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# Ring Structure Formation in Transition-Metal Nitrido Chlorides by Donor−Acceptor Formation

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According to quantum chemical calculations, nitrido chlorides constituted from $d^6$ transition metals form ring structures which are best described as weak donor−acceptor complexes between the lone pair at nitrogen and the empty d orbitals at the transition metal. The stabilities of the ring structures increase in the order $Cr < Mo < W$. The transition metal Cr forms only endothermic ring systems, and these in turn decompose into monomers. A comparison of several homologous oligomers of $NMoCl_3$ shows maximum stability for the tetramer, in agreement with the experimental findings. This particular stability of the tetramer is due to a perfect alignment of the nitrogens between two metal centers. The vibrational analyses reveal that the character of the monomers is nearly conserved in the ring systems. An analysis of the electron densities on the basis of Bader's method of atoms in molecules as well as of the natural bond orbitals (NBO) substantiates the weak ring stabilities.

## Introduction

The nitrido ligand is known as one of the strongest $\pi$ electron donors As a terminal ligand toward a transition metal ($M\equiv N$), it forms a strong bond, as pioneered in 1965 by Dehnicke and Strähle.[1] Meanwhile, various efficient syntheses for the archetypal transition metal nitrides ($M = Mo$, W) $NMCl_3$, **1**, have appeared[2−4] (Chart 1). From the calculation of the force constants a bond order of 2.2 could be deduced[5] for the related $Mo\equiv N$ bond. When the central atom M is a heavier $d^6$ transition metal ($M = Mo$, W), ring structures are observed.[6,7] The matter has been now summarized in recent reviews.[8−11] The best-known ring system is the tetramer, **2**, characterized for $M = Mo$ and W.[8−11] Meanwhile, trimer structures, **3**, have also become known.[12,13] Of the higher homologues, the pentamers and hexamers have not been reported so far. A characteristic feature of these ring structures is bond alternation, i.e. one long and one short MN in the moiety.

In the present publication we explore the bonding features in a series of ring structures, **4**, for $n = 2-6$, $M = Mo$. For the investigation of a variety of ring structures, molybdenum was chosen as the transition metal, since it occupies a central position in the series of $d^6$ transition metals. The investigations were supplemented with studies on a selected variety of ring systems of the other $d^6$ elements, $M = Cr$ and W, to make a suitable comparison with the other ring systems possible. The method of choice for our investigations is the density functional theory in combination with quasirelativistic effective core potential methods and a double-$\zeta$ description for the valence space.

## Methodology

For the quantum chemical investigations we utilized the effective core potentials (ECP's) of Stevens, Basch, and Kraus[14,15] (SBK basis) which are relativistically corrected for the transition elements. For some cases, in particular the investigation of the monomeric structures ($Cl_3MN$ ($M = Cr$, Mo, W), we also used the ECP's developed by the Los Alamos group[16] (LANL2DZ basis) for comparison. In both basis sets the valence spaces refer to a double-$\zeta$ description for the main group elements and a triple-$\zeta$ description for the d orbitals at the transition metals. In some cases, one set of polarization functions was added to chlorine and nitrogen, and its exponents were chosen according to the suggestions of Schmidt et al.[17] To account for proper electron correlation treatment, various procedures to obtain the equilibrium geometries were tested: (a) the three-parameter density function of Becke[18] where the nonlocal correlation is provided by the LYP expression[19,20] (B3LYP), (b) the MP2 procedure[21] and the results were compared with the findings at (c) the RHF level of sophistication. The best results on the geometries of the ring systems were obtained at a B3LYP/ECP level (ECP from Stevens, Basch, and Kraus[14,15]), without

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**Chart 1**

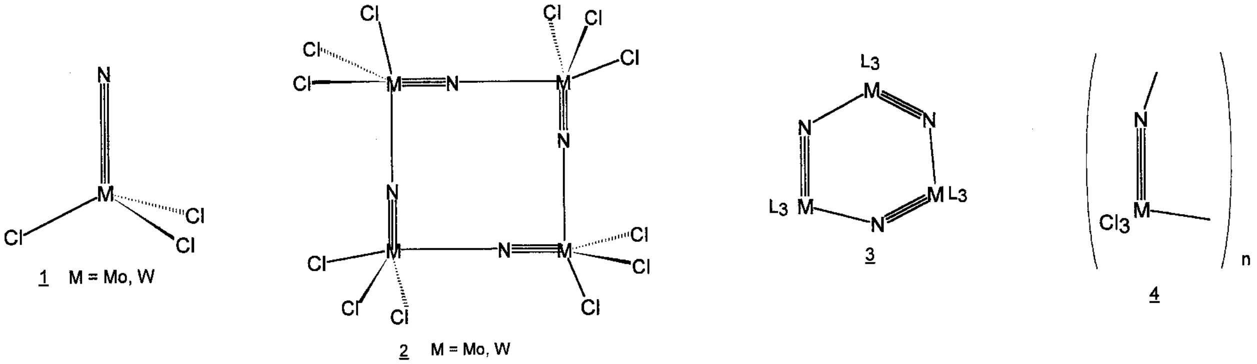
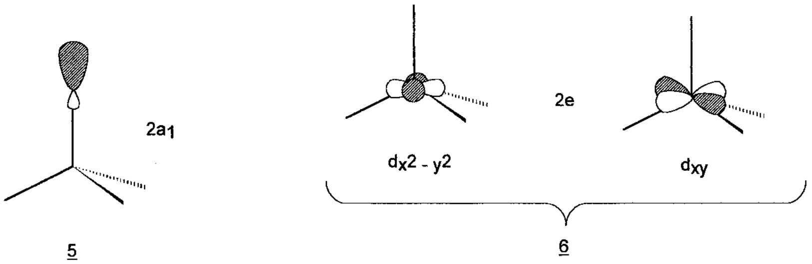


**Chart 2**



inclusion of additional polarization functions at the main group elements nitrogen and chlorine. All quantum chemical calculations were performed with the GAUSSIAN-94 set of programs.[22] A table with results of quantum chemical investigations at various levels of sophistication on the monomers **1** is presented in the Appendix (which includes further discussion of the basis set dependence and the various correlation procedures).

## Results and Discussion

**a. Qualitative Considerations.** We begin our considerations with an analysis of the molecular orbitals of the monomeric **1**. Its bonding feature has been discussed in detail by Hoffmann et al.[23,24] Since the nitrogen is essentially more electronegative than the transition metal, it is informative to discuss the composition of **1** via interaction of $Cl_3Mo^{(3+)}$ (fragment A) with an $N^{(3-)}$ atom (fragment B) (Figure 1).

Interaction of both fragments [C = A−B] leads to the system of molecular orbitals in the monomeric nitride, **1**. For fragment A the energy splitting of the d orbitals at the metal is given by group theoretical considerations.[25,26] At the $Cl_3Mo$ unit (fragment A, $C_{3v}$ symmetry) is at high energy primarily a metal $z$ orbital of $a_1$ symmetry, followed to lower energy by an e set of $x^2-y^2$ and $xy$ character. Below is a second e set with predominantly metal $xy$ and $yz$ character and in addition a $z^2$ orbital, which has $a_1$ symmetry. The nitrogen atom (fragment B) has the three p orbitals, $x$, $y$, $z$, and an $s$ orbital. These belong to another e set and two $a_1$ symmetrical orbitals. The triple-bond character M≡N is obtained here by a strong $\pi$ overlap of the e sets of orbitals of fragments A and B. The HOMO $2a_1$ is a lone pair orbital, **5**, located at nitrogen and directed along the MN axis (Chart 2). On the other hand, the LUMO in the monomeric nitrides refers to an acceptor orbital, **6**, constituted from an e set in C. We will not further discuss all the molecular orbitals in the resulting nitride, as these have, in fact, been discussed in a skillful study by Hoffmann et al.[23,24]

Next we will discuss the formation of the ring systems. A suitable donor−acceptor interaction could occur between the HOMO of one monomeric nitride with the LUMO of another monomeric nitride, as is schematically illustrated in **7** (Scheme 1). This view stresses ring formation as a simple donor−acceptor interaction of monomeric nitrides. In this structure the central transition metal adopts a tetragonal pyramide with the triple bond in the apical position and the chlorines and the other nitrogen in the basal positions, e.g., as illustrated for the tetramer **2**.

Nevertheless such a view is not unique. It may well be possible that the acceptor orbitals share the electrons of the donor orbital to form a strong $\sigma$ bond. In addition **7** does not account for possible $\pi$ delocalization in the formed ring systems. In this case the stabilities should obey Hückel's rule.[23] In more detail the molecular orbital system of nitrides resemble those of phosphazenes which have been the subject of a historical controversy between Dewar[27] and Craig.[28] On this basis the trimer $(Cl_3MN)_3$ (M = $d^6$ transition element), **3**, should exert a particular stability, even though the bond lengths between the nitrogens and the transition metals may alternate. As will be shown by the results of the numerical calculations at SCF level,

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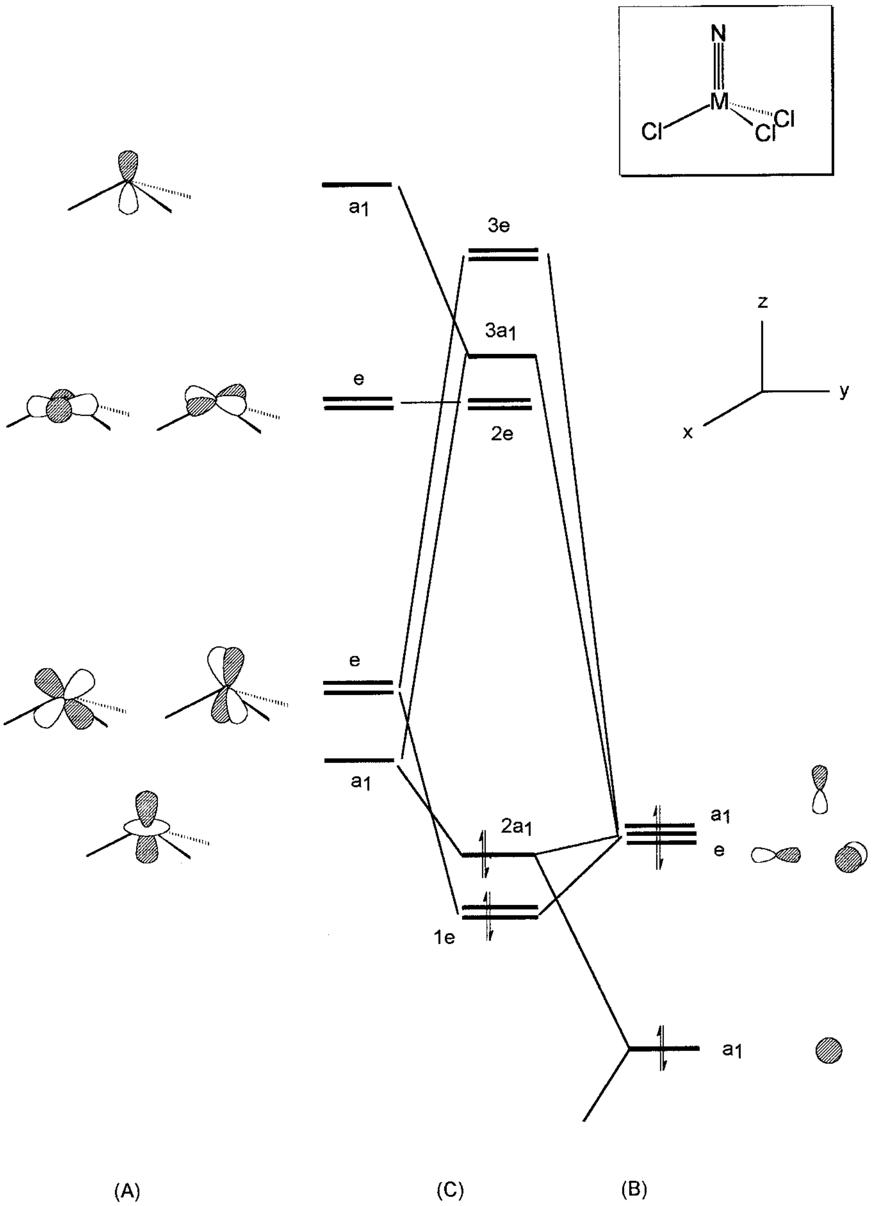
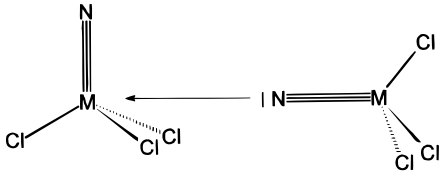


**Figure 1.** Interaction diagram for the frontier orbital composition of monomeric metal nitride [C = A−B] from $MCl_3^{(3+)}$ (A) and $N^{(3-)}$ (B).

**Scheme 1**



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a particular stability of the trimer is not observed. Hence, of the two alternative views, (a) ring formation by donor−acceptor interaction of monomeric nitrides or (b) formation of cyclic π delocalized ring systems, our considerations favor the former.

**b. Equilibrium Geometries of the Ring Structures.** To study the bonding situation in **2** and related homologues we performed a detailed analysis of the ring structures by quantum chemical calculations at SCF level. Of all the tested various procedures (see Appendix) the most successful and also most economically feasible (with regard to the computational effort) appeared to be the density functional approach (B3LYP) with a relativistically corrected effective core potential (SBK) and without further augmentation of the basis set by polarization functions. For the optimization of geometries $C_{nh}$ ($n$ = 2−6) symmetry constraints were assumed. For the trimers and tetramers of M = Mo, a vibrational analysis verified these structures as energy minima on the electronic hypersurfaces. At least for these cases the high symmetry of the structures is thus assured. Given the same ring size for M = Cr, Mo, W, the bonding facets are characteristic, as illustrated for the trimers to the hexamers of the metal nitrides with M = Mo in Figure 2. The nitrogen atoms tend to align between the two metals. One MN bond is short while the other one is long; overall, a strong bond alternation is obtained. For the smaller rings ($n$ = 3) the nitrogen atoms are bent outside while for the larger rings ($n$ = 5, 6) the nitrogens are bent inside the metal−metal axis. More details of the geometries for M = Mo are given in Table 1. For completeness we also included in the table the most important equilibrium parameters (bond lengths in Å, bond angles in deg) of the monomer **1** (M = Mo). Upon ring formation the M≡N bond is only slightly elongated. The effect of ring size is, however, revealed in the long M−N bond. This bond length decreased by almost 10% from the dimer ($n$ = 2)

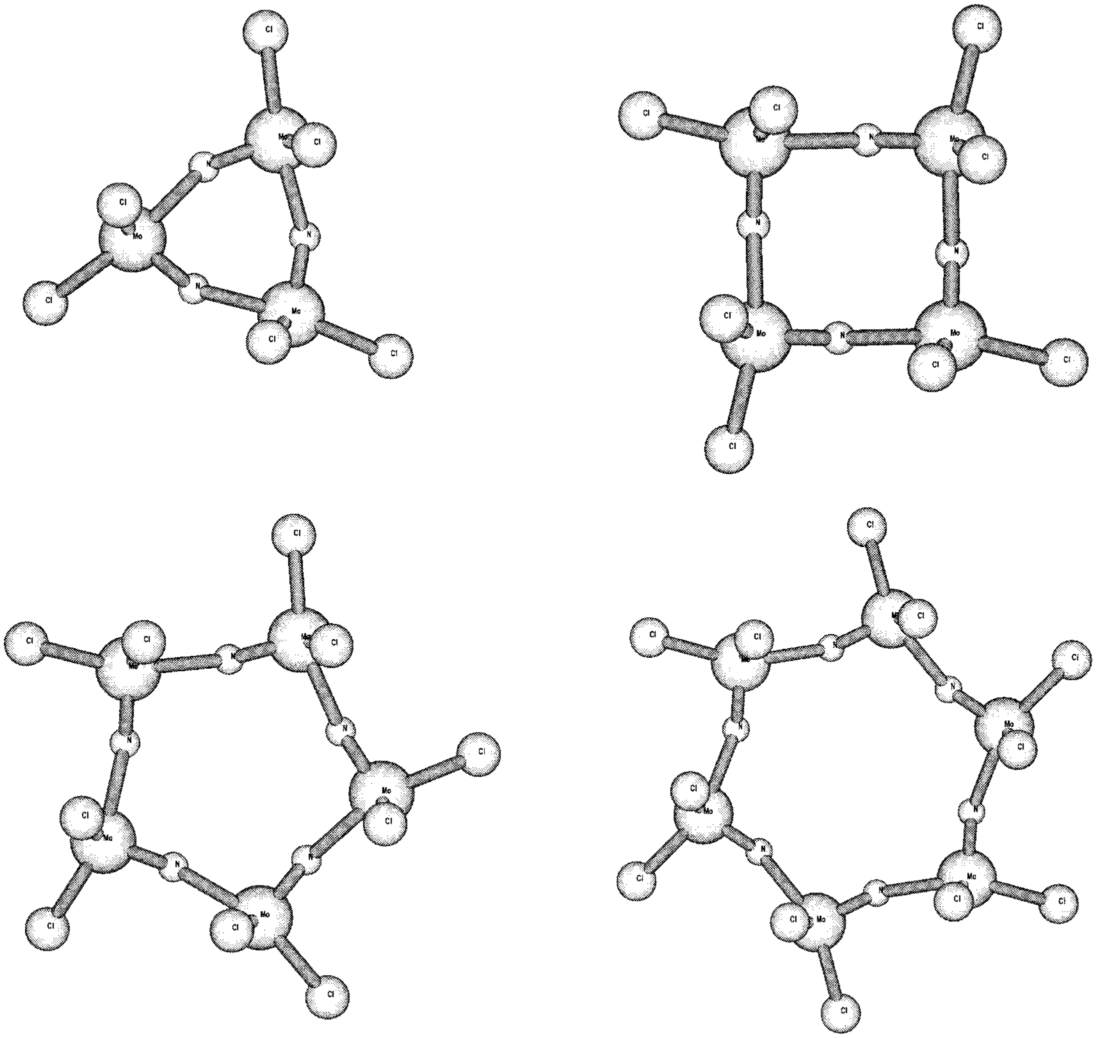

**Figure 2.** Schematic drawing of the ring structures for M = Mo.

**Table 1.** Geometry Parameters (Bond Lengths in Å, Bond Angles in Deg) for Ring Structures, Constituted from M = Mo (at the B3LYP/SBK Level)

| $n$ | Mo≡N | Mo−N | $MoCl_{eq}$ | $MoCl_{ax}$ | ∠Mo≡N−M | ∠N≡Mo−N |
|---|---|---|---|---|---|---|
| 1[a] | 1.669 | − | 2.315 | 2.315 | *b* | − |
| 2 | 1.702 | 2.384 | 2.316 | 2.339 | 101.8 | 78.5 |
| 3 | 1.704 | 2.183 | 2.341 | 2.349 | 155.0 | 85.0 |
| 4 | 1.701 | 2.148 | 2.342 | 2.360 | 173.9 | 96.1 |
| 5 | 1.704 | 2.131 | 2.343 | 2.363 | 173.0 | 101.0 |
| 6 | 1.705 | 2.125 | 2.341 | 2.366 | 165.7 | 105.7 |

[a] $n = 1$ refers to monomer. [b] ∠NMCl = 105.3° ($C_{3v}$ symmetry).

**Table 2.** Geometry Parameters (Bond Lengths in Å, Bond Angles in Deg) for Ring Structures, Constituted from M = W (at the B3LYP/SBK Level)

| $n$ | W≡N | W−N | $WCl_{eq}$ | $WCl_{ax}$ | ∠W≡N−M | ∠N≡W−N |
|---|---|---|---|---|---|---|
| 1[a] | 1.687 | − | 2.321 | 2.321 | *b* | − |
| 2 | 1.752 | 2.153 | 2.344 | 2.350 | 97.4 | 82.6 |
| 3 | 1.738 | 2.060 | 2.364 | 2.353 | 154.1 | 85.9 |
| 4 | 1.733 | 2.032 | 2.359 | 2.368 | 169.9 | 100.1 |

[a] $n = 1$ refers to monomer. [b] ∠NWCl = 104.7° ($C_{3v}$ symmetry).

to the trimer ($n = 3$). The effect of ring formation also significantly increases the length of the MoCl bonds. With increasing ring size the ∠M≡N−M becomes almost linear ($n = 4, 5$) while the ∠N≡M−N is continuously opened.

It is informative to compare these findings with the result for the higher homologue M = W. Only a selected variety of ring systems was investigated, the results for the most important bonding parameters are collected in Table 2. The bonding is similar to the molybdenum case. Here the elongation of the M≡N bond upon ring formation is more pronounced and the M−N bond is significantly shorter in the tetramer ($n = 4$). We note that for the tetramers (M = Mo, W) our computationally derived structures are in good agreement with the experimental results of the crystallography.[8−11] Similarly our values for the trimers, the predicted strong MN bond alternations, are in agreement with the recently reported structures,[12,13] although these ring systems are differently substituted. For the chromium compounds a trimer and a tetramer were investigated: $n = 3$ (4), M≡N 1.562 (1.561), M−N 2.208 (2.069), M−$Cl_{eq}$ 2.187 (2.233), M−$Cl_{ax}$ 2.204 (2.196), ∠M≡N−M 158.9 (175.5), ∠N≡M−N 81.1 (94.5).

**c. Energy Considerations.** How stable are these ring systems? A quantitative measure is given by an analysis of reaction 1.

$$n\mathrm{Cl_3Mn} \rightarrow (\mathrm{Cl_3MN})_n + \Delta E \qquad (1)$$

If the quantity $\Delta E$ is negative, an exothermic ring formation results and then $\Delta E/n$ gives an energy profit for the formed average M−N bond. For all of the calculated ring systems M = Cr, Mo, W, the compiled values for $\Delta E/n$ are collected in Table 3. It is worthwhile to extrapolate our analysis to M = Cr. From the viewpoint of experiment corresponding structures

**Table 3.** Energy Balances (in kJ/mol) for Ring Formation of Transition Metal Nitrides (at the B3LYP/SBK Level)

| | *n* | | | | |
|---|---|---|---|---|---|
| M | 2 | 3 | 4 | 5 | 6 |
| Cr | *a* | +17.7 | +7.6 | − | − |
| Mo | +2.7 | −48.3 | −59.4 | −59.4 | −55.9 |
| W | −29.4 | −99.5 | −115.8 | − | − |

[a] Dissociation into two monomers.

**Table 4.** Disproportionation Energies (in kJ/mol) for Ring Structures (at the B3LYP/SBK Level)

| reaction | Mo | W |
|---|---|---|
| $2(NMCl_3)_2 \rightarrow (NMCl_3)_3 + NMCl_3$ | −156.5 | −180.8 |
| $2(NMCl_3)_3 \rightarrow (NMCl_3)_4 + (NMCl_3)_2$ | +58.9 | +74.6 |
| $2(NMCl_3)_4 \rightarrow (NMCl_3)_5 + (NMCl_3)_3$ | +32.7 | − |
| $2(NMCl_3)_5 \rightarrow (NMCl_3)_6 + (NMCl_3)_4$ | +21.8 | − |

are not known. In the computer experiment these can be traced as stable minima on the energy hypersurface, but their ring formation appears to be endothermic (see Table 3). It is obvious that with increasing atomic number of the transition metal (Cr < Mo < W) the ring systems gain stability, as witnessed in the series of trimers and tetramers.

Our findings rule out a particular role of Hückel's rule on the stabilities of the ring structures. According to our considerations these should rather be described by a donor−acceptor interaction of the lone pair orbital at nitrogen (donor) into the vacant d orbitals (acceptor) at the transition metal. Within a given series of metals (e.g. Mo) the average binding energies differ only in a small amount, which can be accounted for the different geometrical arrangement of the nitrogen bridge (see Figure 1) in bonding toward the metal. The best arrangement of the monomeric nitrides seems to be given in the tetrameric structure.

It is informative to inspect the disproportionation energies for the ring structures. For M = Mo and W these are listed in Table 4. The energy balances are strongly exothermic for the dimers. For all other cases these are strongly endothermic. Hence one expects that these structures are stable entities on the electronic hypersurfaces.

**d. Vibrational Analysis.** Important physicochemical aspects of the transition metal nitrides are their vibrational spectra. If they form stable ring structures then the vibrational spectra should change essentially with respect to the monomers. Experimentally the vibrational spectra of the monomers are difficult to obtain since these undergo easily oligomerization reactions to the ring systems, e.g., the tetramers. However, for $NMoCl_3$ a sharp absorption band at 1045 $cm^{-1}$ has been assigned to the MoN triple bond,[1] while for $NWCl_3$ a single peak appeared at 1086 $cm^{-1}$.[7] Thus the M≡N (M = Mo, W) vibrations differ only slightly. Given the latter value (1086 $cm^{-1}$)[7] For $NWCl_3$ our computed value (1131 $cm^{-1}$) differs by 45 wavenumbers. The MCl vibrations occur at approximately 400 $cm^{-1}$. For the monomeric metal nitrides we obtained the following normal vibrations (Table 5). In these structures no inversion center is present, hence all vibrations are IR and Raman active. We note that in parts a vibrational assignment of the monomers has also been reported previously by quantum chemical investigations of Frenking et al.[29] Their results differ slightly from ours, since a different computational approach was used (MP2 procedure with the Hay−Wadt quasirelativistic effective core potential). Most important is the totally symmetric ($a_1$) M≡N bond vibration. It appears at lower frequencies in the order Cr < Mo < W. In agreement with experiment[1] the MCl vibrations show up at approximately 400 $cm^{-1}$. Upon ring formation (M = Mo) the M≡N vibrations couple for the trimer ($C_{3h}$) to e′ (1104 $cm^{-1}$) and a′ (1028 $cm^{-1}$) and for the tetramer ($C_{4h}$) to $b_g$ (1139 $cm^{-1}$), $e_u$ (1113 $cm^{-1}$), and $a_g$ (1070 $cm^{-1}$). In the trimer only the e′ and in the tetramer only the $e_u$ vibrations are IR active. We do not list here the full vibrational analysis. Full details of the investigations are available on request.

**Table 5.** Vibrations (in $cm^{-1}$) for $NMCl_3$ Compounds (at the B3LYP/SBK Level)

| $\nu_M$ ($cm^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|
| Cr | Mo | W | symm | IR | Raman | assignment |
| 1202 | 1123 | 1131 | $a_1$ | + | + | M≡N valence |
| 486 | 424 | 397 | e | + | + | M−Cl valence |
| 391 | 371 | 374 | $a_1$ | + | + | M−Cl valence |
| 296 | 260 | 258 | e | + | + | M≡N deformation |
| 168 | 133 | 125 | $a_1$ | + | + | M−Cl deformation |
| 122 | 96 | 97 | 3 | + | + | M−Cl deformation |

**Chart 3**

| | | |
|---|---|---|
| $NMoCl_3$ | +1.28 (+2.00) | -0.22 (-0.51) |
| $(NMoCl_3)_3$ | +1.32 (+2.24) | -0.47 (-0.82) |
| $(NMoCl_3)_4$ | +1.33 (+2.28) | -0.49 (-0.86) |

NBO (Bader)

The analysis of the M≡N vibrations in the ring systems and a comparison with the corresponding $a_1$ vibration in the monomers are again an indication of the weak coupling of monomeric units in the rings. It emphasizes the view of a donor−acceptor interaction dictating the stability of the ring structures.

**e. Population Analysis.** Last we will discuss the results of the population analysis for the various structures. Again we restrict our consideration to the cases M = Mo. Analyses of the electron densities were performed utilizing various partitioning schemes, the NBO (natural bond orbital analysis[30] and Bader's method of "atoms in molecules"[31] (values in parentheses, Chart 3). Both procedures result in similar trends, and the metals have strongly donated electron density to the nitrogens and chlorines. To a stronger extent this tendency is pronounced in Bader's approach. (The charges were obtained by an integration of the charge density from the density functional wavefunction over the atomic basins.) These results are in accord with the assignment of a strongly polar metal−nitrogen bond, although the formal oxidation state (+6) in the metal is not achieved. Interestingly the charge separation increases slightly from the monomer to the ring systems. For M = W the electron density distributions are similar. However, the transition metal becomes more electropositive, thus donating slightly more (ca. 0.1) electrons to its more electronegative neighboring atoms.

## Summary

The results of our investigations can be summarized as follows:

(1) The nitrido complexes of the $d^6$ transition metals (Cr, Mo, W) form ring structures which for the heavier elements Mo and W are more stable than their monomers. The element M = Cr is an exception, it does not form ring structures exothermically from the monomers.

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(2) The ring structures are best described as weak donor−acceptor complexes in which the lone pair orbital at nitrogen donates electron density toward the acceptor d orbitals at the transition metal. Donor−acceptor complexes in general possess weak binding energies.[32,33] A special role of Hückel's rule as driving force on the ring stabilities is not substantiated.

(3) As analyzed in detail for M = Mo, most stable are the tetramers and least stable the dimers. The latter should disproportionate easily into trimers and monomers.

(4) The vibrational spectra of $(NMoCl_3)_{n=3.4}$ indicate that upon ring formation the Mo≡N vibration is only slightly changed in the wavenumber. It again makes a weak coupling of monomers evident. The MoCl vibrations are strongly separated from the MoN triple-bond vibration.

(5) The analysis of electron densities reveal an oxidation state of the metal which is lower than (+6), as one expects from formal considerations. It indicates covalency in the metal−nitrogen bond. However, the Bader procedure of atoms in molecules shows a stronger charge separation than the natural bond orbital analysis.

Our investigations on the nitrides are restricted to considerations in the gas phase. In the experiment, however, the crystal structures are mediated by neighboring effects and/or are coordinated by other molecules. With regard to this aspect various structures are known.[34−37] Also our considerations do not give an answer to possible $[NWCl_3]_\infty$ polymerization,[8] as has been found for $NReCl_4$[38] and $NW(t\text{-}BuO)_3$.[39] It is of interest to extend the considerations to $d^7$ and $d^8$ transition elements. Corresponding ring structures are recorded in the literature.[8−11] Investigations on this subject are currently in progress.

## Appendix

For the evaluation of ring structures we have tested various quantum chemical methods. The matter may be first demonstrated for the monomeric $NMoCl_3$ (Table 6). Experimentally two different bond lengths have been assigned to the MoN triple-bond, 1.64 and 1.67 Å.[1] It is the result from investigations on two different crystals. In comparison with at RHF level the MoN triple-bond results too short, in particular when additional d functions are included in the basis set (SBK+d, 1.586 (Å). On the other hand the MP2 procedure tends to overestimate the MoN triple-bond length. This is also shown in a previous study on oxo and nitrido complexes of Mo, W, Ru, and Os.[29] The best results are obtained on the basis of density functional theory.

**Table 6.** Results of Various Methods on $NMoCl_3$ ($C_{3v}$ Symmetry)

| basis set | method | Mo≡N | MoCl | ∠NMoCl |
|---|---|---|---|---|
| SBK[a] | RHF | 1.616 | 2.314 | 104.8 |
| SBK+d[b] | RHF | 1.586 | 2.285 | 105.0 |
| SBK | MP2 | 1.750 | 2.319 | 105.1 |
| SBK | B3LYP | 1.669 | 2.315 | 105.3 |
| SBK+d | B3LYP | 1.646 | 2.284 | 105.4 |
| LANL2DZ[c] | RHF | 1.611 | 2.323 | 103.9 |
| LANL2DZ | MP2 | 1.734 | 2.345 | 105.0 |
| LANL2DZ | B3LYP | 1.664 | 2.318 | 104.7 |

[a] Effective core potential method of Stevens, Basch, and Krauss. [b] Additional one set of d functions (6d) at chlorine and nitrogen. [c] Effective core potential method of Hay and Wadt.

**Table 7.** Results of Various Methods on Tetramer $(NMoCl_3)_4$

| basis set | method | Δ*E*/*n* | Mo≡N | Mo−N |
|---|---|---|---|---|
| SBK | RHF | −24.1 | 1.645 | 2.230 |
| SBK+d | RHF | +86.5 | 1.625 | 2.282 |
| LANL2DZ | RHF | −16.7 | 1.633 | 2.240 |
| SBK | B3LYP | −59.4 | 1.701 | 2.148 |
| SBK+d | B3LYP | −29.9 | 1.678 | 2.215 |

Similarly, the association energies for ring formation depends strongly on the chosen computational level, e.g., for the tetramer $(NMoCl_3)_4$ the following situation results (Table 7). At the density functional level the binding energies ($\Delta E/n$) generally appear higher than at the RHF level. It indicates the importance of an account for electron correlation on the binding energies. Further additional polarization functions at chlorine and nitrogen tend to pronounce destabilization of the ring structures.

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