the blue vanadyl ion. The solid compound does not appear to be at all air sensitive.

Surprisingly, $K_5V(CN)_5$ is diamagnetic; no evidence for paramagnetism is observed, even after diamagnetic corrections are made for potassium and cyanide. Since it would be expected that a complex of vanadium(0) would have either one or five unpaired electrons, the diamagnetism argues against the presence of the $[V(CN)_5]^{5-}$ ion in the solid compound and indicates that a species of higher order is formed in which there is strong vanadium–vanadium interaction. The diamagnetism calls to mind a similar situation for the nickel(I) complex of empirical formula $K_2Ni(CN)_3$, which has been shown to contain $[Ni_2(CN)_6]^{4-}$, where the nickel atoms are bridged by cyanide groups.[23]

The infrared spectrum of the pink compound exhibits three bands in the C–N stretching region, at 2030, 2078, and 2175 cm^{-1} (Table I). By comparison, the starting material shows a single C–N band at 2095 cm^{-1}. Tentatively, the band at 2175 cm^{-1} is assigned to bridged C–N stretching, and those at the two lower frequencies, to terminal C–N stretching. A similar assignment has been made for $K_4Ni_2(CN)_6$ which exhibits C–N bands at 2055, 2079, and 2128 cm^{-1}.[23]

The molar conductance of a freshly prepared 10^{-3} *M* solution of $K_5V(CN)_5$ at 25° was found to be 659 ± 33 ohm^{-1} cm^{-1} (three experiments). This value is to be compared with the corresponding molar conductances obtained for a number of other cyano complexes chosen as standards: $K_3Fe(CN)_6$, 477; $K_4Fe(CN)_6$, 581; $K_4Mo(CN)_8$, 633; $K_4W(CN)_8$, 617; and $K_5V(CN)_5NO$, 634. On the basis of these data, it would be tempting to conclude that $K_5V(CN)_5$ dissociates into six ions in aqueous solution. The conductance value is, however, also consistent with ionization of a dimeric species. Many doubtlessly would find the latter possibility not very palatable since it necessitates the proposal of an ion of extremely large negative charge, $[V_2(CN)_{10}]^{10-}$. In view of the magnetic and spectral properties of the solid and recovery of the compound changed from aqueous solution, the authors regard the dimeric formulation as a distinct possibility.

Acknowledgment.—The authors gratefully acknowledge their debt to the National Science Foundation for financial support of this work.

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Thiocyanato Complexes of Rhodium(I)

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The synthesis of and infrared spectral studies on rhodium(I) thiocyanato compounds of the types $RhL_2(CO)(NCS)$, $RhL_3(NCS)$, $Rh_2L_4(CNS)_2$, and $(R_4N)[Rh(CO)_2(NCS)_2]$, where L is a phosphine, an arsine, a stibine, or a phosphite, are reported. In all of these complexes terminal thiocyanate is bonded through the nitrogen atom, both in the solid state and in solution. The arylarsine and phosphite thiocyanato derivatives dissociate in part in solution with the resultant formation of dinuclear, SCN-bridged complexes of the type $Rh_2(AsR_3)_2(CO)_2(CNS)_2$ and $Rh_2[P(OR)_3]_4(CNS)_2$, respectively. The latter was isolated with triphenyl phosphite.

Introduction

It has been shown that the mode of bonding of the thiocyanate ion in palladium(II) square-planar complexes depends on the nature of other ligands present therein.[1–4] However, in six-coordinate carbonyl compounds investigated in these laboratories the important factors determining the thiocyanate bond type appear to be the oxidation state of the metal[5,6] and the extent of replacement of carbon monoxide by ligands of lesser π-acceptor properties.[7] The nature of the ligand(s) present in conjunction with CO was found to influence the mode of metal–thiocyanate bonding only in those cases where steric interactions are considered important.

In order to compare more directly the results of the aforementioned studies, we have examined the bonding in a number of square-planar rhodium(I) thiocyanatocarbonyl and -noncarbonyl complexes. Reported here are the results of our investigation.

Experimental Section

Materials.—Triphenylphosphine and triphenylstibine, purchased from Metal and Thermit Co., were recrystallized from 95% ethanol. Triphenylarsine and 4-methylpyridine from Eastman Organic Chemicals, triphenyl phosphite from Matheson Coleman and Bell, and tricyclohexylphosphine from Orgmet, Inc., were used without further purification. Reagent grade potassium thiocyanate was dried at 125°.

Dimethylphenylphosphine was prepared as described by Meisenheimer, *et al.*[8] The same general procedure was used to

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[6] A. Wojcicki and M. F. Farona, *J. Inorg. Nucl. Chem.*, **26**, 2289 (1964).

[7] M. F. Farona and A. Wojcicki, *Inorg. Chem.*, **4**, 1402 (1965).

[8] J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt, and W. Samuel, *Ann.*, **449**, 213 (1926).

TABLE I

ANALYTICAL DATA FOR THIOCYANATO- AND CHLORORHODIUM(I) COMPLEXES

		Mol wt		Analyses, %					
				Calcd			Found		
Complex	Mp (dec), °C[a]	Calcd	Found	C	H	N or S	C	H	N or S
$[(n\text{-}C_4H_9)_4N][Rh(CO)_2(NCS)_2]$[b]	84–87					8.12 (N)			8.25 (N)
$Rh[P(C_6H_{11})_3]_2(CO)(NCS)$	237–239	750	751	60.85	8.87	4.28 (S)	60.65	8.81	4.09 (S)
$Rh[P(C_2H_5)_3]_2(CO)(NCS)$	97–99	425	431	39.53	7.11	7.54 (S)	39.80	7.24	7.70 (S)
$Rh[P(CH_3)_2(C_6H_5)]_2(CO)(NCS)$	102–108	465	473			3.03 (N)			2.80 (N)
$Rh[P(p\text{-}ClC_6H_4)_3]_2(CO)(NCS)$	196–198			49.59	2.63	1.52 (N)	49.83	2.90	1.56 (N)
$Rh[As(C_6H_5)_3]_2(CO)(NCS)$	188–190	801	783	56.93	3.78	4.04 (S)	57.18	4.00	3.80 (S)
$Rh[As(p\text{-}ClC_6H_4)_3]_2(CO)(NCS)$	158–159	1008	791, 827	45.27	2.40	3.18 (S)	45.50	2.52	3.00 (S)
$Rh[Sb(C_6H_5)_3]_2(CO)(NCS)$	181–183	895	897	50.95	3.35	3.58 (S)	50.92	3.34	3.39 (S)
$Rh[Sb(p\text{-}ClC_6H_4)_3]_2(CO)(NCS)$	144–147	1102	786	41.42	2.20	2.91 (S)	41.70	2.30	3.25 (S)
$Rh[P(OC_6H_5)_3]_3(NCS)$	144–146	1092	900	60.50	4.15	2.94 (S)	60.66	4.21	2.79 (S)
$Rh_2[P(OC_6H_5)_3]_4(CNS)_2$	175–178	1563	1527	56.86	3.87	4.10 (S)	56.85	4.00	3.97 (S)
$Rh[As(m\text{-}CF_3C_6H_4)_3]_2(CO)Cl$	112–115	1188	1180	43.51	2.04		43.64	2.03	
$Rh(4\text{-}CH_3C_5H_4N)(CO)_2Cl$	98–100	283	295			4.88 (N)			4.74 (N)

[a] Uncorrected. [b] Molar conductivity of a 10^{-3} *M* $C_6H_5NO_2$ solution is 24.7 ohm^{-1} cm^2.

synthesize triethylphosphine. Tris(*p*-chlorophenyl)phosphine was prepared as described in the literature;[9] tris(*p*-chlorophenyl)arsine, tris(*p*-chlorophenyl)stibine, and tris(α,α,α-trifluoro-*m*-tolyl)arsine were obtained by analogous procedures.

To prepare tetrabutylammonium thiocyanate, solutions of $(n\text{-}C_4H_9)_4NBr$ (32 g, 0.10 mole) in 30 ml of $CHCl_3$ and of KSCN (24 g, 0.25 mole) in 50 ml of water were mixed and stirred for 12 hr. The chloroform layer was treated with two more aqueous solutions of KSCN as described above and then was dried over sodium sulfate. Most of the solvent was removed on a rotary evaporator and the viscous residue was dried at 25° under reduced pressure (0.1 mm) for 2 days. The product (mp 119–121°) was obtained in a 93% yield (28 g). Because of its hygroscopic nature, it was stored over P_4O_{10}. *Anal.* Calcd for $C_{17}H_{36}N_2S$: N, 9.33. Found: N, 9.78.

All solvents, with the exception of low-boiling (30–60°) petroleum ether and hexane, were reagent grade. Chromatographic purifications were carried out on Woelm alumina (acid).

The carbonyl $Rh_2(CO)_4Cl_2$ was prepared by the method of Fischer.[10] The complexes $RhL_2(CO)Cl$ (L = $P(C_6H_5)_3$, $P(p\text{-}ClC_6H_4)_3$, $As(C_6H_5)_3$, $As(p\text{-}ClC_6H_4)_3$, $Sb(C_6H_5)_3$, $Sb(p\text{-}ClC_6H_4)_3$) and $Rh[P(OC_6H_5)_3]_2(CO)Cl$ and $Rh[P(OC_6H_5)_3]_3Cl$ were synthesized as described by Vallarino.[11,12] Other compounds $RhL_2(CO)Cl$ (L = $P(C_6H_{11})_3$, $P(CH_3)_2(C_6H_5)$, $As(m\text{-}CF_3C_6H_4)_3$) were prepared by the same general procedure. With the exception of $Rh[As(m\text{-}CF_3C_6H_4)_3]_2(CO)Cl$, for which no thiocyanato complex was isolated, they were not characterized beyond melting points and infrared spectral measurements. The dicarbonyl $Rh(C_5H_5N)(CO)_2Cl$ was prepared as described by Wilkinson;[13] $Rh(4\text{-}CH_3C_5H_4N)(CO)_2Cl$ was synthesized similarly.

Preparation of Thiocyanatorhodium(I) Complexes.[14] **$[(n\text{-}C_4H_9)_4N][Rh(CO)_2(NCS)_2]$.**—A solution of $Rh_2(CO)_4Cl_2$ (0.20 g, 0.51 mmole) in anhydrous methanol (2.7 ml) and glacial acetic acid (0.3 ml) was cooled to −78°. Upon addition of excess tetrabutylammonium thiocyanate (0.75 g, 2.5 mmoles) in anhydrous methanol (2.0 ml) the initial red color of the carbonyl solution changed to purple. This color faded to yellow on subsequent warming slightly above −78°. Further cooling at −78° caused precipitation of yellow crystals, which were collected on a Dry Ice cooled filter under nitrogen and washed with cold anhydrous methanol. The yield was 0.47 g (90%).

$RhL_2(CO)(NCS)$. (a) **L = $P(C_6H_5)_3$, $P(C_6H_{11})_3$, $P(p\text{-}ClC_6H_4)_3$, $As(C_6H_5)_3$.**—These complexes were prepared by a modified procedure of Vallarino for $Rh[P(C_6H_5)_3]_2(CO)(NCS)$,[11] the only previously synthesized thiocyanatorhodium(I) compound in the series studied. The corresponding chlorocarbonyl complex (0.25 mmole) and KSCN (0.097 g, 1.0 mmole) in acetone (50 ml) were refluxed for 30 min. The solvent was then removed under reduced pressure (~20 mm) and the product was extracted into chloroform and precipitated by the addition of 95% ethanol. It was collected on a filter, washed with ethyl alcohol and petroleum ether, and air dried. The yield was 74–98%.

(b) **L = $P(C_2H_5)_3$, $P(CH_3)_2(C_6H_5)$, $Sb(C_6H_5)_3$.**—An acetone solution of the corresponding chlorocarbonyl complex (0.25 mmole) and KSCN (0.097 g, 1.0 mmole) was stirred at room temperature for 15 min, after which time solvent was removed under reduced pressure (~20 mm). The complexes with L = $P(C_2H_5)_3$ and $Sb(C_6H_5)_3$ were extracted into petroleum ether and acetone, respectively, and crystallized by concentrating the solution in a stream of nitrogen. When L = $P(CH_3)_2(C_6H_5)$, the product was extracted into CH_2Cl_2 and precipitated using anhydrous methanol. These compounds were then treated again with KSCN and isolated in the manner just described. The stibine derivative was further purified by two recrystallizations from acetone. The yields ranged from 70 to 83%.

(c) **L = $As(m\text{-}CF_3C_6H_4)_3$.**—The chlorocarbonyl complex (0.15 g, 0.12 mmole) was added to a solution of KSCN (0.03 g, 0.3 mmole) in nitrogen-saturated acetone, and the solvent was immediately removed under reduced pressure (~20 mm). The product was extracted into benzene to record the infrared spectrum, but was not isolated.

(d) **L = $As(p\text{-}ClC_6H_4)_3$, $Sb(p\text{-}ClC_6H_4)_3$.**—A solution of the ligand (0.4 mmole) in anhydrous methanol was added to a cold (−78°) solution of $[(n\text{-}C_4H_9)_4N][Rh(CO)_2(NCS)_2]$ (0.10 g, 0.19 mmole) in anhydrous methanol (10 ml). The product precipitated immediately; it was collected on a Dry Ice cooled filter and washed with cold anhydrous methanol. The low stability of these complexes in solution precluded purification by recrystallization. The yield was 62–80%.

$Rh_2[P(OC_6H_5)_3]_4(CNS)_2$.—Potassium thiocyanate (0.063 g, 0.80 mmole) was added to an acetone solution of $Rh[P(OC_6H_5)_3]_2(CO)Cl$ (0.30 g, 0.38 mmole). After the immediate evolution of gas had ceased, the solvent was removed [25° (~20 mm)] and the product was extracted into benzene. Purification was effected by chromatography on grade V alumina, eluting with benzene. The solution was concentrated in a stream of nitrogen, and the product was precipitated by the addition of 95% ethanol. The yield was 0.25 g (80%).

$Rh[P(OC_6H_5)_3]_3(NCS)$.—An acetone solution of the corresponding chloro complex (0.29 g, 0.27 mmole) and KSCN (0.097 g, 1.0 mmole) was stirred at room temperature for 20 min. The solvent was removed under reduced pressure (~20 mm) and the residue was extracted into CH_2Cl_2; addition of 95% ethanol caused precipitation of the product. The yield was 0.25 g (83%).

This compound was also prepared by treating $Rh_2[P(OC_6H_5)_3]_4$-

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[11] L. M. Vallarino, *J. Chem. Soc.*, 2287 (1957).

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[13] D. N. Lawson and G. Wilkinson, *ibid.*, 1900 (1965).

[14] All analytical data are given in Table I.

$(CNS)_2$ (0.11 mmole) with triphenyl phosphite (0.26 mmole) in benzene (15 ml) at 25° and by the reaction of $[(n\text{-}C_4H_9)_4N]\text{-}[Rh(CO)_2(NCS)_2]$ (0.17 mmole) with triphenyl phosphite (0.58 mmole) in anhydrous methanol (10 ml), also at 25°. The yields were 93 and 95%, respectively.

Attempted Preparation of $RhL(CO)_2(CNS)$ (L = C_5H_5N, 4-$CH_3C_5H_4N$).—The ligand L (*ca.* 0.1 mmole) was added to ~0.1 mmole of $[(n\text{-}C_4H_9)_4N][Rh(CO)_2(NCS)_2]$ in 5 ml of anhydrous methanol. The infrared spectrum of this solution revealed that no reaction had occurred.

After a mixture of ~0.1 g (1.0 mmole) of KSCN and 0.08 g (0.3 mmole) of $Rh(C_5H_5N)(CO)_2Cl$ in 20 ml of acetone had been kept at 25° for 30 min or refluxed for about 20 min, both under nitrogen, no carbonyl-containing product could be detected by infrared spectroscopy.

Properties of the Complexes.—All of the complexes containing a phosphine, an arsine, or triphenyl phosphite are yellow solids; the thiocyanatostibine and chlorostibine complexes form bright orange and dark red crystals, respectively. With the exception of $[(n\text{-}C_4H_9)_4N][Rh(CO)_2(NCS)_2]$ the thiocyanato compounds are stable in the solid state for at least 1 week at room temperature.

The dinuclear $Rh_2[P(OC_6H_5)_3]_4(CNS)_2$ is moderately soluble in benzene, but only sparingly soluble in acetone, chloroform, and methylene chloride. All of the other complexes are moderately to extremely soluble in benzene, chloroform, methylene chloride, and acetone, sparingly soluble in methyl and ethyl alcohols, and insoluble in petroleum ether. The compounds containing $P(CH_3)_2(C_6H_5)$ and $P(C_2H_5)_3$ are moderately soluble in the alcohols; the latter derivative dissolves also in petroleum ether.

Infrared Spectra.—Spectra were recorded on a Beckman Model IR-9 spectrophotometer. Solids were examined in Nujol mulls on KBr plates; solutions were placed in a 0.05-mm KBr cell, with a matched reference cell being used at all times.

Electrical Conductivity.—An Industrial Instruments Co. Model RC 16B2 conductivity bridge and a cell with platinum electrodes were used.

Dipole Moments.—The dipole moment of $Rh[P(C_6H_{11})_3]_2\text{-}(CO)(NCS)$, dissolved in benzene, was determined according to the method of Guggenheim[15] using a Type DM01 Dipolemeter from Wissenschaftlich-Technische Werstätten with a measuring frequency of 2 Mc.

Molecular Weights.—Measurements were made on 8×10^{-3} to 3×10^{-2} *M* benzene or chloroform solutions with a Mechrolab Model 301-A osmometer.

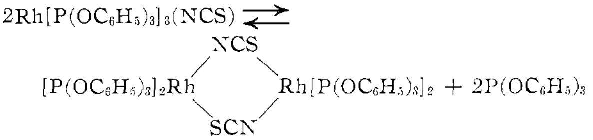
Analyses.—Nitrogen was determined on a Coleman Model 29 analyzer by Mr. P. J. Kovi of these laboratories. Other microanalyses were by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results

The following thiocyanato complexes of rhodium(I) were prepared and characterized in this study: $[(n\text{-}C_4H_9)_4N][Rh(CO)_2(NCS)_2]$, $RhL_2(CO)(NCS)$ (L = a phosphine, an arsine, or a stibine), $Rh[P(OC_6H_5)_3]_3\text{-}(NCS)$, and $Rh_2[P(OC_6H_5)_3]_4(CNS)_2$. In the anion $Rh(CO)_2(NCS)_2^-$ the carbonyl groups occupy *cis* positions, as is evidenced by the presence of two CO stretching frequencies in the infrared spectrum. On the basis of dipole moment measurements, Vallarino[11] assigned *trans* configurations to $Rh[M(p\text{-}XC_6H_4)_3]_2(CO)Cl$ (M = P and As, and X = H, CH_3, Cl, and OCH_3); it is assumed that the structurally analogous compounds $RhL_2(CO)(NCS)$ also exhibit this stereochemistry. In agreement with the existence of a single isomer, these complexes show one CO stretching frequency in their infrared spectra. The only exception is provided by $Rh[P(C_6H_{11})_3]_2(CO)(NCS)$, which exhibits spectral behavior dependent on the nature of the solvent employed. Accordingly, two carbonyl stretching frequencies of approximately equal intensity are observable in chloroform, but only one can be seen in each methylene chloride and benzene. A somewhat similar behavior is found for the corresponding chloride (Table II); for both carbonyls the spectra may reflect the prevalence of *cis–trans* isomerism in certain solvents. However, the dipole moment of 5.4 D. for $Rh[P\text{-}(C_6H_{11})_3]_2(CO)(NCS)$ supports the *trans* structure of this complex in benzene. Vallarino[11] reports the dipole moments of 2.5–4.0 D. for several compounds *trans*-$RhL_2(CO)Cl$ and estimates that the *cis* configurations would give values of 8–9 D. Since the moments of the complexes *trans*-$Pt[P(C_2H_5)_3]_2XCl$ (X = H, CH_3) are *ca.* 3.2 D. lower than those of the corresponding isothiocyanato derivatives,[16,17] it is inferred that $Rh[P\text{-}(C_6H_{11})_3]_2(CO)(NCS)$ exhibits a *trans* arrangement of the phosphines in benzene.

The type of metal–thiocyanate attachment in the complexes is based on the frequencies of the CN and CS stretching modes. A compilation of CN stretching frequencies for palladium(II) complexes containing ligands identical with or similar to the ones used in this study shows the following ranges: M–NCS, 2085–2120 cm^{-1}; M–SCN, 2110–2125 cm^{-1}; M–SCN–M, 2153–2162 cm^{-1}.[3,4,18,19] The position of the CS stretch was determined by comparing the spectra of the thiocyanato and the corresponding chloro complexes. Turco and Pecile[1] give the following values for the frequency of this mode: M–NCS, 780–860 cm^{-1}; M–SCN, 690–720 cm^{-1}. The NCS bending frequencies were also recorded and compared with the diagnostic values given by Sabatini and Bertini:[4] M–NCS, 460–490 cm^{-1}; M–SCN, 410–440 cm^{-1}. These spectral data are presented inTable II.

The infrared spectra of the thiocyanatocarbonyl complexes containing the ion $Rh(CO)_2(NCS)_2^-$, triphenylstibine, and tertiary phosphines are consistent with a common mode of Rh–NCS attachment, both in the solid state and in solution. However, the spectrum of $Rh[P(OC_6H_5)_3]_3NCS$ in benzene exhibits two CN stretching frequencies at 2090 (s) and 2154 (m) cm^{-1}. The ratio of intensities of the high-frequency band to the low-frequency band varies with the solvent in the order: benzene > methylene chloride > nitrobenzene. Gradual addition of triphenyl phosphite to a benzene solution of $Rh[P(OC_6H_5)_3]_3(NCS)$ results in a diminution of intensity of the band at 2154 cm^{-1} and, eventually, complete disappearance of this absorption. The results are consistent with the equilibrium



$$2Rh[P(OC_6H_5)_3]_3(NCS) \rightleftarrows [P(OC_6H_5)_3]_2Rh\overset{NCS}{\underset{SCN}{\diamond}}Rh[P(OC_6H_5)_3]_2 + 2P(OC_6H_5)_3 \qquad (1)$$

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TABLE II

CN, CO, AND CS STRETCHING AND NCS BENDING FREQUENCIES (cm^{-1}) OF RHODIUM(I) COMPLEXES

Complex	CN str[a]	CO str[a]	CS str[b]	NCS bend[b]
$[(n\text{-}C_4H_9)_4N][Rh(CO)_2(NCS)_2]$	~2100 sh	2090 vs, 2032 s	841 m	470 w
$[(n\text{-}C_4H_9)_4N][Rh(CO)_2Cl_2]$		2058 vs, 1974 vs[c]		
$Rh[P(C_6H_5)_3]_2(CO)(NCS)$	2095 s	1993 vs	839 m	472 w
$Rh[P(C_6H_5)_3]_2(CO)Cl$		1979 vs		
$Rh[P(C_6H_{11})_3]_2(CO)(NCS)$	2100 s	1965 s, 1956 s[d]	841 m	466 w
$Rh[P(C_6H_{11})_3]_2(CO)Cl$		1950 s, 1942 ms[e]		
$Rh[P(C_2H_5)_3]_2(CO)(NCS)$	2089 s	1975 vs	828 m	474 w
$Rh[P(C_2H_5)_3]_2(CO)Cl$		1958 vs		
$Rh[P(CH_3)_2(C_6H_5)]_2(CO)(NCS)$	2095 s	1985 vs	840 m	481 w
$Rh[P(CH_3)_2(C_6H_5)]_2(CO)Cl$		1973 vs		
$Rh[P(p\text{-}ClC_6H_4)_3]_2(CO)(NCS)$	2090 s	2000 vs	828 m	487 w
$Rh[P(p\text{-}ClC_6H_4)_3]_2(CO)Cl$		1985 vs		
$Rh[As(C_6H_5)_3]_2(CO)(NCS)$	2149 w, 2093 s	1990 vs	838 m	466 w
$Rh[As(C_6H_5)_3]_2(CO)Cl$		1976 vs		
$Rh[As(p\text{-}ClC_6H_4)_3]_2(CO)(NCS)$	2150 m, 2090 ms	1996 vs	845 m	478 w
$Rh[As(p\text{-}ClC_6H_4)_3]_2(CO)Cl$		1981 vs		
$Rh[As(m\text{-}CF_3C_6H_4)_3]_2(CO)(NCS)$	2143 m, 2100 vw, 2066 m	1998 vs	...[f]	...[f]
$Rh[As(m\text{-}CF_3C_6H_4)\ ]_2(CO)Cl$		1986 vs		
$Rh[Sb(C_6H_5)_3]_2(CO)(NCS)$	2109 s	1986 vs	835 m	450 w
$Rh[Sb(C_6H_5)_3]_2(CO)Cl$		1973 vs		
$Rh[Sb(p\text{-}ClC_6H_4)_3]_2(CO)(NCS)$	2157 vw, 2092 s	1987 vs	837 m	...[g]
$Rh[Sb(p\text{-}ClC_6H_4)_3]_2(CO)Cl$		1974 vs		
$Rh[P(OC_6H_5)_3]_3(NCS)$	2154 m, 2090 s		...[g]	...[g]
$Rh_2[P(OC_6H_5)_3]_4(CNS)_2$	2153 s		...[g]	...[g]

[a] Measured in chloroform solution for $[(n\text{-}C_4H_9)_4N][Rh(CO)_2(NCS)_2]$ and phosphine and stibine complexes, in benzene solution for arsine and phosphite complexes. [b] Measured in Nujol mull. [c] Measured in Nujol mull by L. M. Vallarino, *Inorg. Chem.*, **4,** 161 (1965). However, CO stretching frequencies of 2066 and 2000 cm^{-1} have been reported for $[(CH_3)_4N][Rh(CO)_2Cl_2]$ in Nujol mull.[13] [d] In benzene solution, CO stretch at 1958 cm^{-1} and CN stretch at 2097 cm^{-1}; in methylene chloride solution, CO stretch at 1960 cm^{-1} and CN stretch at 2100 cm^{-1}. [e] In benzene solution, CO stretch at 1941 cm^{-1}; in methylene chloride solution, CO stretches at 1948 and 1944 cm^{-1}. [f] Not measured since compound was not isolated. [g] Masked by other absorptions. Abbreviations: vs, very strong; s, strong; m, medium; w, weak, vw, very weak; sh, shoulder.

TABLE III

CN AND CO STRETCHING FREQUENCIES (cm^{-1}) OF THIOCYANATORHODIUM(I) PHOSPHITE AND ARSINE COMPLEXES WITH EXCESS LIGAND OR THIOCYANATE ION

Complex and added species	CN str[a]	CO str[a]
$Rh_2[P(OC_6H_5)_3]_4(CNS)_2$	2153 s[b]	
$Rh_2[P(OC_6H_5)_3]_4(CNS)_2 + P(OC_6H_5)_3$	2090 s	
$Rh_2[P(OC_6H_5)_3]_4(CNS)_2 + (n\text{-}C_4H_9)_4NSCN$	2106 s, 2097 s, 2066[c]	
$Rh[P(OC_6H_5)_3]_3(NCS)$	2154 m, 2090 s[d]	
$Rh[P(OC_6H_5)_3]_3(NCS) + P(OC_6H_5)_3$	2090 s	
$Rh[P(OC_6H_5)_3]_3(NCS) + (n\text{-}C_4H_9)_4NSCN$	2104 s, 2096 s, 2066[c]	
$Rh[As(p\text{-}ClC_6H_4)_3]_2(CO)(NCS)$	2150 m, 2090 ms[e]	1996 vs
$Rh[As(p\text{-}ClC_6H_4)_3]_2(CO)(NCS) + As(p\text{-}ClC_6H_4)_3$	2090 s	1996 vs
$Rh[As(p\text{-}ClC_6H_4)_3]_2(CO)(NCS) + (n\text{-}C_4H_9)_4NSCN$	2108 s, 2090 s, 2066[c]	1983 vs
$Rh[As(m\text{-}CF_3C_6H_4)_3]_2(CO)(NCS)$	2143 m, 2096 vw, 2066 m	1998 vs
$Rh[As(m\text{-}CF_3C_6H_4)_3]_2(CO)(NCS) + (n\text{-}C_4H_9)_4NSCN$	2106 s, 2097 s, 2066[c]	1985 vs

[a] Measured in benzene. [b] Same value in Nujol mull. [c] Owing to excess of SCN^-. [d] Absorptions at 2105 and 2090 cm^{-1} in Nujol mull. [e] One absorption at 2085 cm^{-1} in Nujol mull.

The isolation of $Rh[P(OC_6H_5)_3]_3(NCS)$ in virtually quantitative yields from a mixture of $Rh_2[P(OC_6H_5)_3]_4(CNS)_2$ (CN stretching frequency at 2153 cm^{-1}) and excess triphenyl phosphite demonstrates the validity of the above scheme.

When a solution of $Rh_2[P(OC_6H_5)_3]_4(CNS)_2$ in benzene is treated gradually with tetrabutylammonium thiocyanate in benzene, the intensity of the absorption band at 2153 cm^{-1} decreases and new peaks appear at 2106 and 2097 cm^{-1}. With a thiocyanate ion:complex ratio of 2, the band at 2153 cm^{-1} disappears completely. Additional tetrabutylammonium thiocyanate does not affect the positions of the two absorptions. A similar behavior is also observed on addition of thiocyanate to $Rh[P(OC_6H_5)_3]_3(NCS)$ and is consistent with the formation of *cis*-$Rh[P(OC_6H_5)_3]_2(NCS)_2^-$ in solution. However, all attempts at the isolation of this species were unsuccessful.

The infrared spectrum of $Rh[As(C_6H_5)_3]_2(CO)(NCS)$ in a Nujol mull shows one strong CN absorption frequency at *ca.* 2100 cm^{-1}. However, in chloroform solution two bands are apparent—one at 2149 cm^{-1} and a more intense one at 2093 cm^{-1}. The former peak gains intensity in a less polar solvent such as benzene but disappears completely in methylene chloride and nitrobenzene. Evaporation of chloroform from solutions of the arsine complex gives a solid whose spectrum shows only the low-frequency CN stretching absorption.

The complex $Rh[As(p\text{-}ClC_6H_4)_3]_2(CO)(NCS)$ exhibits similar but even more pronounced variations in its spectral behavior. Accordingly, the CN stretching absorption at 2150 cm^{-1} is comparable in intensity to that at 2090 cm^{-1} in benzene, and it is still discernible in nitrobenzene. The spectrum of a benzene solution of $Rh[As(m\text{-}CF_3C_6H_4)_3]_2(CO)(NCS)$ exhibits three CN stretching frequencies at 2143, 2096, and 2066 cm^{-1}, the last one reflecting the presence of free thiocyanate ion.

As the tertiary arsine is added gradually to a benzene solution of $Rh(AsR_3)_2(CO)(NCS)$, the high-frequency CN stretching band at *ca.* 2150 cm^{-1} weakens in intensity and eventually disappears. This change is accompanied by an increase in intensity of the peak around 2100 cm^{-1}; the position of the CO stretching frequency is not affected. Addition of tetrabutylammonium thiocyanate to $Rh(AsR_3)_2(CO)(NCS)$ in benzene results in the disappearance of the CN stretching frequencies of the bisarsine complex and the appearance of two new peaks around 2100 cm^{-1}. Concomitantly, the CO stretching frequency moves to lower wavenumbers by 13 cm^{-1}. All of these changes are summarized in Table III, and the infrared spectra in the CN and CO stretching frequency region for $Rh[As(p\text{-}ClC_6H_4)_3]_2(CO)(NCS)$ solutions in benzene are shown in Figure 1.

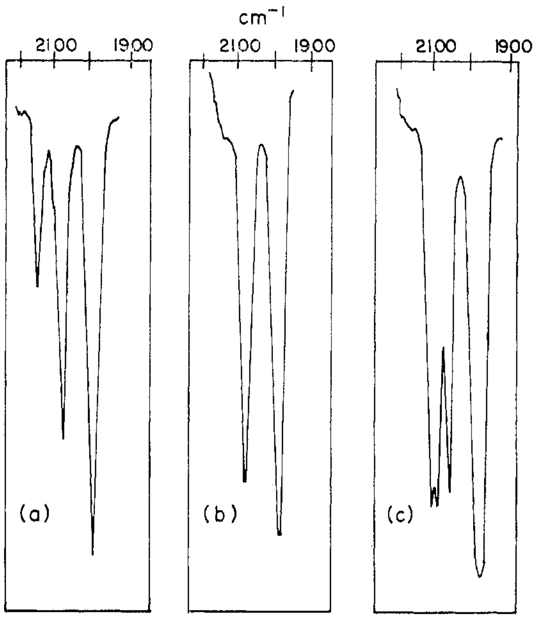
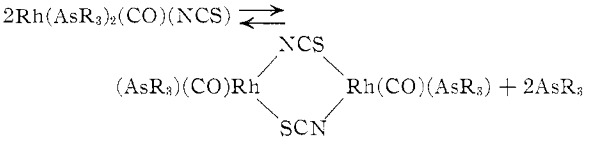


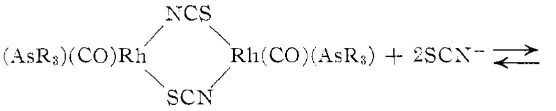
Figure 1.—The infrared spectra in the CN and CO stretching region of $Rh[As(p\text{-}ClC_6H_4)_3]_2(CO)(NCS)$ in benzene: (a) pure complex, (b) complex and excess $As(p\text{-}ClC_6H_4)_3$, (c) complex and excess tetrabutylammonium thiocyanate.

The preceding results reflect the equilibria in solution



$$2Rh(AsR_3)_2(CO)(NCS) \rightleftharpoons (AsR_3)(CO)Rh\overset{NCS}{\underset{SCN}{\;}}Rh(CO)(AsR_3) + 2AsR_3 \quad (2)$$

and



$$(AsR_3)(CO)Rh\overset{NCS}{\underset{SCN}{\;}}Rh(CO)(AsR_3) + 2SCN^- \rightleftharpoons 2Rh(AsR_3)(CO)(NCS)_2^- \quad (3)$$

The presence of two CN stretching bands supports the *cis* formulation of the anion in eq 3, and the decrease in the CO stretching frequency on addition of thiocyanate is consistent with the negative charge of the new species.

Discussion

Two main points of interest emerge from this study. First, all of the rhodium(I) complexes containing terminal thiocyanate are nitrogen bonded. Second, there is a remarkable tendency on the part of the arylarsine and triphenyl phosphite rhodium(I) derivatives to form dinuclear thiocyanato-bridged species.

That terminal thiocyanate bonds to rhodium(I) exclusively through the nitrogen atom is in contrast to its mode of attachment to the isoelectronic palladium(II), where both Pd–NCS and Pd–SCN linkages have been elucidated.[1-4] For example, in a series of compounds $PdL_2(CNS)_2$, Pd–NCS bonds result when L is triphenylphosphine, both $PdL_2(SCN)_2$ and $PdL_2(NCS)_2$ can be isolated with L being triphenylarsine, and Pd–SCN bonding occurs in conjunction with triphenylstibine.[2] However, in the complexes $Rh[M(C_6H_5)_3]_2(CO)(NCS)$ (M = P, As, and Sb), only the nitrogen-bonded species have been detected.

The prevalence of rhodium(I) isothiocyanates may be readily rationalized in terms of π bonding in these square-planar systems. Since all of the isolated complexes contain either carbon monoxide or triphenyl phosphite—good π-bonding ligands—*trans* to the terminal thiocyanate, metal–CNS π interaction will be minimal, promoting isothiocyanato linkages. Thus, the exclusive formation of nitrogen-bonded thiocyanates by rhodium(I) may be ascribed to the dominant influence of these strongly π-bonding ligands. A similar general phenomenon was reported for a variety of manganese(I) thiocyanatocarbonyls, where the degree of substitution of carbon monoxide by neutral ligands of lesser π-bonding ability determined primarily the type of manganese–thiocyanate linkage.[7] Accordingly, the parent pentacarbonyl, $Mn(CO)_5SCN$, and the tetracarbonyls $Mn(CO)_4L(SCN)$ (L = triphenylphosphine, -arsine, and -stibine) are sulfur bonded in the solid state, but the tricarbonyls $Mn(CO)_3L_2(NCS)$ (L = an amine) are nitrogen bonded. Thus highly substituted carbonyl complexes of both rhodium(I) and manganese(I) contain thiocyanate bonded through the nitrogen end. To extend this comparison further, it would be of interest to examine rhodium–thiocyanate bonding in the carbonyls $Rh(CO)_2L(CNS)$ and $Rh(CO)_3(CNS)$. However, attempts at the synthesis of the former were unsuccessful.

The results of our study are also in agreement with those reported elsewhere for palladium(II) thiocyanato complexes of the type *trans*-$PdL_2(CNS)_2$ and *cis*-$Pd(L\text{–}L)(CNS)_2$.[1-4] Since in the latter two systems only ligands of intermediate π-acceptor capacity (phosphines, arsines, 2,2′-bipyridine, etc.) were used in conjunction with SCN^-, π bonding was not the single major factor controlling the type of metal–thiocyanate linkage. Moreover, the effects of π interaction on Pd–CNS bonding in the complexes $PdL_2(CNS)_2$ are expected to be small due to the *trans* positions of the two thiocyanates and the two ligands L. As a result, minor changes in various electronic and steric properties of the ligands employed frequently produce striking effects on the mode of palladium–thiocyanate attachment.

It is surprising that the $RhL_2(CO)(NCS)$ complexes containing tertiary phosphines and triphenylstibine retain their integrity in solution whereas the analogous arsine derivatives undergo partial dissociation with the resultant formation of the dinuclear $Rh_2L_2(CO)_2(CNS)_2$. The extent of dissociation among the arsine complexes increases with L in the order $As(C_6H_5)_3 < As(p\text{-}ClC_6H_4)_3 < As(m\text{-}CF_3C_6H_4)_3$ and thus parallels the increasing π-bonding ability of L (and presumably also decreasing σ bonding), reflected in the values of the CO stretching frequencies.

However, an examination of the carbonyl stretching frequencies of $Rh(MR_3)_2(CO)(NCS)$ (M = P, As, and Sb) reveals that for a given R the extent of Rh–CO π bonding decreases as M changes from antimony to arsenic and to phosphorus. This then indicates that in rhodium(I) complexes the phosphines π bond somewhat better than the arsines and stibines. In the light of these data the ability of $RhL_2(CO)(NCS)$ to undergo loss of the ligand L cannot be ascribed solely to the lability of the Rh–L π bond brought about by a strong π interaction in the *trans*-RhL_2 moiety, but must reflect also a relatively weak Rh–L σ bond.

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Low-Frequency Infrared Spectral Studies on Copper(II) Halide Complexes with Substituted Pyridine N-Oxides[1,2]

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The far-infrared spectra of substituted pyridine N-oxide complexes with copper(II) halides of empirical formula $CuX_2 \cdot L$ and $CuX_2 \cdot 2L$, where X = Cl or Br, have been measured and infrared-active metal–chlorine stretching modes of vibration assigned. The former compounds, which all display subnormal magnetic moments and presumably possess binuclear oxygen-bridged structures, afford terminal metal–chlorine stretching frequencies in the range 342–305 cm^{-1}. The 2:1 chloride complexes may be divided into two types based on their colors and on the position of the metal–chlorine vibrational modes. The first class contains the green compounds and these exhibit metal–chlorine stretching modes at higher frequencies than the corresponding 1:1 complexes. In contrast, the two members of the second class, which are yellow in color, absorb at lower frequencies. These results are compared with the corresponding substituted quinoline N-oxide systems and differences and trends are discussed. Metal–oxygen stretching frequencies are tentatively assigned for the 2:1 derivatives and magnetic susceptibilities at 302, 196, and 77°K are included for several complexes.

Introduction

Recently, we reported the assignment of infrared-active metal–chlorine stretching vibrations for a series of substituted quinoline N-oxide complexes with copper(II) chloride.[3] The use of these frequencies as a criterion of oxygen- or halogen-bridged structural species was proposed. Thus the 1:1 complexes which exhibited subnormal magnetic moments and, by analogy with the parent pyridine N-oxide–copper(II) chloride complex,[4] posssess binuclear oxygen-bridged structures, afforded "terminal" metal–chlorine stretching frequencies in the range 344–325 cm^{-1}. For the condensed compounds which showed normal magnetic behavior the maxima were shifted *ca.* 40 cm^{-1} to lower energy, occurring in the range 308–280 cm^{-1}. This shift was considered to reflect the difference between structural species containing terminal and bridging metal–chlorine bonds. The 2:1 derivatives, which also displayed normal, temperature-independent magnetic moments, afforded maxima in the lower range.

As an extension to this work, the far-infrared spectra of a series of substituted pyridine N-oxide complexes with copper(II) halides have been measured and interpreted, and the results are reported herein. Additionally, magnetic susceptibilities at 302, 196, and 77°K are reported.

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[1] This paper is part V of both the series "Spin–Spin Coupling in Binuclear Complexes" and "Substituted Heterocyclic N-Oxide Complexes."

[2] This material was presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[3] W. E. Hatfield, D. B. Copley, and R. Whyman, *Inorg. Nucl. Chem. Letters*, **2**, 373 (1966); R. Whyman, D. B. Copley, and W. E. Hatfield, *J. Am. Chem. Soc.*, **89**, 3135 (1967).

[4] H. L. Schäfer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).