Nitrido bridges between transition metals and main group elements illustrated by the series [M]NNa to [M]NCl

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A survey is given of the structures and bonding modes of nitrido bridges between transition metals with MN multiple bonds and main group elements. Illustrated by the period row sodium (I) to chlorine (VII) (or a homologue) along with variable transition metals M, characteristic examples are compiled, their principles of synthesis are presented and the step-by-step alterations of the bonding conditions that occur in this period are discussed on the basis of structural parameters. These bonding conditions can be divided into three groups.

- **(1) Electrostatic bond between nitrido ligand and main group element (I, II)**
- **(2) Covalent single bond (III, IV)**
- **(3) Multiple bonds between both neighbouring elements (V–VII)**

One example each is designed to illustrate this aim:

- **(i) $\mathrm{Na_6[MoN_4]}$;**
- **(ii) $\mathrm{[Mg(THF)_4\{NMoCl_4(THF)\}_2]}$;**
- **(iii) $\mathrm{[Re{\equiv}N{-}GaCl_3(PMe_2Ph)(Et_2dtc)_2]}$ (no example with Al is known up to now);**
- **(iv) $\mathrm{Cl_3V{\equiv}N{-}SiMe_3}$;**
- **(v) $\mathrm{O_3Re{=}N{=}PMe_3}$;**
- **(vi) $\mathrm{[Cl_5W{=}N{=}SCl]^-}$;**
- **(vii) $\mathrm{[F_5W{=}NCl]^-}$.**

1 Introduction

Nitrido complexes of transition metals of groups 4 to 8 of the periodic table in high oxidation states are well known in large numbers and in several structural variations.[1] Besides complexes with a terminal nitrido functionality [M]≡N: there are also compounds with nitrido bridges, mostly of the asymmetric type [M]≡N→[M]. Examples with symmetric nitrido bridges [M]=N=[M] are also known. The MN bond to the terminal nitrido ligand is very short and generally described as a triple

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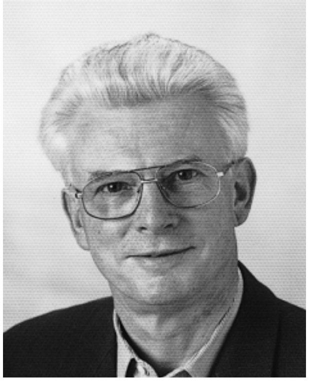

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bond. In the asymmetric nitrido bridges the long N→[M] bond is understood to be of a donor acceptor type.[2] In all cases, the M–N multiple bonds are achieved by participation of unoccupied d-orbitals of the transition metal atoms along with occupied p-orbitals of the nitrido ligand.

Compounds with nitrido bridges between main group elements also often form short element nitrogen bonds [E]=N=[E]. These bonds, however, are to be described essentially as covalent σ-bonds with a strengthening polar contribution. Examples are the borazines,[3] numerous PNP compounds,[3] such as $[R_3PNPR_3]^+$ ions, the adamantane analogue $[P_4N_{10}]^{10-}$,[4] and many sulfur nitrogen cycles such as S_4N_4 and $[S_4N_4]^{2+}$,[3] as well as nitrido derivatives of the higher homologues selenium[5] and tellurium.[6]

Comparative descriptions of the structural features and bonding modes are available for both types of compound [M]=N=[M] and [E]=N=[E], but interest in nitrido bridges of the type [M]=N=[E] between transition metals and main group elements has until now only focused on one particular element E at a time. Examples are compounds with the sequences [M]=N=[P],[7] [M]=N=[S],[8] and [M]≡N–Cl.[9] Here, we are making a first attempt to give a comparative overview of nitrido bridges [M]=N=[E] by varying the elements E in the period from E = Na to E = Cl.

M≡N··Na	M≡N··Mg	M≡N–Al	M≡N–Si	M≡N–P	M≡N–S	M≡N–Cl
(I)	(II)	(III)	↕	↕	↕	↕
			M=N=Si	M=N=P	M=N=S	M=N=Cl
			(IV)	(V)	(VI)	(VII)

In all these cases the transition metal atoms form M–N multiple bonds, while the N–E bonds to the main group elements E exhibit a continuous change from a mainly electrostatic type N··Na to short covalent bonds N–Cl.

2 Nitrido bridges of the type M≡N··Na (I)

Alkali metal nitrido metalates are especially known since the pioneering work of Juza *et al.* on the lithium compounds.[10] They can be successfully synthesized in a high-grade steel autoclave from the transition metal or its binary nitride by reaction with lithium nitride and pure nitrogen. The nitrido metalates mainly of the elements niobium, tantalum, chromium, molybdenum, and tungsten, with the other alkali metals have been known only for a few years. They are usually obtained from sodium amide and the transition metal or its binary nitride. Occasionally alkali metal azides are also used as nitridation reagents at temperatures of 450–600 °C.[11] A typical reaction is given in eqn. (1).

$$Mo + 3\,NaNH_2 \rightarrow Na_3[MoN_3] + 3\,H_2 \qquad (1)$$

The reaction of $NaNH_2$ with WO_3 [eqn. (2)] yields the nitrido oxo metalate $Na_5[WO_4N]$ besides $Na_4[WO_2N_2]$.[12]

$$2\,WO_3 + 9\,NaNH_2 \rightarrow Na_5[WO_4N] + Na_4[WO_2N_2] + 6\,NH_3 \qquad (2)$$

Interestingly, sodium can be intercalated into Ta_3N_5 at temperatures between 450 and 600 °C in sealed Ni tubes to obtain the sodium tantalum nitride, $Na_xTa_3N_5$ ($0 \leqslant x \leqslant 1.4$). At higher temperatures between 600 and 800 °C a disordered rock salt phase $Na_2Ta_3N_5$ is obtained, which transforms above 800 °C to $NaTa_3N_4$.[13]

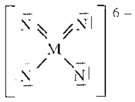
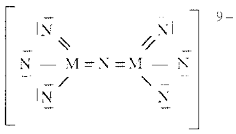
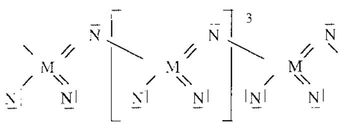
Depending on the reactants and their applied ratio, nitrido metalates with a monomeric or dimeric island structure like $Na_5[WO_4N]$[12] or with a chain structure like $Na_3[MN_3]$ (M = Mo, W),[14] $Na_5A[WN_3]_2$ (A = Rb, Cs[15]), $Na_2K[WN_3]$ or $Na_{11}Rb[WN_3]_4$[16] are formed (Table 1). Beyond these examples, nitrido metalates are also known with a layer structure (*e.g.* $Na_2K_{13}[W_7N_{19}]$[17]) or with a three-dimensional skeletal structure (*e.g.* $Cs_5[Na\{W_4N_{10}\}]$,[18] $Na_2[Ta_3N_5]$, $Na[Ta_3N_4]$[13] or $Na[MN_2]$ with M = Nb,[19] Ta[20]). Thus, these compounds show a significant topological relationship to the structures of silicates.[11] In $Cs_5[Na\{W_4N_{10}\}]$, for example, the anionic part $[Na\{W_4N_{10}\}]^{5-}$ exhibits a β-cristobalite type arrangement.

In the series of nitrido bridges M–N··E, the alkali metal nitrido metalates, discussed here for the case of sodium, show the most strongly marked electrostatic bond relations. Above all, this is demonstrated by the relatively long Na··N distances, which are 251 pm in $Na[TaN_2]$,[20] and between 235 and 299 pm in the example $Na_3[WN_3]$.[14] In the same range are the Na–N distances in the structures of $Na_2K_{13}[W_7N_{19}]$,[17] $Na_5A[WN_3]_2$ (A = Rb, Cs[15]), $Na_2K[WN_3]$ or $Na_{11}Rb[WN_3]_4$.[16]

Unusually short distances between the sodium and nitrogen atoms of 218 and 237 pm are found in the β-cristobalite type arrangement of the anion $[Na\{W_4N_{10}\}]^{5-}$ in $Cs_5[Na\{W_4N_{10}\}]$. The W–N bonds are in the range of 189 pm and the bond angles Na–N–W are 151 and 155°.[18]

$Na[TaN_2]$ crystallizes in the α-$NaFeO_2$-type structure, in which the N atoms adopt cubic close packing and the Ta and Na

Table 1 Examples of nitrido metalates of molybdenum(VI) and tungsten(VI)

		Bonding parameters		
Structure type	Formal description	Bond lengths/pm	Angles/°	Ref.
Isolated tetrahedral anions		Mo–N	187.9(4)	11
$Li_6[MN_4]$		Li···N	203.8(8), 222.7(9)	
		N–Mo–N	105.7(1), 117.3(2)	
Dimeric tetrahedral anions		$Mo–N_t$	183[a]	11
$LiBa_4[M_2N_7]$		$Mo–N_{br}$	195[a]	
		$N_t–Mo–N_t$	108.2[a]	
		Mo–N–Mo	180, 173.58(1)[b]	
Chain structures		$Mo–N_t$	179[a]	11, 14
$Na_3[MN_3]$		$Mo–N_{br}$	194[a]	
		Na···N	235–299	
		Mo–N–Mo	148[a]	
		$W–N_t$	180[a]	11, 14
		$W–N_{br}$	192[a]	
		Na···N	228–301	
		W–N–W	145[a]	

[a] Average value. [b] Two crystallographically independent species.

atoms occupy the octahedral holes in alternating layers. In this structure the N atoms have three Ta atoms with a distance of 211 pm and three Na atoms with a distance of 251 pm as closest neighbours.

In $Na_3[WN_3]$ the tungsten atoms exhibit a tetrahedral coordination, and the WN_4 tetrahedra form infinite chains $[WN_2N_{2/2}]$ (Fig. 1) which are also observed in the structures of the nitrido tungstates $Na_5A[WN_3]_2$ (A = Rb, Cs[15]), $Na_2K[WN_3]$ or $Na_{11}Rb[WN_3]_4$.[16] While these chains are stretched in the cases of $Na_3[WN_3]$, $Na_2K[WN_3]$, and $Na_{11}Rb[WN_3]_4$, they form a zig-zag arrangement in $Na_5A[WN_3]_2$ (A = Rb, Cs).

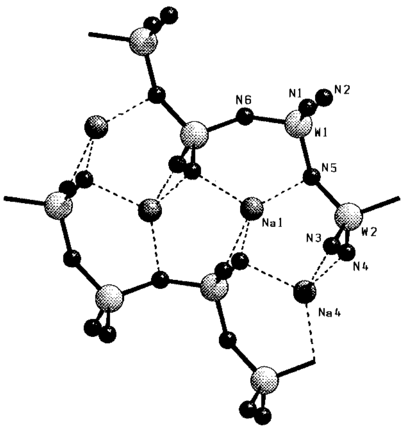
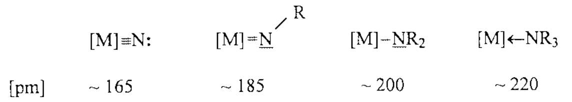


Fig. 1 Section of the chain structure of $Na_3[WN_3]$ with the Na··N contacts, linking the chains.

The shorter Na–N distances are usually with the terminal N atoms, which are to be regarded as the preferred charge carriers of the anion chain (*cf.* Table 1). The terminally bonded nitrido ligand atoms achieve WN distances that are approximately in the range of double bonds, while the bridging N atoms exhibit distances of shortened WN single bonds. This estimation is based upon the knowledge of MN bond lengths for numerous 4d



and 5d elements in high oxidation states. In this connection, it is of interest that the M–N distances in the homoleptic dications $[M(NPR_3)_4]^{2+}$ of molybdenum and tungsten are quite similar to those in the $[MN_4]^{6-}$ anions [Table 1; see also section 6]. Both types of compounds can be understood as Ψ-isolobal MN_4 units.

In the nitrido oxo tungstate $Na_5[WO_4N]$[12] with isolated square pyramidal anions $[WO_4N]^{5-}$, which are isoelectronic with the fluoro derivative $[WF_4N]^-$, all of the oxygen and nitrogen ligand atoms form short bonds to the sodium cations (Fig. 2). With respect to the closest neighbour atoms (< 300 pm) the ligand atoms O and N possess distorted terahedral arrangements. The W–N distance of 177 pm to the apical N atom indicates a multiple bond, while the W–O bonds are considerably longer (194 to 195 pm).

3 Nitrido bridges of the type M≡N··Mg (II)

Whereas nitrido bridges M–N–E with the heavier alkaline earth metals E = Ca, Sr, and Ba are known in great number and variety, nitrido bridges of the type M–N··Mg are described so far only by the example $[Mg(THF)_4\{NMoCl_4(THF)\}_2]$ with a molecular structure,[21] and for $Mg_{2.67-x}Ta_{1.33+x}N_4$ (x = 0.3–1.0), as well as $Mg_{1-x}Ta_{2+x}N_3$ (x = 0.0–0.06) with a three-dimensional skeletal structure.[22]

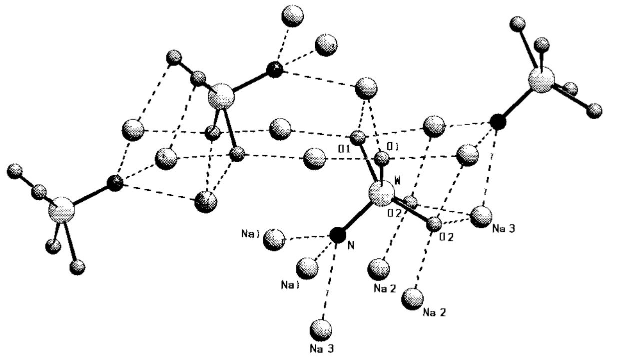


Fig. 2 Structure of $Na_5[WO_4N]$ with O··Na and N··Na contacts < 300 pm. O··Na contacts are between 224.7 and 253.0 pm, N··Na contacts between 238.3 and 287.2 pm.

The complex $[Mg(THF)_4\{NMoCl_4(THF)\}_2]$ has been prepared by the reaction of molybdenum nitride chloride with magnesium chloride in a dichloromethane suspension with an equivalent amount of tetrahydrofuran [eqn. (3)].

$$2\ MoNCl_3 + MgCl_2 + 6\ THF \longrightarrow [Mg(THF)_4\{NMoCl_4(THF)\}_2] \quad (3)$$

Fig. 3 shows its molecular structure, in which the magnesium atom is coordinated octahedrally by the oxygen atoms of the four THF molecules and by the *trans*-positioned nitrogen atoms of the two $[:N{\equiv}MoCl_4(THF)]^-$ groups. With an angle of 177.3° the axis N–Mg–N is virtually linear, and the Mg–N distances of 224.3 pm correspond to the expected value for donor–acceptor bonds. Considering the ionic radius of the magnesium ion which is smaller by 30 pm than that of Na^+, the Mg–N distances approximately correspond to the mean value of the Na··N contacts as observed in the structure of $Na_3[WN_3]$ (see above). Therefore, one has to assign a comparable bond polarity to the Mg–N bonds in $[Mg(THF)_4\{NMoCl_4(THF)\}_2]$. This is also indicated by the fact that the Mo≡N bond in the magnesium complex is only slightly stretched to 165.1 pm compared with $PPh_4[MoNCl_4]$ which has isolated $[MoNCl_4]^-$ ions and a distance of 163.7 pm.[1a]

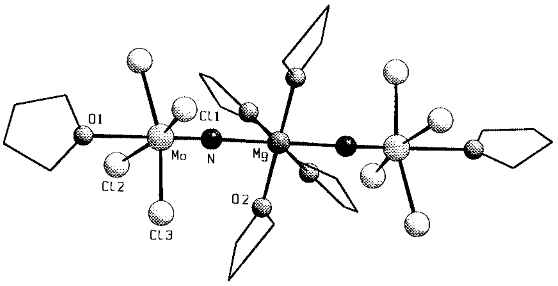


Fig. 3 Molecular structure of $[Mg(THF)_4\{N{\equiv}MoCl_4(THF)\}_2]$.

The magnesium nitrido tantalates $Mg_{2.67-x}Ta_{1.33+x}N_4$, and $Mg_{1-x}Ta_{2+x}N_3$ are obtained from Mg_3N_2 or $Mg(NH_2)_2$ and Ta_3N_5 at temperatures between 900 and 1350 °C. The type of compound formed depends on the molar ratio Mg:Ta. $Mg_{2.67-x}Ta_{1.33+x}N_4$ is obtained with a large excess of magnesium, whereas $Mg_{1-x}Ta_{2+x}N_3$ is produced when a molar ratio of 3:2 is used. $Mg_{2.67-x}Ta_{1.33+x}N_4$ crystallizes in the cubic NaCl-type structure with disordered cations, and a Mg,Ta–N distance of approximately 218 pm.

The structure of $Mg_{1-x}Ta_{2+x}N_3$ is composed of $[TaN_2]^{3-}$ layers between which Mg^{2+} ions and additional Ta atoms occupy octahedral holes formed by nitrogen atoms. Within the $[TaN_2]^{3-}$ layers the Ta atoms are in a trigonal prismatic coordination. It is assumed that the prismatic holes are occupied by Ta^{3+} and the octahedral holes by Ta^{5+} with distances for Ta^{3+}–N of 219 and 221 pm and for Ta^{5+}–N of 212 pm. The Mg–N distances are 216 pm. The nitrogen atoms are in an octahedral environment of two Mg and four Ta atoms with bond angles Mg–N–Ta of 90.9 and 177.0°.

4 Nitrido bridges of the type M≡N–Al(Ga) (III)

Up to now no examples have been found of a nitrido bridge with aluminium as the main group element component. However, nitrido complexes of rhenium readily interact with gallium trichloride or boron trichloride. Examples of the products include $[Cl_3Ga–N≡ReCl_2(PMe_2Ph)_3]$,[23] which is shown in Fig. 4, $[Cl_3Ga–N≡ReCl(PMe_2Ph)_3(CH_3CN)]^+[GaCl_4]^-$,[23] and $[Cl_3Ga–N≡Re(Et_2dtc)_2(PMe_2Ph)]$,[24] as well as $[Cl_3B–N≡ReCl_2(PMe_2Ph)_3]$.[25] In all cases the Re–N bond is only slightly stretched (~2 pm) compared with the $GaCl_3$ or BCl_3 free reactants so that its triple bond character is maintained. This is also indicated by the axis ReNB or ReNGa, which are still largely linear (Fig. 4). However, the strong *trans* influence deriving from the nitrido ligand is considerably weakened by the formation of the bridge to the Lewis acid. This is revealed by the Re–Cl bond of the chlorine atom Cl(2) *trans* to the nitrido ligand in the complex $[Cl_3Ga–N≡ReCl_2(PMe_2Ph)_3]$, which is 15 pm shorter compared with that in $[ReNCl_2(PMe_2Ph)_3]$. This bond now is only 5.6 pm longer than the Re–Cl(1) bond of the *cis* chlorine atom. We explain these findings by a clear covalent component of the Ga–N bond so that these complexes take an intermediate position between nitrido and imido complexes of rhenium.

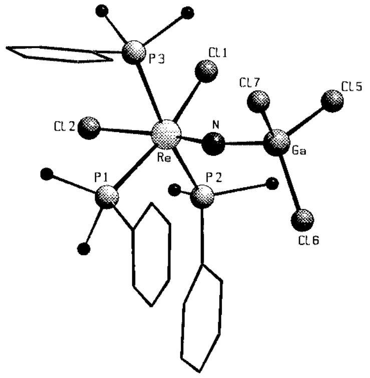


Fig. 4 Molecular structure of $[Cl_3Ga–N≡ReCl_2(PMe_2Ph)_3]$.

5 Nitrido bridges of the type M≡N–Si (IV)

A representative, and at the same time very reactive, molecule with this atomic sequence is $Cl_3V≡N–SiMe_3$. It originates from the reaction of vanadium tetrachloride with trimethylsilyl azide in carbon tetrachloride according to eqn. (4).[26]

$$VCl_4 + Me_3SiN_3 \rightarrow Cl_3V≡N–SiMe_3 + N_2 + \tfrac{1}{2}\,Cl_2 \quad (4)$$

It forms orange–red very volatile crystals with a monomeric molecular structure of C_s symmetry and an almost linear axis VNSi with a bond angle of 177.5° (Fig. 5). The VN bond of 159.4 pm is very short and is interpreted as a triple bond, while the Si–N bond with a length of 179.3 pm represents a relatively long but largely covalent bond. Nevertheless, it is very reactive. With elemental chlorine it reacts under elimination of trimethylchlorosilane and formation of the *N*-chloroimido complex[27] [eqn. (5)] (see also section 8).

$$Cl_3V≡N–SiMe_3 + Cl_2 \rightarrow Cl_3V≡N–Cl + ClSiMe_3 \quad (5)$$

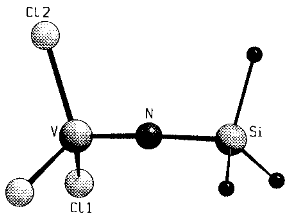


Fig. 5 Molecular structure of $Cl_3V≡N–SiMe_3$.

Surprisingly, reactions of strong Lewis bases such as pyridine also lead to the elimination of trimethylchlorosilane to give the nitrido complex $[Cl_2VN(Py)_2]$ which is associated in linear chains V≡N–V≡N– with strongly alternating bond lengths [eqn. (6)].[28] Trimethylazidosilane was also used for the

$$Cl_3V≡N–SiMe_3 + 2\ Py \rightarrow [Cl_2VN(Py)_2] + ClSiMe_3 \quad (6)$$

synthesis of molybdenum and tungsten silylimido complexes $Cl_2L_3M≡NSiMe_3$ (L = PR_3).[29]

The titanium compound $[Cl_3Ti≡N–SiMe_3]^-$, which is isoelectronic to $Cl_3V≡N–SiMe_3$ can be obtained from the polymeric $[TiCl_2(NSiMe_3)]_\infty$[30] by reaction with tetraphenylphosphonium chloride [eqn. (7)].[31]

$$TiCl_2(NSiMe_3) + PPh_4Cl \rightarrow PPh_4[Cl_3Ti(NSiMe_3)] \quad (7)$$

Surprisingly, the anion has a dimeric structure (Fig. 6) with a trigonal bipyramidal surrounding of the titanium atoms. The Ti–N bonds of the centrosymmetric Ti_2N_2 four-membered ring, however, are of different lengths, namely, 177.4 and 200.1 pm. This implies noticeable multiple bond character for the short bond. The same structure as in $[TiCl_3(NSiMe_3)]_2{}^{2-}$ is found in the isoelectronic molecular compound of the phosphoraneiminato complex (see section 6) $[TiCl_3(NPMe_3)]_2$[7b] (Fig. 6).

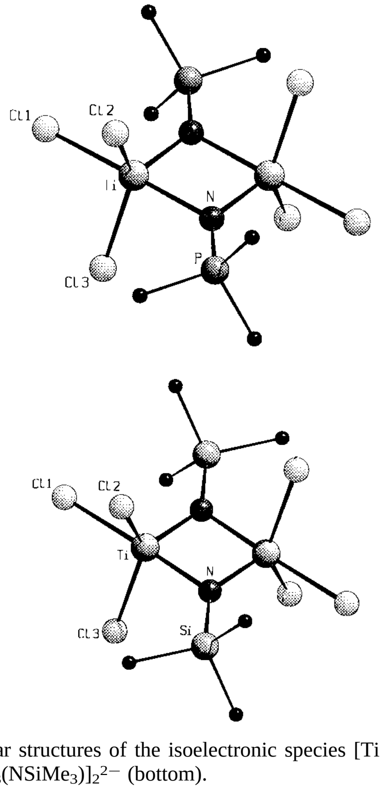


Fig. 6 Molecular structures of the isoelectronic species $[TiCl_3(NPMe_3)]_2$ (top) and $[TiCl_3(NSiMe_3)]_2{}^{2-}$ (bottom).

Here, the Ti–N bonds of the Ti_2N_2 four-membered ring are a little longer, *viz.* 184.3 and 208.2 pm, due to the lower charge of the $(NPMe_3)^-$ ligand compared with $(NSiMe_3)^{2-}$.

Niobium and tantalum dimethylsilyl imido complexes $[(Me_2HSi)_2N]_3M≡NSiHMe_2$ have been obtained from the metal pentachlorides and $LiN(SiHMe_2)_2$.[32]

The reaction of the tantalum imido complex [Ta(NSiMe$_3$)Cl$_3$(py)$_2$] with sodium cyclopentadienide led to an interesting result: on using a large excess of NaCp this reaction resulted in the substitution of all three chloro ligands and in a displacement of the pyridine molecules [eqn. (8)].[33]

$$[\mathrm{Ta(NSiMe_3)Cl_3(py)_2}] + 3\ \mathrm{NaCp} \rightarrow [\mathrm{Cp_3Ta(NSiMe_3)}] + 3\ \mathrm{NaCl} + 2\ \mathrm{py} \quad (8)$$

According to the crystal structure analysis[33] two of the Cp ligands are η^5-bonded, the third Cp ligand is η^1-bonded (Fig. 7).

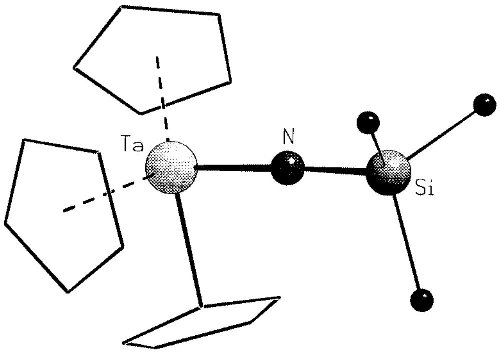


Fig. 7 Molecular structure of [Cp$_3$Ta(NSiMe$_3$)].

Provided that the 18-electron rule is obeyed, the (NSiMe$_3$)$^{2-}$ ligand acts as a four-electron donor, corresponding to the formation of a Ta–N double bond; this is in accord with the observed distance of 179.6 pm. Since the bond axis TaNSi is almost linear with a bond angle of 171.9°, and the Si–N bond is very short with 170.1 pm (in comparison with 179.3 pm in [Cl$_3$V≡N–SiMe$_3$]), this implies the unusual bonding mode [Ta]=N=SiMe$_3$ for the silylimido ligand.

The bis(silylimido) tantalum complex [(py)$_2$MeTa(NSi^{t}Bu$_3$)$_2$][34] has been synthesized from Me$_3$TaCl$_2$ with two equivalents of LiNHSi^{t}Bu$_3$ in hexane and subsequent reaction with pyridine [eqn. (9)]

$$\mathrm{Me_3TaCl_2} \xrightarrow[-\mathrm{MeH}]{\mathrm{LiNHSi^tBu_3}} (^t\mathrm{Bu_3SiNH})\mathrm{Me_2Ta(NSi^tBu_3)} \xrightarrow[-\mathrm{MeH}]{\mathrm{pyridine}} [\mathrm{(py)_2MeTa(NSi^tBu_3)_2}] \quad (9)$$

The crystal structure determination[34] revealed a trigonal bipyramidal molecule with the imido groups in equatorial positions (Fig. 8). The bond angles TaNSi are almost linear (176.3 and 168.1°), and the short average bond lengths for Ta–N of 182 pm and for Si–N of 171 pm indicate multiple bonds for both Ta–N and again Si–N. According to the observed structural parameters such a bonding mode can be assumed also in the heteroleptic tris(imido)tungsten complex [W(NSiMe$_3$)(NMes)$_2$(PMe$_3$)$_2$].[35] This complex is formed as dark red crystals by oxidation of the tungsten(IV) complex [W(NMes)$_2$(PMe$_3$)$_3$] with trimethylsilyl azide [eqn. (10)].[33] The crystal structure

$$[\mathrm{W(NMes)_2(PMe_3)_3}] + \mathrm{Me_3SiN_3} \xrightarrow[20\,^\circ\mathrm{C}]{\mathrm{toluene}} [\mathrm{W(NSiMe_3)(NMes)_2(PMe_3)_2}] + \mathrm{PMe_3} + \mathrm{N_2} \quad (10)$$

analysis[35] exhibited a trigonal bipyramidal coordination for the tungsten atom with the three imido ligands in equatorial positions (Fig. 9). With values of 181.0 pm for the (NSiMe$_3$)$^{2-}$ ligand and 183.0 and 182.2 pm, respectively, for the mesityl imido ligands there is hardly a difference between the WN distances, and they are typical for double bonds. For the tungsten atom this would agree with a 16-electron balance. As in the tantalum imido complexes described above the Si–N bond is again very short with 171.3 pm, and the bond angle WNSi is stretched with 178.8°.

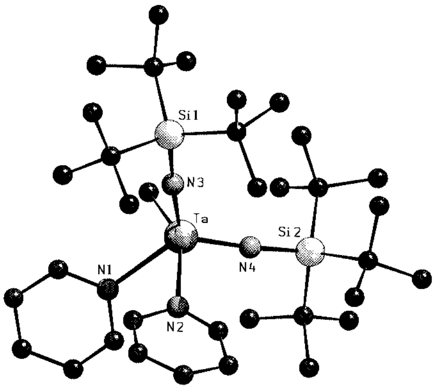


Fig. 8 Molecular structure of [(py)$_2$MeTa(NSi^{t}Bu$_3$)$_2$].

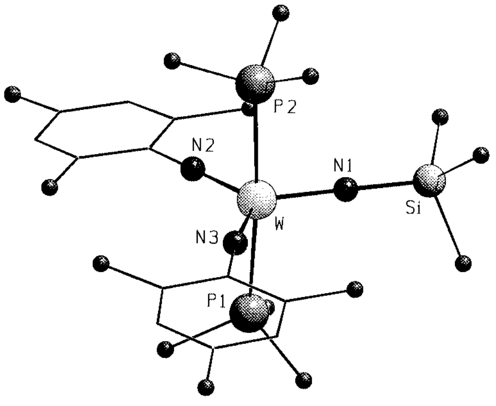


Fig. 9 Molecular structure of [W(NSiMe$_3$)(NMes)$_2$(PMe$_3$)$_2$].

An interesting, fully chlorinated *N*-silylimido amido tungsten complex has been prepared by the reaction of LiN(SiCl$_3$)$_2$ with tungsten hexachloride in dichloromethane at −78 °C [eqn. (11)].[36]

$$\mathrm{WCl_6} + 2\ \mathrm{LiN(SiCl_3)_2} \xrightarrow{-\mathrm{LiCl},\,-\mathrm{SiCl_4}} \mathrm{Cl_3W(NSiCl_3)\{N(SiCl_3)_2\}]} \quad (11)$$

Compounds of this type are promising candidates for molecular preorganization leading to novel polymeric ternary nitrides. The tungsten complex [Cl$_3$W(NSiCl$_3$){N(SiCl$_3$)$_2$}] exhibits a pseudo square-pyramidal arrangement of the ligands with the imido group in apical position (Fig. 10). The corresponding W–N bond length of 171.8 pm is close to the expected value for a triple bond, whereas the W–N bond to the amido ligand (200.7 pm) is in agreement with a single bond.[36]

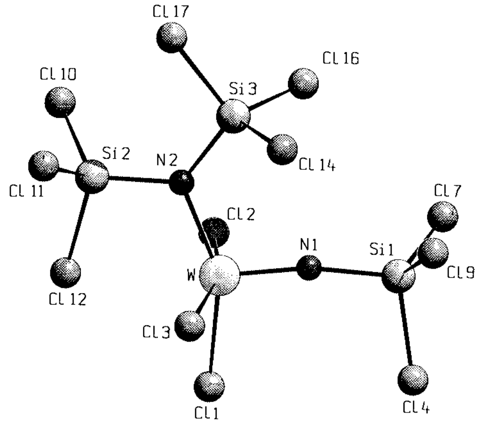


Fig. 10 Molecular structure of [Cl$_3$W(NSiCl$_3$){N(SiCl$_3$)$_2$}].

In comparison with the bonding in the silylimido complexes the M–N bonds in the numerous organoimido compounds with a linear MNC arrangement are always considerably shorter[1a,37] and can be formulated according to **C** as triple bonds, whereas in the complexes with silylimido ligands, because of the partial SiN multiple bond character, the bonding corresponds to the formulae **A** and **B**.

$$\underset{\textbf{A}}{[M]\equiv N\text{–}SiMe_3} \leftrightarrow \underset{\textbf{B}}{[M]{=}N{=}SiMe_3}$$

$$\underset{\textbf{C}}{[M]\equiv N\text{–}R}\ (R = \text{organic substituent})$$

6 Nitrido bridges of the type M–N–P (V)

Compounds of this type contain the phosphoraneiminato ligand (NPR_3^-) (R = organic substituent, Cl, NR_2), which can easily be introduced by reaction of transition metal halides or transition metal oxides with the silylated phosphaneimines Me_3SiNPR_3,[7] as is shown for example in the eqns. (12) and (13). Besides these, the reactions of metal halides with the alkali metal derivatives $LiNPR_3$ and $NaNPR_3$ are also significant as they yield derivatives of rare earth elements [eqn. (14)],[7b] and a threefold substitution was also observed in the reactions with niobium and tantalum pentahalides [eqn. (15)].[38]

$$TiCl_4 + Me_3SiNPR_3 \rightarrow TiCl_3(NPR_3) + ClSiMe_3 \quad (12)$$

$$Re_2O_7 + 2\ Me_3SiNPR_3 \rightarrow 2\ ReO_3(NPR_3) + O(SiMe_3)_2 \quad (13)$$

$$3\ MCp_2Cl + 3\ LiNPPh_3 \xrightarrow{\text{toluene}} [M_2Cp_3(NPPh_3)_3] + MCp_3 + 3\ LiCl \quad (14)$$

$$(M = Y, Dy, Er)$$

$$MCl_5 + 3\ LiNPR_3 \xrightarrow{-LiCl} MCl_2(NPR_3)_3 \quad (15)$$

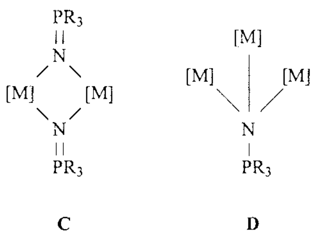
$$(M = Nb, Ta;\ R = {}^tBu, NMe_2)$$

Recently the redox reactions of metals with the *N*-iodo phosphaneimine $INPPh_3$ have also been successfully used [eqn. (16).[39]

$$7\ Yb + 8\ INPPh_3 \xrightarrow{\text{THF}} 2\,[I\text{–}Yb\{Yb(NPPh_3)_4\}(THF)_2] + 3\ YbI_2 \quad (16)$$

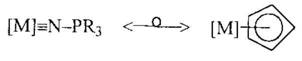
Linear or largely linear MNP bridges are achieved mainly by metals in high oxidation states which can be described by the bonding modes **A** and **B**, respectively. In complexes with metal atoms in medium oxidation states, on the other hand, the dimeric type **C** with μ-N bridging function is found, and with metal atoms in low oxidation states the μ_3-N bridging type **D** occurs leading to structures with a heterocubane skeleton.[7]

$$\underset{\textbf{A}}{[M]\equiv N\text{–}PR_3} \leftrightarrow \underset{\textbf{B}}{[M]{=}N{=}PR_3}$$



C **D**

Examples of bonding mode **A** are found in the molecular complexes $[Cl_3TiNPPh_3]$ and $[O_3ReNPPh_3]$ (Fig. 11).[7] The titanium complex has a stretched bonding axis TiNP (180°) and a very short TiN bond of 171.9 pm, which comes close to a triple bond, while the rhenium complex has an ReNP bond angle of 162.0° and the ReN distance of 179.3 pm lies between the expected value for a double and a triple bond. Bonding mode **A**, which is expected in compounds of this type, implies for the $[NPR_3]^-$ ligand a (σ, 2π)-donor set of six electrons, as it also exists for the bond mode of η^5-cyclopentadienyl ligands in transition metal complexes. It, therefore, suggests, by analogy with the comparison developed for imido complexes,[40] the idea of considering both complex types to be ψ-isolobal to one another. Since both ligand groups show the same charge, direct comparisons can be drawn with the same transition metal; so in this case with $[Cl_3Ti(C_5H_5)]$ and with $[O_3Re(C_5H_5)]$. Indeed, quantum chemical calculations show a striking analogy in the bonding behaviour of these two complex species.[41] The bonding energies calculated on the basis of the model molecules $[Cl_3TiNPH_3]$ and $[O_3ReNPH_3]$ at the BP86/TZ(2)P level of nonlocal density functional theory (DFT) can best be described for both complex chemical series as partial triple bonds which dissociate homolytically into the neutral radical fragments. Compared with this, the heterolytic dissociation is more strongly endothermic by about 200 kcal mol^{-1}. In spite of their strongly differing spatial/steric configuration, the metal–ligand bonding mechanisms of NPH_3 and Cp are astonishingly similar even on closer inspection of the real interaction and of its σ and π components.



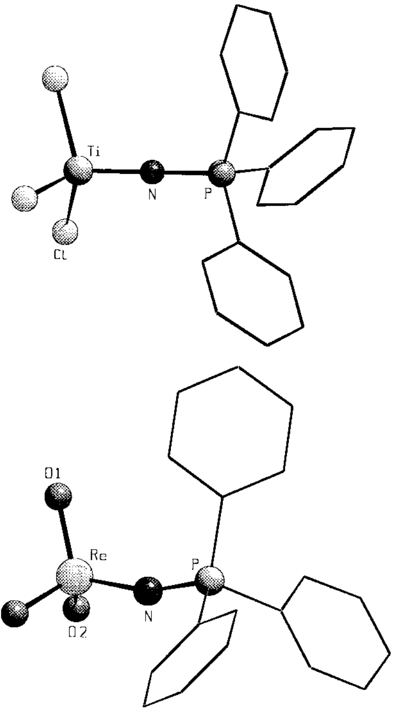


Fig. 11 Molecular structures of $[Cl_3TiNPPh_3]$ (top) and $[O_3ReNPPh_3]$ (bottom).

An exploration of the energy hypersurface of the phosphoraneiminato complexes showed a very flat shape in terms of the MNP bond angle. This means that minor changes within the system, *e.g.* the kind of substituents at the phosphorus atom or packing effects in the crystalline state, can lead to relatively large variations of the MNP bond angle.[41]

Among the numerous known phosphoraneiminato complexes of transition metals,[7] the homoleptic representatives of the same type as the molecular compound $Ti(NPPh_3)_4$, which have been known for some time, attract special interest. The molecular compound $Ti(NPPh_3)_4$ cannot be prepared by fourfold metathesis reaction from titanium(IV) chloride and the silylated phosphaneimine $Me_3SiNPPh_3$, but it can well be obtained from

$TiCl_2(NPPh_3)_2$ and organolithiums in toluene solutions according to eqn. (17). The Ti–N bond lengths are now enlarged to 187

$$[TiCl_2(NPPh_3)_2] \xrightarrow[(R=CH_3,\,C_5H_5)]{LiR} [Ti(NPPh_3)_4] + \text{other products} \quad (17)$$

pm compared with that in $[TiCl_3(NPPh_3)]$ (171.9 pm). The complex is isoelectronic with the monocation $[V(NPPh_3)_4]^+$, which has been prepared as its simple chloride by treatment of $[VCl_2(NPPh_3)_3]$ with dry ammonia in dichloromethane.[42] Compared with $[VOF_2(NPPh_3)]$ (172.7 pm[43]) the VN distances (176.0–177.6 pm) are also stretched, even if to a smaller extent than in $[Ti(NPPh_3)_4]$. It can be assumed that the MN bond lengths are enlarged due to steric hindrance imposed by the phosphoraneiminato moieties (Fig. 12).

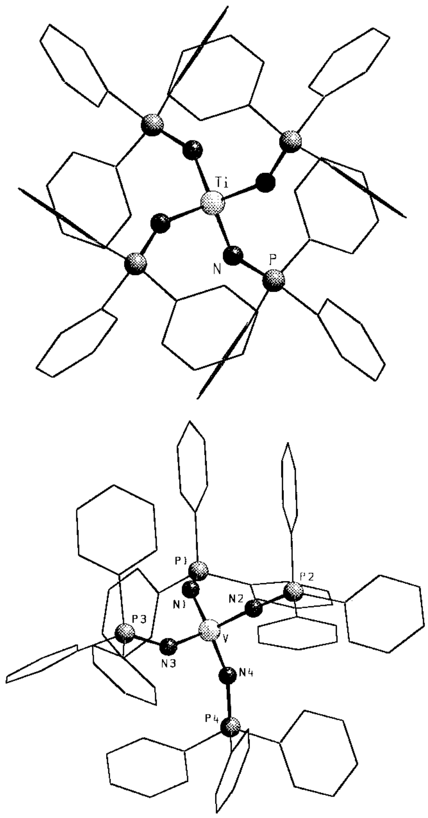
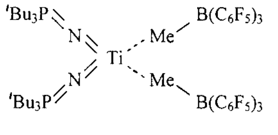


Fig. 12 Molecular structures of the isoelectronic complexes $[Ti(NPPh_3)_4]$ (top) and $[V(NPPh_3)_4]^+$ (bottom).

Whereas the reaction (17) does not result in a stable dialkyl derivative, the dimethyl complexes $[CpTi(NPR_3)Me_2]$ (R = ^{t}Bu, ^{i}Pr, Cy) and $[(^tBu_3PN)_2TiMe_2]$ can easily be obtained by reaction (18).[44] Both types of compounds are catalyst precursors for olefin polymerisation. The reaction of $[(^tBu_3PN)_2TiMe_2]$ with the Lewis acid $B(C_6F_5)_3$ affords the zwitterionic

$$[(^tBu_3PN)_2TiCl_2] \xrightarrow[OEt_2]{MeMgBr} [(^tBu_3PN)_2TiMe_2] \quad (18)$$

species $[(^tBu_3PN)_2TiMe(\mu\text{-}Me)B(C_6F_5)_3]$ which is an active catalyst for ethene polymerisation.[44a] This activity decreases dramatically through the use of an excess of $B(C_6F_5)_3$, which leads to the unprecedented di-zwitterionic complex $[(^tBu_3PN)_2Ti\{\mu\text{-}MeB(C_6F_5)_3\}_2]$.[44b] According to the crystal structure



determination of this pseudo-tetrahedral species both bond angles TiNP = 176.3° and Ti···C–B = 175.0° are nearly linear. The Ti–N bond lengths of 175.7 pm are significantly shorter than the corresponding Ti–N distance in the neutral precursor $[(^tBu_3PN)_2TiMe_2]$ (182.7 pm[44a]), and they are also somewhat shorter than in the dichloro derivatives $[(Ph_3PN)_2TiCl_2]$ (179.0 pm[7b]) and $[(^tBu_3PN)_2TiCl_2]$ (179.1 pm[44a]). These TiN distances do not, however, reach the extremely short bond length of 171.6 pm found in the complex $[TiCl_3(NPPh_3)(TiCl_4)]_2$ activated by the Lewis acid $TiCl_4$.[7b]

$[Ta(NPPh_3)_4]^+$, valence isoelectronic with $[V(NPPh_3)_4]^+$, is also known and has been structurally examined as the corresponding dications of molybdenum and tungsten, $[M(NPPh_3)_4]^{2+}$.[7] These are formed in good yield [eqns. (19)–(21) by exposure of $TaCl_5$, $MoNCl_3$, and WO_2Cl_2 to

$$[TaCl_5]_2 + 4\,Me_3SiNPPh_3 \rightarrow [Ta(NPPh_3)_4][TaCl_6] + 4\,ClSiMe_3 \quad (19)$$

$$MoNCl_3 + 4\,Me_3SiNPPh_3 \rightarrow [Mo(NPPh_3)_4]Cl_2 + ClSiMe_3 + N(SiMe_3)_3 \quad (20)$$

$$WO_2Cl_2 + 4\,Me_3SiNPPh_3 \rightarrow [W(NPPh_3)_4]Cl_2 + 2\,O(SiMe_3)_2 \quad (21)$$

silylated phosphaneimines. The metal–nitrogen distances in the dications $[M(NPR_3)_4]^{2+}$ (M = Mo, W) are only slightly shorter than those in the alkali metal nitrido metalates $[MN_4]^{6-}$ (see Table 1), while the MNP bond angles of all the homoleptic representatives of this series reflect bonding mode **B**. Fig. 13 shows the structure of the $[W(NPPh_3)_4]^{2+}$ ion.

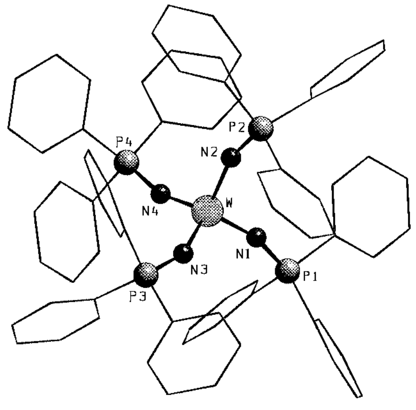


Fig. 13 Molecular structure of the dication $[W(NPPh_3)_4]^{2+}$.

Surprisingly, examples of the bonding modes **A/B** were also found for phosphoraneiminato complexes of the trivalent rare earth elements despite of their large ionic radii and of their small formal charge +3. The resulting small metal–nitrogen distances, which are unprecedented for the rare earth elements, lead to molecular structures with small coordination numbers for the metal atoms. Thus, in the ytterbium complex $[Yb(NPPh_3)_3]_2$ the two metal atoms are μ-N bridged by two $NPPh_3^-$ ligands (bonding mode **C**), whereas the terminal $NPPh_3^-$ ligands exhibit an almost linear arrangement YbNP corresponding to the bonding type **A/B**.[45] The corresponding lanthanum compound crystallises from thf as the solvate $[\{La(NPPh_3)_3\}_2\cdot thf]$ with the oxygen atom bridging in addition to the metal atoms causing a folded butterfly arrangement of the four-membered La_2N_2 ring (Fig. 14).[45] The reason for this probably is the different ionic radius of La^{3+}, which is 13 pm larger than that of Yb^{3+}.

The ytterbium as well as the lanthanum complex are both highly efficient catalysts for the ring opening polymerisation of ε-caprolactone and δ-valerolactone. It is shown that the complexes are active as dimers. Therefore, it can be assumed that the O atoms of the keto and ether functions of the lactones bridge the metal atoms as the primary reaction.[45]

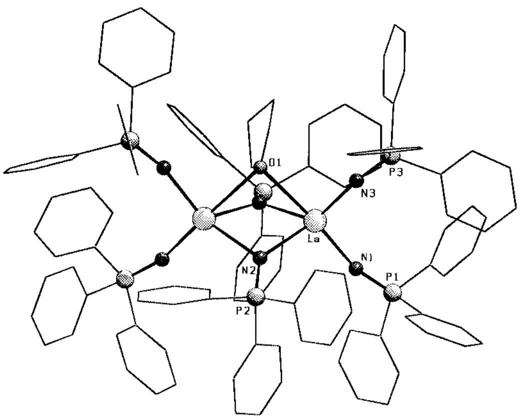


Fig. 14 Molecular structure of $[\{La(NPPh_3)_3\}_2\,(thf)]$.

7 Nitrido bridges of the type M–N–S (VI)

Nitrido bridges of this type are known in five different species, which are listed in Table 2. Besides the thionitrosyl complexes [M]=N=S, which are known for some time and in which this ligand group is generally understood as a NS^+ ligand because of its special bonding modes,[46] the η^1 ligand group $[NSCl]^{2-}$ is known,[8a] which can be described as an imido derivative, as well as the dinitrido sulfate(II) $[NSN]^{4-}$, which serves only as a μ-bridging ligand.[8a] Of the two bidentate chelating ligands $N_3S_2{}^{3-}$ and $N_2S_2{}^{4-}$, the first forms fairly stable planar metalacyclothiazeno complexes with vanadium, molybdenum, tungsten, and rhenium[8b] whereas the second is only known in rhenium(VII) complexes.[8a]

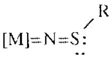
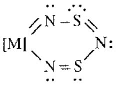
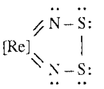
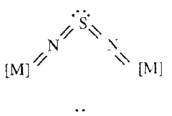
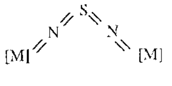
Thionitrosyl complexes are easily obtained by reaction of nitrido complexes with elemental sulfur or disulfur dichloride[46] [eqn. (22)], with polysulfides[47] [eqn. (23)], or by reaction of metal chlorides with trithiazyl chloride[48] [eqn. (24)]. An interesting variant has been described recently by the reaction of the nitrido complex *cis-/trans-*$[Os^{VI}(tpy)(Cl_2)(N)]^+$ with $SPPh_3$ which leads to a phosphoraneiminato complex as well as to a thionitrosyl complex[49] according eqn. (25). The reaction is accompanied by reduction of Os^{VI} to Os^{IV} and Os^{II}, respectively.

$$2[ReNCl_2(PR_3)_2] + S_2Cl_2 \rightarrow 2[Re(NS)Cl_3(PR_3)_2] \quad (22)$$

$$PPh_4[OsNCl_4] + 3\,Na_2S_4 \xrightarrow{DMF-H_2O} PPh_4[Os(NS)(S_4)_2(H_2O)] + 4\,NaCl + Na_2S_3 \quad (23)$$

$$OsCl_3 \xrightarrow{(NSCl)_3,\ THF} Os(NS)Cl_3 \xrightarrow{PPh_4Cl-H_2O} PPh_4[Os(NS)Cl_4(H_2O)] \quad (24)$$

Table 2 Ligand groups with M–N–S sequences

Structure type	Formal description	Nomenclature
$[M]{=}N{=}\ddot{S}$	(NS^-)	Thionitrosyl
	(NSR^{2-}) [R = Cl, Br, CH_3]	R-thioimido [R-thionitreno (2−)]
	$(N_3S_2{}^{3-})$	Iminodithiodiimido (3−) [cyclothiazeno (3−)]
	$(N_2S_2{}^{4-})$	Dithiodiimido (4−)
	(NSN^{4-})	Thiodiimido (4−) [dinitridosulfate(II)]
	(NSN^{2-})	Thiodiimido (2−) [dinitridosulfate(IV)]

$$[Os^{VI}(tpy)(Cl_2)(N)]^+ + SPPh_3 \rightarrow [Os^{IV}(tpy)(Cl_2)(NPPh_3)]^+ + [Os^{II}(tpy)(Cl_2)(NS)]^+ \quad (25)$$

In Fig. 15 the structure of the thionitrosyl complex produced according to eqn. (23) is given as an example. It shows the NS ligand in the typical linear arrangement [M]=N=S with bond lengths Os–N of 175.2 and N–S of 151.3 pm, corresponding approximately to double bonds. The *trans* influence deriving from the short OsN bond is shown in the long Os–(OH_2) bond of 219.8 pm; its effect, however, is clearly reduced compared with the nitrido ligand, since the Os–O distance found in $K[OsNCl_4(H_2O)]^1$ is 250 pm.

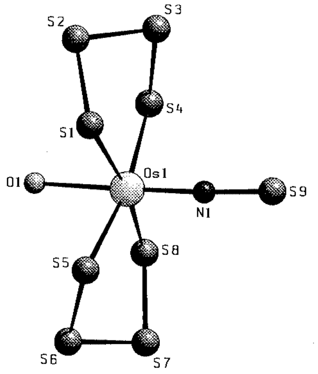
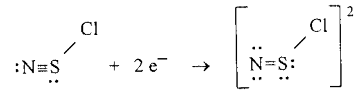


Fig. 15 Molecular structure of the complex ion $[Os(NS)(S_4)_2(H_2O)]^-$.

Complexes with the chlorothionitreno ligand (chlorothioimido ligand) $[NSCl]^{2-}$ are of further preparative interest. The latter is to be regarded as the reduced form of the thiazyl chloride which is monomeric in the gas phase [eqn. (26)]. Up to now, complexes with this ligand group are known for only molybdenum, tungsten, rhenium, and osmium. They can be prepared by exposure of the anhydrous chlorides to trithiazyl chloride according to the following example [eqn. (27)].[8a] The compound has a centrosymmetric molecular structure with asymmetric W–Cl–W bridges with bond lengths of 244.1 and 265.0 pm (Fig. 16). The longer of the two bonds is in a *trans*-position to the shorter W–N bond of the $(NSCl)^{2-}$ ligand. Just as in the thionitrosyl complexes the short W–N bond (176 pm) corresponds to a double bond. At 158 pm the NS bond is a little



$$:N{\equiv}S{-}Cl + 2\,e^- \rightarrow [N{=}S{-}Cl]^{2-} \quad (26)$$

$$2\,WCl_6 + {}^2\!/_3\,(NSCl)_3 \rightarrow [WCl_4(NSCl)]_2 + 2\,Cl_2 \quad (27)$$

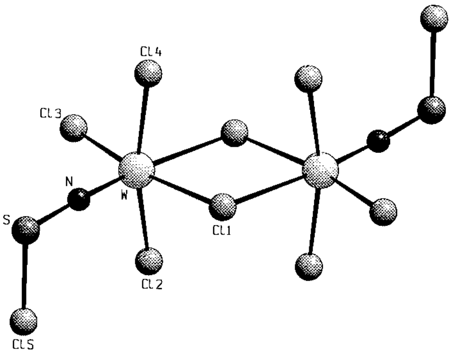


Fig. 16 Molecular structure of the centrosymmetric dimer complex $[WCl_4(NSCl)]_2$.

longer than in thionitrosyl complexes, yet it can still be understood as a double bond. The bond angle NSCl of 104.0° is in accord with the electronic structure of the $(NSCl)^{2-}$ ligand described in eqn. (26).

While $[WCl_4(NSCl)]_2$ can be sublimed undecomposed *in vacuo* and obtained as bright red crystals, the corresponding molybdenum compound undergoes decomposition already at 100 °C [eqn. (28)]. This, however, can be used as an easy route

$$[MoCl_4(NSCl)]_2 \rightarrow 2\ MoNCl_3 + 2\ SCl_2 \qquad (28)$$

for the synthesis of molybdenum nitride chloride. For molybdenum and tungsten only complexes with one $(NSCl)^{2-}$ group are known, rhenium pentachloride, on the other hand, can be converted with trithiazyl chloride to give the disubstituted derivative with heptavalent rhenium [eqn. (29)].[8a] The black

$$ReCl_5 + {}^{2}/_{3}\ (NSCl)_3 \rightarrow ReCl_3(NSCl)_2 + Cl_2 \qquad (29)$$

product insoluble in dichloromethane dissolves readily in donor solvents such as acetonitrile, and also in dichloromethane in the presence of $AsPh_4Cl$ or S_4N_3Cl. Dissolving with the latter produces the corresponding tetrachlororhenate complexes $[ReCl_4(NSCl)_2]^-$. Depending on the cation this results in a cisoid ($S_4N_3^+$) or a transoid ($AsPh_4^+$) conformation of the chlorine atoms bound to the sulfur atoms (Fig. 17).[8a]

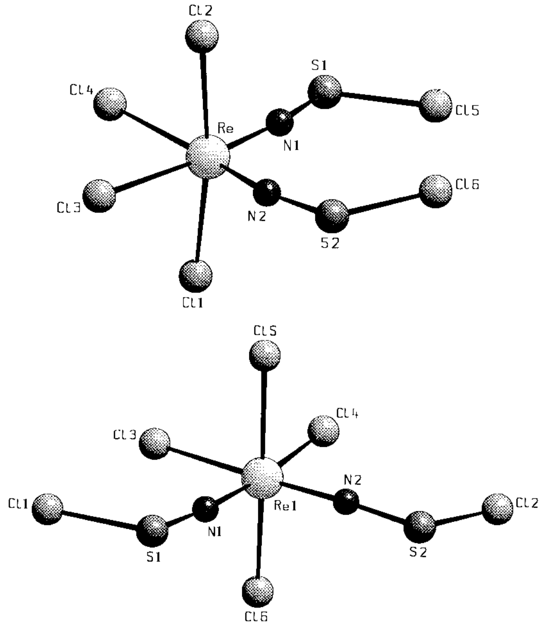


Fig. 17 Molecular structures of the two conformeric species $[ReCl_4(NSCl)_2]^-$.

With reducing agents (formally with loss of Cl_2) the two *cis* $(NSCl)^{2-}$ ligands can be transformed into the remarkable ReN_2S_2 heterocycle, the only example of which is known for rhenium [eqns. (30) and (31)]:[8a]

$$ReCl_3(NSCl)_2 + PPh_3 \rightarrow (ClPPh_3)^+[Cl_4ReN_2S_2]^- \qquad (30)$$

$$[ReCl_4(NSCl)_2]^- + Ph\text{–}C{\equiv}C\text{–}Ph \rightarrow [Cl_4ReN_2S_2]^- + Ph\text{–}C(Cl){=}C(Cl)Ph \qquad (31)$$

The $[Cl_4ReN_2S_2]^-$ ion contains a planar ReN_2S_2 five-membered ring with short Re–N bonds of 182 pm and S–N distances of 152 pm, which agree with double bonds, and a significantly long S–S bond of 253 pm in length, which approximately correspond to the transannular S··S contacts in the S_4N_4 molecule (258 pm) (Fig. 18). But from MO calculations it clearly follows that it is a heterocycle and not an 'open' di-thionitrosyl complex.[50] The short Re=N bonds cause a strong *trans* effect, which can be used for a Cl/F ligand exchange with sodium fluoride in boiling acetonitrile. In this process only the two *trans* chloro ligands are exchanged for fluoro ligands. As a result the Re–N bonds are shortened by seven pm, as is the S–S bond by 10 pm.[8a]

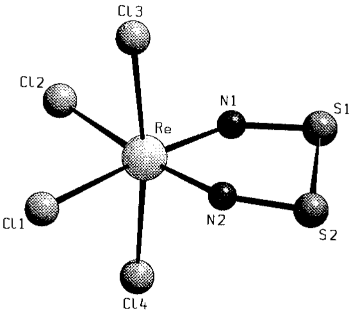


Fig. 18 Molecular structure of the complex anion $[ReCl_4(N_2S_2)]^-$.

Attempts to introduce a second $(NSCl)^{2-}$ ligand into the $(NSCl)^{2-}$ complexes of molybdenum and tungsten by using an excess of trithiazyl chloride lead to the formation of metalacyclothiazene six-membered rings [eqn. (32)].[8b] Reactions

$$[WCl_4(NSCl)]_2 + {}^{4}/_{3}\ (NSCl)_3 \rightarrow [Cl_3WN_3S_2]_2 + 2\ Cl_2 + 2\ SCl_2 \qquad (32)$$

suitable for the synthesis of such complexes are that of $WOCl_4$ with trithiazyl chloride as well as those of the metal chlorides VCl_4, $MoCl_5$, and WCl_6 with S_4N_4. In all cases structure determinations show largely planar MN_3S_2 six-membered rings with metal–N distances that approximately correspond to double bonds and with S–N bonds that are of only slightly different lengths from each other. Therefore, the $(N_3S_2)^{3-}$ chelating rings can be understood as fragments with delocalized π bonds. While $Cl_2VN_3S_2$ forms polymeric chains in which the complex units are connected alternately *via* chloro and nitrogen bridges,[51] the tungsten complex formed according to eqn. (32) has a dimeric molecular structure (Fig. 19).[52]

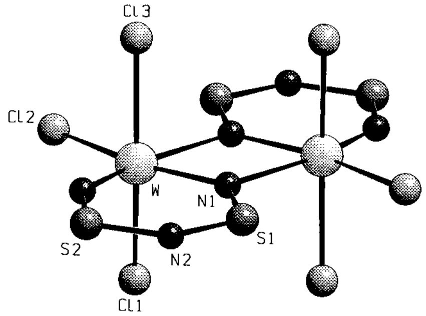


Fig. 19 Molecular structure of the centrosymmetric dimeric complex $[Cl_3W(N_3S_2)]_2$.

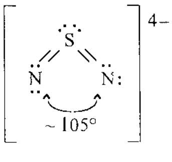
The centrosymmetric W_2N_2 four-membered ring is formed by W–N bonds of different lengths (193.3 and 228.8 pm), with the longer of these bonds corresponding to the donor–acceptor type. This longer bond is easily dissolved by donor molecules such as acetonitrile or tetrahydrofuran as well as by chloride ions in the presence of large cations. As a result, monomeric complex units of the type $[Cl_3WN_3S_2{\cdot}D]$ (D = donor molecule) and $[Cl_4WN_3S_2]^-$, respectively, are formed.[8b]

Exposure to strong bases can lead to the decomposition of the rigid MN_3S_2 six-membered ring with loss of S_4N_4. Thus, the reaction of $Cl_2VN_3S_2$ with pyridine leads to the polymeric nitrido complex [eqn. (33)],[53] which can also be obtained in another way (*cf.* section 5), and $[Cl_3MoN_3S_2]_2$ reacts with $LiNPPh_3$ to give the monomeric nitrido complex $[MoN(NPPh_3)_3]$ [eqn. (34)].[54]

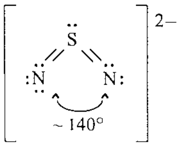
$$Cl_2VN_3S_2 + 2\ Py \rightarrow Cl_2VN(Py)_2 + {}^{1}/_{2}\ S_4N_4 \qquad (33)$$

$$Cl_3MoN_3S_2 + 3\ LiNPPh_3 \rightarrow MoN(NPPh_3)_3 + {}^{1}/_{2}\ S_4N_4 + 3\ LiCl \qquad (34)$$

For the $(NSN)^{4-}$ ligand (**I**), which has to be described as a dinitridosulfate(II) and which is not known in the ionic form, only complexes with μ-bridging function are known. This ligand differs from the $(NSN)^{2-}$ ion (**II**), with tetravalent sulfur,[55] most of all by its smaller bond angle at the sulfur atom. Its potassium salt could be isolated.



(I)



(II)

The electronic structure of complexes of the type $[Cl_4MN_3S_2]^-$ (M = Mo, W) has recently been studied and classified according to C_{2v} symmetry.[56] The MO diagram for the interaction of a $[Cl_4M]^{2+}$ fragment with a $[N_3S_2]^{3-}$ group shows a splitting pattern of the transition metal d orbitals. The M–N σ bond is formed by orbitals of a_1 and b_1 symmetry. π-Bonding results from interaction of fragment orbitals of a_2 and b_2 symmetry.[56] According to the results of a population analysis the transition metal atom acts as an acceptor towards the thiazeno ligand. As the corresponding donor orbitals have N–S antibonding character, this charge transfer causes a strengthening of the N–S bonds. Depending on the π-acidity of the transition metal atom, the electronic structure of the metalacyclothiazenes may be described by the Lewis formula given in Table 2.[56]

$[MoCl_2(NSN)(THF)_2]_2$[57] is an example of a complex with ligand group **I**. The complex forms a centrosymmetric eight-membered ring (Fig. 20). At 175.2 and 180.2 pm the MoN bonds are of slightly different length; they correspond to double bonds. In the structure of $[Hg_2(NSN)_2(NH_3)_2]_\infty$[58] with ligand group **II** the NSN bond angle is 123°; this agrees well with one lone pair at the sulfur atom. The corresponding NSN bond angle, 108.3°, in $[MoCl_2(NSN)(THF)_2]_2$ with the type **I** ligand group is in accordance with two lone pairs at the sulfur atom. $[MoCl_2(NSN)(THF)_2]_2$ can easily be obtained from the *S*-chlorosulfimido complex of molybdenum with *N*,*N*,*N*′-tris-(trimethylsilyl)benzamidine as the nitridation reagent [eqn. (35)].

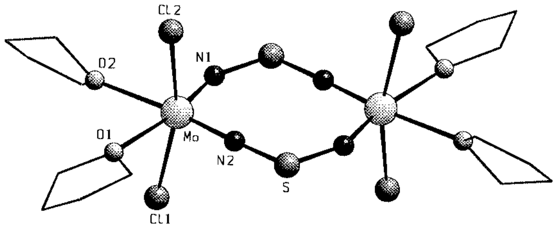


Fig. 20 Molecular structure of the centrosymmetric dimeric complex $[MoCl_2(NSN)(THF)_2]_2$.

$$[MoCl_4(NSCl)]_2 + 2\,[PhC(NSiMe_3)\{N(SiMe_3)_2\}] \xrightarrow{THF} [MoCl_2(NSN)(THF)_2]_2 + 6\,ClSiMe_3 + 2\,PhCN \quad (35)$$

8 Nitrido bridges of the type M≡N–Cl (VII)

Nitrido bridges of this type (*N*-chloroimido complexes) have been reviewed recently along with those of the other halogen atoms.[9] Examples are known for the transition metals vanadium, molybdenum, tungsten, rhenium, and osmium. With the exception of F_5OsNCl, in all cases the transition metal atoms are in their highest oxidation states. Partly they are characterized by *ab initio* calculations. The calculated charge distribution indicates negative partial charge for the N atom if the halogen atom is Cl, Br, or I. A corresponding picture results for the halogen atoms of the M–N–X groups, which show a positive sign for the halogen atoms X. The amount of the positive partial charge decreases along the sequence I → Br → Cl.[9]

These results are in accordance, for example, with the reaction of the $[Cl_5W{\equiv}N{-}Cl]^-$ ion with additional chloride (as the PPh_4^+ salt) which links two of them to form the dinuclear complex with a linear Cl··Cl··Cl bridge [eqn. (36) and Fig. 21]

$$2\,PPh_4[Cl_5W{\equiv}N{-}Cl] + PPh_4Cl \rightarrow (PPh_4)_3[Cl(Cl{-}N{\equiv}WCl_5)_2] \quad (36)$$

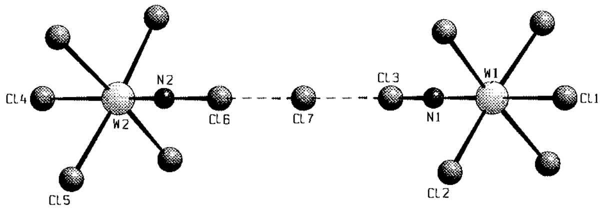


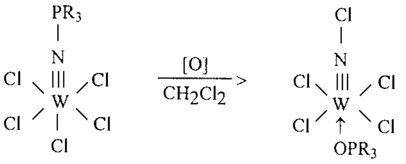
Fig. 21 Molecular structure of the complex anion $[Cl(Cl{-}N{\equiv}WCl_5)_2]^{3-}$.

The Cl··Cl··Cl distances amount to 288 and 278 pm and are noticeably shorter than the sum of the van der Waals distance of 350 pm. Thus, the association can be interpreted by mainly electrostatic bonding modes. The WN triple bond of the W≡N–Cl group is thus affected only marginally.

The *N*-chloroimido derivatives of molybdenum and tungsten are particularly well characterized since they are easily accessible. They can be obtained by reaction of an excess of nitrogen trichloride dissolved in carbon tetrachloride on the metal carbonyls [eqn. (37)]

$$2\ M(CO)_6 + 4\ NCl_3 \xrightarrow{CCl_4} [Cl_4M{\equiv}N{-}Cl]_2 + 12\ CO + N_2 + Cl_2 \quad (37)$$

There is an interesting synthesis reaction, which shows the connection to phosphoraneiminato complexes, by exposure to pyridine *N*-oxide as oxidizing agent [eqn. (38)].[59]



$$Cl_5W{-}N{\equiv}PR_3 \xrightarrow[CH_2Cl_2]{[O]} Cl_4(R_3PO)W{\equiv}N{-}Cl \quad (38)$$

(R = Me, Ph)

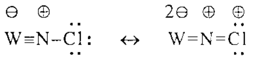
The partially electropositive character of the chlorine atom in the *N*-chloroimido complexes is also documented in the reaction of $[Cl_4W{\equiv}N{-}Cl]_2$ with elemental fluorine; in this reaction [eqn. (39)] the chloro ligands bonded to the tungsten atom can be fluorinated, but not so the *N*-bonded chlorine atom.[60]

$$Cl_4W{\equiv}N{-}Cl + 2\ F_2 \rightarrow F_4W{\equiv}N{-}Cl + 2\ Cl_2 \quad (39)$$

The high tendency for formation of the W≡N–Cl group is also seen in the reaction of molybdenum and tungsten nitride chloride with elemental fluorine [eqn. (40)]. Surprisingly, this reaction does not lead to the nitride fluorides MNF_3 but to the formation of the M≡N–Cl moiety.

$$MNCl_3 + 2\ F_2 \rightarrow F_4M{\equiv}N{-}Cl + Cl_2\ (M = Mo, W) \quad (40)$$

The degree of association of the fluoro derivatives $F_4M{\equiv}N{-}Cl$ is not known. However, the tungsten compound can be isolated as a monomeric acetonitrile solvate complex (Fig. 22).[59] At 178.6° the W≡N–Cl axis is linear; the W–N distance of 172.2 pm is a little longer than in the terminal nitride functionality W≡N: (~165 pm) as expected; however, at 161.1 pm the N–Cl distance is significantly short. This is compatible



with the notation and with the partial positive charge character at the Cl atom. The strong *trans*-influence of the W≡N multiple

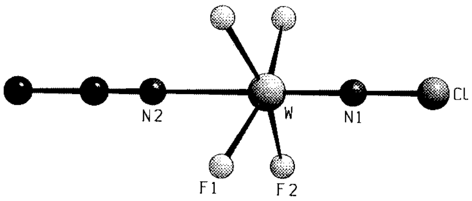


Fig. 22 Molecular structure of the acetonitrile complex $[CH_3CN–WF_4(NCl)]$.

bond only permits a long W–N bond to the acetonitrile molecule of 226.7 pm.

9 Acknowledgement

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