

Se was prepared by precipitation from an acidified solution of KSeCN . Vitreous Se was prepared by pouring molten gray Se into water. The powder was purified by repeated leaching with concentrated aqueous solutions of KCN until acidification of the solution gave no red Se.

Pseudohalide Preparation.—Cyano, isocyanato, and isothiocyanato derivatives of triorganosilanes and -germanes were prepared by refluxing ethereal solutions of the corresponding bromides or iodides over the silver salts. Selenocyanates were prepared by simple addition of excess KSeCN to the organometal halide, either neat or in ether solution.³⁰ Yields on the preparations varied from 40 to 95%. Table III lists physical constants and analytical data for previously unreported compounds. The extreme sensitivity of these compounds to hydrolysis and the toxicity of the hydrolysis product HCN make caution absolutely necessary in their handling.

TABLE III
ANALYTICAL DATA

Compound	Bp, °C (mm)	% calcd.		% found	
		C	H	C	H
$(\text{C}_6\text{H}_{13})_3\text{SiCN}$	225 (125)	73.7	12.7	74.4	12.8
$(\text{C}_4\text{H}_9)_3\text{GeCN}$	292–294	57.8	10.1	58.2	10.3
$(\text{C}_6\text{H}_{13})_3\text{SiNCSe}$	307–308 (250)	58.7	10.1	58.8	10.4
$(\text{CH}_3)_3\text{GeNCSe}^a$	118–119 (232)	21.6	4.1	22.1	4.5
$(\text{C}_2\text{H}_5)_3\text{GeNCSe}$	175–176 (240)	31.8	5.7	32.1	5.9
$(\text{C}_4\text{H}_9)_3\text{GeNCSe}$	221–222 (100)	44.8	7.8	45.2	8.0

^a Mp 13–14°.

Chalcogenation Procedures.—Pure cyanosilanes or -germanes in 1-ml quantities was placed in a 25-ml standard taper Bantamware flask, treated with the desired chalcogenating agent, and allowed to sit in a desiccator. If heating was required, a 25-ml

round-bottomed flask would be used, fitted with a reflux condenser and drying tube, and refluxed using a heating mantle. The sulfur used for quenching experiments was heated in a porcelain boat until liquid and was then poured immediately into the cyanide. For the CS_2 experiments, a weighed quantity of the cyanide would be dissolved in 15 ml of CS_2 taken directly from an unopened bottle, the stoichiometric amount of sulfur was added, and the entire system was refluxed. Progress of room-temperature reactions could be followed by removal of samples for infrared spectra.

Bromination.—Liquid bromine was added to pure I in a dropwise fashion at room temperature. Reaction was vigorous and exothermic. The system remained colorless until excess Br_2 was present. Some cyclohexene was added, whereupon the bromine color disappeared and a grayish solid precipitated out. The cyclohexene was decanted and shaken with an aqueous solution of AgNO_3 . A yellowish solid precipitated; this was shown by infrared and analytical techniques to be AgBr with traces of AgCN . The grayish solid, after drying in air, dissolved readily in water. This solution was acidified, treated with NaI , and shaken with CCl_4 , whereupon the violet color of iodine appeared immediately.

Infrared Spectra.—All spectra were run on a Perkin-Elmer Model 337 grating spectrophotometer, linear in wave number and covering the range 4000–400 cm^{-1} . The great majority of samples were run as liquid smears, using NaCl or CsBr plates. Certain samples were run as CCl_4 solutions, using 0.1-mm KBr cells. All peak positions were determined to $\pm 5 \text{ cm}^{-1}$, using polystyrene for calibration.

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The Question of Isomerism in Rhenium(IV) Chloride

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The previously proposed structures for α - and β - ReCl_4 are significant in being two of the few examples of a transition element halide appearing in isomers displaying different halogen:metal coordination numbers and warrant reinvestigation. Preparative, chemical, and X-ray powder diffraction studies now support the more plausible NbCl_4 -like structure for α - ReCl_4 . It is suggested that α - and β - ReCl_4 are quite closely related stereochemically in that both consist of pairs of ReCl_6 octahedra joined by a shared edge or face, respectively.

Introduction

Two separate studies indicated that rhenium(IV) chloride adopted, firstly, a proposed trigonal cluster structure¹ $(\text{Re}_3\text{Cl}_9)\text{Cl}_3$, similar to that established for $\text{Cs}_3\text{Re}_3\text{Cl}_{12}$, and, secondly, a dimeric form established by X-ray crystallography² and containing Re_2Cl_9 groups, similar to the chloro groups found in $\text{K}_3\text{W}_2\text{Cl}_9$. It is convenient to designate these different materials as α and β forms, respectively,³ but provisionally on the basis of preparative origin since we believe their

structures are still an open issue. α - and β - ReCl_4 are obtained, respectively, from refluxing thionyl chloride and hydrated rhenium dioxide and from the pyrolytic disproportionation of rhenium pentachloride. The reported Cl:Re and Re:Re coordination numbers are 5 and 2 and 6 and 1, respectively.

The adoption of two structures by a particular transition element halide, each displaying different halogen:metal coordination numbers, is remarkable since it has been restricted to halides of silver and mercury in the past, and the present possibility of isomerism in ReCl_4 deserves to be confirmed. On the one hand, α - ReCl_4 is reported to be amorphous to X-rays so that a direct refutation or confirmation of

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(3) F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 223 (1967).

TABLE I
 THE COMPOSITION AND PROPERTIES OF THE PRODUCT FROM REFLUXING SOCl_2 AND $\text{ReO}_2 \cdot n\text{H}_2\text{O}$

Prepn no.	Reflux time, hr	Yield, %	% compn					Cl:Re	% chloride release		Solution color ^b			Remarks
			Cl ^a	Re	C	H	S		0.1 M NaOH	0.1 M HNO ₃	6 M HCl	CH ₃ CN	Acetone	
1	6	50	28.7								r-v	r-b	g-b	SOCl_2 used directly from bottle
2	6	...	21.9								v	v	g	SOCl_2 used as recovered
3	24	31	17.2	73.8				1.22	17.0		v	r-v	g	Anhydrous ReO_2 used
4	6	35	34.9	46.9				3.9			v	r-b	r-b	Sealed tube, 120°
5	48	...	34.1	44.5				4.0	(33.1) ^c		v	r-v	g-b	Sealed tube, 120°
6	24	63	36.6	48.7	0.64	0.51	0.72	4.0	35.1	8.9	r-b	g	g-b	N ₂ atmosphere
7	50	95	38.9	41.7	0.79	0.85	0	4.85	35.5	12.4	N ₂ atmosphere
8	96	...	36.1	48.2				4.0	(30.9) ^c	17.6	r-b	r-b	g	N ₂ atmosphere
9	6	50	29.3								r-b	r-b	g-b	
10	6	50	31.0								r-b	r-b	g-b	
11	96	59	27.6	6.26				2.3	27.8	23.5	v	r-b	g-b	
12	192	67	31.7	56.3				3.0	32.6		r-b	r-b	g-b	
13	384	84	31.5	55.8				3.0	32.4		g	g-b	g-b	
14	0.5	<<5	30.5								Ratio $\text{SOCl}_2:\text{ReO}_2 \cdot n\text{H}_2\text{O}$ (v/w) = 20
15	0.5	8	37.2		1.73	0.57	3.48		35.5		v	10
16	1	<5	35.1								20
17	1	9	35.6	4.96	1.68	0.44	2.89	3.8	35.5		v	10
18	2	<5	35.1								20
19	2	9	37.0	48.0	1.84	0.55	2.80	4.0	34.8		v	r-b	g	10
20	4	23	30.4	52.3	1.35	0.84	3.12	3.0	32.8		v	g-b	g	5
21	4	8	38.8	48.3	1.47	...	2.52	4.2	38.1		v	g-b	g	10
22	4	<5									100
23	6	20	36.2	47.5				4.0	39.3		20
24	8	11	37.8	47.4	2.65	0.93	2.71	4.2	35.8		v	g-b	g	10
25	8	<5									100
26	48	24	32.3	44.6				3.8	31.6		v	20
27	72	52	41.4	57.0				3.8	41.5		v	v ^d	g	20
28	72	49	42.8	56.0				4.0	47.5		v	v ^d	g	20

^a Obtained by NaOH fusion. ^b v, violet; g, green; r-v, red-violet; r-b, red-brown; g-b, green-brown. ^c Hydrolysis with water. ^d Slowly soluble.

structure seems remote, and, on the other, $\beta\text{-ReCl}_4$ appears not to have been prepared in a laboratory since its unexpected delivery from a commercial source.³ This paper reports an extensive series of attempted preparations of ReCl_4 and the light they throw on the isomerism in this chloride.

Results and Discussion

The Products of Hydrated Rhenium Dioxide in Refluxing Thionyl Chloride.—We have carried out the $\text{SOCl}_2\text{-ReO}_2 \cdot 2\text{H}_2\text{O}$ reaction a total of 24 times under a variety of conditions. The results are given in Table I. Consistently very dark solid separated from the dark refluxing solution and a majority of samples possessed a Cl:Re ratio distinctly close to 4.0 as required by ReCl_4 . (Rather notable exceptions are samples 12 and 13 which were obtained after very long reflux times and possessed a ratio of 3.0.) Moreover a number of samples at least superficially resembled the original $\alpha\text{-ReCl}_4$ ^{1,4} since we find they are soluble in methyl cyanide and acetone giving red-brown solutions. Additionally we find similar colors after solution in 6 M hydrochloric acid. In dilute alkali most of our samples dissolved to give the persistent and significant red-brown color described for $\alpha\text{-ReCl}_4$. These colors are important since they contrast with the violet or green solutions generated by $\beta\text{-ReCl}_4$ in hydrochloric acid or in acetone, respectively.

We were disappointed to find, however, that almost all of our samples contained additional material to Re and Cl since their total content was usually only 85%. Moreover, the samples left appreciable black residue

after solution in hydrochloric acid or acetone, and selected samples contained appreciable quantities of sulfur, hydrogen, and carbon (*viz.*, Table I).

It is now apparent that the reported preparation⁴ of $\alpha\text{-ReCl}_4$ is unique in the claim of forming a pure transition metal halide *in situ*, without the need of further purification, by the action of thionyl chloride on an oxide or hydroxide. *E.g.*, Bagnall and Brown found⁵ that niobium, tantalum, and protactinium hydroxides could react in the cold with thionyl chloride and they warned against overheating of the thionyl chloride and of the impure products that would result. These workers nonetheless purified their chlorides by sublimation. Uhlemann and Fischbach found⁶ 7% sulfate in the trichloride resulting from heated chromium trioxide and thionyl chloride.

We have confirmed the general deficiencies of the refluxing thionyl chloride method of converting hydroxides to chlorides by investigating the products from seven first transition element hydroxides. The results are given in Table II. The reactions were carried out over 2, 6, and 24 hr and in nearly all cases the product was of the same composition for each hydroxide indicating complete reaction. The near to integral chlorine:metal ratio supports that reaction was complete and that the actual composition did not result from occluded hydroxide. The results provide two surprises. Hydroxychlorides result in some cases and most samples possess ir absorption at 3600–3340 and 1645–1595 cm^{-1} indicating residual aquo groups. Of greater relevance is the observation that the total

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TABLE II
THE PRODUCTS OF REFLUXING THIONYL CHLORIDE ON
FIRST TRANSITION ELEMENT HYDROXIDES

Hydroxide	Reflux time, hr	% compn			Cl:M
		Cl	Metal	Cl + metal	
Ni(OH) ₂ ·nH ₂ O	2	46.3	36.9	83.2	2.1
	6	44.9	35.7	80.6	2.1
	24	45.4	38.4	83.8	2.0
Cu(OH) ₂ ·nH ₂ O	2	41.6	35.3	75.9	2.1
	6	42.7	41.7	84.4	1.8
	24	44.2	32.5	76.7	2.4
Cr(OH) ₃ ·nH ₂ O	2	37.5	25.8	2.1	2.1
	6	39.6	26.8	2.2	2.2
	24	38.9	25.2	2.3	2.3
Co(OH) ₂ ·nH ₂ O	2	30.3	45.5	1.1	1.1
	6	30.2	47.2	1.1	1.1
	24	31.2	45.5	1.1	1.1
Mn(OH) ₂ ·nH ₂ O	2	25.2	41.7	0.9	0.9
	6	25.8	41.3	1.0	1.0
	24	28.4	46.8	0.9	0.9
Fe(OH) ₃ ·nH ₂ O	2	60.3	27.1	87.4	3.5
	6	57.8	29.0	86.8	3.1
	24	57.2	29.0	86.2	3.1
Zn(OH) ₂ ·nH ₂ O	2	36.3 ^a			
	6	34.8			
	24	37.4			

^a Required by ZnCl₂, 52.1%.

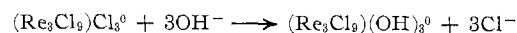
metal, chlorine, and hydroxide content is well short of 100%. We conclude therefore that the refluxing thionyl chloride method is not at all reliable for the preparation of pure transition metal chlorides *in situ*. Although one is predisposed to accept that thionyl chloride must remove all water, we are not even certain that this is actually true. Some but not all of our α -ReCl₄ possessed ir aquo group absorption bands. There is a qualitative report⁷ that [CrCl₂(H₂O)₄]Cl·2H₂O does not produce anhydrous CrCl₃ with refluxing SOCl₂.

In view of the nature of our results and conclusions we were grateful to be informed by Fergusson and Hickford that their independent study⁸ of the SOCl₂-ReO₂·nH₂O reaction led them also to conclude that it gave variable products, sometimes containing Re(III), sometimes aquo groups, and usually low in over-all rhenium and chlorine. Moreover they found the corresponding reaction with technetium dioxide fails, in a very similar way to rhenium dioxide, to give a pure tetrachloride. We have only recently found a reference⁹ by Schäfer, *et al.*, to their failure to prepare ReCl₄ by the SOCl₂-ReO₂·nH₂O method and their observations seem very similar to ours and those of Fergusson and Hickford.

The important conclusions at this stage are, firstly, that the reported properties of α -ReCl₄ are probably confused by impurities and, secondly, that *at least some of our preparations must contain a similar chloride of rhenium to that found by Colton and Brown*. We do not contest their claim to have prepared a pure sample of ReCl₄, since we ourselves achieved nearly as much in samples 27 and 28 (Table I), but suggest they enjoyed some good fortune in the samples chosen for analysis.

The Properties of α -ReCl₄.—The most diagnostic chemical property reported for the trimeric formulation

is the 25% release of chloride when α -ReCl₄ is dissolved in dilute alkali since this supports the reaction scheme



However this striking observation did not warrant a mention in the first two papers^{4,10} and appears as a *post hoc* justification of the trimer proposition in the third paper¹ and without quantitative support. On the other hand, early mention was made of the rather low chlorine figures obtained for samples of α -ReCl₄ which in our view is equally well explained by poor products of the sort we find. Our observations are that all samples gave virtually the same chloride release in cold 0.1 M hydroxide, even water, as in fused alkali. This is quite inconsistent with our samples, albeit impure, containing any quantity of trimer. Moreover we cannot accept the validity that a fractional release of chloride from α -ReCl₄ implies some structure or other, when it is also reported⁴ that α -ReCl₄ easily hydrolyzes giving some rhenium dioxide (which does not appear in the above equation) and that the apparently characteristic and significant resistance to complete hydrolysis of α -ReCl₄ is similar to that of TcCl₄, which is now known¹¹ not to possess a cluster-type structure at all. It is unprecedented for a neutral and non-electrolyte hydroxychloride such as (Re₃Cl₉)(OH)₃⁰ to be soluble in aqueous solution and it is unprecedented for a cluster chloro compound to require fusion with alkali for complete decomposition. Nonetheless we observe the persistently colored solutions that result when α -ReCl₄ is dissolved in aqueous alkali, but we suppose these to result from some form of colloidal rhenium(IV) oxide since a brown precipitate is immediately given on acidification or on long standing. It is significant that yellow colloidal solutions of rhenium(IV) oxide are given by the acid reduction of per-rhenate.¹² It has been pointed out that the violet solutions given by β -ReCl₄ in hydrochloric acid or methanol and the green solutions in acetone provide some of the grounds for supposing that α -ReCl₄ is probably of a different structure since it does not give these colors. We now report that *most of our samples of α -ReCl₄ did give, not only the same violet or green colors, but also all of the derivative reactions³ of β -ReCl₄*. These were conducted on a qualitative and test-tube basis since we are familiar at first hand with the chemistry of β -ReCl₄ by virtue of partially successful syntheses of it (*vide infra*).

We conclude that there are no adequate grounds for maintaining that α -ReCl₄ is either of trimer form or of stereochemistry greatly different from β -ReCl₄.

The Structure of α -ReCl₄.—Our samples of α -ReCl₄ have consistently given rather diffuse but discernible and extensive X-ray powder diffraction patterns, which are very similar to those observed by Fergusson and Hickford⁸ and which bear an unmistakable resemblance

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to the patterns for niobium(IV),¹³ α -molybdenum(IV),¹⁴ and tungsten(IV)¹⁵ chlorides. Table III lists the d spacings and relative intensities in a comparative form for the four tetrachlorides.

TABLE III
X-RAY POWDER DIFFRACTION DATA FOR
Nb(IV), W(IV), Mo(IV), AND Re(IV) CHLORIDES

NbCl ₄ ¹³		WCl ₄ ¹⁵		MoCl ₄ ¹⁴		α -ReCl ₄	
d	Intens	d	Intens	d	Intens	d	Intens
6.02	10	5.97	vvs	6.00	s	5.84	vs
				5.75	s		
				5.30	w	5.27	w
4.45	9	4.45	vvs	4.41	s	4.36	m
4.09	8	4.02	vvs	4.04	m	4.00	m
3.43	2						
		3.23	vs	3.28	m	3.21	vw
2.95	3	3.08	vw				
		2.85	vw	2.86	w	2.82	vw
2.71	8	2.77	w	2.72	vw		
2.61	9	2.62	vs	2.63	vs	2.59	vs
2.57	5	2.58	s	2.59	s	2.53	vs
		2.54	w	2.54	m		
2.22	7	2.23	s	2.20	m	2.18	m
2.17	2	2.18	vw				
2.14	3	2.13	vw	2.12	w		
		2.10	w	2.10	m	2.08	m
2.03	7	2.02	s	2.01	s	1.99	m
		1.98	vw				
1.92	1	1.93	vw				
						1.89	vs
1.87	4	1.86	vw			1.85	s

A brief report¹⁶ gives the essential stereochemistry of NbCl₄ as consisting of pairs of octahedra joined by an edge. The niobium atoms are displaced toward each other in these pairs.

It is now certain that there are two modifications of MoCl₄: (i) that prepared at low temperatures (refluxing chloro- or hydrocarbons on MoCl₅)¹⁷⁻¹⁹ and (ii) that prepared at relatively high temperatures (molybdenum metal or trichloride heated in MoCl₅ vapor).^{20,21} The designations α and β have been assigned¹⁹ to the former and latter. The β form consists of widely separated molybdenum atoms (3.50 Å) octahedrally coordinated by chloride,²¹ but powder diffraction patterns of the two forms differ and that of the α form closely resembles^{14,18,19} that of NbCl₄. It has been demonstrated¹⁹ that the β form contains Mo₂ pairs since the diffraction data are inconsistent with a halved b axis, *i.e.*, assuming molybdenum atoms equispaced along it.

The data of Table III do not firmly establish the structure type for α -ReCl₄ nor indicate whether Re₂ pairs exist in it but nevertheless do provide for the reasonable proposal that α -ReCl₄ resembles NbCl₄.

The Magnetic Properties of α -ReCl₄.—We have not measured the susceptibility with any thoroughness since (i) we have not obtained a pure material and (ii) we do not see how this resolves the structural issue. The room-temperature susceptibility of several impure

samples indicates an effective moment of 2.0 BM *per* Re atom; while this is consistent with a weak Re–Re bond as suggested by an NbCl₄-type structure, it is not particularly strong support for it.

The principal grounds advanced for the trimeric¹ formulation of ReCl₄ was a rather ingenious but speculative model for the interpretation of the temperature variation of magnetic susceptibility. On similar grounds it was proposed²² that MoCl₃, MoCl₄, WCl₅, and WBr₅ would contain M₃ trigonal clusters. Since these proposals, the structures or structure types of α - and β -MoCl₃,²¹ α - and β -MoCl₄ (*vide supra*), and WCl₅²³ have been established with reasonable certainty and yet none has been found to contain M₃ clusters. Even if the temperature–susceptibility observations on our materials did prove identical with those previously reported¹⁰ and discussed,¹ we see no reason to accept this as evidence for the (Re₃Cl₃)Cl₃ structure until the model has been shown to have any structure-predicting ability.

The Reaction of Hydrated Rhenium Dioxide with Carbon Tetrachloride at High Temperature.— α -ReCl₄ is formed in refluxing SOCl₂ (bp 77°) and apparently β -ReCl₄ was produced at 350–375°. It is possible that the appearance of these different forms depends on the formation temperature and we judged a worthwhile attempt at the synthesis of β -ReCl₄ would be a chlorination reaction of ReO₂· n H₂O with CCl₄, rather than SOCl₂, at 350°. Some initial success prompted us to carry out the reaction under a variety of conditions some 40 times but we have to conclude the method is unsatisfactory. As in the thionyl chloride reaction, the product displays low total Re and Cl content, ~90%, and the products are found to contain several per cent of carbon. The Cl:Re ratio varies from 3.0 to 4.2 with a reasonable proportion of samples giving ratios close to 4.0. As expected by the wide variation in composition, the materials give a number of different X-ray powder diffraction patterns but none of them resembles that of α -ReCl₄. We have been unable to verify if these high-temperature reaction products contain β -ReCl₄ directly since it appears²⁴ that a powder photograph of the original β -ReCl₄ is not available and no intensity data have been published to facilitate the comparison of our powder photographs with the published² unit cell data. Nonetheless the CCl₄–ReO₂·2H₂O reaction gives an appreciable quantity of some rhenium chloride which undergoes every reaction published³ as characteristic of β -ReCl₄, even to the extent of giving appropriate yields. Table IV lists the derivative compounds from our high-temperature chlorination products.

In the absence of any direct evidence to the contrary, we tentatively propose that the form of ReCl₄ present in our materials is the β form. On the other hand, we have at least established that ReCl₄ can be readily formed in two reactions from ReO₂· n H₂O with the

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TABLE IV
 DERIVATIVES CHARACTERISTIC OF β - ReCl_4 AND OBTAINED WITH THE PRODUCT OF CCl_4 - $\text{ReO}_2 \cdot n\text{H}_2\text{O}$ AT HIGH TEMPERATURE

Derivative	Yield, %		% compn									
	Found	Lit.	C		H		N		S		Cl	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{Re}_2\text{Cl}_8$	36	39	33.8	33.7	6.4	6.6	2.5	2.7	24.9	24.4
$[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{Re}_2\text{Cl}_8$	46	...	32.7	32.7	6.1	6.0	2.4	2.7	27.2	26.5
$[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Re}_2\text{Cl}_8$	50	46
$[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Re}_2\text{Cl}_8$	44	52
$\text{ReCl}_5(\text{tu})_2 \cdot \frac{1}{2}(\text{CH}_3\text{COCH}_3)^a$	8.9	8.2	2.6	3.4	15.5	15.3	17.8	17.8	19.7	18.8
$\text{ReCl}_5(\text{C}_6\text{H}_5)_3\text{P}$	32	50	39.0	38.9	7.7	3.4	10.2	18.3
$\text{ReOCl}_3 \cdot \text{bipy}^b$	25.8	26.2	1.7	2.0	6.0	6.1	22.9	22.5
$\text{ReOCl}_3(\text{C}_6\text{H}_5)_3\text{P}$	32	...	52.0	51.0	3.6	4.2
$(\text{bipy})\text{HReOCl}_4$	23.9	23.3	1.8	2.1	5.6	4.9
$\text{Re}_2\text{O}_5(\text{C}_6\text{H}_5\text{N})_4\text{Cl}_4$	27.3	27.5	2.33	2.33	6.3	5.4
Green ppt from ReCl_4^- , $\text{C}_6\text{H}_5\text{N}-\text{C}_5\text{H}_5\text{O}$	18.2 ^a	16.2	1.9 ^a	1.9	2.9 ^a	3.3

^a tu = thiourea. ^b bipy = 2,2'-bipyridyl.

chemical properties of β - ReCl_4 so that these methods are now available as starting points for examining new derivatives unique to ReCl_4 .

Experimental Section

Thionyl Chloride.—This was purified by the linseed oil-quinoline method²⁵ and fractionated (bp 75–76°, lit.²⁵ bp 77°). The origin of carbon in our α - ReCl_4 clearly results from contaminated thionyl chloride, possibly from the ingredients used in purifying it. However, some purification of SOCl_2 is essential since very poor results are obtained with crude or recovered SOCl_2 (*viz.*, preparations 1 and 2, Table I). Colton, *et al.*, did not state how they purified their SOCl_2 .

Hydrated Rhenium Dioxide.—Preparations 1–13 employed dioxide from the reduction of KReO_4 with zinc and hydrochloric acid. Although this material contains detectable amounts of zinc (probably as metallic fragments), the over-all results were the same as in preparations 14–28 where dioxide from the hy-

drolysis of ReCl_5 was employed. The precipitated dioxide was washed with water and acetone and then vacuum dried at room temperature.

The First Transition Element Hydroxides.—The colloidal precipitates from the action of alkali on the appropriate chloride were washed (assisted by centrifugation for separation) and dried as for $\text{ReO}_2 \cdot n\text{H}_2\text{O}$.

Analyses.—Cl was determined by potentiometric titration and Re by the α -furyl dioxime method.²⁶ The remaining transition elements were analyzed by flame spectrophotometry against standard solutions; C, H, N, and S were determined by commercial microanalyses.

Reaction Products.—These were efficiently separated from the SOCl_2 phase by centrifugation and decantation. The chloride products were handled under dry nitrogen and dried in vacuum.

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Crystallographic Studies on Polynuclear Rhenium Carbonyl Hydrides and Anions. II.¹ The Characterization of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Re}_4(\text{CO})_{16}]$

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The tetra-*n*-butylammonium salt of the hexadecacarbonyltetrarhenium dianion— $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Re}_4(\text{CO})_{16}]$ —crystallizes as deep red parallelepipeds in the centrosymmetric monoclinic space group $\text{C}2/c$ (no. 15; C_{2h}^6) with $a = 24.65 \pm 0.04 \text{ \AA}$, $b = 12.93 \pm 0.02 \text{ \AA}$, $c = 19.49 \pm 0.03 \text{ \AA}$, $\beta = 107.7 \pm 0.2^\circ$, $Z = 4$. Observed and calculated densities are 1.89 ± 0.01 and 1.887 g cm^{-3} , respectively. A single-crystal X-ray diffraction study has been completed. Data to $\sin \theta = 0.37$ ($\text{Mo K}\alpha$ radiation) were collected with a 0.01° -incrementing Buerger automated diffractometer, and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. The final discrepancy index is $R_F = 10.65\%$ for 2696 independent nonzero reflections. The crystal consists of discrete $\text{Re}_4(\text{CO})_{16}^{2-}$ and $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ ions. The $\text{Re}_4(\text{CO})_{16}^{2-}$ ion has crystallographically imposed C_2 symmetry with the rhenium atom skeleton defining two fused, coplanar, approximately equilateral triangles. Individual rhenium-rhenium bond distances range from 2.956 ± 0.007 to $3.024 \pm 0.007 \text{ \AA}$. Each rhenium atom is associated with four terminal carbonyl ligands, two of which are approximately *axial* and two approximately *equatorial*. The $\text{Re}_4(\text{CO})_{16}^{2-}$ ion distorts from idealized D_{2h} symmetry, probably as a result of intramolecular oxygen...oxygen contacts. The tetra-*n*-butylammonium ions have the expected configuration, but one of the *n*-butyl chains appears to have a disordered $-\text{CH}_2-\text{CH}_3$ moiety.

Introduction

The reaction of dirhenium decacarbonyl with sodium borohydride (in tetrahydrofuran) gives rise to a solu-

tion with an intense red coloration.³ Evidence that this solution contains a number of different rhenium-carbonyl species comes from (i) the highly complicated infrared absorption spectrum in the carbonyl stretching

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