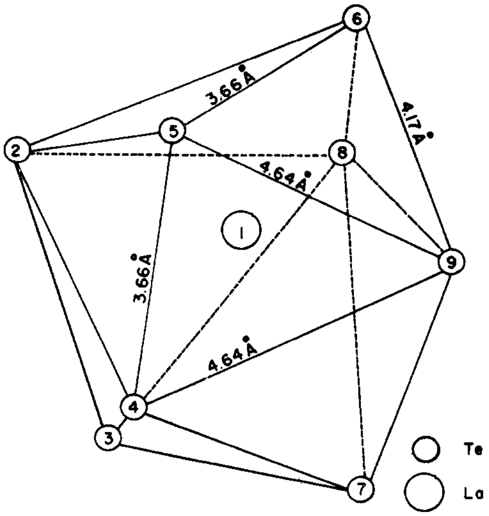

Figure 1.—Eightfold coordination of La in La_2Te_3. The coordination polyhedron can be considered as composed of two tetrahedra, one elongated and one flattened, or as an irregular octaverticon.

also calculated as a function of composition over the solid solution range La_3Te_4 to La_2Te_3, and the smallest value occurred for the composition La_2Te_3 for which the crystals had been originally selected.

Discussion of Structure

There are two different La–Te bond distances, 3.244 ± 0.0028 Å. and 3.418 ± 0.0028 Å., in the structure. The coordination polyhedron around La can be described in terms of two tellurium tetrahedra, an elongated one formed by atoms 6, 7, 3, 5 and a flat one formed by atoms 2, 8, 9, 4, Figure 1, or by the irregular octaverticon shown in Figure 1. Surrounding one La are eight other lanthanum atoms, all at a distance of 4.50 Å. from the central atom. The anion in this structure is coordinated to six lanthanum atoms which form a distorted octahedron.

Pauling's relation for bond length and bond number, $D_n = D_1 - 0.6 \log n$, was used to determine the relative strengths of the LaTe bonds. The term D_1 represents the sum of empirically derived metallic single bond radii and the values given by Pauling are 1.69 and 1.37 Å. for La and Te, respectively[8]; D_n is the observed bond length and n is the bond number. In Table III indicated electrostatic bond summations utilizing the derived parameter $x = 0.075$ are compared with those fixed by the idealized parameter of $^1/_{12}$. The sum of the bond numbers for each atom is very close to the formal valence when $x = 0.075$. It should be noted that these calculations do not take into account the missing lanthanum atoms in the deficient La_2Te_3 structure. One out of every nine La is absent and this produces a vacancy in the Te polyhedron. The polyhedra associated with the eight La closest neighbors to any given La polyhedron share with it one face from one or another of two nonequivalent sets of four triangular faces. Any instance of vacancy in two adjacent polyhedra would reduce electrostatic bond summations about some Te atoms to 1.25 (2, 4, 8, or 9 in Figure 1). When no two adjacent polyhedra are vacant, the minimum sum is 1.75. It seems probable that vacant sites are in fact ordered, at least locally. The over-all average Te bond number sum is 2. Occupancy of the polyhedra of the eight nearest La neighbors and the four next near La neighbors achieves this average in a smallest possible volume, *i.e.*, three-fourths of one unit cell.

TABLE III

RELATIVE BOND STRENGTHS OF La–Te BONDS IN La_2Te_3

Central atom	Coordinating atoms	D_n	n
		$x = 0.075$	
La	4 Te	3.24	0.5
	4 Te	3.42	0.25
			$\Sigma n = 3.0$
Te	3 La	3.24	0.5
	3 La	3.42	0.25
			$\Sigma n = 2.25$
		$x = 0.083$	
La	8 Te	3.33	0.354
			$\Sigma n = 2.83$
Te	6 La	3.33	0.354
			$\Sigma n = 2.12$

Holtzberg, Okaya, and Stemple[9] have reported a single crystal determination of the positional parameter in the compound Gd_2Se_3 of 0.0715 and in the compound La_3Se_4 (which contains no vacancies) of 0.075. These findings indicate that in rare earth compounds having a thorium phosphide structure considerable covalent bonding exists and the variable positional parameter deviates from the ideal value of 0.083 and is near 0.075.

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(8) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

(9) F. Holtzberg, Y. Okaya, and N. Stemple, Abstracts, American Crystallographic Association Meeting, Gatlinburg, Tenn., 1965.

CONTRIBUTION FROM SHELL DEVELOPMENT COMPANY,
EMERYVILLE, CALIFORNIA

Reaction Product from Rhodium Trichloride and Acrylonitrile

BY K. C. DEWHIRST

Received September 16, 1965

The reduction of rhodium trichloride by ethanol in the presence of olefins[1-3] has frequently been employed for the preparation of π complexes of rhodium(I). We now wish to report that the use of acrylonitrile in this reaction gives rise to a stable σ complex of rhodium(III). Only a few organorhodium complexes of this general type are known[4,5] and have been prepared by different routes.

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(1) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

(2) R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

(3) G. N. Schrauzer and K. C. Dewhirst, *J. Am. Chem. Soc.*, **86**, 3265 (1964).

(4) R. F. Heck, *ibid.*, **86**, 2796 (1964).

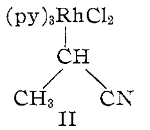
(5) J. Chatt and A. E. Underhill, *J. Chem. Soc.*, 2088 (1963).

Results

Treatment of ethanolic rhodium trichloride with acrylonitrile produces a voluminous yellow precipitate of approximate composition I in 87% yield. This material is diamagnetic, insoluble in organic solvents, and extremely stable. It does not react with phosphines, arsines, or cyclopentadienylsodium, but slowly dissolves in warm pyridine to give, after careful chromatography on silicic acid, compound II in 53% yield. This complex, although somewhat hygroscopic, is extremely air-stable (dec. pt. >250°) and resistant to hydrolysis.

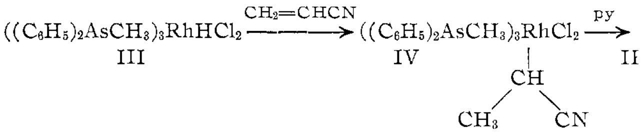
$[(CH_2{=}CHCN)_2RhCl_2]_n$

I


$(py)_3RhCl_2CH(CH_3)CN$

II

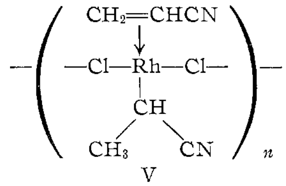
The infrared spectrum (potassium bromide) of II exhibits a nitrile band at 2225 cm.$^{-1}$ (doublet), but none attributable to either rhodium hydride or olefin. The n.m.r. spectrum (carbon tetrachloride, internal TMS) showed the usual aromatic resonances in the region δ 7–10 and two alkyl resonances centered near δ 4.0 (multiplet) and 1.1 (doublet), with intensity ratios of 15:1:3, respectively. Although the occurrence of extra bands in both the infrared and n.m.r. spectra indicates a mixture of isomers, the spectra nevertheless are consistent with the proposed structure. This structure is further supported by the following synthetic sequence.


$((C_6H_5)_2AsCH_3)_3RhHCl_2 \xrightarrow{CH_2=CHCN} ((C_6H_5)_2AsCH_3)_3RhCl_2CH(CH_3)CN \xrightarrow{py}$ II

III IV

Monohydride III[6] reacted smoothly with acrylonitrile in benzene solution to give the σ complex IV in good yield. Treatment of IV with excess pyridine gave rise to rapid ligand exchange and formation of complex II, identical with that prepared by the alcohol route, except for the melting point, which differs by 20°. This almost certainly reflects a difference in isomer distribution.

Little can be said concerning the structure of compound I due to its insolubility. The presence of a normal nitrile band at 2270 cm.$^{-1}$ in the infrared spectrum (potassium bromide) and none attributable to rhodium hydride or terminal olefin suggests the chloro-bridged structure V.



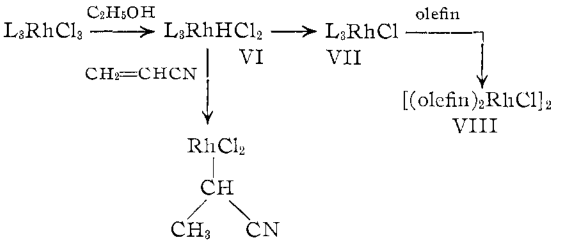
V

Attempts to isolate a complex containing the second acrylonitrile moiety by use of the mild ligand *p*-toluidine[7] failed.

Attempts to utilize this reaction for the preparation of similar complexes with crotononitrile, methacrylonitrile, cinnamonitrile, methyl vinyl ketone, methyl vinyl sulfone, and isoprene failed.

Discussion

The formation of σ complexes in this reaction is most readily explained by ethanolic reduction of rhodium trichloride to the monohydride VI, followed by Michael addition to acrylonitrile. Such reductions have been extensively studied in the iridium series,[8] and we have trapped VI in the present case by addition of diphenylbutylphosphine to an ethanolic solution of rhodium trichloride. Similar additions to acrylonitrile have been reported[9] for iron and cobalt complexes.


$L_3RhCl_3 \xrightarrow{C_2H_5OH} L_3RhHCl_2$ (VI) $\longrightarrow L_3RhCl$ (VII) $\xrightarrow{olefin} [(olefin)_2RhCl]_2$ (VIII); $L_3RhHCl_2 \xrightarrow{CH_2=CHCN} RhCl_2CH(CH_3)CN$

In the absence of a good hydride acceptor, further reduction can occur[10] to give compounds of type VII, which can then coordinate with olefin[10] to give the normal π complexes such as VIII.

Experimental Section

Reaction of Rhodium Trichloride with Acrylonitrile.—Rhodium trichloride trihydrate, 3.0 g., 10 ml. of acrylonitrile, and 75 ml. of ethanol were refluxed overnight. The resulting yellow solid was filtered to give 2.7 g. (87%) of composition I, m.p. 220° dec.

For analysis, the sample was washed repeatedly with ethanol and benzene and dried under high vacuum.

Anal. Found: C, 27.7; H, 2.6; N, 8.6; Rh, 35.9; Cl, 24.9. This corresponds to $C_{6.6}H_{7.6}N_{1.8}Rh_{1.0}Cl_{2.1}$

The infrared spectrum (potassium bromide) exhibited a nitrile band at 2270 cm.$^{-1}$, but none attributable to either terminal olefin or metal hydride.

Dichloro(1-cyanoethyl)trispyridinerhodium(III).—Compound II, 3.0 g., was warmed to 55° in excess pyridine for 0.5 hr. The reaction mixture was cooled, filtered, and evaporated *in vacuo* to give 2.6 g. of yellow complex. This material was dissolved in methylene chloride and adsorbed on a column of silicic acid. Elution with 20% ether–methylene chloride gave several fractions whose infrared spectra were identical. These fractions were combined, evaporated, and reprecipitated from benzene–pentane to give yellow crystals, m.p. 90°.

Anal. Calcd. for $C_{18}H_{14}N_4RhCl_2$: C, 46.4; H, 4.1; Cl, 15.3; Rh, 22.2; mol. wt., 465. Found: C, 46.3; H, 4.3; Cl, 15.3; Rh, 22.4; mol. wt., 560 (ebullioscopic in dichloroethane, 0.02 *M*).

Dichloro(1-cyanoethyl)tris(diphenylmethylarsine)rhodium(III).—Dichlorohydridotris(diphenylmethylarsine)rhodium(III), 2.0 g., 2.4 ml. of acrylonitrile, and 40 ml. of benzene were refluxed under nitrogen for 1 hr. The cooled reaction mixture was con-

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[6] J. Lewis, R. S. Nyholm, and G. K. N. Reddy, *Chem. Ind.* (London), 1386 (1960).

[7] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

[8] (a) L. Vaska, and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961); (b) J. Chatt and B. L. Shaw, *Chem. Ind.* (London), 931 (1960).

[9] (a) J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 2976 (1963); (b) J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, **3**, 421 (1965).

[10] J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun.* (London), 131 (1965).

centrated and diluted with pentane to give 2.3 g. of product, m.p. ~142°.

Anal. Calcd. for $C_{42}H_{43}As_3Cl_2NRh$: C, 52.6; H, 4.5; As, 23.4; Cl, 7.4; N, 1.5; Rh, 10.7; mol. wt., 960. Found: C, 50.6; H, 4.3; As, 22.0; Cl, 9.0; N, 1.3; Rh, 12.8; mol. wt., 1360 (ebullioscopic, 0.02 *M*).

This corresponds to $L_{2.4}Rh(C_3H_4N)Cl_2$ and could not be improved by carrying out the reaction in excess diphenylmethylarsine. Attempts at chromatography resulted in even greater loss of ligand.

The infrared spectrum of this material (chloroform) showed the presence of a nitrile band at 2230 cm.$^{-1}$ and absence of hydride in the 2000 cm.$^{-1}$ region.

Treatment of Dichloro(1-cyanoethyl)tris(diphenylmethylarsine)rhodium(III) with Pyridine.—The subject complex was dissolved in excess pyridine under nitrogen and warmed to 100° for 4 hr. The cooled reaction mixture was stripped and diluted with pentane, and the resulting solid was adsorbed on a column of silicic acid. Elution with 20% ether–methylene chloride gave the pyridine compound II, m.p. ~110°. The compound was identical in infrared and n.m.r. spectra with a sample prepared by the rhodium trichloride–ethanol route.

Hydridodichlorotris(diphenylbutylphosphine)rhodium(III).—To a solution of 0.5 g. of rhodium trichloride trihydrate in 50 ml. of ethanol was added 2.0 ml. of diphenylbutylphosphine under nitrogen. After stirring for 15 min., the small amount of solid formed was filtered off, and the filtrate was allowed to stir under nitrogen for 2 days. The resulting yellow solid was filtered, washed with hexane, and dried *in vacuo* to give product (99%), m.p. *ca.* 140° dec.

The infrared spectrum (methylene chloride) exhibited a weak rhodium hydride band at 2090 cm.$^{-1}$ which disappeared on heating with carbon tetrachloride.

Anal. Calcd. for $C_{48}H_{58}Cl_2P_3Rh$: C, 63.8; H, 6.4; Rh, 11.4. Found: C, 63.4; H, 6.7; Rh, 10.8.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Exchange of Oxygen-18 between Water and Orthotungstate and between Water and 12-Tungstocobaltate(III)[1]

BY GERHARD GEIER AND C. H. BRUBAKER, JR.[2]

Received August 16, 1965

In order to understand more completely the mechanism of electron exchange between 12-tungstocobaltate-(II) and -(III),[2] we felt that we should determine whether or not oxygen exchange occurs between water and the 12-tungstocobaltates. Hall and Alexander[4] and Spitsyn[5] have reported complete exchange of oxygen between water and orthotungstate in 1 hr. or more at 95–100°.

Before we could undertake an investigation of the exchange between water and the 12-tungstocobaltates, it seemed necessary to determine whether oxygen exchange between water and tungstate would be appreciable at 25°. This is a report of our findings on the oxygen exchange between water and orthotungstate and water and 12-tungstocobaltate(III) at 25° by means of an oxygen-18 tracer study.

Experimental Section

Materials.—Oxygen-18 enriched water (1.59 ± 0.03 atom % by our analysis) was obtained from Yeda Research and Development Co., Rehoveth, Israel. The 12-tungstocobaltate-(III), as $K_4HCoW_{12}O_{40} \cdot 16H_2O$, was prepared and purified as described previously.[3] All other reagents were of reagent grade and were used without further purification.

Measurement of ^{18}O Content.—The ^{18}O content of water, anhydrous barium and sodium tungstates, and anhydrous tetramethylammonium 12-tungstocobaltate(III) was measured by converting the oxygen to carbon dioxide by the method of Anbar and Guttman,[6] in which the oxygen-containing compound (hereafter called oxide) is heated in a sealed tube with mercury(II) chloride and cyanide. The gaseous products are purified over zinc amalgam and the ^{18}O content is determined mass spectrometrically. A Consolidated Type 21-103C mass spectrometer was employed.

In the cases of barium and sodium tungstates and the tetramethylammonium 12-tungstocobaltate(III), satisfactory conversion of the oxides to CO_2 could not be effected unless large excesses by weight (4:1:1 or 5:1:1) of the oxide, compared to $HgCl_2$ and $Hg(CN)_2$, were used. With water, nearly equal proportions by weight or excess mercury salts gave good conversion. The reason for the need to use excess oxide is not understood, but has been observed by others.[7] Samples of Na_2WO_4 of 200 mg.; $BaWO_4$, 200–250 mg.; $[(CH_3)_4N]_5[CoW_{12}O_{40}]$, 250 mg.; and H_2O, 5–10 mg. were used.

In order to obtain anhydrous tungstates and 12-tungstocobaltate for conversion to CO_2, it was necessary to heat the hydrated $BaWO_4 \cdot {}^1/_2H_2O$, $Na_2WO_4 \cdot 2H_4O$, and the unknown hydrate of $[(CH_3)_4N]_5[CoW_{12}O_{40}]$ under a stream of "prepurified" nitrogen to avoid exchange of oxygen with the atmosphere. Sodium and barium tungstates were heated at 550° and the 12-tungstocobaltate at 200° to constant weight and no residual water.

In order to verify the necessity of heating in nitrogen, several series of experiments were run in which labeled $BaWO_4$ samples were heated in the air at 550° and then were converted to CO_2 and checked mass spectrometrically (see Table I).

TABLE I

LOSS OF ^{18}O FROM $BaWO_4$ BY EXCHANGE WITH OXYGEN OF THE AIR AT 550 ± 10°[a,b]

Length of time heated, min.	Sample 1	Sample 2	Sample 3	Sample 4
	^{18}O content (atom %) of $BaWO_4$			
0	1.41	1.41	1.41	1.41
30	0.81	0.89	0.85	0.99
60	0.61	0.64	0.60	0.73
90	0.42	0.57	0.54	0.53
120	0.30	. . .	0.46	0.50

[a] $BaWO_4 \cdot {}^1/_2H_2O$ heated to remove water. Samples 1 and 2, $BaWO_4$ was precipitated from freshly prepared Na_2WO_4 solutions; samples 3 and 4, from solutions 23–24 hr. old. [b] ^{18}O content at zero time calculated from content of Na_2WO_4 and $BaCl_2$ solutions and the assumption of rapid, complete exchange.

Exchange Reaction Procedures.—Weighed samples of $Na_2WO_4 \cdot 2H_2O$ (natural abundance of ^{18}O) were dissolved in ^{18}O-labeled water containing 1 *M* NaCl and a small amount of NaOH (10^{-2} *M* or less) to make a 0.1 *M* WO_4^{2-} solution. Solution was complete in 30 sec. or less.

Two methods of separating tungstate from water were em-

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[1] Support by the U. S. Atomic Energy Commission under grant AT(11-1)-1001 is gratefully acknowledged.

[2] To whom correspondence should be addressed.

[3] P. G. Rasmussen and C. H. Brubaker, Jr., *Inorg. Chem.*, **3**, 977 (1964).

[4] N. F. Hall and O. R. Alexander, *J. Am. Chem. Soc.*, **62**, 3455 (1940).

[5] V. I. Spitsyn, *Russ. J. Inorg. Chem.*, **3**, 217 (1958).

[6] M. Anbar and S. Guttman, *Intern. J. Appl. Radiation Isotopes*, **5**, 233 (1959).

[7] G. Gordon, private communication.