Theor Chem Acc (1999) 102:300–308
DOI 10.1007/s00214980m165

Theoretical
Chemistry Accounts

*Regular article*

# The Lewis basicity of nitrido complexes. Theoretical investigation of the structure and bonding of $Cl_2$ $(PH_3)_3ReN{-}X$ (X = $BH_3$, $BCl_3$, $BBr_3$, $AlH_3$, $AlCl_3$, $AlBr_3$, $GaH_3$, $GaCl_3$, $GaBr_3$, O, S, Se, Te)*,**

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Received: 27 July 1998 / Accepted: 26 October 1998 / Published online: 16 March 1999

**Abstract.** Quantum chemical calculations using gradient-corrected density functional theory (B3LYP) and ab initio methods at the MP2 level are reported for the geometries and bond energies of the nitrido complexes $Cl_2$ $(PH_3)_3ReN{-}X$ (X = $BH_3$, $BCl_3$, $BBr_3$, $AlH_3$, $AlCl_3$, $AlBr_3$, $GaH_3$, $GaCl_3$, $GaBr_3$, O, S, Se, Te). The theoretical geometries are in excellent agreement with experimental values of related complexes which have larger phosphine ligands. The parent nitrido complex $Cl_2(PH_3)_3ReN$ is a very strong Lewis base. The calculated bond dissociation energy of $Cl_2(PH_3)_3ReN{-}AlCl_3$ is $D_e = 43.7$ kcal/mol, which is nearly as high as the bond energy of $Me_3N{-}AlCl_3$. The donor-acceptor bonds of the other $Cl_2(PH_3)_3ReN{-}AY_3$ complexes are also very strong. Even stronger N—X bonds are predicted for most of the nitrido-chalcogen complexes, which exhibit the trend $X = O \gg S > Se > Te$. Analysis of the electronic structure shows that the parent compound $Cl_2(PH_3)_3ReN$ has a Re—N triple bond. The Re—N $\sigma$ bond is clearly polarized towards nitrogen, while the two $\pi$ bonds are nearly nonpolar. The Re—N $\sigma$ and $\pi$ bonds become more polarized toward nitrogen when a Lewis acid or a chalcogen atom is attached. Bonding in $AY_3$ complexes should be described as $Cl_2(PH_3)_3Re{\equiv}N{\rightarrow}AY_3$, while the chalcogen complexes should be written with double bonds $Cl_2(PH_3)_3Re{=}N{=}X$. The charge-decomposition analysis indicates that the nitrogen-chalcogen bonds of the heavier chalcogen complexes with X = S, Se, Te can also be interpreted as donor-acceptor bonds between the nitrido complex acting as a Lewis base and the chalcogen atom with an empty $p(\sigma)$ orbital acting as a Lewis acid. The nitrido oxo complex $Cl_2(PH_3)_3$ $Re{=}N{=}O$ has a covalent N—O double bond.

**Key words:** Lewis basicity – Nitrido complexes – Transition–metal bonding

## 1 Introduction

Transition-metal compounds with terminal nitrido groups show a fascinating variety of chemical reactions [1, 2]. The nitrogen atom of $L_nM{\equiv}N$ is capable of binding other transition-metal fragments and main-group elements which leads to molecules with coordination numbers 2–4 at nitrogen [2]. Transition-metal nitrido complexes are strong Lewis bases. This becomes obvious from experimental studies which show that complexes of $L_nM{\equiv}N{-}X$, where X is a Lewis acid, are stable compounds which can readily be synthesized [2–6]. In the course of our theoretical studies of donor-acceptor complexes [7–9] and transition-metal compounds with multiple metal-ligand bonds [10], we became interested in the nature and the strength of the nitrido-Lewis acid interactions. While main group compounds with triply bonded nitrogen such as nitriles are rather weak Lewis bases [7, 11], the bonding in transition-metal nitrido compounds apparently makes the nitrogen atom become a strong Lewis base; however, there are no experimental data on the strength of the donor-acceptor bond in $L_nMN{-}X$ compounds. Also, theoretical studies on these complexes have not been published so far.

We decided to carry out a theoretical investigation of the structure and bond strength of complexes with nitrido bridges between main-group atoms and transition metals. The choice was made to study the complexes $Cl_2(PH_3)_3ReN{-}X$ with the Lewis acids X = $BH_3$, $BCl_3$, $BBr_3$, $AlH_3$, $AlCl_3$, $AlBr_3$, $GaH_3$, $GaCl_3$, $GaBr_3$, and with the chalcogens X = O, S, Se, Te. The chalcogen compounds have been included in this study in order to

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* Contribution to the Kenichi Fukui Memorial Issue

** Theoretical studies of inorganic compounds. VII. Part VI: Boehme C, Frenking G. Chem Europ J (in press)

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compare the bonding situation with that of the donor-acceptor complexes. The experimental work of Abram and coworkers [4–6] makes it possible to compare the calculated geometries with measured data obtained from X-ray structure analysis. The focus of this work is on the calculation of the nitrido-acceptor bond strength at a level of theory which has proven to give accurate results for donor-acceptor complexes [8, 9]. We also present a detailed analysis of the bonding situation in the $L_nM{\equiv}N{-}X$ moiety using the charge-decomposition analysis (CDA) [12] and the natural bond orbital (NBO) partitioning scheme [13].

## 2 Theoretical methods

The geometry optimizations were carried out using two different methods. One method is gradient-corrected density functional theory (DFT) with the three-parameter fit of hybrid functionals introduced by Becke (B3LYP) [14]. The second method is Møller–Plesset perturbation theory terminated at second order (MP2) [15]. For both methods we used our standard basis set II [16], which has a relativistic effective core potential (ECP) [17] with a (441/2111/21) valence basis set for Re and a 6-31G(d) all-electron basis sets for H, B, and N [18]. An ECP has been employed with a (31/31/1) valence basis set for the heavier main-group elements Al, Ga, S, Se, Te, P, Cl, and Br [19]. The vibrational frequencies and zero-point vibrational energies were calculated at B3LYP/II. All structures reported here are minima on the potential energy surface (only positive eigenvalues of the Hessian matrix). Additional single-point energy calculations were carried out at the CCSD(T) level [20] using B3LYP/II optimized geometries for the bond energies of the boron complexes $Cl_2(PH_3)_3ReN{-}X$ ($X = BH_3, BCl_3, BBr_3$).

The analysis of the donor-acceptor interactions was performed using the CDA [12]. In the CDA method the (canonical, natural of Kohn–Sham) molecular orbitals (MOs) of the complex are expressed in terms of the MOs of appropriately chosen fragments. In the present case, the Kohn–Sham orbitals of the B3LYP/II calculations of $Cl_2(PH_3)_3ReN{-}X$ are formed by a linear combination of the orbitals of $Cl_2(PH_3)_3ReN$ and X in the geometry of $Cl_2(PH_3)_3ReN{-}X$. The orbital contributions are divided into the mixing of the occupied MOs of $Cl_2(PH_3)_3ReN$ and the unoccupied MOs of X [donation $N \rightarrow X$], the occupied MOs X and the unoccupied MOs of $Cl_2(PH_3)_3ReN$ [backdonation $N \leftarrow X$], and the mixing of the occupied MOs of X and the occupied MOs of $Cl_2(PH_3)_3ReN$ [repulsive polarization $X \leftrightarrow N$]. A more detailed presentation of the method and the interpretation of the results is given in Ref. [18]. Further examples where the CDA method was used for the analysis of donor-acceptor complexes can be found in the literature [8, 9].

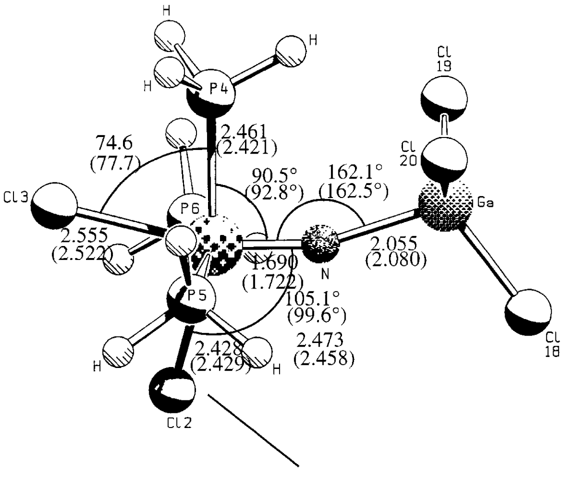
The geometry optimizations and frequency calculations were carried out with the program package Gaussian 94 [21]. The CDA calculations were performed using the program CDA 2.1 [22].

## 3 Geometries and bond energies

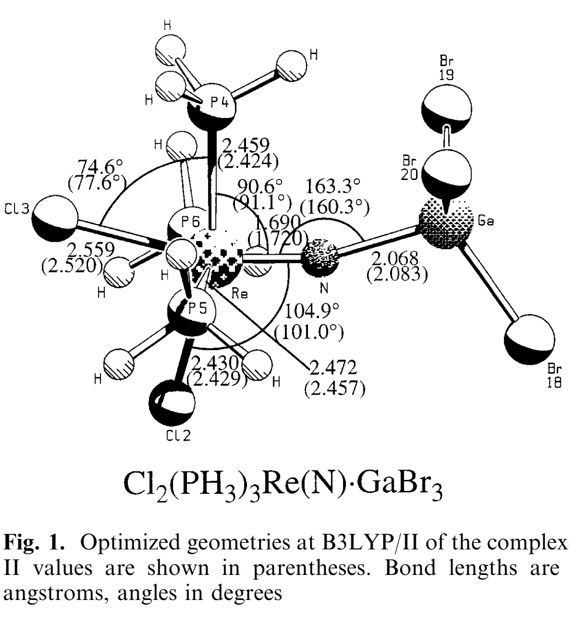
The optimized structures of the calculated complexes at the B3LYP/II level of theory are shown in Fig. 1. The calculated bond lengths and bond angles at MP2/II are given in parentheses.

The theoretically predicted geometry of the parent compound $Cl_2(PH_3)_3ReN$ shall be compared with the X-ray structure analysis of the related complex $Cl_2(PMe_2Ph)_3ReN$ [23]. The agreement of the B3LYP/II values with the experimental values is very good. The most important bond lengths are Re—N = 1.668 Å (exp. 1.660 Å), Re—P = 2.440 and 2.460 Å (exp. 2.42–2.46 Å), and $Re{-}Cl_{cis}$ = 2.455 Å (2.442 Å). The MP2/II values are similar, but the Re—N bond length (1.703 Å) is slightly too long. It has been noted before that MP2 gives bond lengths for transition metal-ligand multiple bonds which are too long [10].

The calculated geometries of the nitrido complexes with Lewis acids $Cl_2(PH_3)_3ReN{-}$ X compare generally quite favorably with available experimental data. An

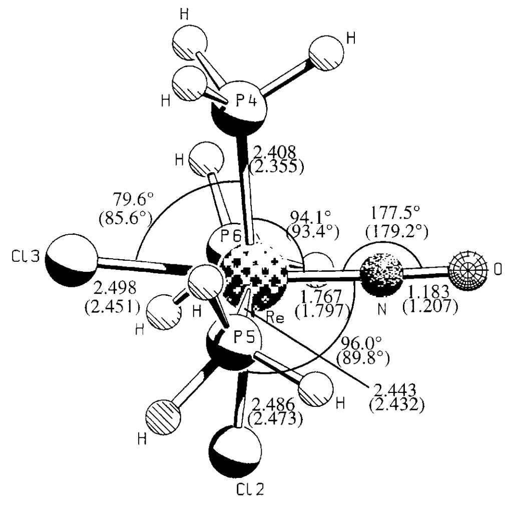


$Cl_2(PH_3)_3Re(N){\cdot}GaCl_3$

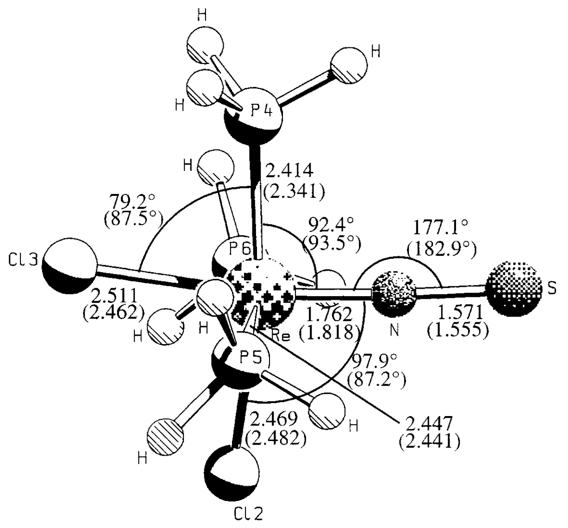


$Cl_2(PH_3)_3Re(N){\cdot}GaBr_3$

**Fig. 1.** Optimized geometries at B3LYP/II of the complexes. MP2/II values are shown in parentheses. Bond lengths are given in angstroms, angles in degrees

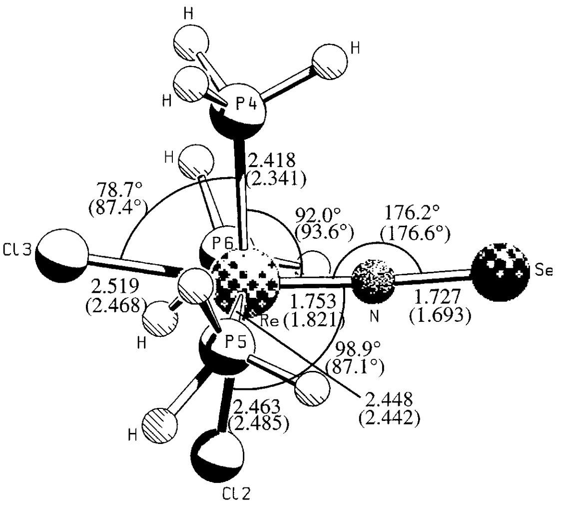


$Cl_2(PH_3)_3Re(N\text{-}O)$

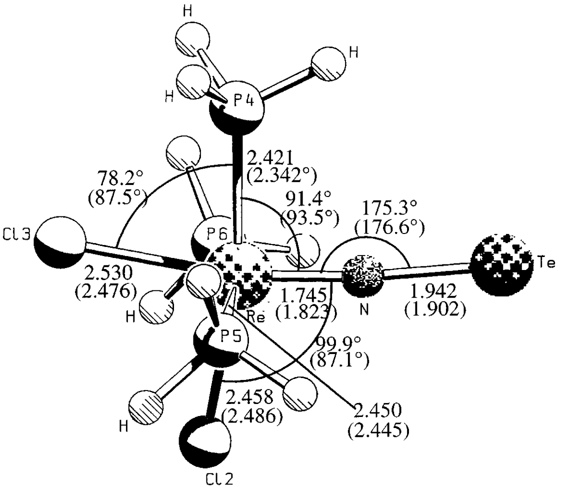


$Cl_2(PH_3)_3Re(N\text{-}S)$

**Figure 1** Continued



$Cl_2(PH_3)_3Re(N\text{-}Se)$

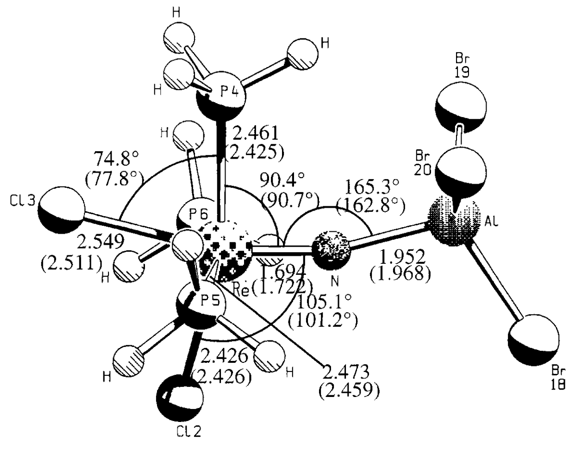


$Cl_2(PH_3)_3Re(N\text{-}Te)$

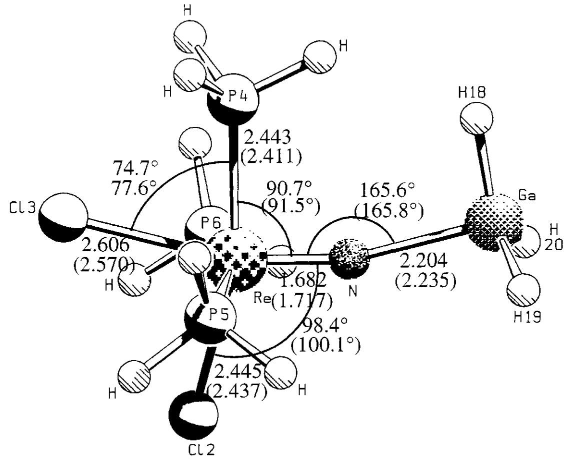
**Figure 1** Continued

X-ray structure analysis has been reported for $Cl_2(PMe_2Ph)_3ReN{-}GaCl_3$, which shows that the Re—N distance becomes a little longer (1.68 Å) than in the parent compounds (1.660 Å) [5]. This is in agreement with the calculated data, which predict at both levels of theory that the Re—N bond of $Cl_2(PH_3)_3ReN{-}GaCl_3$ is about 0.02 Å longer than in the parent compound (Fig. 1). The calculations show that the complexation of $Cl_2(PH_3)_3ReN$ by $GaCl_3$ leads to a significant shortening of the Re—Cl bond which is trans to the nitrido ligand by about 0.13 Å. The experimentally observed $Re{-}Cl_{trans}$ bond length of $Cl_2(PMe_2Ph)_3ReN{-}GaCl_3$ is 0.15 Å shorter than in the parent compount [5]. The calculated Re—N—Ga bond angle is 162°; the experimental value is 168°. A significant difference between theory and experiment is only found for the N—Ga bond length. The X-ray structure analysis gives a value of 1.97 Å, which is clearly shorter than the calculated values of 2.0555 (B3LYP/II) and 2.080 Å (MP2/II). We do not think that the disagreement between experiment and theory is caused by an insufficient level of the calculation. It has been shown that donor-acceptor bond lengths are always shorter in solids than in the free molecule [7]; this is because intermolecular forces yield a shortening of bonds between Lewis acids and Lewis bases. We believe that the calculated results for the N—Ga bond length are closer to the value for the free complex than the result obtained from X-ray structure analysis.

The calculated structures of the nitrogen-chalcogen complexes show that the Re—N distances are significantly longer (1.767–1.745 Å) than in the parent compound (1.668 Å, Fig. 1). This is in agreement with the measured Re—N bond lengths for $Cl(PMe_2Ph)_2(Et_2dtc)ReNS$ [1.72(1) and 1.795(9) Å], which are clearly longer than in the parent nitrido complexes [6]. The elongation of the Re—N bond in the chalcogen complexes is a first hint that these compounds might be

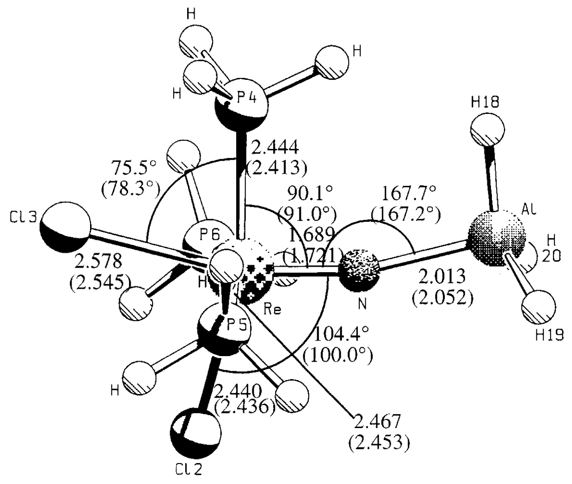


$Cl_2(PH_3)_3Re(N)\cdot AlBr_3$

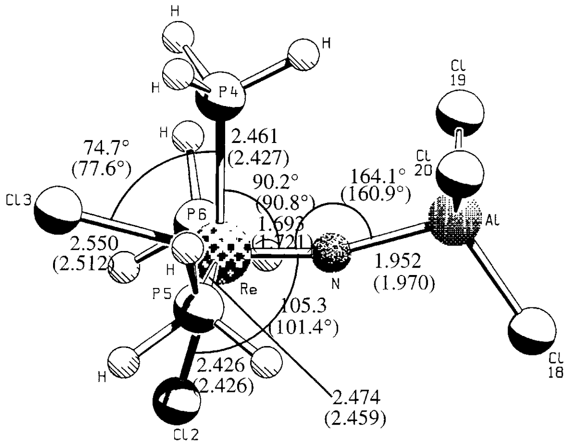


$Cl_2(PH_3)_3Re(N)\cdot GaH_3$

**Figure 1** Continued



$Cl_2(PH_3)_3Re(N)\cdot AlH_3$ ($C_1$)



$Cl_2(PH_3)_3Re(N)\cdot AlCl_3$

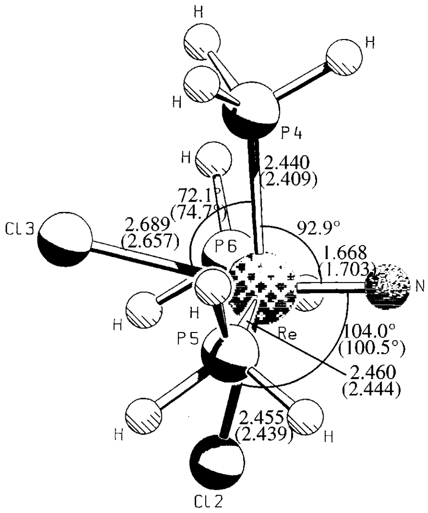
**Figure 1** Continued

better described with double bonds $L_nRe{=}N{=}S$. This will be discussed below. We want to point out that the calculated geometries of the nitrogen-chalcogen complexes show a trend with increasing $L_nRe{-}NY$ bond length Y = Te < Se < S < O, which suggests that the N—Y binding interactions become stronger. The calculated geometries of the complexes demonstrate that the theoretical values of the model compounds may be used to calculate bond energies, and they may also be used to discuss the bonding situation in the experimentally observed molecules.

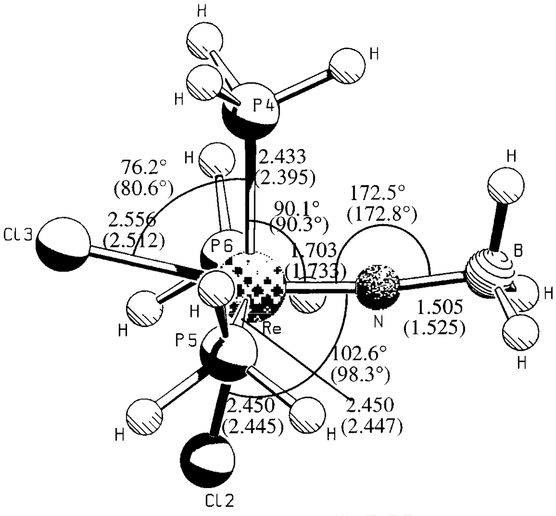
The calculated bond dissociation energies for the $Cl_2(PH_3)_3ReN{-}X$ bonds are given in Table 1. Since there are no experimental values available to assess the accuracy of the theoretical bond energies, we use previously reported bond energies at the same level of theory as benchmarks. We could show that calculated bond energies of main-group donor-acceptor complexes at MP2/6-31G(d) deviate less than 4 kcal/mol from experimental values [7]. Since the valence basis set of the heavier atoms has the same quality as 6-31G(d), we expect that the calculated bond energies at MP2/II should have an error margin of perhaps ±5 kcal/mol. The accuracy of B3LYP for calculating donor-acceptor bond energies is less known. Thus, the MP2/II data are also helpful to give information about the reliability of B3LYP/II bond energies.

The calculated bond energies of the $L_nReN$-chalcogen bonds are nearly the same at both levels of theory. The differences between the MP2/II and B3LYP/II values are only $\leq 1$ kcal/mol (Table 1). Larger differences between B3LYP/II and MP2/II are found for the donor-acceptor bonds $Cl_2(PH_3)_3ReN{-}X$. The theoretically predicted bond energies at B3LYP/II for the aluminum and gallium complexes are clearly lower than the MP2/II values. The largest difference is found for the bond energy of $Cl_2(PH_3)_3ReN{-}GaBr_3$, which is underestimated by 10 kcal/mol at B3LYP/II. It is known that DFT methods have difficulties with bond energies of weak bonds. Although the donor-acceptor bonds investigated here have moderate strength, it seems that the inherent weakness of DFT to describe van der Waals interactions yields bond energies for the complexes that are too low.

The strongest donor-acceptor bond of the complexes investigated is calculated for $Cl_2(PH_3)_3ReN{-}AlCl_3$. We want to point out that the strongest bonded donor-

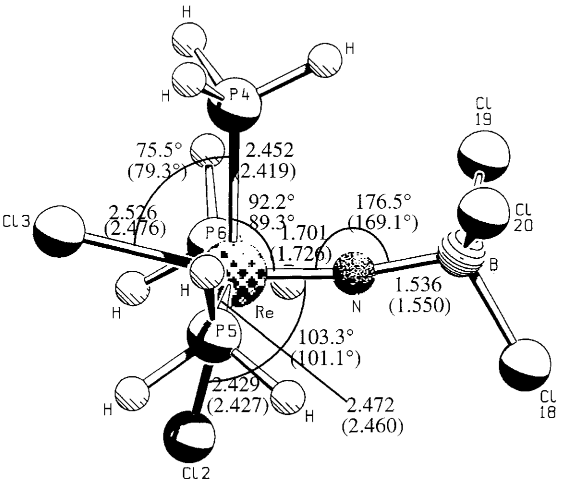


$Cl_2(PH_3)_3Re(N)$

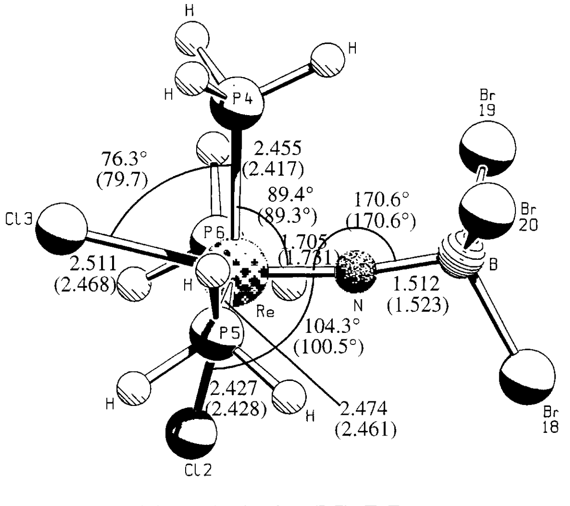


$Cl_2(PH_3)_3Re(N){\cdot}BH_3$

**Figure 1** Continued



$Cl_2(PH_3)_3Re(N){\cdot}BCl_3$



$Cl_2(PH_3)_3Re(N){\cdot}BBr_3$

**Figure 1** Continued

acceptor complex with a bond between main-group elements which is experimentally known is also a complex with $AlCl_3$ as a Lewis acid [24].[1] The bond dissociation energy of $Me_3N{-}AlCl_3$ has been measured as 47.5 ± 2 kcal/mol [25]. Calculations at MP2/6-31G(d) gave $D_o$ = 47.6 kcal/mol [7]. The theoretical value for the bond energy of $Cl_2(PH_3)_3ReN{-}AlCl_3$ shows that the nitrogen atom of the Re nitrido complex has a similar Lewis basicity as $Me_3N$: this is a remarkable result.

The calculated bond energies of the nitrido-boron complexes $Cl_2(PH_3)_3ReN{-}X$ with X = $BH_3$, $BCl_3$ and $BBr_3$ show a different trend than the aluminum and gallium analogues, which increase in the order $XH_3 \ll XBr_3 < XCl_3$ (Table 1). MP2/II predicts that the three boron complexes should have similar bond energies, and that $BBr_3$ should have slightly stronger interactions with $Cl_2(PH_3)_3ReN$ than $BCl_3$. The reader may note that the $AlCl_3$ and $GaCl_3$ complexes have significantly stronger N—X bonds than the $AlH_3$ and $GaH_3$ complexes, respectively, while the $BCl_3$ and $BH_3$ about the same bond energy complexes have at MP2/II. The halogen atoms have two opposing effects upon the Lewis acidity. The $p(\pi)$ donation leads to lower acidity, and the higher electronegativity than hydrogen increases the acidity [26]. The net effect of the bond energy depends on the nature of the Lewis base. $BCl_3$ binds the hard acid CO much less ($D_e$ = 2.0 kcal/mol) than $BH_3$ ($D_e$ = 25.6 kcal/mol), while the soft Lewis base $Me_3N$ has similar binding interactions with $BCl_3$ ($D_e$ = 36.7 kcal/mol) and $BH_3$ ($D_e$ = 41.3 kcal/mol) [7]. Since the Lewis basicity of $Cl_2(PH_3)_3ReN$ is comparable with that of $Me_3N$, it seems reasonable that MP2/II gives similar bond energies for $Cl_2(PH_3)_3ReN{-}BH_3$ and $Cl_2(PH_3)_3ReN{-}BCl_3$. It is disturbing, however that not only the absolute values of the B3LYP/II predicted bond energies are different from the MP2/II results, but also the trend is different.

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[1] Even stronger Lewis acidity than for $AlCl_3$ has theoretically been predicted for BeO, see Ref [9 e]

**Table 1.** Dissociation energies $D_e$ and zero-point energy corrected values $D_0$ of the rhenium nitrido-bridged complexes $Cl_2(PH_3)_3Re$-$N{\cdot}X$ [kcal/mol] with respect to $Cl_2(PH_3)_3ReN$ and X at the B3LYP and MP2 levels using basis set II. For the $Cl_2(PH_3)_3Re(N{-}X)$ chalcogen complexes the dissociation energies correspond to formation of $Cl_2(PH_3)_3ReN$ and X in its $^3P$ state

| Complex | B3LYP/II | | MP2/II | | CCSD(T)/II[a] | |
|---|---|---|---|---|---|---|
| | $D_e$ | $D_0$ | $D_e$ | $D_0$ | $D_e$ | $D_0$ |
| $Cl_2(PH_3)_3ReN{\cdot}BH_3$ | 33.1 | 30.4 | 31.9 | 29.3 | 31.8 | 29.2 |
| $Cl_2(PH_3)_3ReN{\cdot}BCl_3$ | 23.8 | 22.4 | 32.6 | 31.2 | 30.2 | 28.8 |
| $Cl_2(PH_3)_3ReN{\cdot}BBr_3$ | 25.3 | 24.1 | 36.2 | 35.0 | 31.6 | 30.4 |
| $Cl_2(PH_3)_3ReN{\cdot}AlH_3$ | 25.4 | 23.6 | 27.1 | 25.3 | | |
| $Cl_2(PH_3)_3ReN{\cdot}AlCl_3$ | 36.8 | 35.7 | 43.7 | 42.6 | | |
| $Cl_2(PH_3)_3ReN{\cdot}AlBr_3$ | 33.9 | 32.9 | 42.0 | 41.0 | | |
| $Cl_2(PH_3)_3ReN{\cdot}GaH_3$ | 14.9 | 13.4 | 18.5 | 17.0 | | |
| $Cl_2(PH_3)_3ReN{\cdot}GaCl_3$ | 28.3 | 26.8 | 35.0 | 33.5 | | |
| $Cl_2(PH_3)_3ReN{\cdot}GaBr_3$ | 23.3 | 22.0 | 33.2 | 31.9 | | |
| $Cl_2(PH_3)_3Re(N{-}O)$ | 101.2 | 98.6 | 100.2 | 97.6 | | |
| $Cl_2(PH_3)_3Re(N{-}S)$ | 65.1 | 63.6 | 66.5 | 65.0 | | |
| $Cl_2(PH_3)_3Re(N{-}Se)$ | 47.2 | 46.3 | 47.3 | 46.4 | | |
| $Cl_2(PH_3)_3Re(N{-}Te)$ | 36.3 | 35.8 | 35.2 | 34.7 | | |

[a] Using B3LYP/II optimized geometries

In order to make sure that MP2/II gives indeed the correct order and trend for the bond energies, we carried out single-point energy calculations of the nitrido-boron complexes and the fragments at CCSD(T)/II using B3LYP/II optimized geometries. The results are also shown in Table 1. It becomes obvious that the MP2/II results for the bond energies are supported by the CCSD(T)/II calculations. The results for the $BH_3$ and $BCl_3$ complexes are very similar, while the MP2/II value for the $BBr_3$ complex is slightly too high. It follows that the complexes of $Cl_2(PH_3)_3ReN$ with $BH_3$, $BCl_3$, and $BBr_3$ have nearly the same bond dissociation energy, while $AlH_3$ and $GaH_3$ are more weakly bonded than the chlorides and bromides.

## 4 Bonding analysis

In order to analyze the bonding situation in the nitrido complexes, we used several methods to gain insight into the electronic structure. First, we were interested in the charge distribution of the compounds and in the polarization and hybridization of the Re—N and N—X bonds, which are given by the NBO method [13]. Second, we wanted a quantitative analysis of the $L_nReN{-}X$ donor-acceptor interaction in terms of $L_nReN{\rightarrow}X$ donation and $L_nReN{\leftarrow}X$ backdonation. To this end we used the CDA method [12]. Finally, we were looking for information regarding the ionic/covalent characters of the Re—N and N—X bond, which are given by the Wiberg covalent bond orders.

The results of the NBO partitioning scheme are shown in Table 2. The NBO methods find three Re—N bonds for all compounds: one $\sigma$ bond and two $\pi$ bonds. Since the molecules have only $C_s$ symmetry, the Re—N $\pi$ bonds are not degenerate. The Re—N $\sigma$ bond of the parent compound $Cl_2(PH_3)_3ReN$ is clearly polarized toward the nitrogen end (only 36.3% at Re, Table 2), while the $\pi$ bonds are nearly nonpolar with a slightly greater weight at the rhenium end. The hybridization at the metal end of the Re—N $\sigma$ bond is $sd^{4.7}$. The Re—N $\sigma$ bond becomes even more polarized toward nitrogen when a Lewis acid or a chalcogen atom is attached. Also the Re—N $\pi$ bonds of the $Cl_2(PH_3)_3ReN{-}X$ complexes gain slightly more weight at the nitrogen atom. This can be explained by the donation of electronic charge from the nitrogen long-pair $\sigma$ orbital to the acceptor orbital at X, which makes the nitrogen atom more electron deficient.

The $L_nReN{-}X$ ($X = BY_3$, $AlY_3$, $GaY_3$) donor-acceptor bonds are strongly polarized toward the nitrogen donor atom (Table 2). The bonds of the aluminum and gallium complexes are more polarized (about 90% at N) than those of the boron complexes (about 77% at N) which is in agreement with the electronegativities of B, Al, and Ga. Also the charge donation $Cl_2(PH_3)_3ReN{\rightarrow}X$ is a little higher and the bond orders of the N—X bonds are larger for the boron complexes than for the aluminum and gallium analogues. The Wiberg covalent bond order for the Re—N triple bond, which has a value of 2.44 in the parent compound, becomes somewhat smaller in the complexes.

The results for the chalcogen complexes are interesting. The NBO partitioning scheme gives a Re—N triple bond and a N—X single bond, although the Wiberg bond orders indicate that the Re—N and N—X bonds are rather double bonds, which is in agreement with the changes in the Re—N bond lengths. The NBO method fails in this case, because the best description would be a Lewis structure with two 4-electron-3-center $\pi$ bonds for the Re—N—X moiety. Thus, the $AY_3$ complexes should be written as $Cl_2(PH_3)_3Re{\equiv}N{\rightarrow}AY_3$, while the chalcogen complexes should be written as $Cl_2(PH_3)_3Re{=}N{=}X$.

The results of the CDA calculations for the $Cl_2(PH_3)_3ReN{-}X$ complexes ($X = BY_3$, $AlY_3$, $GaY_3$) are given in Table 3. Note that the absolute numbers of the donation and backdonation are not so important, more relevant is the donation/backdonation ratio. Figure 2a shows schematically the most important orbital contributions between $L_nM{\equiv}N$ and $AY_3$. As expected, the calculations show strong N→X donation. Significant backdonation N←X is only found for the complexes

**Table 2.** Results of the natural bond orbital analysis of the rhenium nitrido-bridged complexes at the B3LYP/II level

| Molecule | Re—N Bond | | | | | N—X Bond | | | | | Charge | | | Wiberg bond indiees | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Occup. | %Re | %*s* | %*p* | %*d* | Occup. | %N | %*s* | %*p* | %*d* | $XY_3$ | X | N | Re—N | N—X |
| Parent | $\sigma$: 1.95 | 36.3 | 17.5 | 1.0 | 81.5 | – | – | | | | – | – | −0.27 | 2.44 | – |
| | $\pi$: 1.97 | 52.1 | 0.7 | 0.2 | 99.1 | | | | | | | | | | |
| | $\pi$: 1.97 | 55.5 | 1.5 | 0.1 | 98.4 | | | | | | | | | | |
| [$BH_3$] | $\sigma$: 1.95 | 29.1 | 22.3 | 0.3 | 77.4 | 1.99 | 76.7 | 57.4 | 42.6 | 0 | −0.25 | −0.26 | −0.25 | 2.04 | 0.87 |
| | $\pi$: 1.97 | 48.2 | 0.6 | 0.2 | 99.2 | | | | | | | | | | |
| | $\pi$: 1.97 | 52.6 | 1.0 | 0.1 | 98.9 | | | | | | | | | | |
| [$BCl_3$] | $\sigma$: 1.95 | 28.5 | 23.0 | 0.3 | 76.7 | 1.99 | 77.3 | 55.4 | 44.6 | 0 | −0.34 | +0.28 | −0.41 | 2.04 | 0.71 |
| | $\pi$: 1.97 | 44.4 | 0.3 | 0.1 | 99.6 | | | | | | | | | | |
| | $\pi$: 1.99 | 48.7 | 0.9 | 0.1 | 99.0 | | | | | | | | | | |
| [$BBr_3$] | $\sigma$: 1.95 | 28.1 | 22.9 | 0.3 | 76.8 | 1.99 | 77.1 | 56.0 | 43.9 | 0 | −0.30 | +0.06 | −0.43 | 2.00 | 0.75 |
| | $\pi$: 1.97 | 44.1 | 0.9 | 0.1 | 99.0 | | | | | | | | | | |
| | $\pi$: 1.96 | 48.6 | 0.3 | 0.1 | 99.6 | | | | | | | | | | |
| [$AlH_3$] | $\sigma$: 1.95 | 31.6 | 21.4 | 0.4 | 78.1 | 1.97 | 90.3 | 57.2 | 48.4 | 0 | −0.14 | +0.99 | −0.44 | 2.21 | 0.37 |
| | $\pi$: 1.98 | 47.0 | 0.7 | 0.1 | 99.2 | | | | | | | | | | |
| | $\pi$: 1.97 | 51.0 | 1.1 | 0.1 | 98.8 | | | | | | | | | | |
| [$AlCl_3$] | $\sigma$: 1.95 | 30.7 | 22.1 | 0.4 | 77.4 | 1.97 | 90.2 | 54.8 | 45.2 | 0 | −0.16 | +1.52 | −0.56 | 2.17 | 0.35 |
| | $\pi$: 1.98 | 44.8 | 0.4 | 0.1 | 99.5 | | | | | | | | | | |
| | $\pi$: 1.97 | 48.8 | 1.0 | 0.1 | 98.9 | | | | | | | | | | |
| [$AlBr_3$] | $\sigma$: 1.95 | 30.7 | 22.0 | 0.4 | 77.6 | 1.97 | 90.3 | 55.9 | 44.1 | 0 | −0.15 | +1.34 | −0.56 | 2.16 | 0.35 |
| | $\pi$: 1.98 | 44.7 | 0.4 | 0.1 | 99.5 | | | | | | | | | | |
| | $\pi$: 1.97 | 48.8 | 1.0 | 0.1 | 98.9 | | | | | | | | | | |
| [$GaH_3$] | $\sigma$: 1.95 | 32.5 | 21.2 | 0.4 | 78.4 | 1.96 | 91.0 | 54.9 | 45.1 | 0 | −0.14 | +0.77 | −0.36 | 2.28 | 0.33 |
| | $\pi$: 1.98 | 48.5 | 1.0 | 0.1 | 98.9 | | | | | | | | | | |
| | $\pi$: 1.97 | 52.3 | 1.2 | 0.1 | 98.7 | | | | | | | | | | |
| [$GaCl_3$] | $\sigma$: 1.95 | 30.8 | 22.4 | 0.4 | 77.2 | 1.96 | 89.6 | 51.6 | 48.4 | 0 | −0.19 | +1.41 | −0.50 | 2.20 | 0.35 |
| | $\pi$: 1.98 | 45.5 | 0.6 | 0.1 | 99.3 | | | | | | | | | | |
| | $\pi$: 1.97 | 49.4 | 1.1 | 0.1 | 98.9 | | | | | | | | | | |
| [$GaBr_3$] | $\sigma$: 1.95 | 27.7 | 21.5 | 0.5 | 78.0 | 1.97 | 91.1 | 53.7 | 46.3 | 0 | −0.17 | +1.34 | −0.47 | 2.26 | 0.30 |
| | $\pi$: 1.98 | 41.4 | 0.8 | 0.2 | 99.0 | | | | | | | | | | |
| | $\pi$: 1.98 | 49.3 | 1.2 | 0.1 | 98.7 | | | | | | | | | | |
| [O] | $\sigma$: 1.97 | 24.4 | 24.8 | 0.1 | 75.1 | 2.00 | 45.2 | 36.4 | 63.5 | 0 | – | −0.27 | +0.18 | 1.57 | 1.70 |
| | $\pi$: 1.96 | 53.2 | 2.9 | 0.1 | 97.0 | | | | | | | | | | |
| | $\pi$: 1.96 | 57.9 | 0.9 | 0.1 | 99.0 | | | | | | | | | | |
| [S] | $\sigma$: 1.96 | 25.0 | 23.9 | 0.2 | 75.9 | 1.99 | 69.6 | 41.9 | 57.9 | 0.2 | – | +0.21 | −0.51 | 1.56 | 1.46 |
| | $\pi$: 1.97 | 46.2 | 1.5 | 0.1 | 98.4 | | | | | | | | | | |
| | $\pi$: 1.97 | 50.9 | 0.8 | 0.0 | 99.2 | | | | | | | | | | |
| [Se] | $\sigma$: 1.96 | 26.0 | 23.2 | 0.3 | 76.5 | 1.99 | 73.2 | 41.9 | 57.9 | 0.2 | – | +0.20 | −0.55 | 1.64 | 1.34 |
| | $\pi$: 1.97 | 45.5 | 2.0 | 0.1 | 97.9 | | | | | | | | | | |
| | $\pi$: 1.97 | 50.5 | 0.8 | 0.0 | 99.2 | | | | | | | | | | |
| [Te] | $\sigma$: 1.96 | 27.0 | 22.8 | 0.3 | 76.9 | 1.99 | 77.9 | 42.9 | 57.0 | 0.1 | – | +0.20 | −0.60 | 1.71 | 1.17 |
| | $\pi$: 1.97 | 45.0 | 2.0 | 0.1 | 97.9 | | | | | | | | | | |
| | $\pi$: 1.97 | 50.1 | 0.9 | 0.0 | 99.1 | | | | | | | | | | |

with $BH_3$, $BBr_3$, $AlH_3$, and $GaH_3$. The occupied orbitals of $BCl_3$, $AlCl_3$, $AlBr_3$, $GaCl_3$, and $GaBr_3$. are too low in energy, and they are more polarized toward the halogen atoms to be available for N←X backdonation. The residue term is approximately 0, which indicates that the $L_nMN—AY_3$ bonds can be discussed in terms of closed-shell interactions. We also analyzed the bonds of the chalcogen complexes $Cl_2(PH_3)_3ReN—X$ (X = O, S, Se, Te) with the CDA method using the chalcogen atom in the singlet electronic state where the valence *s* and valence $p(\pi)$ orbitals are doubly occupied, and the $p(\sigma)$ orbital is empty (Fig. 2b). We wanted to know if the nitrogen-chalcogen bonds of the complexes may also be interpreted as donor-acceptor interactions. Table 3 shows that this may be a valid interpretation of the heavier chalcogen complexes with X = S, Se, Te, but not for oxygen. The residue term for the nitrido-oxygen compound is very large, which means that the bonding between the two fragments should not be considered as a donor-acceptor bond, but rather as a covalent double bond between two triplet fragments. For the complexes with X = S, Se, Te, it is found that the $Cl_2(PH_3)_3ReN \leftarrow X$ $\pi$ backdonation is much more important than for the $AY_3$ complexes. This is reasonable, because the chalcogen atoms have two occupied $p(\pi)$ orbitals which are available for backdonation (Fig. 2b).

## 5 Summary and conclusion

The calculated geometries of the nitrido complexes $Cl_2(PH_3)_3ReN—X$ with Lewis acids and chalcogen atoms X are in excellent agreement with experimental data. The Re—N bond becomes slightly longer and the $Re—Cl_{trans}$ bond becomes significantly shorter when a Lewis acid is attached to nitrogen. Even longer Re—N bonds are calculated for the nitrogen chalcogen complexes. The nitrogen atom of the nitrido complexes is a strong Lewis base. Calculations show that the Lewis basicity of $Cl_2(PH_3)_3ReN$ is nearly as high as that of

**Table 3.** Results of the charge decomposition analysis for the rhenium nitrido-bridged complexes at the B3LYP/II level[a]

| Complex | N→X donation | X→N back-donation | Repulsion | Residue term |
|---|---|---|---|---|
| [$BH_3$] | 0.551 | 0.327 | −0.258 | 0.004 |
| [$BCl_3$] | 0.461 | 0.014 | −0.538 | 0.020 |
| [$BBr_3$] | 0.552 | 0.204 | −0.472 | 0.026 |
| [$AlH_3$] | 0.417 | 0.179 | −0.151 | −0.007 |
| [$AlCl_3$] | 0.520 | 0.048 | −0.225 | −0.007 |
| [$AlBr_3$] | 0.534 | 0.074 | −0.249 | −0.004 |
| [$GaH_3$] | 0.330 | 0.141 | −0.120 | −0.012 |
| [$GaCl_3$] | 0.485 | 0.006 | −0.205 | −0.013 |
| [$GaBr_3$] | 0.424 | 0.018 | −0.195 | 0.017 |
| [O] | 0.294 | 0.499 | −0.390 | 0.152 |
| [S] | 0.502 | 0.451 | −0.403 | 0.047 |
| [Se] | 0.472 | 0.387 | −0.426 | 0.033 |
| [Te] | 0.480 | 0.324 | −0.374 | 0.025 |

[a] For $Cl_2(PH_3)_3Re(NX)$ complexes (X = O, S, Se, Te) the singlet state of X was used for the calculation, with the unoccupied *p* orbital oriented along the Re—N bond

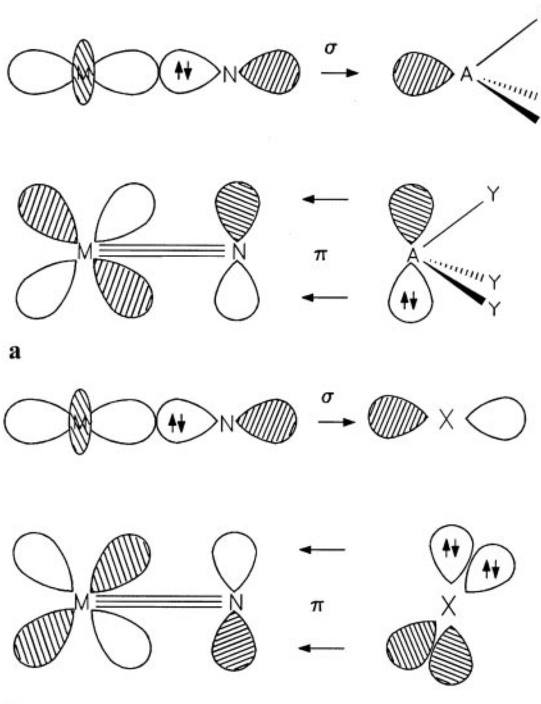

**Fig. 2.** Schematic representation of the dominant orbital interactions between the nitrido complexes and **a** the Lewis acids $AY_3$ and **b** chalcogen atoms $X$ in the singlet state with the empty $p(\sigma)$ atomic orbital along the $N$-$X$ axis. The doubly occupied valence *s* orbital of the chalcogen atom is not shown. Only one of the two degenerate components of the $\pi$ backdonation is shown

trimethylamine. This becomes obvious from the theoretically predicted bond dissociation energy for the $Cl_2(PH_3)_3ReN{-}AlCl_3$ bond $D_e$ = 43.7 kcal/mol. The $Cl_2(PH_3)_3ReN$-chalcogen bonds are strong and exhibit the trend O $\gg$ S > Se > Te. The bonding analysis indicates that $Cl_2(PH_3)_3ReN$ has a $\sigma$ bond which is clearly polarized toward nitrogen, while the two $\pi$ bonds are nearly nonpolar. The Re—N $\sigma$ and $\pi$ bonds become more polarized toward nitrogen when a Lewis acid or a chalcogen atom is attached. The nitrogen-chalcogen bonds in the heavier chalcogen complexes with S, Se, and Te, may also be considered as donor-acceptor interactions with the chalcogen atom in a singlet state with two doubly occupied $p(\pi)$ orbitals. The nitrido-oxygen complex, however, should be described with a $Cl_2(PH_3)_3Re{=}N{=}O$ covalent double bond.

*Acknowledgements*. This work was supported by the Deutsche Forschungsgemein-schaft and by the Fonds der Chemischen Industrie. Excellent service by HRZ Marburg is gratefully acknowledged. Additional computer time was given by HLRZ Stuttgart and HHLR Darmstadt.

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