weight: theoret, 908; found, 889. [e] Complex decomposed before analysis could be obtained.

found to contain N-bonded pseudohalide groups, as evidenced by the solid-state and solution infrared data shown in Table III. With respect to the free-ion values, the ν_{CX} and ν_{CN} frequencies of the complexes have been shifted to higher frequencies, the integrated absorption intensities of the ν_{CN} bands are larger, and the δ_{NCX} frequencies are little changed, as would be expected for N-bonded pseudohalide groups.[7,16]

Although steric control of the bonding mode of the selenocyanate ion in square-planar palladium(II) complexes has been firmly established,[17] cooperative electronic ligand control of the bonding mode of the ion in square-planar complexes has heretofore never been observed; *i.e.*, only Se bonding has been found to occur in the sterically unhindered complexes of palladium(II),[5,18] platinum(II),[18,19] and gold(III).[20] The *trans*-$Rh(P(C_6H_5)_3)_2(CO)NCSe$ complex, reported here for the first time, represents the first example of an N-bonded selenocyanate group in a d^8 square-planar complex.

A very recent study[21] has emphasized the importance of steric factors in determining the bonding mode adopted by the thiocyanate ion in palladium(II) complexes, even those containing ligands having coordinated atoms, *e.g.*, P and As, which have been considered to be π acceptors. Thus, as noted earlier,[4] the switch from S to N bonding in the complexes $Pd(SCN)_4^{2-}$ and *trans*-$Pd(P(C_6H_5)_3)_2(NCS)_2$ can be attributed to either the steric hindrance of the phenyl groups of the phosphine to the formation of the nonlinear Pd–SCN linkage or the π withdrawal by the phosphines,[3] or a combination of both. The observation applies equally well to the *trans*-$M(P(C_6H_5)_3)_2(CO)NCS$ (M = Rh, Ir) complexes. However, in comparing the complexes



one sees that the steric factor remains essentially constant in both, and the switch to N bonding in the latter complex must therefore be due to an electronic effect, most probably the greater π-withdrawal by the trans CO group. Moreover, if steric control of the bonding modes were completely dominant, a switch to N bonding would be anticipated to be more likely in the complex $Pd(P(C_6H_5)_3)_2(SeCN)_2$, due to the greater size of the selenium atom. Instead, it is the thiocyanate complex which is found to be N bonded. If some of the steric crowding is relieved, but a strongly electron-with-

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TABLE III
INFRARED DATA FOR Rh(I), Ir(I), Au(I), AND Au(III) COMPLEXES

				ν_{CN}	
M or L	X	ν_{CX},[a] cm^{-1}	δ_{NCX},[a] cm^{-1}	Freq, cm^{-1}	$10^{-4}A$,[b] M^{-1} cm^{-2}
		trans-$M(P(C_6H_5)_3)_2(CO)X$ Complexes			
Rh	NCO	1340 m	605, 589 m	2233 s[c] 1985 s (ν_{CO})[c]	18[c]
Rh	NCS	829 w	470 w	2096 s[c] 1993 s (ν_{CO})[c]	12[c]
Rh	NCSe	565 w	?	2096 s[c] 1996 s (ν_{CO})[c]	9[c]
Ir	NCO	1352 m	610, 581 m	2245 s[c] 1970 s (ν_{CO})[c]	18[c]
Ir	NCS	845 m	480 w	2096 s[c] 1981 s (ν_{CO})[c]	12[c]
Ir	NCSe	560 w (?)	440 w (?)	2094 s[c] 1985 s (ν_{CO})[c] 1712 m[c,d]	7[c]
		LAuX Complexes			
$(C_6H_5)_3P$	NCO	1348 w	621, 599 m	2211 s[e]	25[e]
$(C_6H_5)_3P$	SCN	*f*	448 w (?)	2131 s[e]	1.5[e]
$(C_6H_5)_3P$	SeCN	529 w	?	2135 s[e]	0.70[e]
$(C_6H_5)_3As$	NCO	1345 w	625, 599 m	2207 s[e]	20[e]
$(C_6H_5)_3As$	SCN	*f*	?	2132 s[e]	1.0[e]
$(C_6H_5)_3As$	SeCN	?	?	2132 s[e]	0.54[e]
		LAu_2X_2 Complexes			
diphos	NCO	1350 w	592, 580 w	2210 s[e]	23[e]
diphos	SCN	*f*	?	2131 s[e]	1.5[e]
diphos	SeCN	?	?	2131 s[e]	0.80[e]
		$LAuBr_2X$ Complexes			
$(C_6H_5)_3P$	NCO	1339 w	595, 588 w	2152 s[a] 2171 s[e]	... 17[e]
$(C_6H_5)_3As$	NCO	1340 w	618, 592 w	2155 s[a]	...
		$LAu_2Br_4X_2$ Complexes			
diphos	NCO	1342 w	600 w	2155 s[a]	...
diphos	SCN	720, 690 w	?	2127 s[a]	...
		Other Complexes and Ionic Pseudohalides			
$(C_6H_5)_3PAu(SCN)_2Cl$		*f*	?	2142 sh, 2137 s[a]	...
trans-$Pd(CH_3P(C_6H_5)_2)_2(C_6F_5)NCS$		...	...	2092[g]	10[g]
Ionic cyanate		1300, 1205[h]	636, 626[h]	2158[i]	8.4[i]
KNCS		749	486, 471	2060[j]	4.4[j]
KNCSe		558	424, 416	2069[j]	3.1[j]

[a] Nujol mull. Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. [b] Integrated absorption intensity, calculated per mole of coordinated pseudohalide. [c] Chloroform solution. [d] ν_{CO} of acetone carbonyl. [e] Dichloromethane solution. [f] Band obscured by phenyl ring absorption. [g] Acetone solution. [h] As KNCO. [i] As $[(C_6H_5)_4As]NCO \cdot 2H_2O$ (acetone solution); data taken from ref 7. [j] Butanone solution.

TABLE IV
ELECTRONIC SPECTRAL DATA FOR Rh(I), Ir(I), AND Au(III) COMPLEXES

M	X	ν_{max},[a] kK ($10^{-3}\epsilon_{max}$)
	trans-$M(P(C_6H_5)_3)_2(CO)X$ Complexes	
Rh	Cl	27.4 (3.63) 34.0 (14.0)
Rh	NCO	27.1 (3.97) 36.4 (19.5)
Rh	NCS	27.0 (4.13) 34.2 (18.0)
Rh	NCSe	26.7 (3.82) 33.4 (15.2)
Ir	Cl	22.8 (0.665) 25.8 (3.24) 29.5 (2.71) 36.4 (17.2)
Ir	NCO	22.6 (0.781) 25.8 (3.44) 29.5 (2.62) 36.3 (18.6)
Ir	NCS	22.6 (1.80) 25.3 (3.85) 28.9 (3.55) 33.7 (16.5)
Ir[c]	NCSe[c]	20.0 (0.200) 22.1 (0.961) 25.1 (4.05) 28.1 (4.23) 32.6 (12.2)

L	X	ν_{max},[b] kK ($10^{-3}\epsilon_{max}$)
	$LAuBr_2X$ Complexes	
$(C_6H_5)_3P$	Cl	29.1 (9.41)
$(C_6H_5)_3P$	NCO	29.4 (9.12)
$(C_6H_5)_3P$	Br	24.5 (3.86) 29.0 (8.78)
$(C_6H_5)_3As$	Cl	21.2 sh *d* 25.3 *d*
$(C_6H_5)_3As$	Br	21.1 sh *d* 25.1 *d*
	$LAu_2Br_4X_2$ Complexes	
diphos	Cl	24.9 (4.87) 29.1 (8.80)
diphos	NCO	29.9 (15.8)
diphos	SCN	25.7 (7.87) 30.2 (8.60)
diphos	Br	25.5 (10.8) 30.1 (13.5)
	$(C_6H_5)_3PAu(SCN)_2Cl$	
...	...	21.4 *d*
...	...	31.6 *d*

[a] Chloroform solution. [b] Dichloromethane solution. [c] Contains 1 mol of coördinated acetone (*vide infra*). [d] Decomposes in solution.

drawing group is placed in the trans position, as in the complex *trans*-$Pd(CH_3P(C_6H_5)_2)_2(C_6F_5)NCS$, N bonding (see Table III) is still observed. All of these observations lend further credence to the π-bonding hypothesis first suggested by Turco and Pecile.[3]

The isoselenocyanatorhodium(I) complex was precipitated from a chloroform solution by adding ethanol. However, when the same procedure was applied to the iridium analog, the complex decomposed before it could be isolated. Consequently, the iridium(I) complex had to be isolated rapidly and directly from an acetone solution, the result being that the complex was isolated as a five-coordinate species containing 1 mol of acetone, as well as an N-bonded selenocyanate group. The formulation of the product as a five-coordinate complex is supported by its infrared spectrum (Table III). The 1712-cm^{-1} band, which does not shift appreciably upon dissolution in chloroform, appears in the region of the carbonyl stretching frequency of acetone. Even after drying the complex for 8 hr at 40° *in vacuo*, the infrared spectrum showed that the acetone band had not decreased in intensity, also indicating that the acetone is coordinated to the metal.

The proton nuclear magnetic resonance spectrum of the complex in deuterated chloroform exhibited two resonances at δ 6.8–8.1 (m, 32) and 2.17 (s, 6) ppm. The multiplet is assigned to the phenyl protons, while the singlet is assigned to the methyl protons. The integration of the bands (32/6) was found to be in close agreement with the actual value (30/6).

The rhodium(I) complexes exhibit two main bands in their electronic spectra (Table IV), whereas the iridium(I) complexes exhibit four strong bands. Further examination of the spectra of the iridium(I) complexes shows that the isoselenocyanato complex exhibits an additional band at lower energy. This offers further support for the hypothesis that the isoselenocyanato complex is five-coordinate.

Gold(I) Complexes.—The addition of an ethanolic solution of 2 equiv of triphenylphosphine or triphenylarsine to a yellow solution of tetrachloroauric acid in ethanol results in the immediate disappearance of the color and the precipitation of a white solid.[22] The loss of color is due to the reduction of gold(III) to gold(I) and the switch from a d^8 system to a d^{10} system. The product of the reaction is chloro(triphenylphosphine)- or chloro(triphenylarsine)gold(I). These complexes

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[22] F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1828 (1937).

are two-coordinate, as would be expected for gold(I), and are reasonably stable. The diphosphine, 1,2-bis(diphenylphosphino)ethane, reacts with tetrachloroauric acid in the same manner to yield the dinuclear diphosphine-bridged complex ClAu(diphos)AuCl.[23]

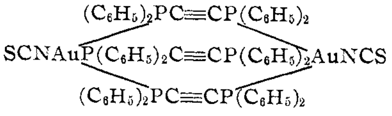
If an ethanolic solution of triphenylphosphine or diphos is added to a blood red solution of $Au(SCN)_4^-$, the color is lost immediately, and the corresponding thiocyanate complexes are formed. The substitution of triphenylarsine in this reaction yielded a white solid which showed a strong absorption band in the ν_{CN} region but always gave poor analytical results. An attempt to prepare selenocyanato(triphenylphosphine)gold(I) by the addition of triphenylphosphine to a cold solution of $Au(SeCN)_4^-$ resulted in the formation of triphenylphosphine selenide. [$(C_6H_5)_3P{=}Se$ was identified by its melting point (185–188°) and infrared spectrum ($\nu_{P=Se}$ 561 cm^{-1}); lit. values:[24] mp 184–186°; $\nu_{P=Se}$ 560 cm^{-1}.] Consequently, the preparations of the LAuSeCN and diphosAu$_2$(SeCN)$_2$ complexes were carried out by metathetical reactions between the corresponding chloro complex and sodium selenocyanate. The corresponding isocyanato complexes, along with the thiocyanatoarsinegold(I), were prepared by reaction of the chloro complexes with the appropriate silver pseudohalide.

With the exception of the three gold chlorides,[22,23] the thiocyanatophosphinegold(I),[25] whose bonding mode was not determined, and the isocyanatophosphinegold(I)[12,26] complexes, the remaining gold(I) complexes have not been previously reported.

It was expected that the removal of steric hindrance, coupled with the increased d-electron density on the metal, would create a coordination site which would exhibit a strong preference for S or Se bonding (and N bonding, in the case of the cyanate, which exhibits O bonding only when coordinated to highly charged, very hard metal ions[27,28]). That this expectation was realized is clearly demonstrated by the data in Table III. The cyanate complexes exhibit the same trends in infrared behavior described earlier and are, therefore, shown to contain N-bonded groups. The thiocyanate and selenocyanate complexes, however, exhibit ν_{CN} integrated absorption intensities which are *lower* than the free-ion values and are thus shown[16] to contain X-bonded groups.

Recently, Carty and Efraty[29] reported a series of copper(I) and gold(I) complexes in which 1,2-bis(diphenylphosphino)acetylene (DPPA) acts as a bridging ligand. These complexes are similar to the diphos complexes reported here. Of particular interest are two gold(I)–thiocyanate complexes having the molecular formulas

$NCSAuP(C_6H_5)_2C{\equiv}CP(C_6H_5)_2AuSCN$



$$\begin{array}{c} (C_6H_5)_2PC{\equiv}CP(C_6H_5)_2 \\ SCNAuP(C_6H_5)_2C{\equiv}CP(C_6H_5)_2AuNCS \\ (C_6H_5)_2PC{\equiv}CP(C_6H_5)_2 \end{array}$$

Although they did not reach any definite conclusions regarding the nature of the gold–thiocyanate bonds in these complexes, on the basis of the solid-state infrared data reported, it would appear that the (DPPA)Au$_2$(SCN)$_2$ complex is S bonded (ν_{CN} 2112 cm^{-1} (s, sp)), while the (DPPA)$_3$Au$_2$(NCS)$_2$ complex is N bonded (ν_{CN} 2095 cm^{-1} (s)). Although the authors noted the latter possibility, they stated that, in the former case, S bonding was not predictable because M–NCS bonding has been found to predominate in metal–thiocyanate–phosphine complexes.

However, these assignments of the bonding modes of the thiocyanate groups agree perfectly with the results of our study. In the case where only one π-acceptor ligand (DPPA or diphos) is coordinated to gold(I), it is insufficient to switch gold(I) from a class b metal to a class a metal; therefore, S bonding is observed. When three π-acceptor ligands are incorporated into the coordination sphere, as in (DPPA)$_3$Au$_2$(NCS)$_2$, the gold(I) is converted to a class a metal, and N bonding is observed. It must be pointed out that an unequivocal assignment of the bonding mode cannot be made on the basis of solid state ν_{CN} frequency data alone. It should also be noted that the increased steric hindrance created by the six phenyl groups about each gold(I) in the latter complex would also tend to promote the formation of a linear Au–NCS bond.

Gold(III) Complexes.—As noted earlier, the addition of 2 equiv of a phosphine, arsine, or diphosphine to tetrachloroauric acid results in the reduction of gold(III) to gold(I). However, the use of oxidative addition reactions with gold(I) complexes enabled us to prepare gold(III) complexes containing such ligands. Only four reports dealing with the oxidation of gold(I) to gold(III) *via* oxidative addition reactions have appeared in the literature.[26,30–32]

When bromine was added to carbon tetrachloride slurries of the gold(I) complexes discussed above, a series of four-coordinate dibromogold(III) complexes was obtained. The reactions proceeded rapidly and were essentially quantitative. The addition of bromine to the chloro- and isocyanatogold(I) complexes yielded the expected dibromochloro- and dibromoisocyanatogold(III) complexes. However, the addition of bromine to the monothiocyanato- and selenocyanatogold(I) complexes resulted in the replacement of the pseudohalide group and the formation of the tribromogold(III) derivatives. In the case of the dithiocyanato- and diselenocyanatodigold(I)–1,2-bis(diphenylphosphino)ethane complexes, the pseudohalide groups were replaced in only the selenocyanate complex, yielding the bridged hexabromogold(III)–1,2-bis(diphenylphosphino)ethane complex. The thiocyanate groups remained intact, and the tetrabromodithiocyanatogold(III)–1,2-bis(diphenylphosphino)ethane complex was isolated.

The replacement of certain pseudohalide groups by bromine can be explained by taking the oxidizing power of the halogens and pseudohalogens into consideration. The halides and pseudohalides can be arranged in the following order of *increasing* reducing power: F$^-$,

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[27] J. L. Burmeister, E. A. Deardorff, A. Jensen, and V. H. Christiansen, *Inorg. Chem.*, **9**, 58 (1970).

[28] R. A. Bailey and S. L. Kozak, *J. Inorg. Nucl. Chem.*, **31**, 689 (1969).

[29] A. J. Carty and A. Efraty, *Inorg. Chem.*, **8**, 543 (1969).

[30] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1235 (1940).

[31] C. E. Wymore and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **14**, 42 (1960).

[32] L. G. Vaughan and W. A. Sheppard, *J. Amer. Chem. Soc.*, **91**, 6151 (1969).

ONC^-, NCO^-, Cl^-, N_3^-, Br^-, CN^-, SCN^-, I^-, $SeCN^-$. The oxidizing power of the free halogens and pseudohalogens should *decrease* in the same order.[33] Since bromine is a weaker oxidizing agent than chlorine and oxycyanogen, $(NCO)_2$, it cannot oxidize chloride and isocyanate to chlorine and oxycyanogen and hence does not replace them during the oxidative addition reactions. On the other hand, bromine is a stronger oxidizing agent than thiocyanogen and selenocyanogen, and it can oxidize thiocyanate and selenocyanate to form these compounds. Therefore, bromine would tend to replace thiocyanate and selenocyanate during the oxidative addition reactions. That bromine does not replace thiocyanate in the diphos complex might be due to the fact that, since diphos is a more basic phosphine than triphenylphosphine, the gold(III) coordination site would be softer and, hence, the Au–SCN bond would be stronger.

It was anticipated that the effect of an increased positive charge in square-planar d^8 systems would serve to diminish the effects of potential π-acceptor ligands. This, too, was realized in that (Table III) only an Au–NCO, Au–SCN bonding pattern was observed for the gold(III) complexes. Admittedly, the gold(III) complexes prepared do not provide an entirely appropriate comparison with the palladium(II) phosphine complexes, since the former contain only one phosphine group coordinated to the metal atom, and steric effects would also be expected to be of less importance. Solubility and/or decomposition problems prevented the acquisition of solution infrared data for all of the gold(III) complexes except $(C_6H_5)_3PAuBr_2NCO$.

Oxidative addition reactions of thiocyanogen to a series of rhodium(I)–carbonyl complexes have recently been reported.[34] The products of the reactions were the corresponding dithiocyanatorhodium(III)–carbonyl complexes. When thiocyanogen was added to chloro(triphenylphosphine)gold(I), an orange solid was isolated, which analyzed for $(C_6H_5)_3PAu(SCN)_2Cl$, with what appear (Table III) to be S-bonded thiocyanates.

The electronic spectral data for all of the gold(III) complexes are listed in Table IV. The bands appear to be charge-transfer bands in view of their large ϵ_{max} values. As one proceeds from the first transition series downward, the value of Δ (the energy separation between the d orbitals) increases. Since gold is in the third transition series, it might be expected that the d–d absorption bands would be shifted to higher energies due to the increased value of Δ and are thereby covered by the more intense charge-transfer bands.

Complexes of the type MAB_2C can exist as either the cis or trans isomer. Although the complex $(C_6H_5)_3PAu(SCN)_2Cl$ does exhibit two ν_{CN} bands in its solid-state infrared spectrum, the assignment of a cis configuration is not unequivocal because the in-phase ν_{CN} frequency of a trans configuration in the solid state may be active if the site symmetry of the complex is not centrosymmetric.

Conclusions

The results of this study have shown that cooperative electronic ligand effects due to π-acceptor ligands are, as predicted, more pronounced in d^8 complexes in which the metal is in a lower oxidation state. Nitrogen bonding was noted for both the thiocyanate and selenocyanate complexes of iridium(I) and rhodium(I) whereas, in sterically similar palladium(II) complexes, N bonding is only observed for the thiocyanate. The cyanate ion remains insensitive to the electronic effects of other ligands in the coordination sphere and continues to be bonded through the nitrogen.

The thiocyanate and cyanate complexes of gold(III) are S and N bonded, respectively. Since gold(III) is a class b metal, it prefers to bond to the soft sulfur and the relatively soft nitrogen (compared to oxygen) in these complexes. Since gold(I) is a d^{10} system, it is an even softer Lewis acid than gold(III). Consequently, the incorporation of only one π-acceptor ligand is not sufficient to change gold(III) (due to its higher charge) or gold(I) (due to its greater d-electron density) to class a metals, and S, Se, and N bondings are found for the thiocyanate, selenocyanate, and cyanate complexes, respectively. In the case of the gold(I) and gold(III) complexes, however, the inferences relating to the importance of π bonding are less conclusive because of concurrent steric effects which would also tend to initiate the bonding trends observed.

The $Pd(SeCN)_4^{2-}$[18] and $Rh(P(C_6H_5)_3)_2(CO)NCSe$ complexes, when compared with the complexes $Fe(NCSe)_4^{2-}$[18] and $C_5H_5Fe(CO)_2SeCN$,[35] provide the first examples involving the selenocyanate ion of a paradoxical bonding trend which has been known to exist in thiocyanate complexes for some time. In mixed-ligand complexes of class a metals, symbiotic[36] behavior is generally observed, *e.g.*, $Co(NH_3)_5NCS^{2+}$[37] *vs.* $Co(CN)_5SCN^{3-}$,[38] whereas antisymbiotic behavior is generally observed for complexes of class b metals, *e.g.*, $Pd(SCN)_4^{2-}$ *vs.* $Pd(P(C_6H_5)_3)_2(NCS)_2$.[4] A satisfactory explanation for the existence of the opposing trends has yet to be presented.

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