CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CINCINNATI, CINCINNATI, OHIO 45221

The Chalcogenation of Organometallic Cyanides[1]

BY JOHN S. THAYER

Received July 15, 1968

Trialkylcyanosilanes and -germanes are readily converted to the isochalcocyanates R_3MNCX (M = Si, Ge; X = O, S, Se), using a variety of reagents under different reaction conditions. Introduction of oxygen and sulfur requires heating, but selenium reacts at room temperature and shows a marked "allotrope effect." There is no reaction with tellurium. The mechanism of chalcogenation is discussed in connection with the long-standing "normal–iso" structural uncertainty of cyanosilanes and cyanogermanes.

Ever since its initial report in 1951[2,3] the structure of trimethylcyanosilane, $(CH_3)_3SiCN$ (I), has been a source of controversy and uncertainty. Previous workers proposed the "normal" form[4] or an equilibrium between the two, with the "normal" form predominating[5]

$$2(CH_3)_3SiCN \rightleftharpoons 2(CH_3)_3SiNC \tag{1}$$

A similar equilibrium was suggested for $(CH_3)_3GeCN$ (II) on the basis of spectral and chemical resemblance to (I).[6] This "normal–iso" equilibrium was based on two pieces of evidence: (a) infrared spectroscopy which showed a strong band at 2190 cm^{-1} and a much weaker band at 2100 cm^{-1} in various organocyanosilanes[2,3,5] and II;[6] (b) the chemical reactions

$$(CH_3)_3SiCN + H_2 \xrightarrow{Ni} [(CH_3)_3Si]_2NH + NH_3 + CH_4 \tag{2}$$

$$(CH_3)_3SiCN + LiAlH_4 \longrightarrow (CH_3)_3SiH \tag{3}$$

$$(CH_3)_3SiCN + Cl_2 \xrightarrow{CHCl_3} \text{“}(CH_3)_3SiNCCl_2\text{”} \tag{4}$$

$$(CH_3)_3SiCN + S \longrightarrow (CH_3)_3SiNCS \tag{5}$$

$$(CH_3)_3SiCN + Fe(CO)_5 \longrightarrow (CH_3)_3SiNCFe(CO)_4 + CO \tag{6}$$

Reactions 5 and 6 have also been reported for II.[6,7] More recently, Allerhand and Schleyer[8] studied the hydrogen-bonding interaction between I and phenol. They reported that the shift in the O–H stretching band caused by I was more typical of a cyanide than an isocyanide.

This paper reports further investigations on the chemical properties of trialkylcyanosilanes and -germanes, particularly their reactions with chalcogenating agents (species able to give up an atom of a group VI element). Chalcogenation was studied under different conditions in an effort to provide mechanistic evidence for or against the proposed "normal–iso" equilibrium.

Results

Infrared Spectra.—Each pseudohalide group has its own distinct infrared bands, which may be readily used for structural diagnosis[2,9] (see Table I). A preliminary band assignment of the C=Se stretching mode in $(CH_3)_3SiNCSe$ (III)[10] has been shown to be incorrect by Bürger and Goetze.[11] In general, asymmetric stretching bands are very intense for all pseudohalides, while the other bands are usually appreciably weaker. The weak band at 2100 cm^{-1} in certain trialkylcyanosilanes or -germanes varies in appearance, depending on the conditions under which the spectrum is run.

TABLE I

PSEUDOHALIDE INFRARED BANDS

Compound	$\nu_{asym}(NCX)$	$\nu_{sym}(NCX)$	$\delta(NCX)$	$\nu(M–Ps)$	Ref
$(CH_3)_3SiCN$	2198 (2100)	...	?	644	2, 3, 4, 5
$(C_6H_{13})_3SiCN$	2192 (2110)	...	?	m	
$(CH_3)_3GeCN$	2197 (2100)	...	?	?	2, 6
$(C_4H_9)_3GeCN$	2175	...	?	?	
$(CH_3)_3SiNCO$	2290	1435	616	521	2, 9
$(C_6H_{13})_3SiNCO$	2275	1425	m	m	
$(CH_3)_3GeNCO$	2240	1415	606	454	2, 9
$(CH_3)_3SiNCS$	2080	956	470	436	2, 9
$(C_6H_{13})_3SiNCS$	2063	950 sh	475 sh	m	
$(CH_3)_3GeNCS$	2075	892	476	m	2, 9
$(CH_3)_3SiNCSe$	2055	800	449	371	10, 11
$(C_2H_5)_3SiNCSe$	2065	826	m	?	10
$(C_6H_{13})_3SiNCSe$	2050	830	430 sh	?	
$(C_6H_5)_3SiNCSe$	2070	830	m	?	10
$(CH_3)_3GeNCSe$	2052	795	430	?	
$(C_2H_5)_3GeNCSe$	2050	?	430	?	
$(C_4H_9)_3GeNCSe$	2047	m	425 sh	?	

[a] Abbreviations: ?, peak not visible or cannot be assigned with certainty; sh, shoulder; m, masked by another peak.

Chalcogenation Studies.—The results of various chalcogenation experiments are given in Table II. When reaction occurred, the corresponding isochalcocyanates formed and were isolated. These were compared to the compounds prepared from the halosilanes and silver chalcocyanates; in all cases, they were identical.

Conversion of a cyanide to an isocyanate requires a strong oxidizing agent. HgO and Ag_2O, which con-

---

[1] (a) This work was partially supported by a Frederick Gardner Cottrell grant from the Research Corp. (b) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

[2] For a review of structural and chemical studies on organometallic cyanides, see J. S. Thayer and R. West, *Advan. Organometal. Chem.*, **5**, 181 (1967).

[3] J. J. McBride and H. C. Beachell, *J. Am. Chem. Soc.*, **74**, 5247 (1952).

[4] R. Linton and E. R. Nixon, *J. Chem. Phys.*, **28**, 990 (1958).

[5] T. A. Bither, W. H. Knox, R. V. Lindsay, and W. H. Sharkey, *J. Am. Chem. Soc.*, **80**, 4151 (1958).

[6] D. Seyferth and N. Kahlen, *J. Org. Chem.*, **25**, 809 (1960).

[7] D. Seyferth and N. Kahlen, *J. Am. Chem. Soc.*, **82**, 1080 (1960).

[8] A. Allerhand and P. von R. Schleyer, *ibid.*, **85**, 866 (1963).

[9] J. S. Thayer and D. P. Strommen, *J. Organometal. Chem.* (Amsterdam), **5**, 383 (1966).

[10] J. S. Thayer, *ibid.*, **9**, P30 (1967).

[11] H. Bürger and U. Goetze, *ibid.*, **10**, 380 (1967).

TABLE II

CHALCOGENATION STUDIES OF R_3MCN

Cyanide	Chalcogenating agent	Temp, °C	Time, hr	Product[a]	Ref
$(CH_3)_3SiCN$	Air	200–250	3	NR[b]	3
	PbO_2	118	0.5	siNCO–siCN	
	MnO_2	118	4	siNCO–siCN	
$(C_6H_{13})_3SiCN$	MnO_2	25	135	Trace siNCO	
	MnO_2	Warming	26	siNCO–siCN	
	MnO_2	Reflux	5	Complete decomposition	
$(C_4H_9)_3GeCN$	Na_2O_2	25	29	NR	
$(CH_3)_3SiCN$	Rhombic S	25	720	NR	
	Rhombic S	118		siNCS	3
	Plastic S	25	120	NR	
	Molten S	[c]	0.1	Trace siNCS	
	S_8–CS_2	46	48	Trace siNCS	
$(C_6H_{13})_3SiCN$	Plastic S	25	48	NR	
	Molten S	[c]	0.1	NR	
	S_8–CS_2	46	2	Trace siNCS	
$(C_6H_5)_3SiCN$	Molten S	150	1	siNCS	5
$(CH_3)_3GeCN$	Molten S	170–185	5	geNCS	6
$(C_4H_9)_3GeCN$	S_8–CS_2	46	48	NR	
$(CH_3)_3SnCN$	Molten S	150–160	1	snNCS	6
$(C_4H_9)_3SnCN$	Molten S	170		snNCS	15
	S_8–CS_2	46	8	snNCS	15
$(CH_3)_3SiCN$	Gray Se	25	168	siNCSe–siCN	
	Gray Se	118	2	siNCSe–siCN	
	Red Se	25	240	Trace siNCSe	
	Vitreous Se	25	240	Trace siNCSe	
$(C_6H_{13})_3SiCN$	Gray Se	25	240	siNCSe–siCN	
	Red Se	25	240	siCN–siNCSe	
	Vitreous Se	25	240	Trace siNCSe	
$(CH_3)_3GeCN$	Gray Se	25	[d]	geNCSe–geCN	
$(C_4H_9)_3GeCN$	Gray Se	25	96	geNCSe–geCN	
$(CH_3)_3SiCN$	Te powder	25	120	NR	
$(C_6H_{13})_3SiCN$	Te powder	25	240	NR	

[a] The symbols si, ge, and sn represent triorganosilyl, -germyl, and -stannyl, respectively; thus siCN is any triorganocyanosilane. The more abundant component of a mixture is listed first. [b] NR means no reaction occurred. [c] The sulfur was melted and quenched by pouring into the liquid cyanide. [d] Six months.

vert organic isocyanides (but not nitriles) to isocyanates,[12] give exchange with I[13]

$$2(CH_3)_3SiCN + HgO \longrightarrow [(CH_3)_3Si]_2O + Hg(CN)_2 \quad (7)$$

Stronger oxidizing agents, such as PbO_2, MnO_2, or Na_2O_2, did not react at room temperature but readily converted cyanides to isocyanates upon heating. Siloxane or germoxane formed as by-products. Vigorous heating of $(C_6H_{13})_3SiCN$ with MnO_2 caused extensive cleavage of the hexyl groups to form an amorphous black sludge. There was no indication of any organometallic fulminate, R_3MCNO,[2,14] even in trace amounts.

Previous reports on the reaction of sulfur with organometallic cyanides[3,5,6,15] have almost always involved heating to temperatures of about 150°; one exception is the conversion of $(C_4H_9)_3SnCN$ to $(C_4H_9)_3SnNCS$ by refluxing in S-containing CS_2.[15] Oxidation of cyanides to isothiocyanates apparently requires fairly vigorous heating; little or no reaction will occur at room temperature. Attempts to form isothiocyanates by quenching molten sulfur in pure liquid cyanide gave only trace quantities of product. No reaction occurred between $(C_4H_9)_3GeCN$ and sulfur in refluxing CS_2, while only minute quantities of cyanosilanes reacted to form isothiocyanatosilanes under the same conditions.

Organic isoselenocyanates may be formed in good yields by gentle heating of isocyanides with selenium.[16,17] The corresponding reaction with cyanosilanes or -germanes goes very readily at room temperature. Infrared spectra indicate that small amounts of the isoselenocyanate are present within 1 min after gray Se is added to the neat cyanide. Heating speeds up the reaction considerably. Selenium has two additional allotropes that are metastable at room temperature: red selenium and vitreous selenium.[18] Comparative studies on the reaction rates of these allotropes with I and $(C_6H_{13})_3SiCN$ could be made by comparing the ratios of the CN and NCSe infrared absorbances over a period of time. The three allotropes gave markedly different rates of reaction. Gray Se reacted rapidly at room temperature, though some cyanide remained even after 10 days. Red Se reacted very much more slowly, giving only slight conversion, while vitreous Se gave only barely detectable traces, even upon long standing.

No reaction occurred when organocyanosilanes were treated with purified tellurium powder, either at room temperature or with mild heating. When unpurified tellurium was used, the cyanide reacted with the traces of selenium present to form isoselenocyanate. Attempts to prepare organic isotellurocyanates by this method also failed,[16] and KNCTe is unstable at room temperature.[19] Apparently the stabilizing power of the organometallic residues is not sufficient to allow the existence of isotellurocyanates at room temperature, but they might very well be stable at lower temperatures.

Other Reactions.—In an effort to study the thermal and chemical stability of the C–Se bond, pyrolysis experiments were carried out. When III was heated at 200° for 1 hr in dry air, selenium was formed and the liquid was converted to a mixture of I, $(CH_3)_3SiNCO$, and starting material. Other organosilyl isoselenocyanates gave similar results. The germanium compounds appeared to decompose at somewhat lower temperatures. Such thermal stability is considerably greater than for KSeCN or the corresponding organic isoselenocyanates,[16,17] a phenomenon observed in the analogous azides and fulminates.[2] Heating III in the presence of $(C_6H_5)_3P$ gives partial deselenation

$$(CH_3)_3SiNCSe + (C_6H_5)_3P \xrightarrow{\Delta} (CH_3)_3SiCN + (C_6H_5)_3PSe \quad (8)$$

This reaction is also known for KSeCN.[20] However, the greater thermal stability of III requires that the mixture be heated for several hours, and reaction is not complete. $(C_6H_5)_3PSe$ may be identified by the strong P=Se band at 562 cm^{-1}.[20]

Bromine will react with I in the manner described

---

(12) A. Gautier, *Ann. Chim.*, **17**, 229 (1869).
(13) C. Eaborn, *J. Chem. Soc.*, 2755 (1949).
(14) W. Beck and E. Schuierer, *Chem. Ber.*, **97**, 3517 (1964).
(15) R. A. Cummins and P. Dunn, *Australian J. Chem.*, **17**, 411 (1964).
(16) W. J. Franklin and R. L. Werner, *Tetrahedron Letters*, 3003 (1965).
(17) K. A. Jensen, G. Felbert, C. T. Pedersen, and U. Svanholm, *Acta Chem. Scand.*, **20**, 278 (1966).
(18) K. W. Bagnall, "The Chemistry of Selenium, Tellurium, and Polonium," Elsevier Publishing Co., Amsterdam, 1966, pp 33–38.
(19) N. N. Greenwood, R. Little, and M. J. Sprague, *J. Chem. Soc.*, 1292 (1964).
(20) P. Nicpon and D. W. Meek, *Inorg. Chem.*, **5**, 1297 (1966).

by McBride and Beachell.[3] The solution remains colorless until excess Br_2 is added, whereupon it turns brown. A mixture of I and extra Br_2 was treated with cyclohexene, whereupon the color disappeared and small amounts of solid settled out. Part of the cyclohexene solution was shaken with aqueous $AgNO_3$, giving a precipitate of yellow AgBr. An infrared spectrum of the cyclohexene solution showed no cyanide band at 2190 cm^{-1}. The solid was separated and dried. It gave a weak band at 2185 cm^{-1} (BrCN has an absorption at 2194 cm^{-1})[21] and dissolved in water to give a solution that, upon acidification, would oxidize iodide ion to free iodine. These data would suggest that eq 4 should better be written

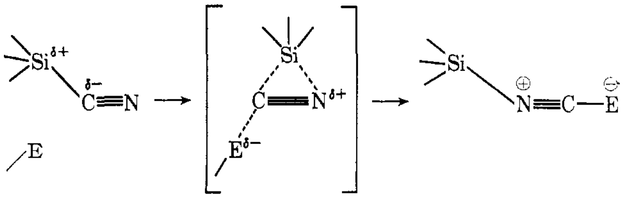
$$(CH_3)_3SiCN + Br_2 \longrightarrow (CH_3)_3SiBr + BrCN \qquad (9)$$

Presumably a similar reaction occurs for chlorine.

Discussion

The "normal–iso" equilibrium was originally proposed by Bither, *et al.*,[5] to explain the infrared spectra and chemical reactions of organocyanosilanes. Presence of an iso species was postulated by analogy to organic chemistry, where isocyanides, but not nitriles, may be oxidized to the corresponding isochalcocyanides. Since all presently known chalcocyano derivatives of silicon and germanium have been shown to be bonded exclusively through nitrogen,[2,22] such a postulation was reasonable. Recent research, however, has shown that there is a major difference between organic nitriles or isocyanides and the silicon or germanium analogs: the properties of the bond between the cyanide group and the rest of the molecule. C–CN or C–NC bonds are covalent and rather unreactive, while Si–CN and Ge–CN linkages are polar and quite labile. Cyanide groups bonded to Si or Ge have been shown to be very similar to Cl in lability toward exchange.[23] In any mechanism that is considered for the reaction of organosilanes or -germanes, this lability must be taken into consideration.

The various chalcogenation reactions apparently require an activation energy, usually in the form of heat. Even the cyanide–gray selenium reaction, which proceeds at an appreciable rate at room temperature, accelerates markedly upon heating. From what is known about other reactions of sulfur and selenium,[18,24] the most reasonable explanation for this would be cleavage of a sulfur–sulfur or selenium–selenium bond, followed by reaction of the electrophilic chalcogen intermediate and the nucleophilic cyanide. Available evidence is insufficient to indicate the nature of the cyanide species; it is quite possible that there is isocyanide present, particularly at higher temperatures. However, *such a species is not required to explain the reaction.* The lability of the Si–CN (or Ge–CN) bond and the ease with which organosilyl groups undergo migration[25] suggest that chalcogenation might proceed through an intermediate (IV) in which the negatively polarized cyanide carbon reacts with an electrophilic chalcogen species, followed by migration of the organosilyl or germyl group from carbon to nitrogen



IV, E = chalcogen intermediate

Such an intermediate has been previously suggested by Ebsworth.[26] Organic isocyanides isomerize to the more stable nitriles upon heating *via* unimolecular migration of the organic group from nitrogen to carbon.[27] Thus the proposed mechanism is not unreasonable, and may be extended to the other reactions shown in eq 2, 3, and 6. The reaction with bromine (and with other halogens) is much more likely to proceed *via* bond cleavage than by the addition reaction suggested by McBride and Beachell.[3] The reaction of cyanides with metal carbonyls, which also requires elevated temperatures,[7] can be explained by assuming loss of one CO molecule, giving an electrophilic metal carbonyl residue which reacts with the cyanide in a fashion analogous to that of the chalcogens. Reduction under mild conditions (such as in eq 3) proceeds *via* Si–CN bond cleavage

$$(CH_3)_3SiCN \xrightarrow{[H]} (CH_3)_3SiH + HCN \qquad (10)$$

Under more extreme conditions reported by McBride and Beachell,[3] the HCN initially produced would probably be reduced to CH_4 and NH_3;[28] the ammonia would then react with $(CH_3)_3SiH$ to form hexamethyldisilazane and hydrogen.

More research is needed to establish details of this reaction and to verify or disprove the proposed mechanism, which does have the advantage of being consistent with presently known organosilicon and organogermanium chemistry and does not require the postulation of a species (*i.e.*, the isocyano form) for which there is no single piece of unequivocal evidence.

Experimental Section

Reagents and Purification.—$(C_4H_9)_3GeI$ and $(CH_3)_3GeCl$ were purchased from Alfa Inorganics, as were KSeCN, $(C_6H_5)_3P$, Se powder, and Te powder. AgCN, $(CH_3)_3SiBr$, $(C_2H_5)_3SiBr$, and $(C_6H_{13})_3SiBr$ were obtained from K & K Laboratories, while $(C_2H_5)_3GeCl$ was obtained from Metallomer Laboratories. Organometallic reagents were generally used without further purification, as were AgCN and gray Se. KSeCN was purified by precipitation from acetonitrile upon addition of ether. Red

---

[21] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, New York, N. Y., 1963, p 80.

[22] It has recently been suggested that small quantities of H_3GeOCN are formed, in the reaction of H_3GeBr with AgOCN, along with the major product, H_3GeNCO: J. E. Griffiths, *J. Chem. Phys.*, **48**, 278 (1968).

[23] K. Moedritzer, *Advan. Organometal. Chem.*, **6**, 224 (1968).

[24] W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 59–64.

[25] R. West, M. Ishikawa, and R. E. Bailey, *J. Am. Chem. Soc.*, **89**, 4068, 4072 (1967).

[26] E. A. B. Ebsworth, "Volatile Silicon Compounds," Pergamon Press Ltd., London, 1963, pp 148–155.

[27] J. Casanova, N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3473 (1966).

[28] V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, pp 151–153.

Se was prepared by precipitation from an acidified solution of KSeCN. Vitreous Se was prepared by pouring molten gray Se into water. Te 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.[10] 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 C	% calcd H	% found C	% found H
$(C_6H_{13})_3SiCN$	225 (125)	73.7	12.7	74.4	12.8
$(C_4H_9)_3GeCN$	292–294	57.8	10.1	58.2	10.3
$(C_6H_{13})_3SiNCSe$	307–308 (250)	58.7	10.1	58.8	10.4
$(CH_3)_3GeNCSe$[a]	118–119 (232)	21.6	4.1	22.1	4.5
$(C_2H_5)_3GeNCSe$	175–176 (240)	31.8	5.7	32.1	5.9
$(C_4H_9)_3GeNCSe$	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 ±5 cm^{-1}, using polystyrene for calibration.

Acknowledgments.—It is a pleasure to acknowledge helpful discussions with Drs. Joyce Corey and Robert West.

CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY,
UNIVERSITY OF ADELAIDE, ADELAIDE, SOUTH AUSTRALIA

The Question of Isomerism in Rhenium(IV) Chloride

BY I. R. ANDERSON AND J. C. SHELDON

Received July 8, 1968

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 structure[1] $(Re_3Cl_9)Cl_3$, similar to that established for $Cs_3Re_3Cl_{12}$, and, secondly, a dimeric form established by X-ray crystallography[2] and containing Re_2Cl_9 groups, similar to the chloro groups found in $K_3W_2Cl_9$. 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 disproportion 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

---

(1) R. Colton and R. L. Martin, *Nature*, **205**, 239 (1965).

(2) M. J. Bennett, F. A. Cotton, B. M. Foxman, and P. F. Stokely, *J. Am. Chem. Soc.*, **89**, 2759 (1967).

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