

N-Halogenoimido Complexes of Transition Metals

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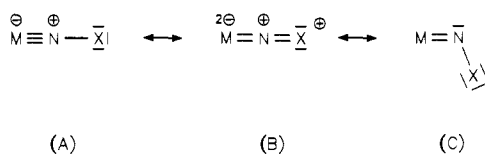
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I. Introduction

N-Halogenoimido complexes of the transition metals are compounds with the structural element MNX (X = halogen), its characteristics are a short metal–nitrogen bond, a relatively short nitrogen–halogen bond, and a large bond angle MNX. These characteristics can be represented by the formulations:



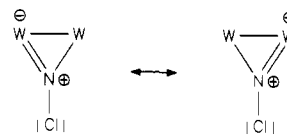
Examples are known for the elements vanadium, molybdenum, tungsten, rhenium, and osmium. Because of its π -donor character the $[\text{NX}]^{2-}$ ligand stabilizes the high oxidation states of these metals. The N-halogenoimido complexes are special cases of the numerous known organoimido complexes with the building unit MNR.¹ However, except for the SiMe_3 -substituted derivatives, these complexes can only be described with the forms A and C. Chemically the N-halogenoimido complexes differ from the organoimido complexes especially by the reactivity of the nitrogen–halogen bond, and therefore they represent a synthetic potential.

The $[\text{NX}]^{2-}$ ligand is isolobal with the oxo group O^{2-} as well as the ligands $[\text{NSR}]^{2-}$ ² and $[\text{NSEr}]^{2-}$ ³ (R =

Cl, organic residue). Close chemical and structural relations as well as similarities of the bonding properties exist especially between the chlorothionitreno ligand $[\text{NSCl}]^{2-}$ and the chlorimido ligand $[\text{NCl}]^{2-}$. This is discernible in the following formulas:



N-Halogenoimido groups usually act as terminal ligands. Only one example of a bridging group is known; a μ_2 -NCl ligand bridges a W–W bond of a dinuclear tungsten complex:⁴



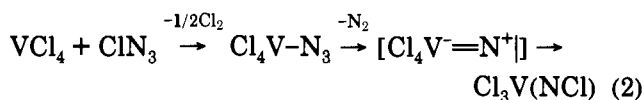
II. Synthetic Routes

A. Vanadium

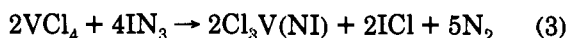
The first example of the synthesis of a N-halogenoimido compound of a transition metal was that of $\text{Cl}_3\text{V}(\text{NCl})$, which yields from the reaction of chlorine azide with vanadium tetrachloride:⁵



$\text{Cl}_3\text{V}(\text{NCl})$ forms orange crystals, which are very sensitive to humidity and, like V_2O_5 , are weakly paramagnetic. Reaction with water affords chlorine amine, and therefore it occurs explosively. For the mechanism of eq 1 a nitrene intermediate was postulated, which is formed from the isolable azide Cl_4VN_3 and is stabilized by the migration of a Cl^- to the nitrene nitrogen (eq 2).



The subsequent synthesis of the corresponding N-I compound from vanadium tetrachloride and iodine azide⁶ showed that the preservation of the N–I bond of the iodine azide can be assumed. Therefore in this case another mechanism can also be discussed. In this



mechanism the formation of an intermediate donor–acceptor complex $\text{Cl}_3\text{V} \leftarrow \text{N}(\text{N}_2)\text{I}$ is postulated, in which



Kurt Dehnicke is Professor of Inorganic Chemistry at the University of Marburg, Germany. Born in Cologne in 1931, he studied chemistry at the University of Leipzig from 1950 to 1955, when he graduated with a Diplom. He did his doctoral dissertation with J. Goubeau on boron trifluoride adducts on amino acids at the University of Stuttgart and received the Dr. rer. nat. from this institution in 1957. In 1965 he received his Habilitation with a work on the chemistry of compounds with electropositive chlorine. In 1967 he was appointed Full Professor at the Philipps University of Marburg. In 1989 he was awarded the Wilhelm Klemm Preis of the Gesellschaft Deutscher Chemiker (German Chemical Society). His main fields of research are transition metal complexes of metal multiply bonded to nitrogen, alkyne complexes of transition metals in high oxidation states, and polyselenido and polytellurido complexes.



Joachim Strähle, born in Dresden, Germany, in 1937, studied chemistry at the University of Stuttgart and graduated with a thesis on metal azido and nitrido halides in the group of K. Dehnicke at the Institute of Inorganic Chemistry of this university in 1965. From 1965 to 1968 he worked as a post-doc with G. Brauer at the University of Freiburg and thereafter with H. Bärnighausen at the University of Karlsruhe for five years. In Karlsruhe he was introduced to the method of crystal structure determination. In 1973 he finished his habilitation with a thesis on syntheses and crystal structures of transition metal–nitrogen compounds. In the same year he was offered chairs at the Universities of Hannover and Tübingen. He took that at Tübingen, where he became full professor in 1976. In 1987 he refused a chair for Inorganic Chemistry and the University of Stuttgart. He is active in the synthesis and crystal structure determination of coordination compounds with nitrogen donor ligands, metal nitride fluorides, and transition metal–gold clusters.

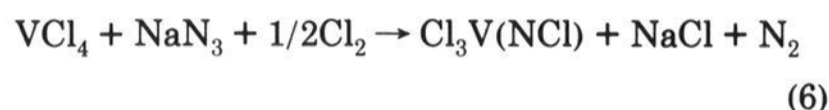
the iodine azide is bound via its α -N atom and which under the influence of a second mole of iodine azide subsequently decomposes with separation of N_2 . An indirect support for this mechanism is provided by the observation that the thermolysis of the tetrachloride monoazides of niobium and tantalum, $[MCl_4(N_3)]_2$, which form dinuclear complexes with azido groups bridging via the α -N atoms, does not result in the

formation of a $M\equiv N-Cl$ moiety.⁷

$Cl_3V(NI)$ synthesized according to eq 3 can easily be transformed with bromine or chlorine to the corresponding NBr (eq 4) or NCl (eq 5) compounds:⁶



Since iodine azide can be handled more easily than chlorine azide⁸ the synthesis of $Cl_3V(NCl)$ via $Cl_3V(NI)$ is preferable. Considering the necessary safety regulations $Cl_3V(NCl)$ can also be obtained by the direct reaction of vanadium tetrachloride and chlorine with sodium azide at 80 °C (eq 6):⁹



For the synthesis of small amounts of $Cl_3V(NCl)$, the reaction of vanadium nitride with chlorine at 120–140 °C is also possible (eq 7):¹⁰



This synthesis has been used for the generation of single crystals via the gas phase.

Especially interesting is the recently reported synthesis of $Cl_3V(NCl)$ by slow reaction of $[N-(trimethylsilyl)imide]vanadium trichloride$ with excess chlorine in dichloromethane (eq 8):¹¹



In the educt the Cl_3VN moiety is already preformed. The relatively long N–Si bond of the monomeric $Cl_3V(NSiMe_3)$ ¹² (Figure 1) assists this reaction. The syn-

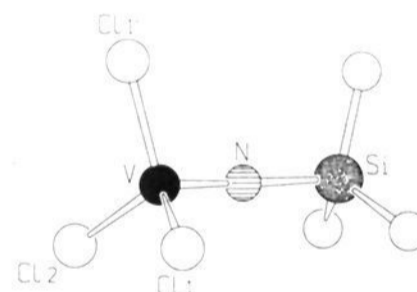
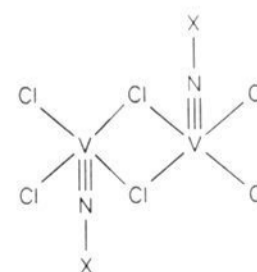


Figure 1. Structure of $Cl_3V(NSiMe_3)$.

thetic route according to reaction 8 could gain importance for the synthesis of N-halogenoimido complexes of other metals. It also shows that the $V\equiv NSiMe_3$ group parallels the $V\equiv NCl$ group as the $SiMe_3$ residue exhibits, like the N-bound Cl atom, a partial positive character.

$Cl_3V(NCl)$ and $Cl_3V(NI)$ form dimeric structures in the solid state (section III) with the NX ligand in axial position of the square-pyramidal coordination:^{13,14}

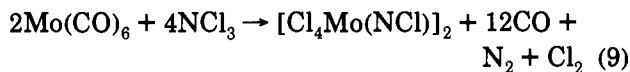


According to spectroscopic findings $Cl_3V(NBr)$ has a

corresponding structure.⁶ In the gas-phase $\text{Cl}_3\text{V}(\text{NCl})$ is monomeric.¹⁵

B. Molybdenum

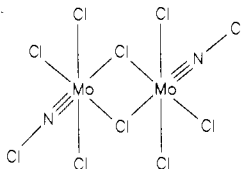
While molybdenum hexacarbonyl reacts with nitrogen trichloride in a molar ratio of 1:1 in tetrachloromethane as solvent to yield MoNCl_3 ¹⁶ an excess of nitrogen trichloride affords $\text{Cl}_4\text{Mo}(\text{NCl})$ at 0 °C¹⁷ (eq 9). The compound is a moisture-sensitive, diamagnetic,



red crystalline powder, sparingly soluble in tetrachloromethane, decomposing to MoNCl_3 via elimination of chlorine at 100 °C¹⁷ (eq 10).

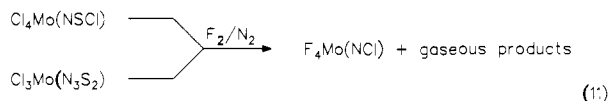


According to the IR spectrum $[\text{Cl}_4\text{Mo}(\text{NCl})]_2$ is dimerized by chlorine bridges with the *N*-chloroimido group in equatorial position as in the case of all the other imido complexes of this type.



The molybdenum complexes $[\text{MoCl}_4(\text{NSCl})]_2$ ¹⁸ and $[\text{MoCl}_4(\text{O})]_2$ ¹⁹ exhibit entirely analogous structures, as well. The ligand groups $[\text{NSCl}]^{2-}$ and $[\text{O}]^{2-}$, which are isolobal with $[\text{NCl}]^{2-}$, cause strongly asymmetric chlorine bridges, owing to their trans influence.

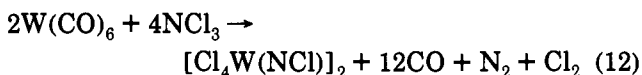
The corresponding fluoro derivative $[\text{F}_4\text{Mo}(\text{NCl})]_x$, with an unknown degree of association, can be obtained from the chlorothionitreno complex¹⁸ as well as from the cyclothiazeno complex²⁰ of molybdenum by treatment with a diluted stream of fluorine gas at 20 °C²¹ (eq 11). The nitrogen bound chlorine atom is not



substituted even with excess of fluorine. $\text{F}_4\text{Mo}(\text{NCl})$ is a pale yellow, very moisture-sensitive crystalline powder, soluble only in solvating solvents. It is stable up to 200 °C.

C. Tungsten

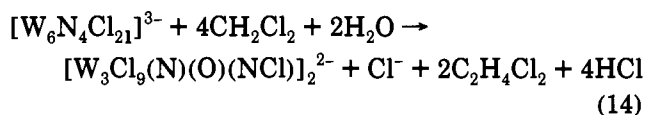
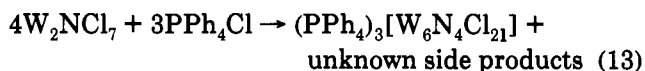
The synthesis of the corresponding tungsten compound turns out to be analogous to that described for $\text{Cl}_4\text{Mo}(\text{NCl})$. However, it exhibits a much higher thermal stability. The completion of the synthesis reaction even requires treatment in boiling tetrachloromethane.²² The decomposition of the brownish-red,



moisture-sensitive crystalline powder of $[\text{Cl}_4\text{W}(\text{NCl})]_2$ to yield WNCl_3 occurs only at 200 °C. Because of the

high stability of the tungsten complex a relatively large number of derivatives of it are known and structurally characterized (see sections III and IV).

The only known complex in which the $[\text{NCl}]^{2-}$ ligand functions as a μ_2 bridging ligand is $[\text{W}_3\text{Cl}_9(\text{N})(\text{O})(\mu_2\text{-NCl})]_2^{2-}$, which is formed by the reaction of PPh_4Cl with W_2NCl_7 in dichloromethane in the presence of traces of water. The not completely clarified route of formation of this compound occurs presumably upon participation of the solvent:⁴



According to the crystal structure analysis⁴ the $[\text{NCl}]^{2-}$ ligand bridges a W–W axis in the centrosymmetrical $[\text{W}_3\text{Cl}_9(\text{N})(\text{O})(\mu_2\text{-NCl})]_2^{2-}$ ion (Figure 2). The two W–N

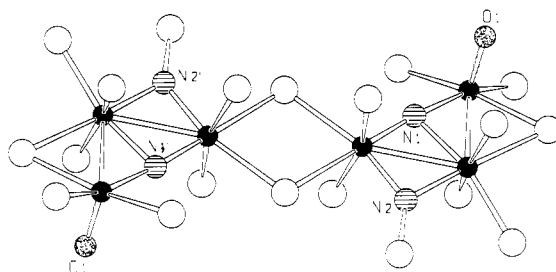
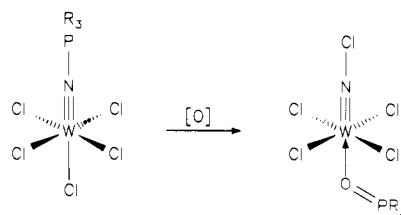


Figure 2. Structure of the trinuclear tungsten complex $[\text{W}_3\text{Cl}_9(\text{N})(\text{O})(\mu_2\text{-NCl})]_2^{2-}$ with a bridging $[\text{NCl}]^{2-}$ ligand.

bond lengths of 196 and 189 pm are somewhat shorter than the expected value for a single bond. At the same time the chlorine atom of the *N*-chloroimido group deviates from the W_2N plane by 15 pm, indicating an intermediate form between sp^2 and sp^3 hybridization at the N atom. In accordance with this observation the N–Cl distance of 173 pm is relatively long. It is longer than the distance in complexes with a linear $\text{M}\equiv\text{NCl}$ arrangement and only a little shorter than in NCl_3 (175 pm²³) with pyramidal structure.

The reaction of the phosphoraneiminato complex $\text{W}(\text{NPMe}_3)\text{Cl}_5$ ²⁴ with a large excess of chlorine, which presumably contained traces of HOCl and/or Cl_2O ,²⁴ results in the interesting formation of donor–acceptor complexes of tungsten with a NCl group.



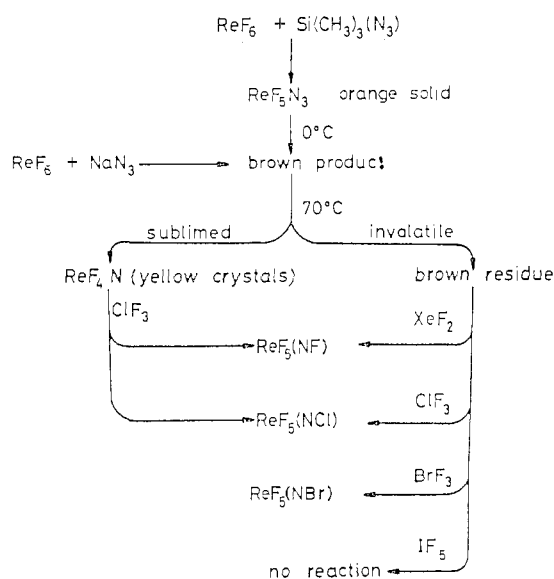
The reaction proceeds better if pyridine *N*-oxide is used as oxidizing agent. In this way $\text{W}(\text{NPMe}_3)\text{Cl}_5$ ²⁴ and $\text{W}(\text{NPPH}_3)\text{Cl}_5$ ^{24,25} can be transformed into the donor–acceptor complexes $[\text{W}(\text{NCl})\text{Cl}_4(\text{OPR}_3)]$ ($\text{R} = \text{Me}, \text{Ph}$)²⁴ with good yields at room temperature in dichloromethane. The structure of these complexes is discussed in section III. The synthesis according to the

above reaction is obviously associated with the migration of a chloro ligand from the tungsten to the nitrogen atom.

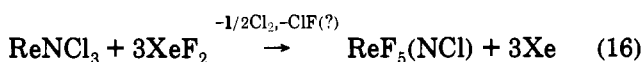
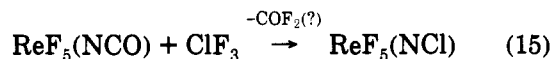
D. Rhenium

The first examples of *N*-halogenoimido complexes of rhenium of the type $F_4Re(NX)$ ($X = F, Cl, Br$) have been synthesized and characterized by R. D. Peacock et al.²⁶⁻²⁸ The authors reacted rhenium hexafluoride with trimethylsilyl azide at $-50^\circ C$ in genetron (1,1,2-trichlorotrifluoroethane), which primarily yielded orange colored ReF_5N_3 . The latter decomposes at $0^\circ C$ to a brownish product, which presumably is a mixture of $ReNF_3$ and ReF_5N_3 , from which at $70^\circ C$ a small amount of $ReNF_4$ can be sublimed as yellow crystals. Subsequent reaction with XeF_2 , ClF_3 , as well as BrF_3 , affords the *N*-halogenoimido derivatives $ReF_5(NF)$, $ReF_5(NCl)$, and $ReF_5(NBr)$ (see Scheme I).²⁸

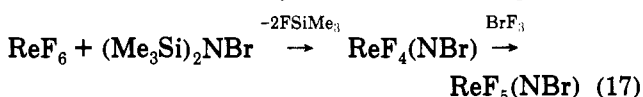
Scheme I



$ReF_5(NCl)$ is also formed by the reaction of chlorine trifluoride with $ReF_5(NCO)$ (eq 15), which itself yields from ReF_6 and Me_3SiNCO .²⁸ Another synthesis for $ReF_5(NCl)$ is the reaction of $ReNCl_3$ ²⁹ with xenon difluoride (eq 16).²⁸



Finally, the $[NBr]^{2-}$ ligand can also be introduced with the aid of bromine bis(trimethylsilyl)amine. The reaction with ReF_6 presumably affords primarily $ReF_4(NBr)$, which subsequently can be oxidized with bromine trifluoride to yield $ReF_5(NBr)$ (eq 17):²⁸



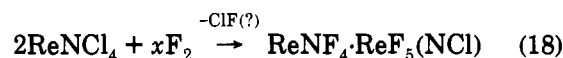
The *N*-halogenoimido complexes $ReF_5(NX)$ of rhenium form colorless ($X = F$) or dark red ($X = Cl, Br$), moisture-sensitive, and, in vacuum, easily sublimable crystals, which have monomeric molecular structures.^{26,28}

Table I. Experimental Distances and Bond Angles of *N*-Halogenoimido Complexes^a

complex	M-N	N-X	M-N-X	ref(s)
$[VCl_3(NCl)]_2$	164.2(9)	158.8(9)	175.2(3)	13
$VCl_3(NCl)$ (gas)	165.0(2)	159.7(3)	170(1)	15
$VCl_3(NCl)(SbCl_5)_2$	165.5(3)	160.3(3)	179.5(2)	41
$VCl_3(NCl)(bipy)$	168.8(6)	158.5(6)	175.0(4)	41
$[VCl_3(NI)]_2$	165(2)	193(2)	163(1)	14
$[(MeCN)MoF_4(NCl)]$	171.5(9)	159(1)	175.8(6)	21
	172.6(7)	161.7(9)	177.7(7)	
$[Na(15-crown-5)][MoF_5(NCl)]$	172.9(3)	161.8(3)	175.8(2)	47
$[Na(15-crown-5)][WF_5(NCl)]$	173.3(6)	162.2(7)	176.1(5)	49
$[K(18-crown-6)][WF_5(NCl)]$	172.4(7)	162.7(7)	170.7(5)	50
$[WCl_5(NCl)]^-$	168.7(8)	160.2(8)	174.9(7)	51
$[WCl_4(N_3)(NCl)]^-$	177(1)	159(1)	170.0(6)	73
$[Cl_5W(NCl)Cl(CIN)WCl_5]^{3-}$	196(5)	141(5)	180.0	51
	153(3)	183(4)	180.0	
$[(MeCN)WCl_4(NCl)]$	172(1)	161(1)	176(1)	22
$[(Me_3PO)WCl_4(NCl)]$	173.7(6)	160.8(6)	167.0(4)	24
$[(Ph_3PO)WCl_4(NCl)]$	173.2(5)	160.6(5)	175.8(4)	24
	173.1(6)	160.8(5)	172.2(4)	
$[W_3Cl_9(N)(O)(\mu-NCl)]_2^{2-}$	196(3)	173(3)	131(2)	4
	189(3)		136(2)	
$ReF_5(NF)$	172(1)	126(1)	178(1)	26,28
$ReF_5(NCl)$	173(2)	156(2)	177(1)	26,28
$ReNF_4 \cdot ReF_5(NCl)$	164(2)	160(3)	177(2)	31

^a Values are in picometer and degree.

The reaction of $ReNCl_4$, which can easily be obtained from rhenium pentachloride and nitrogen trichloride,³⁰ with excess fluorine gas without a solvent affords as main product the ruby-red, mixed nitride fluoride-*N*-chloroimido complex $ReNF_4 \cdot ReF_5(NCl)$, the components of which are linked together by a linear fluorine bridge.³¹



E. Osmium

The only known halogenoimido complex of osmium is $OsF_5(NCl)$. It was characterized by its IR and mass spectrum. Surprisingly it forms colorless crystals. The synthesis proceeds in a manner analogous to eq 15 by the reaction of osmium hexafluoride with Me_3SiNCO and treatment of the intermediate $OsF_5(NCO)$ or $OsF_4(NCO)$ with chlorine trifluoride (caution!) in genetron as solvent. The compound is stable up to its melting point, $170-174^\circ C$.³²

III. Structures of the Basic Types

Structure determinations of the basic types of the *N*-halogenoimido complexes are known only of a few examples. In these the building unit MNX is characterized by very short MN distances and relatively short NX bond lengths as well as by large MNX bond angles (Table I). These are usually close to 180° . In contrast, complexes of the main group elements have much smaller ENX bond angles like 118° in $SF_4(NF)$.³³

Both vanadium compounds $VCl_3(NCl)$ and $VCl_3(NI)$ crystallize isotypically in the space group $P\bar{1}$ forming centrosymmetrical dimers, which are generated by slightly asymmetric VCl_2V bridges (Figures 3 and 4).^{13,14} The $(NX)_2^{2-}$ ligands occupy axial positions in the distorted square-pyramidal complexes. While the $VNCl$ group is almost linear with a bond angle of 175.2° , the bond angle VNI amounts only to 163° . Nevertheless, in both complexes the N atoms can be characterized

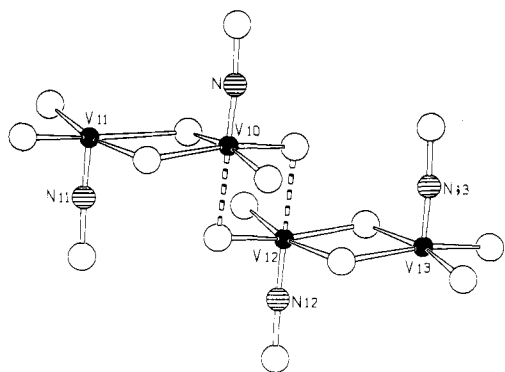


Figure 3. Structure of $[\text{Cl}_3\text{V}(\text{NCl})]_2$ showing the (5 + 1) coordination.

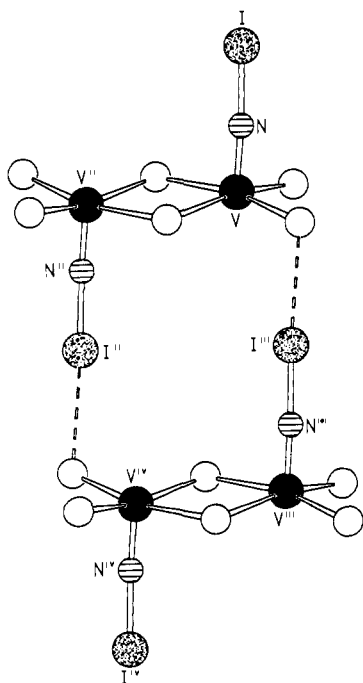


Figure 4. Structure of $[\text{Cl}_3\text{V}(\text{NI})]_2$ showing the $\text{V}\equiv\text{N}-\text{I}\cdots\text{Cl}$ interaction.

as sp hybridized. This is also shown by the short nitrogen-halogen distances of 158.8 pm (NCl) and 193 pm (NI). The latter is the shortest N-I distance measured so far. Within the experimental error both VN distances are equal, at 164 pm they correspond to the expected value for a triple bond.³⁴ VN distances of 157–160 pm are also observed in nitrido complexes of vanadium and are interpreted as triple bonds.^{35,36} As a consequence of the strong π -bond character a strong trans influence results, which allows only a weak bond for a sixth ligand. In the solid-state structures of $\text{VCl}_3(\text{NCl})$ and $\text{VCl}_3(\text{NI})$ this situation is expressed by the packing of the dimers, in which one of the chlorine atoms of the neighboring molecule forms a contact distance of 260¹³ and 263 pm,¹⁴ respectively, such that a (5 + 1) coordination can be assumed (Figure 3). The π bond of the VNX group also causes a repulsion of the cis-arranged Cl atoms, and the vanadium atom therefore does not form a common plane with them.

Finally, the noticeably shorter distances between the N-bound halogen atoms and an equatorial chloro ligand of a neighboring complex deserve attention. In $\text{VCl}_3(\text{NCl})$ with $\text{Cl}\cdots\text{Cl}(1) = 325$ pm, they are markedly shorter than the van der Waals distance of 362 pm;¹³

in $\text{VCl}_3(\text{NI})$ (Figure 4), however, with $\text{I}\cdots\text{Cl}(1) = 307$ pm, it is considerably shorter than the van der Waals contact of 410 pm.¹⁴ These contacts express the partial positive charge of the N-bound halogen atoms.

According to the structure analysis with electron diffraction $\text{VCl}_3(\text{NCl})$ forms monomeric molecules with symmetry C_s in the gas phase.¹⁵ Remarkable is the preservation of the characteristic bonding parameters of the VNX group, which exhibit almost unchanged distances VN (165 pm) and NCl (161 pm) and an only slightly reduced bond angle of 170°.

Crystal structure analyses of the complexes $\text{ReF}_5(\text{NF})$ (Figure 5) and $\text{ReF}_5(\text{NCl})$ revealed monomeric

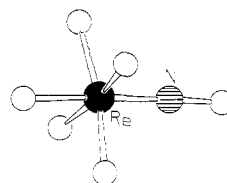


Figure 5. Structure of $\text{ReF}_5(\text{NF})$.

complexes.^{26,28} In both compounds the group ReNX is nearly linear with bond angles of 177.5° ($X = \text{F}$) and 176.7° ($X = \text{Cl}$), so that the molecular symmetry C_{4v} is fairly well achieved. The fluorine atom in trans position forms a slightly longer Re-F bond than the equatorial F atoms. The difference amounts to 3.2 pm in $\text{ReF}_5(\text{NF})$ and 5 pm in $\text{ReF}_5(\text{NCl})$. In spite of the short Re-N bond of 172 pm the trans influence of the $[\text{NX}]^2-$ ligand is only weakly developed, which is also expressed in the NReF_{eq} bond angles being 94° in average.^{26,28} The small trans influence is possibly connected with the short distances NF (126 pm) and NCl (156 pm), since in the imido complex of tungsten $[\text{WCl}_5(\text{NC}_2\text{Cl}_5)]^-$ with analogous structure, the N-C distance of which corresponds to a normal single bond, a markedly larger trans influence is observed while the WN distance is 168.4 pm. The difference in the bond lengths $\text{WCl}_{trans}-\text{WCl}_{cis}$ amounts to 10 pm.³⁷

IV. Chemical Reactions

A. Reactions with Lewis Acids

The molecular complex $\text{ReNF}_4\cdot\text{ReF}_5(\text{NCl})$, being formed by the reaction of ReNCl_4 with fluorine, can be interpreted as the reaction product of $\text{ReF}_5(\text{NCl})$ with the Lewis acid ReNF_4 (eq 18). According to the crystal structure analysis³¹ (Figure 6) the two components are

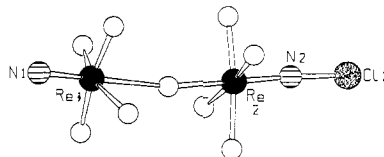
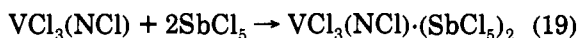


Figure 6. Structure of $\text{ReNF}_4\cdot\text{ReF}_5(\text{NCl})$.

linked together by a largely linear (bond angle $\text{ReRe} = 168^\circ$) and strongly asymmetric fluoro bridge. Of the two Re-F bonds the shorter one (188 pm) is located in trans position to the N-chloroimido group, whereas the longer bond (228 pm) is trans to the nitrido ligand. This example therefore supplies a direct possibility of comparing the extent of the trans influence of the nitrido and imido ligand. It confirms the experience that the terminally bound nitrido ligand performs the strongest

trans influence of all known ligands.^{38,39} The structure of the $\text{ReF}_5(\text{NCl})$ component in $\text{ReNF}_4 \cdot \text{ReF}_5(\text{NCl})$ remains largely unchanged in comparison with $\text{ReF}_5(\text{NCl})$.^{26,28} Only the ReN bond length is shortened from 172 to 164 pm.³¹ With that it has approximately the same length as the ReN bond of 169 pm in the imido complex $[(\text{POCl}_3)\text{ReCl}_4(\text{NC}_2\text{Cl}_5)]$.⁴⁰ The ReNF_4 unit in $\text{ReNF}_4 \cdot \text{ReF}_5(\text{NCl})$ forms a square pyramid with the Re atom being shifted from the basic plane in direction of the nitrido ligand.³¹ The short ReN distance of 159 pm corresponds to a triple bond as it was also found with 158 pm in ReNCl_4 .³⁰

A second example of a reaction of a Lewis acid with a *N*-halogenoimido complex investigated in detail is the reaction of $\text{VCl}_3(\text{NCl})$ with antimony pentachloride⁴¹ (eq 19). The compound crystallizes upon cooling



of the deep red, saturated solution in antimony pentachloride to form orange, extremely moisture-sensitive crystals being stable only up to 30 °C. According to the crystal structure analysis,⁴¹ the complex exhibits a molecular structure in which the $\text{VCl}_3(\text{NCl})$ molecule is connected with two SbCl_5 molecules via asymmetric chloro bridges VCl_2Sb (Figure 7). In that way both

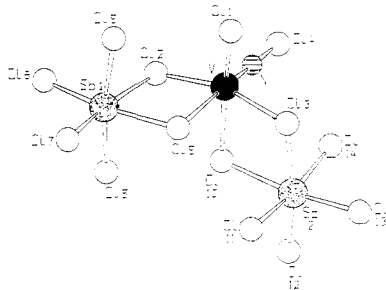


Figure 7. Structure of $\text{Cl}_3\text{V}(\text{NCl})(\text{SbCl}_5)_2$.

metal atoms achieve the coordination number six in the form of distorted octahedra. The VNCl group does not undergo a noticeable change by this complexation. Because of the bridging function of the chlorine atoms $\text{Cl}(2,3,9,10)$ the $\text{V}-\text{Cl}$ bonds are markedly weakened in comparison with free $\text{VCl}_3(\text{NCl})$. The distance $\text{V}-\text{Cl}(9)$ of 259.7 pm is particularly large; therefore, one can speak of a (5 + 1) coordination for the vanadium atom. The reason for this is on the one hand the trans position to the $\text{V}=\text{NCl}$ group and on the other hand the bridging function of the chlorine atom $\text{Cl}(9)$. The vanadium atom itself in $\text{VCl}_3(\text{NCl})$ achieves a comparable coordination by intermolecular interactions in the lattice (Figure 3). To a large extent it obviously does not make any difference to the vanadium atom if its coordination is completed by neighboring SbCl_5 or $\text{VCl}_3(\text{NCl})$ molecules. The SbCl_5 octahedra are also distorted because of the formation of the chlorine bridges, whereby the Sb atoms tend to form as large distances to the vanadium atom as possible.

B. Reactions with Lewis Bases

Reactions of the *N*-halogenoimido complexes with Lewis bases can only be expected for compounds with metal atoms that have achieved a complete coordination by association via halogen bridges, which can be cleaved

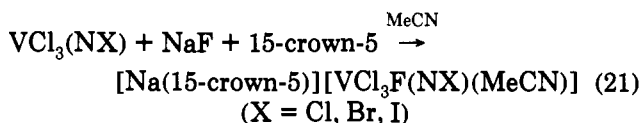
by an attack of Lewis bases. This applies for the complexes of vanadium, molybdenum, and tungsten, whereas the monomeric compounds of rhenium, $\text{ReF}_5(\text{NX})$, do not exhibit Lewis acidic properties because of the coordination number six at the rhenium atom.

Thus $\text{VCl}_3(\text{NCl})$, which is dimerized by chlorine bridges, reacts with tetraphenylarsonium chloride in dichloromethane under formation of the $[\text{VCl}_4(\text{NCl})]^-$ ion with tetragonal symmetry C_{4v} (eq 20).⁴² According

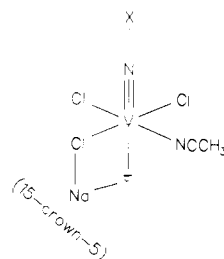


to the IR spectrum and to a comparison of its X-ray powder diagram with that of $\text{AsPh}_4[\text{VCl}_4\text{O}]$, whose crystal structure was determined using single crystals, the complex crystallizes in the space group $P4/n$ with the $[\text{NCl}]^{2-}$ ligand in apical position.⁴²

The *N*-halogenoimido complexes of vanadium react with sodium fluoride in acetonitrile as solvent in the presence of 15-crown-5 to yield anionic monofluoro complexes, which according to the IR spectra form ion pairs (eq 21).⁴³ In these complexes the vanadium atom



exhibits a distorted octahedral coordination:



A distorted octahedral coordination of the vanadium atom is also observed in the crystallographically characterized bipyridine complex $[\text{VCl}_3(\text{NCl})(\text{bipy})]$ ⁴¹ (Figure 8). The N atoms of the bipyridyl ligand occupy one

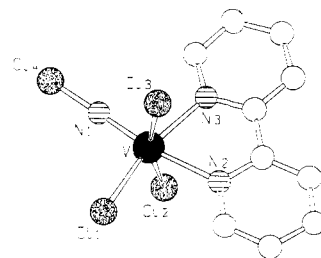


Figure 8. Structure of $\text{Cl}_3\text{V}(\text{NCl})(\text{bipy})$.

position trans and one cis to the $[\text{NCl}]^{2-}$ ligand, the $\text{V}-\text{N}$ bond in trans arrangement with 218.5 pm being slightly longer than the one in cis position with 213.0 pm. The bond lengths and the bond angle of the $\text{V}=\text{NCl}$ group are only marginally changed by the coordination with the bipyridine ligand.⁴¹ Only the $\text{V}=\text{N}$ bond length is slightly elongated from 164.2 pm in $\text{VCl}_3(\text{NCl})$ to 168.8 pm in bipyridine complex.

$\text{MoF}_4(\text{NCl})$ which is associated by fluoro bridges dissolves easily in acetonitrile, affording the acetonitrile

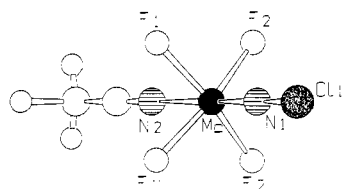
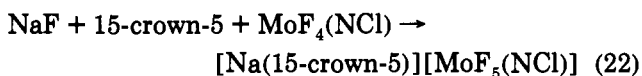


Figure 9. Structure of [(MeCN)MoF₄(NCl)].

adduct [(MeCN)MoF₄(NCl)], which forms yellow, moisture-sensitive crystals.²¹

The compound forms monomeric molecules, in which the molybdenum atom is surrounded in a distorted octahedral arrangement by four fluoro ligands, the N atom of the chloroimido group, and, in trans position to it, the N atom of an acetonitrile molecule (Figure 9). Two slightly different, independent molecules with the symmetry C_s are situated in the unit cell. Not considering the H atoms, the symmetry C_{4v} is almost fulfilled. The differences between the two molecules are especially revealed in the bond lengths Mo-N(acetonitrile) of 238 and 222 pm and in the bond angles Mo-N-C (167°, 178°) of this group. The long Mo-N distance is correlated with the smaller bond angle (molecule I). Presumably this is a consequence of the packing of the molecules, which does not allow the acetonitrile molecule of molecule I the ideal coordination in a linear arrangement Mo⁻-N⁺≡C-Me; thus the Mo-N distance is also elongated. In contrast the Mo-N(acetonitrile) distance of 222 pm in molecule II corresponds to the length of a normal donor acceptor bond as it is also observed in the ion [MoBr₅(MeCN)]⁻ (223 pm⁴⁴). The MoNCl group is linear in both individuals (176° and 178°). The MoN distance of 172 pm is slightly longer than in nitrido complexes with terminal nitrido ligands Mo≡N: (~165 pm^{38,39}). It corresponds, however, approximately to the MoN bond lengths in *N*-organoimido complexes of molybdenum.¹ According to Pauling, a distance of 170 pm can be assumed for a MoN triple bond,³⁴ while Bart and Ragaini⁴⁵ discuss a bond order of 2.5 for this distance. The N-Cl bond length in [(MeCN)MoF₄(NCl)] of 159 and 162 pm, respectively, corresponds to the expectation. The high electron density of the Mo≡N bond causes a considerable steric effect, which manifests itself in large bond angles NMoF with an average value of 98°; as a consequence the fluorine atoms can not form a common plane with the molybdenum atom. The Mo-F distances are in the range of 186 to 190 pm; thus being somewhat longer than in MoF₆ (177–186 pm⁴⁶).

In the presence of 15-crown-5 also sodium fluoride can be added to MoF₄(NCl), forming the yellow ion pair [Na(15-crown-5)][MoF₅(NCl)], which is readily soluble in acetonitrile.⁴⁷ A F/Cl exchange at the



chloroimido group does not occur, even with an excess of sodium fluoride. The ion pair is formed by two Na-F interactions (Figure 10). A very short Na-F contact of 228.3 pm exists with the fluorine atom F(4) of the [MoF₅(NCl)]⁻, which is in trans position to the NCl group. This contact is even slightly shorter than the Na-F distance in sodium fluoride (230.7 pm⁴⁸). There is another, however, markedly weaker Na...F contact of

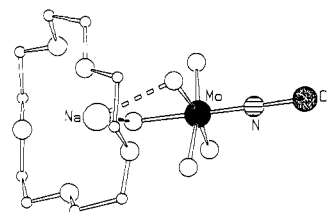
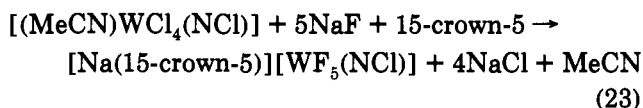


Figure 10. Structure of the ion pair [Na(15-crown-5)][MoF₅(NCl)].

249.6 pm to one of the equatorial fluorine atoms so that together with the five Na-O bonds to the crown ether molecule a (6 + 1) coordination results for the Na ion. In the anion [MoF₅(NCl)]⁻ the molybdenum atom exhibits a distorted octahedral coordination by five fluoro ligands and the [NCl]²⁻ group, which corresponds approximately to the symmetry C_{4v} . The distances MoN = 172.9 pm and NCl = 161.8 pm as well as the bond angle MoNCl = 175.8° are analogous to the corresponding values in [(MeCN)MoF₅(NCl)]. The bond angles N≡MoF_{eq}, on average, amount to 95.6°; thus they are slightly smaller than in the acetonitrile adduct. The fluorine atom arranged in trans position to the Mo≡NCl group forms a Mo-F bond which is 7.7 pm longer than that of the equatorial F atoms, but it is also effected by the bond weakening bridging function to the sodium atom.

The corresponding tungsten compound [Na(15-crown-5)][WF₅(NCl)]⁴⁹ crystallizes isotypically with the molybdenum compound. This tungsten complex can be obtained in the same way as [K(18-crown-6)][WF₅(NCl)]⁵⁰ by the reaction of excess alkali metal fluoride in the presence of the crown ether in acetonitrile solution (eq 23). The ion pair [Na(15-crown-5)][WF₅(NCl)]



(NCl)] exhibits a structure, which is completely analogous to that of the corresponding molybdenum compound; the structural parameters of the W≡NCl group are WN = 173.3 pm, N-Cl = 162.2 pm, WNCl = 176.1°. ⁴⁹ [K(18-crown-6)][WF₅(NCl)], too, has the structure of an ion pair (Figure 11).⁵⁰ It is formed by two K-F

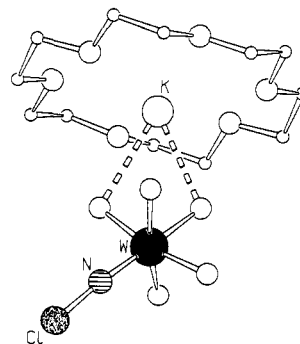


Figure 11. Structure of the ion pair [K(18-crown-6)][WF₅(NCl)].

contacts of 272.4 and 288.6 pm; the shorter of the two contacts corresponds approximately to the K-F distance in potassium fluoride (266.4 pm⁴⁸). The bond angle WNCl of 170.7° is slightly smaller than in the two ion

pairs described above; the distances WN and NCl, however, are comparable.

The educt [(MeCN)WCl₄(NCl)] taken as a basis for eq 23 has a molecular structure analogous to that of [(MeCN)MoF₄(NCl)].²² The molecule possesses a mirror plane along the axis ClNWCC (symmetry C_s), the deviation from the symmetry C_{4v} (without H atoms) is, however, only small, because of the large bond angle WNCI of 175.5°. The bond lengths WN = 172 and NCl = 161 pm are in accord with the expectation.

The triorganophosphine oxides OPR₃ (R = Me, Ph), too, form stable 1:1 adducts with WCl₄(NCl), which have been characterized crystallographically.²⁴ While the bond lengths WN and NCl are almost equal in both complexes and show no deviations from the values of the tungsten complexes hitherto described, the WNCI bond angle in [W(NCl)Cl₄(OPMe₃)] of 167.0° is noticeably small.²⁴ The reason for this is possibly based on the strongly asymmetric coordination of the OPMe₃ molecule, which is expressed by the small WOP angle of 151.2° (Figure 12). In contrast the WNCI bond angle

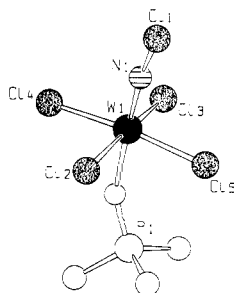
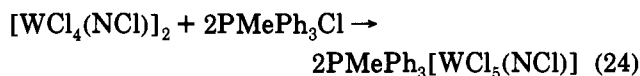


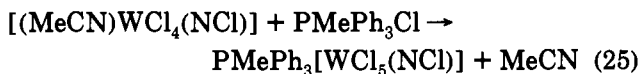
Figure 12. Structure of [WCl₄(NCl)(OPMe₃)].

of 174.0° (average of two crystallographically independent molecules) in the triphenylphosphine oxide derivative [W(NCl)Cl₄(OPPh₃)] is normal, but at the same time the WOP bond angle of 163.5° on average is also markedly larger than that in the trimethylphosphine oxide compound.²⁴

By using chlorides of bulky cations like PPh₄⁺ or PMePh₃⁺, [WCl₄(NCl)]₂ can be transformed into the anionic pentachloro *N*-chloroimido complexes upon cleavage of the chloro bridges in dichloromethane (eq 24).⁵¹ The complex can also be obtained from the



adduct [(MeCN)WCl₄(NCl)] by substitution of acetonitrile.⁵¹ According to the crystal structure analysis,



the symmetry C_{4v} is almost fulfilled for the anion [WCl₅(NCl)]⁻ (Figure 13).⁵¹ The negative charge only slightly influences the WNCI group in comparison with the molecular complex [(MeCN)WCl₄(NCl)]. The distances WN and NCl are even somewhat shortened (169 and 160 pm) so that the influence of the bond weakening charge is concentrated on the WCl bonds. The trans influence of the [NCl]²⁻ group becomes noticeable by the long WCl distance of 239 pm of the chlorine atom in trans position, while the distances

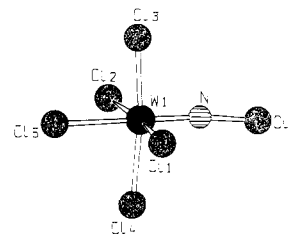


Figure 13. Structure of the anionic complex [WCl₅(NCl)]⁻.

WCl_{cis} amount to 233 pm on average. The perceptibly electropositive character of the N-bound chlorine atom in the chlorimido complexes is expressed by the reaction of [WCl₅(NCl)]⁻ ions with an additional chloride ion, which according to the crystal structure analysis links the two Cl atoms of the two WNCI groups in a linear coordination (Figure 14).⁵¹ The bonding properties can

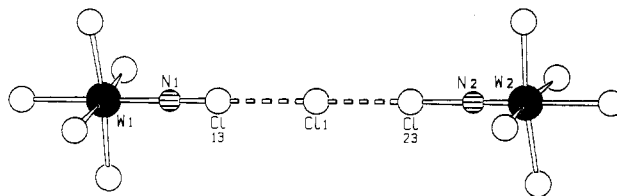
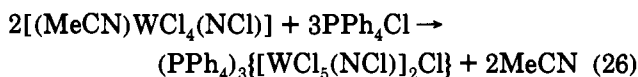
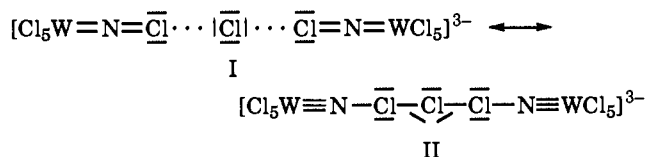


Figure 14. Structure of the dinuclear complex [Cl₅W(NCl)...Cl...Cl(N)WCl₅]³⁻ with a bridging Cl₃ unit.



be described in a formal way as follows:



The Cl...Cl...Cl distances amount to 288 and 278 pm. Thus they are noticeably shorter than the van der Waals distance of 350 pm according to Bondi⁵² (spherical Cl atoms) or than the sum of the ionic radius of Cl⁻⁵³ and the van der Waals radius, which amounts to 339 pm according to Nyburg and Faerman⁵⁴ (flattened Cl atom). The association can be interpreted as mainly electrostatic in the sense of formula I; it clearly shows the electrophilic character of the chlorine atom of the WNCI group. Covalent bonds in the sense of formula II, which shows an analogy to the Cl₃⁻ ion, can, however, to a certain extent, also be assumed. In the Cl₃⁻ ion of AsPh₄Cl₃ two bonds of different lengths are also observed (223 and 231 pm⁵⁵), which, however, are markedly shorter than in our case. The Cl...Cl contacts of different lengths correspond to differently long W-Cl distances of the chlorine atoms being in trans position to the WNCI groups: the shorter contact Cl(1)...Cl(23) is related to the longer bond W(2)-Cl(21) of 252 pm, while the longer contact Cl(1)...Cl(13) corresponds to the shorter bond W(1)-Cl(11) of 241 pm. The [WCl₅(NCl)] building units, however, differ only slightly from the anion in PPh₃Me[WCl₅(NCl)].

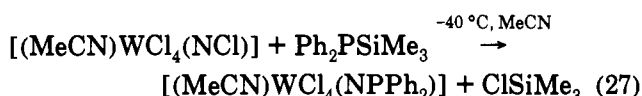
(PPh₄)₃{[WCl₅(NCl)]₂Cl} crystallizes upon inclusion of one molecule of CCl₄ and four molecules of MeCN per formula unit. The {[WCl₅(NCl)]₂Cl}³⁻ ions and the included CCl₄ molecules alternate along the 4-fold axis

of the space group $P4/n$. The tetrahedral structure of the CCl_4 molecule is, however, not consistent with the 4-fold rotational symmetry, therefore the CCl_4 molecule is disordered.

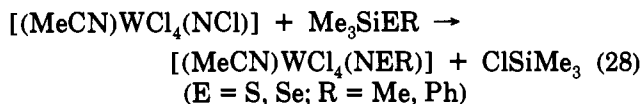
The PPh_4^+ ions are stacked along the $\bar{4}$ axes. This is an arrangement which, along with the space group $P4/n$, is frequently observed with tetraphenylphosphonium salts, always exhibiting the lattice parameter c in the stacking direction of about 780 pm.⁵⁶ Since the ion $\{[\text{WCl}_5(\text{NCl})]_2\text{Cl}\}^{3-}$ is longer than the stacking height of two PPh_4^+ ions three PPh_4^+ ions per anion are necessary along the direction of c in order to retain at the same time the electroneutrality. The lattice constant c therefore is tripled in comparison with other tetraphenylphosphonium salts ($3 \times 780 \text{ pm} = 2340 \text{ pm}$). In addition it is elongated to 2720 pm by the inclusion of MeCN molecules. The insertion of MeCN molecules in the cation stack and of CCl_4 molecules between the anions serves for a compensation of the different lengths of the $(\text{PPh}_4^+)_3$ stacks and the $\{[\text{Cl}_5\text{W}(\text{NCl})]_2\text{Cl}\}^{3-}$ ions.

C. Substitution Reactions at the N Atom

Substitution reactions at the N atom of halogenoimido compounds have so far only been successful with silylated thio and seleno compounds. In one case the reaction with a silylated phosphido compound was also possible (eq 27).⁵⁷



The silylated thio and seleno ethers Me_3SiSR ($\text{R} = \text{Me, Ph}$) and Me_3SiSeMe react with $\text{WCl}_4(\text{NCl})$ in acetonitrile solution at -40°C under separation of trimethylchlorosilane and formation of a N-S or N-Se bond (eq 28).^{3,58} The resulting (organothio)- and



(organoseleno)nitrene complexes, respectively, form monomeric red complexes, which are moisture-sensitive and easily soluble in organic solvents. The crystal structure of $[(\text{MeCN})\text{WCl}_4(\text{NSMe})]$ is known (Figure 15).⁵⁸ The 176° WNS axis of the (methylthio)nitrene

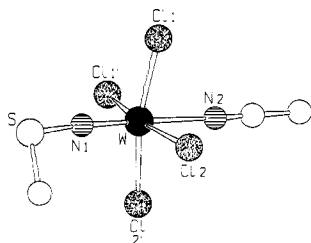


Figure 15. Structure of $[(\text{MeCN})\text{WCl}_4(\text{NSMe})]$.

group $[\text{NSMe}]^{2-}$ is almost linear, the WN bond length of 174 pm is only slightly longer than those in the N-chloroimido complexes of tungsten. The bond angle at the S atom amounts only to 102° , so that in agreement with the Gillespie-Nyholm model⁵⁹ two lone pairs at the S atom can be assumed. The bonding properties

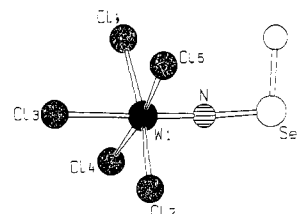
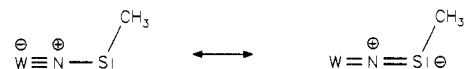


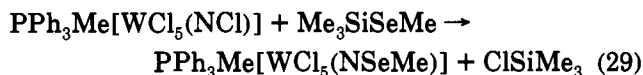
Figure 16. Structure of $[\text{WCl}_5(\text{NSeMe})]^-$.

can therefore be formulated according to the following formula:



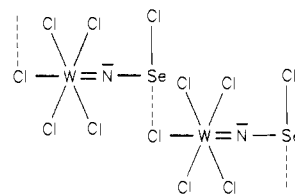
The structural and bonding situation is very similar to that in (chlorothio)nitrene complexes. In the structure of $[\text{WCl}_4(\text{NSCl})]_2$, for example, bond lengths of $\text{WN} = 176 \text{ pm}$ and $\text{NS} = 158 \text{ pm}$, and a bond angle of 104° at the S atom are observed.⁶⁰ The bond distance $\text{W}-\text{N}$ of 229 pm to the acetonitrile ligand is virtually of the same length as in $[(\text{MeCN})\text{WCl}_4(\text{NCl})]$ (228 pm),²² therefore in both complexes an equally strong trans influence exists.

In an analogous way as in eq 28 the anionic N-chloroimido complex of tungsten can be substituted at the N atom with Me_3SiSeMe .³ This reaction proceeds quantitatively at room temperature in dichloromethane solution (eq 29):



In the structure isolated anions $[\text{WCl}_5(\text{NSeMe})]^-$ are present (Figure 16), in which the WN distance of 172 pm (average of the two symmetry independent units) corresponds approximately to the WN distance in the ion $[\text{WCl}_5(\text{NCl})]^-$ (169 pm).⁵¹ The $\text{Se}-\text{N}$ bond length of 180.6 pm is a little shorter than the expected value of a single bond (186 pm), even though it is longer than that of a SeN double bond (164 pm⁴⁸). Since the bond angle WNSe is 173.7° just as it is in the comparable thio compound and the bond angle at the Se atom is only 98.3° , the bonding properties can be described according to formula shown above.

Interestingly the (chloroseleno)nitrene complex included in the anion of $\text{PPh}_3\text{Me}[\text{WCl}_5(\text{NSeCl})]$ does not form isolated units, the $[\text{WCl}_5(\text{NSeCl})]^-$ ions are associated via chloro bridges to build up chains according to the following formula:⁶¹



These chloro bridges can be degraded with an additional chloride anion forming isolated anions $[\text{WCl}_5(\text{NSeCl}_2)]^{2-}$.⁶²



The crystal structure analysis of the PPh_4^+ salt (Figure 17) shows an almost linear WNSe axis (bond angle 175°)

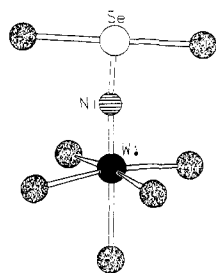
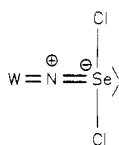
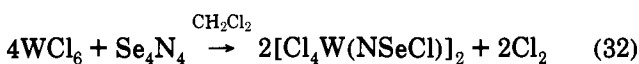
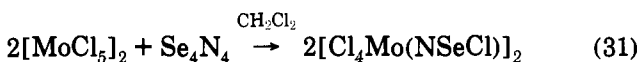


Figure 17. Structure of $[\text{WCl}_5(\text{NSeCl}_2)]^{2-}$.

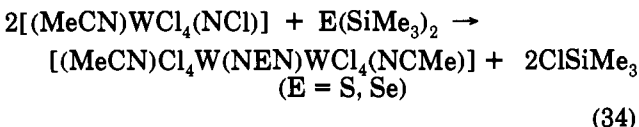
for the anion with bond distances WN of 176 pm and SeN of 174 pm, which correspond approximately to double bonds. The selenium atom exhibits a ψ -trigonal bipyramidal surrounding with the two lone pairs and the N atom in equatorial positions, and the chlorine atoms are in axial arrangements.⁶² The WNSeCl₂ group can therefore be described according to the following formula:



The methyl compound $[\text{Cl}_5\text{W}(\text{NSeMe})]^-$ in contrast is not able to add a chloride at the selenium atom. It should be noted that the (chloroseleno)nitrene complexes of molybdenum and tungsten can be obtained^{61,64,65} by the reaction of molybdenum pentachloride or tungsten hexachloride with the long known but very explosive Se_4N_4 , or even better with Se_4N_2 .⁶³ With

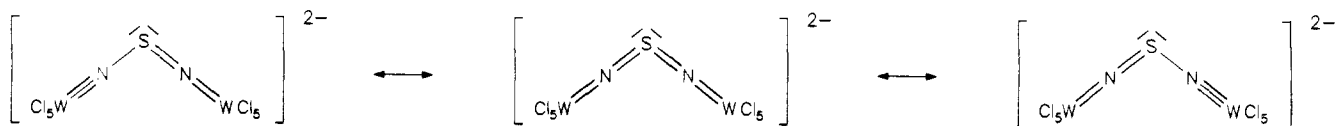


the bis(trimethylsilyl)chalcogenides $\text{E}(\text{SiMe}_3)_2$ ($\text{E} = \text{S}, \text{Se}$) the *N*-chloroimido complex of tungsten can be reacted in acetonitrile at room temperature to the μ -dinitridosulfato or μ -dinitridoselenato complexes, in which the formal building unit $[\text{NEN}]^{4-}$ is present.⁵⁸

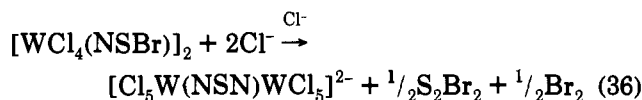
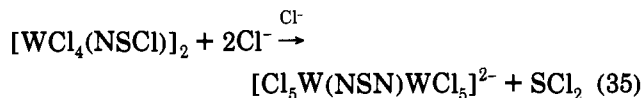


With tetraphenylphosphonium or -arsonium chloride, the dianions $[\text{Cl}_5\text{W}(\text{NEN})\text{WCl}_5]^{2-}$ can be synthesized, the representatives of which with $\text{E} = \text{S}$ are also obtainable from the (halogenothio)nitrene complexes,

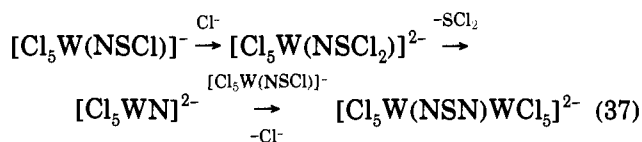
Scheme II



which are related to the *N*-chloroimido complexes, if excess chloride is supplied.^{66,67}



Presumably the reaction proceeds via a primary nucleophilic attack of chloride at the S atom of the first-formed chlorothionitrene complex $[\text{Cl}_5\text{W}(\text{NSCl})]^-$ leading to the separation of SCl_2 whereafter the liberated nitrido complex $[\text{Cl}_5\text{WN}]^{2-}$ can react with further $[\text{Cl}_5\text{W}(\text{NSCl})]^-$ forming the NSN bridge.⁶⁶



In the case of the seleno compound the primary product of eq 37 could be established by isolation of $(\text{PPh}_4)_2[\text{Cl}_5\text{W}(\text{NSeCl}_2)]$, being stable in this case (see eq 30).

While the anion in $(\text{AsPh}_4)_2[\text{Cl}_5\text{W}(\text{NSN})\text{WCl}_5]$ is disordered and therefore its structure could be determined only relatively inaccurately,⁶⁶ the structure of $(\text{PPh}_4)_2[\text{Cl}_5\text{W}(\text{NSN})\text{WCl}_5] \cdot \text{CH}_2\text{Cl}_2$ could be ascertained without problems (Figure 18).⁶⁷ The two tungsten

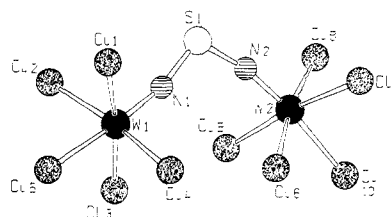


Figure 18. Structure of $[\text{Cl}_5\text{W}(\text{NSN})\text{WCl}_5]^{2-}$ with a bridging $[\text{NSN}]^{4-}$ group.

atoms are connected by a folded NSN bridge with the skeletal atoms WNSNW lying nearly in one plane. The WN and SN distances approximately correspond to double bonds, while the bond angle of 104.0° at the S atom indicates the stereochemical influence of two lone pairs, which is in agreement with the assumption of a $[\text{NSN}]^{4-}$ ligand; see Scheme II.⁶⁷

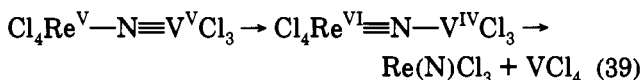
On the other hand for the $[\text{NSN}]^{2-}$ ion, being isolable as dipotassium salt,⁶⁸ a NSN bond angle of $\sim 125^\circ$ is estimated from the vibrational frequencies,⁶⁷ while from MO calculations a bond angle of 118° is expected.⁶⁹

A reaction for which primarily the substitution at the N atom of Cl_3VNCl has to be assumed is present in the synthesis of ReNCl_5 from ReCl_5 , which proceeds

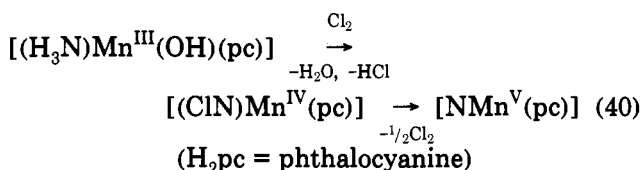
in tetrachloromethane saturated with chlorine.⁷⁰ In



this reaction, upon separation of chlorine, the substitutional product $\text{Cl}_4\text{Re}-\text{N}=\text{VCl}_3$ is formed first. Because of the more favorable π -overlap it is transformed by an internal redox reaction to $\text{Cl}_4\text{Re}=\text{N}-\text{VCl}_3$, which then, after a 1,3-shift of chlorine from rhenium to vanadium leads to the separation of VCl_4 .⁷⁰

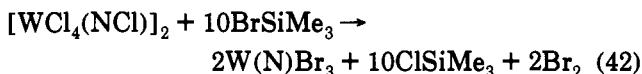
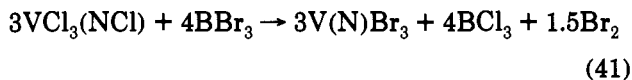


A *N*-chloroimido compound is a factor, too, as an intermediate product in the synthesis of (nitrido)-(phthalocyaninato)manganese(V); here the ammine complex is chlorinated to form the NCl compound first, and the nitrido complex is produced afterward upon separation of chlorine:⁷¹

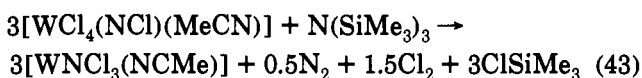


D. Substitution Reactions at the Metal Atom

Substitution reactions at the metal atom of *N*-halogenoimido complexes have so far been studied only to a small extent. These also include the fluoridation of $[\text{Cl}_4\text{W}(\text{NCl})_2]$ with NaF and KF in the presence of crown ethers (reaction 23), which represents a combination of an acid/base and a substitution reaction. The *N*-halogeno function is not always preserved by attempts to exchange the halogeno ligands at the metal atom. Thus the bromidation reactions with boron tribromide or trimethylbromosilane lead to the nitridobromides VNBBr_3 ⁷² and WNBBr_3 ⁵⁸ when solvents are not used:



$[\text{WCl}_4(\text{NCl})]_2$ reacts also with tris(trimethylsilyl)-amine in acetonitrile solution to form the nitrido derivative:⁵⁸



The resulting nitrido complex exhibits the tetrameric structure, being typical for the solvates of the nitridechlorides $\text{M}(\text{N})\text{Cl}_3\text{-L}$ ($\text{M} = \text{Mo}, \text{W}, \text{Re}$)^{38,39} with alternating long MN bonds in the $\text{M}=\text{N}-\text{M}$ bridge and with the solvate molecule in the position trans to the short MN bond.⁵⁸

The reactions of $[\text{WCl}_4(\text{NCl})(\text{NCMe})]$ or $[\text{WCl}_5(\text{NCl})]^-$ with trimethylsilyl azide in contrast—however with stoichiometric direction of the reaction—proceed easily upon Cl/N_3 exchange of one chlorine atom and

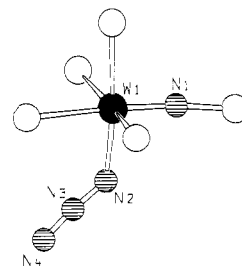
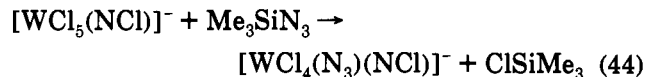


Figure 19. Structure of $[\text{WCl}_4(\text{N}_3)(\text{NCl})]^-$.

formation of the corresponding azido derivatives:⁷³



As the (triphenylmethyl)phosphonium salt the complex could be isolated as red, nonexplosive crystals. According to the crystal structure analysis⁷³ the azido group occupies a position cis to the WNCl group (Figure 19). Presumably because of its influence the WN bond of the *N*-chloronitreno group with 174 pm is longer by 5 pm than in $\text{PPh}_3\text{Me}[\text{WCl}_5(\text{NCl})]$,⁵¹ whereas the 204-pm $\text{W}-\text{N}$ distance of the azido group, which is oriented in the direction of the free space between the two neighboring chlorine atoms, corresponds approximately to a single bond.

V. Vibrational Spectra

The expected spectrum of the characteristic fragment $\text{M}=\text{N}-\text{X}$ of *N*-halogenoimido complexes depends on the bond angle at the *N* atom. With the ideal linear arrangement it possesses the local symmetry $C_{\infty v}$, with smaller angles the symmetry C_s . According to the selection rules⁷⁴ the following correlation results:

type	$C_{\infty v}$		C_s
ν_{as}	Σ	\rightarrow	A'
ν_{s}	Σ	\rightarrow	A'
δ	Π	\rightarrow	A''
		\rightarrow	A'

In each case all fundamental vibrations are active in the IR and Raman spectra.⁷⁴ Since the bond angles of most of the *N*-halogenoimido complexes exhibit only small deviations from the linear arrangement $\text{M}=\text{N}-\text{X}$ the splitting of the Π -vibration into the type modes A' and A'' is in general not observed.

Because of the large bond angles a strong coupling of the two stretching vibrations has to be expected.⁷⁴ $\nu_{\text{as}}(\text{MNX})$ mainly has the character of a MN vibration; $\nu_{\text{s}}(\text{MNX})$ on the other hand has mainly that of a NX vibration. The larger the mass of the halogen atom *X*, the longer the wavelength of $\nu(\text{NX})$ is to be expected, and the smaller its coupling influence on $\nu(\text{MN})$. This can clearly be shown with the examples of the VNX stretching vibrations of $\text{Cl}_3\text{V}=\text{N}-\text{X}$ with $\text{X} = \text{Cl}, \text{Br}, \text{I}$ (values in cm^{-1}):

	$\text{VCl}_3(\text{NCl})$ ⁵	$\text{VCl}_3(\text{NBr})$ ⁶	$\text{VCl}_3(\text{NI})$ ⁶
$\nu(\text{VN})$	1107	1032	963
$\nu(\text{NX})$	510	435	390

The influence of the coupling can also be recognized indirectly, since e.g. the WN stretching vibration of $[\text{WCl}_4(\text{NCl})]_2$ is observed at 1207 cm^{-1} (see Table II),

Table II. IR Spectra of *N*-Halogenoimido Complexes^a

complex	$\nu(\text{MN})$	$\nu(\text{NX})$	$\delta(\text{MNX})$	ref(s)
VCl ₃ (NCl)	1107	510	375, 238	5
VCl ₃ (NBr)	1032	435	285	6
VCl ₃ (NI)	963	390	265	6
VCl ₃ (NCl)(SbCl ₅) ₂	1108	498		41
VCl ₃ (NCl)(bipy)	1110	498		41
AsPh ₄ [VCl ₄ (NCl)]	1114	520	320	42
MoF ₄ (NCl)	1175	495		21
[MoF ₄ (NCl)(MeCN)]	1165	550		21
MoCl ₄ (NCl)	1145	638	420	17
WCl ₄ (NCl)	1207	531		22
[WCl ₄ (NCl)(MeCN)]	1203			22
PPh ₃ Me[WCl ₅ (NCl)]	1165			51
(PPh ₄) ₃ [WCl ₅ (NCl)] ₂ Cl	1142			51
[Na(15-crown-5)][WF ₅ (NCl)]	1200	520		49
[K(18-crown-6)][WF ₅ (NCl)]	1192	532		50
ReF ₅ (NCl)	1205			26, 28
ReNF ₄ ·ReF ₅ (NCl)	1221	475		31
OsF ₅ (NCl)	1215	495 (?)		32

^a Values in cm⁻¹.

while it appears at 1036 cm⁻¹³⁸ in the nitrido complex [WCl₄(N)]⁻ with a terminal W≡N: group. The comparison between the corresponding stretching vibrations of [MoCl₄(NCl)]⁻ (1145 cm⁻¹) and [MoCl₄(N)]⁻ (1054 cm⁻¹)³⁸ has a similar result. The characteristic vibrations of *N*-halogenoimido complexes are summarized in Table II.

VI. Ab Initio Calculations

Preliminary ab initio calculations have been carried out for the fictitious monomeric *N*-halogenoimido complexes VCl₃(NX), WCl₄(NX), and MoCl₄(NCl).⁷⁵ The monomeric gas-phase structure is known only for VCl₃(NX) with X = Cl. The results of the optimization of the geometries⁷⁶ are presented in Table III. For the

Table III. Calculated Geometries^a of *N*-Halogenoimido Complexes^a

complex	M-N	N-X	M-Cl	M-N-X	N-M-Cl	<i>E</i> _{total}
VCl ₃ (NF)	156.1	129.1	213.2	179.1	106.3	-268.093 767
VCl ₃ (NCl)	156.2	162.0	213.6	179.2	106.3	-183.948 480
VCl ₃ (NBr)	155.9	181.8	213.2	179.1	106.6	-181.673 673
VCl ₃ (NI)	154.7	197.7	214.3	179.3	106.2	-180.418 980
WCl ₄ (NH)	166.0	100.0	230.4	180.0	103.5	-181.139 214
WCl ₄ (NF)	166.0	129.7	230.0	180.0	103.0	-279.356 309
WCl ₄ (NCl)	167.0	162.1	230.3	180.0	103.1	-195.219 604
WCl ₄ (NBr)	167.0	181.5	230.1	180.0	103.7	-192.951 331
WCl ₄ (NI)	166.4	197.6	230.8	180.0	103.0	-191.694 943
[WCl ₄ (N)] ⁻	161.6		237.8		102.4	-180.689 639
MoCl ₄ (NCl)	165.1	161.2	231.0	180.0	102.3	-194.852 044
[MoCl ₄ (N)] ⁻	157.7		239.2		101.4	-180.356 957

^a Distances in pm; bond angles in deg; energies in atomic units (Hartrees).

vanadium complexes *C*_{3v} symmetry is approximately obtained, and for those of molybdenum and tungsten *C*_{4v} symmetry. The calculated bond lengths MN and NX are in good agreement with the results of crystal structure analyses of comparable complexes (see Table I, section III). The calculations for the hypothetical WCl₄(NH) fit well into the general trend. In comparison with the nitrido complexes [MCl₄(N)]⁻ (M = Mo, W) of the same symmetry,^{38,39} the MN distances in the *N*-halogenoimido complexes are somewhat longer. This agrees quite well with the experiment.

Table IV. Partial Charges at the Atoms of *N*-Halogenoimido Complexes⁷⁷

complex	<i>q</i> (M)	<i>q</i> (N)	<i>q</i> (Cl)	<i>q</i> (X)
VCl ₃ (NF)	1.10	+0.14	-0.37	-0.14
VCl ₃ (NCl)	1.19	-0.38	-0.37	+0.31
VCl ₃ (NBr)	1.19	-0.52	-0.36	+0.40
VCl ₃ (NI)	1.21	-0.60	-0.39	+0.56
MoCl ₄ (NCl)	1.54	-0.45	-0.36	+0.36
[MoCl ₄ (N)] ⁻	1.59	-0.37	-0.56	
WCl ₄ (NH)	1.90	-0.77	-0.40	+0.47
WCl ₄ (NF)	2.06	-0.32	-0.40	-0.14
WCl ₄ (NCl)	1.91	-0.66	-0.39	+0.32
WCl ₄ (NBr)	1.92	-0.80	-0.39	+0.43
WCl ₄ (NI)	1.92	-0.88	-0.41	+0.58
[WCl ₄ (N)] ⁻	2.05	-0.79	-0.57	

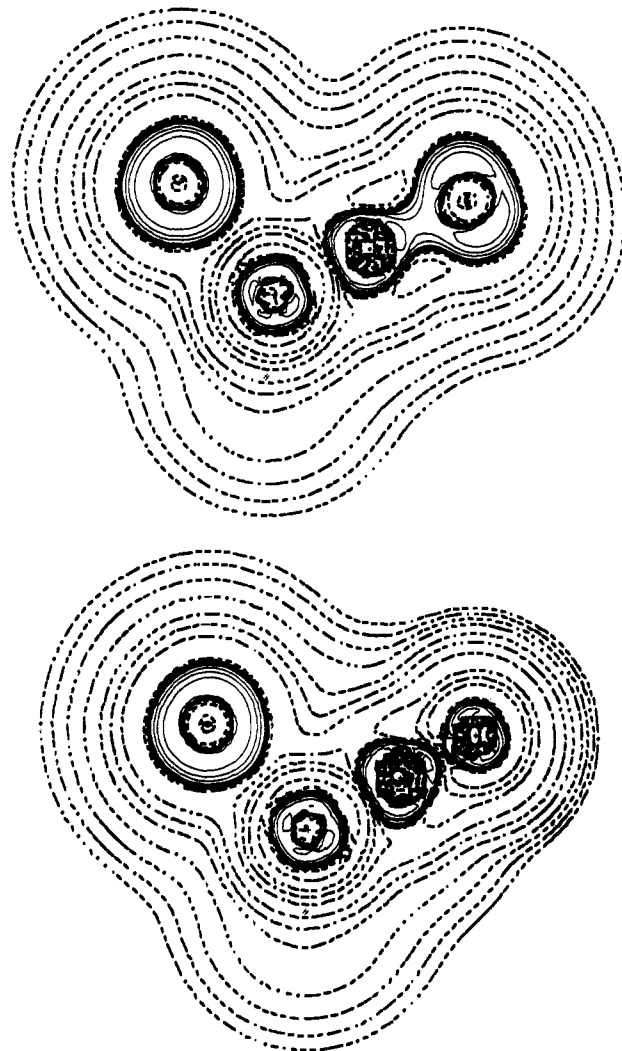


Figure 20. Laplacian distribution of the electron density in intersecting planes Cl—V≡N—X in the molecules VCl₃(NF) (above) and VCl₃(NCl) (below).

In the case of the vanadium complexes the calculation of the charge distribution⁷⁷ (Table IV) indicates negative amounts of the partial charge for the N atom if X = Cl, Br, I; a positive charge, however, if X = F. In the case of the tungsten complexes the imido nitrogen atoms actually always have a negative partial charge, the amount for WCl₄(NF), however, is much smaller. A corresponding picture results for the halogen atoms of the M≡N—X groups, which have a negative sign for X = F only. In the sequence I → Br → Cl the amount of the positive partial charge decreases. The amount

of $q(\text{Cl}) = +0.32$ for $\text{WCl}_4(\text{NCl})$ is sufficient to fix a chloride ion between two $\text{W}\equiv\text{N}-\text{Cl}$ groups, as the example of the $\{[\text{WCl}_4(\text{NCl})]_2\text{Cl}\}^{3-}$ ion shows (see section III, Figure 14).

Changing from $\text{V}\equiv\text{N}^{\delta+}-\text{F}^{\delta-}$ to $\text{V}\equiv\text{N}^{\delta-}-\text{Cl}^{\delta+}$ a reversion of the partial charge results. This is supported by the analysis of the Laplacian distribution of the electron density.⁷⁸ In Figure 20 intersections of the electron density distributions of the planes $\text{Cl}-\text{V}\equiv\text{N}-\text{X}$ ($\text{X} = \text{F}, \text{Cl}$) in the molecules $\text{VCl}_3(\text{NF})$ and $\text{VCl}_3(\text{NCl})$ are represented. For the $\text{N}-\text{Cl}$ bond a covalent bond results, while for the $\text{N}-\text{F}$ compound a polar, weak covalent bond situation is found by investigating the electron density of the $\text{N}-\text{F}$ bond.

VII. Future Directions

N-Halogenoimido complexes are only known for a few transition metals. With the development of additional synthetic routes more examples also of other metals will presumably be obtained. In addition—as the N-halogenoimido complexes comprise a high synthetic potential—interesting new transition metal nitrogen compounds can be synthesized; they may be useful for the synthesis of organic compounds e.g. as catalysts or specific oxidizing agents. Further development on the field of N-halogenoimido complexes therefore seems to be worthwhile.

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