The Nature of the M≡E Bond: Theoretical Investigation of the Molecules $[(RO)_3M{\equiv}E]$ (M = Mo, W; E = N, P, As, Sb, Bi; R = H, Me) and $[(Me_3CO)_3Mo{\equiv}P]$

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The electronic and molecular structures of the metal-pnicogen complexes $[(RO)_3M{\equiv}E]$ (M = Mo, W; E = N, P, As, Sb, Bi; R = H, Me) and $[(Me_3CO)_3M{\equiv}P]$ have been investigated at the DFT level using the exchange correlation functionals B3LYP and BP86. The nature of the M≡E interactions was analyzed with charge and energy decomposition methods. The bonding analyses show that the metal-pnicogen bonds are genuine triple bonds containing a σ- and a degenerate π-bond. The M–E σ-bonds are always polarized towards the pnicogen atom E, particularly for the nitrogen complexes. The M–N π-bonds are also polarized towards nitrogen, while the π-bonds of the heavier pnicogens P–Bi show a small polarization towards the metal atom. The M–E σ-bonds at the pnicogen E are sp^n-hybridized; the p character is always > 80% of the total AO contribution. The hybridization of the metal atoms in the nitrido complexes is approximately sd^2 and that in the heavier homologues, approximately sd. The ratio of the energy contributions of the σ- and π-orbitals to the covalent bonding in $[(HO)_3M{\equiv}E]$ is about 50:50 for all pnicogen atoms E. The metal–nitrido bonds in $[(HO)_3M{\equiv}N]$ are more covalent than electrostatic. The covalent character becomes smaller when the pnicogen atom becomes heavier with the trend N >> P > As > Sb > Bi. The $[(HO)_3M{\equiv}E]$ tungsten complexes have stronger bonds that are slightly less covalent than the molybdenum complexes, the π-bonding contribution in the former species is slightly larger than in the latter.

Introduction

Triple bonding between transition metals is a feature commonly encountered in several classes of dinuclear complexes.[1] Molecules that have a σ- and a degenerate π-bond are also known to form between transition metals and main group elements as exemplified in carbyne,[2−9] nitrido,[10−20] and germylyne[21−25] complexes. The coordination chemistry of transition metal complexes with a terminal nitrido ligand has blossomed in the last 25 years, during which much knowledge of their properties has been obtained.[10−20]

For the heavier group 15 elements P, As, Sb, and Bi there are only a small number of complexes with a terminal phosphorus atom as a ligand known from the literature.[26−32] An intermediate metal phosphido complex [(O-*t*Bu)3 W≡P] was first suggested in 1985 by Becker et al.[33] from the reaction of [W2(O-*t*Bu)6] with t-BuC≡P. In 1987, Chisholm and coworkers proposed the formation of an intermediate phosphido complex [(NpO)3 W≡P] (Np = neopentyl).[34] The existence of metal-arsenido complexes [Cp(CO)2M≡As] (M = Mo, W] as intermediates was suggested by Ziegler et al.[35] Rheingold and coworkers reported on metal-stibido complexes $[(CO)_nM{\equiv}Sb]$ (n = 4, M = Cr, Mo, W; n = 3, M = Fe) as intermediates.[36]

Until ten years ago, no examples of stable, fully characterized complexes with a terminal M≡E bond (E = P, As, Sb, Bi) were known. In 1995, the groups of Cummins[37] and Schrock[38] independently reported representative examples of complexes containing metal−phosphorus triple bonds in $[(ArRN)_3Mo{\equiv}P]$, $[(R_2N)_3Mo{\equiv}P]$ {R = $C(CD_3)_2(CH_3)$, Ar = 3,5-$C_6H_3Me_2$} and $[(N_3N)M{\equiv}P]$ {M = Mo, W; N_3N = $(Me_3SiNCH_2CH_2)_3N$}. Schrock et al. also isolated the first examples of metal-arsenido complexes $[(N_3N)M{\equiv}As]$ (M = Mo, W).[38,39] Scheer and coworkers synthesized $[(N_3N)W{\equiv}E]$ (E = P, As) by a different synthetic route.[40] Recently, Cummins et al. reported on the phosphido complex $[(RO)_3Mo{\equiv}P]$ (R = 1-methylcyclohexyl).[41]

Several theoretical studies on metal nitrido complexes have been published[14−20] but little theoretical work has been performed on the heavier homologues. Four computational investigations on phosphido complexes have been reported. Wagener and Frenking optimized the geometries of the model compounds $[(H_2N)_3M{\equiv}P]$, $[(H_2N)3(NH_3)M{\equiv}P]$, $[(HNCH_2CH_2)_3M{\equiv}P]$ (M = Mo, W) at the HF, MP2, and B3LYP levels of theory[42] ^{31}P NMR

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chemical shielding calculations for phosphido complexes were carried out by Morokuma et al.[43] and by Cummins et al.[41] Geometries of $[(N_3N)W{\equiv}E]$ (E = P, As) were optimized at the DFT/BP86/SVP level of theory by Scheer et al.[40] Ab initio MP2 calculations on the $[(CO)_4Mo{\equiv}Sb]^-$ anion were reported by Rheingold et al.[36] A comparative study of complexes with terminal metal−pnicogen triple bonds $L_nM{\equiv}E$ has not been published until now.

In this paper, 21 metal-pnicogen complexes $[(RO)_3M{\equiv}E]$ (M = Mo, W; E = N, P, As, Sb, Bi; R = H, Me) and $[(Me_3CO)_3M{\equiv}P]$ have been investigated using density functional theory at the B3LYP and BP86 levels of theory. We report on the charge and energy decomposition analysis of the metal−pnicogen triple bonds in $[(MeO)_3M{\equiv}E]$ (M = Mo, W; E = N, P, As, Sb, Bi), which gives, for the first time, the energies that are associated with the M→E σ-donation and M←E π-bonding. The relative strength of the electrostatic and covalent contributions to the bond strength will be also reported. The following questions are addressed in this work: (i) how are the M≡E σ- and π-bonds polarized, and what is the hybridization at the metal and pnicogen atoms; (ii) how strong are the contributions of the M−E σ-bonding and M−E π-bonding to the total M≡E bonding energy; (iii) what are the relative strengths of the covalent and electrostatic interactions?

Computational Methods

Calculations on all complexes have been performed using the hybrid B3LYP density functional method, which uses Becke's 3-parameter nonlocal exchange functional[44] mixed with the exact (Hartree−Fock) exchange functional and Lee−Yang−Parr's nonlocal correlation functional.[45] The geometries of the molecules were optimized without any symmetry restrictions with standard 6−311G(d) basis sets[46] for H, C, O, N and P atoms. For As, Sb, Bi, Mo and W, quasi-relativistic effective core potentials (ECP) determined by Hay−Wadt have been used.[47] The valence basis sets for Mo and W have triple-ζ quality (10s10p4d1f/3s3p3d1f), which include $(n+1)$p functions[48] that were augmented by an additional set of f orbitals with an exponent of 1.043 for Mo and 0.823 for W.[49] For As, Sb and Bi, the standard (3s4p1d/2s3p1d) valence basis functions of Hay and Wadt have been used.[50] This basis set is denoted TZP. Frequency calculations were performed at B3LYP/TZP to determine whether the optimized geometries were minima on the potential energy surface. The electronic structures of the complexes were examined by NBO analysis.[51] The B3LYP/TZP calculations were carried out with the Gaussian98 program.[52] All MO pictures were made by using the MOLDEN program.[53]

Calculations on the model complexes $[(HO)_3M{\equiv}E]$ have also been performed at the nonlocal DFT level of theory using the exchange functional of Becke[54] and the correlation functional of Perdew[55] (BP86). Scalar relativistic effects have been considered using the ZORA formalism.[56] Uncontracted Slater-type orbitals (STOs) using triple-ζ basis sets augmented by two sets of polarization functions were employed for the SCF calculations.[57] The $(1s)^2$ core electrons of carbon and nitrogen, $(1s2s2p)^{10}$ core electrons of phosphorus, $(1s2s2p3s3p)^{18}$ core electrons of arsenic, $(1s2s2p3s3p3d)^{28}$ core electrons of molybdenum, $(1s2s2p3s3p3d4s4p)^{36}$ core electrons of antimony, and $(1s2s2p3s3p3d4s4p4d)^{46}$ core electrons of bismuth and tungsten were treated by the frozen-core approximation.[58] An auxiliary set of s, p, d, f and g STOs was used to fit the molecular densities, and to present the coulomb and exchange potentials accurately in each SCF cycle.[59] A numerical integration accuracy of INTEGRATION = 10 was used throughout. The geometries of $[(HO)_3M{\equiv}E]$ were optimized at BP86/TZ2P with C_3 symmetry. The latter calculations were performed utilizing the program package ADF-2002.01.[60]

The binding interactions in the complexes $[(HO)_3M{\equiv}E]$ between the fragment radicals in the electronic quadruplet states ($^4A_1$) $[(HO)_3Mo]$ and ($^4\Sigma^-$) E have been analyzed with C_3 symmetry using the energy decomposition scheme of ADF, which is based on the methods of Morokuma,[61] and Ziegler and Rauk.[62] According to the ETS method, the bond energy ΔE between the $[(HO)_3Mo]$ and E fragments is:

$$\Delta E = \Delta E_{int} + \Delta E_{prep} \quad (1)$$

Here, ΔE_{prep} is the energy required to promote the structures of the free fragments from their equilibrium structure in the electronic ground state to the geometry and electronic state that they take up in the molecule:

$$\Delta E_{prep} = E_{total}(\text{distorted fragments}) - E_{total}(\text{fragments in the equilibrium structure}) \quad (2)$$

ΔE_{int} in Equation (1) is the instantaneous interaction energy between the two fragments in the molecule. It is comprised of three main components as shown in Equation (3).

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \quad (3)$$

ΔE_{elstat} describes the classical Coulomb interaction between the fragments, which is attractive in most cases. The term ΔE_{Pauli}, which is called exchange repulsion or Pauli repulsion, takes into account the destabilizing two-orbital three- or four-electron interactions between occupied orbitals of both fragments. ΔE_{Pauli} is calculated by enforcing the Kohn−Sham determinant of the molecule, which results from superimposing both fragments, to obey the Pauli principle through antisymmetrization and renormalization. The last term ΔE_{orb} in Equation (1) gives the stabilizing orbital interactions between occupied and virtual orbitals of the two fragments. ΔE_{orb} can be further partitioned into contributions from the orbitals that belong to different irreducible representations of the point group of the system. It

has been suggested that the covalent and electrostatic character of a bond is given by the ratio $\Delta E_{elstat}/\Delta E_{orb}$.[23,63−65]

Results and Discussion

Geometries

Figure 1 shows the optimized geometries of $[(RO)_3Mo{\equiv}P]$ (R = H, Me, CMe_3). Table 1 gives the most important bond lengths and angles that have been computed for the eleven molybdenum-pnicogen complexes $[(RO)_3Mo{=}E]$ (R = H, Me; M = Mo; E = N, P, As, Sb, Bi) and $[(Me_3CO)_3Mo{=}P]$. The geometrical data for the ten tungsten-pnicogen complexes $[(RO)_3W{=}E]$ (R = H, Me; M = W; E = N, P, As, Sb, Bi) are presented in Table 2.

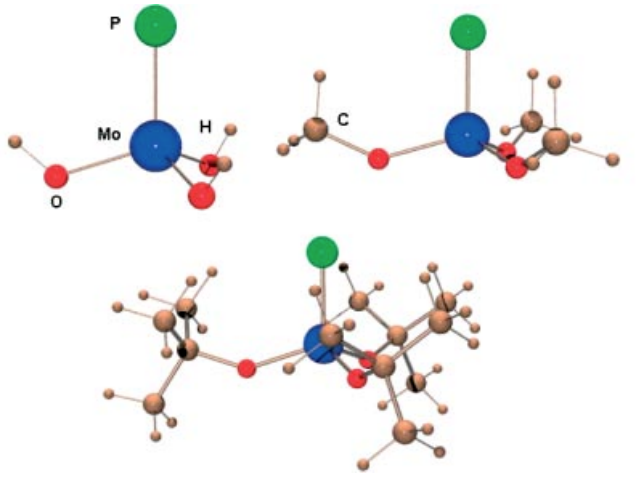

Figure 1. Optimized geometries of $[(RO)_3Mo{\equiv}P]$ (R = H, Me, CMe_3)

Experimental values are available for a large number of stable nitrido complexes of molybdenum and tungsten. From these structural data, the M≡N triple bond lengths are between 1.6−1.7 Å.[10−20] The calculated Mo≡N and W≡N bond lengths at B3LYP/TZP in $[(HO)_3Mo{\equiv}N]$ (1.634 Å), $[(MeO)_3Mo{\equiv}N]$ (1.639 Å), $[(HO)_3W{\equiv}N]$ (1.665 Å), and $[(MeO)_3W{\equiv}N]$ (1.670 Å) agree quite well with the experimental values. The calculated Mo≡P and W≡P bond lengths in $[(HO)_3Mo{\equiv}P]$ (2.094 Å), $[(MeO)_3Mo{\equiv}P]$ (2.102 Å), $[(Me_3CO)_3Mo{\equiv}P]$ (2.112 Å), $[(HO)_3W{\equiv}P]$ (2.118 Å) ,and $[(MeO)_3W{\equiv}P]$ (2.126 Å) are also very close to experimental values found by X-ray diffraction for $[(ArRN)_3Mo{\equiv}P]$ [2.119(4) Å], $[(RO)_3Mo{\equiv}P]$ [2.1144(16) Å], and $[(N_3N)W{\equiv}P]$ [2.162(4) Å]. We note that as the size of R increases, the M≡E bond lengthens. In arsenido complexes, the calculated M≡As bond lengths in $[(HO)_3Mo{\equiv}As]$ (2.217 Å), $[(MeO)_3Mo{\equiv}As]$ (2.224 Å), $[(HO)_3W{\equiv}As]$ (2.237 Å), and $[(MeO)_3W{\equiv}As]$ (2.245 Å) are slightly shorter than those found by X-ray diffraction for $[(N_3N)Mo{\equiv}As]$ [2.252(3) Å] and $[(N_3N)W{\equiv}As]$ [2.2903(11) Å]. The BP86/TZ2P values are very similar to the B3LYP/TZP data.

There are no experimental data for the length of M≡Sb and M≡Bi triple bonds. A bond length of 2.55 Å in $[(CO)_4Mo{\equiv}Sb]^-$ has been calculated at the MP2 level.[36] Using the relationship between bond order and bond lengths suggested by Pauling,[66] we find the estimated Mo≡E (Mo≡N = 1.81 Å, Mo≡P = 2.12 Å, Mo≡As = 2.25 Å, Mo≡Sb = 2.44 Å, and Mo≡Bi = 2.49 Å) and W≡E bond lengths (W≡N = 1.82 Å, W≡P = 2.13 Å, W≡As = 2.26 Å, W≡Sb = 2.45 Å, and W≡Bi = 2.50 Å) for triple bonds from the M−E single bond lengths based on covalent radii predictions (covalent radius, Mo = 1.40 Å, W = 1.41 Å, N = 0.75 Å, P = 1.06 Å, As = 1.19 Å, Sb = 1.38 Å, Bi = 1.43 Å).[67] It is interesting to note that the calculated M≡E bond lengths in the calculated molyb-

Table 1. Selected optimized geometrical parameters for the $[(RO)_3Mo{\equiv}E]$ (R = H, Me; E = N, P, As, Sb, Bi) complexes; distances are in Å and angles are in degrees

E =	N			P				As			Sb			Bi		
R =	H		Me	H		Me	$C(Me)_3$	H		Me	H		Me	H		Me
	B3LYP	BP86	B3LYP	B3LYP	BP86	B3LYP	B3LYP	B3LYP	BP86	B3LYP	B3LYP	BP86	B3LYP	B3LYP	BP86	B3LYP
Bond lengths																
Mo−E	1.634	1.657	1.639	2.094	2.117	2.102	2.112	2.217	2.226	2.224	2.429	2.443	2.436	2.484	2.523	2.488
Mo−O	1.902	1.906	1.893	1.893	1.893	1.881	1.889	1.893	1.893	1.880	1.892	1.891	1.878	1.893	1.893	1.879
O−H	0.963	0.973		0.962	0.971			0.962	0.971		0.962	0.971		0.962	0.971	
O−C			1.415			1.413	1.443			1.413			1.411			1.411
Bond angles																
E−Mo−O	106.2	107.1	105.3	107.1	107.8	105.5	107.9	107.2	107.8	105.5	107.3	107.7	105.2	107.2	107.9	104.9
O−Mo−O	112.5	111.8	113.3	111.8	111.0	113.1	111.1	111.7	111.1	113.1	111.5	111.2	113.4	111.6	111.1	113.6
M−O−H	122.5	119.9		124.9	122.1			125.2	121.8		125.7	121.8		125.9	122.1	
M−O−C			134.2			139.3	144.2			140.0			141.5			141.6

Table 2. Selected optimized geometrical parameters for the [(RO)$_3$W≡E] (R = H, Me; E = N, P, As, Sb, Bi) complexes; distances are in Å and angles are in degrees

E =	N			P			As			Sb			Bi		
R =	H		Me	H		Me	H		Me	H		Me		H	Me
	B3LYP	BP86	B3LYP	B3LYP	BP86	B3LYP	B3LYP	BP86	B3LYP	B3LYP	BP86	B3LYP	B3LYP	BP86	B3LYP
Bond lengths															
Mo−E	1.665	1.686	1.670	2.118	2.133	2.126	2.237	2.237	2.245	2.446	2.448	2.455	2.502	2.539	2.508
Mo−O	1.888	1.907	1.878	1.877	1.898	1.865	1.876	1.896	1.863	1.876	1.892	1.860	1.876	1.894	1.861
O−H	0.962	0.971		0.961	0.970		0.961	0.970		0.961	0.970		0.961	0.970	
O−C			1.420			1.418			1.418			1.417			1.417
Bond angles															
E−Mo−O	106.4	106.7	105.5	107.6	107.7	106.3	107.6	107.7	106.4	108.0	107.7	106.4	107.9	107.8	106.1
O−Mo−O	112.9	112.1	113.1	111.3	111.1	112.5	111.3	111.2	112.3	110.9	111.2	112.4	111.0	111.1	112.6
M−O−H	124.9	119.4		127.1	121.7		127.1	121.8		128.2	121.6		128.2	121.7	
M−O−C			135.3			140.2			141.0			142.5			143.2

denum-pnicogen and tungsten-pnicogen complexes correspond to a Pauling bond order of approximately 3.

Bonding Analysis of M≡E Bonds

We begin the analysis of the bonding situation in the pnicogen complexes [(MeO)$_3$M≡E] (M = Mo, W; E = N, P, As, Sb, Bi) with a discussion on the conventional indices that are frequently used in order to characterize the bonding situation in molecules, i.e. bond orders and atomic charges. Table 3 gives the Wiberg bond indices (WBI)[68] and the results of the natural bond orbital (NBO) analysis.

Table 3 shows that the WBI values of the M≡E bonds in the pnicogen complexes are significantly higher (2.47−2.65) than the WBI values of the M−O single bond (0.81−0.85).

Table 3. Wiberg bond indices and results of the NBO analysis of the [(RO)$_3$M≡E] (M = Mo, W; E = N, P, As, Sb, Bi) complexes

	Mo							W				
E =	N	P			As	Sb	Bi	N	P	As	Sb	Bi
R =	Me	H	Me	CMe_3	Me	Me	Me	Me	Me	Me	Me	Me
Wiberg bond indices												
M−E	2.65	2.59	2.53	2.48	2.51	2.49	2.47	2.58	2.56	2.55	2.54	2.54
M−O	0.81	0.85	0.83	0.83	0.83	0.83	0.84	0.81	0.84	0.84	0.84	0.83
O−C	0.92		0.91	0.86	0.91	0.91	0.91	0.90	0.89	0.89	0.89	0.89
C−H	0.93		0.93	0.92	0.93	0.93	0.93	0.93	0.93	0.93	0.93	0.93
NBO charges												
M	1.63	1.07	1.09	1.14	1.03	0.99	1.06	1.94	1.39	1.33	1.25	1.29
E	−0.46	0.02	−0.01	−0.09	0.02	0.08	0.01	−0.66	−0.23	−0.18	−0.10	−0.10
O	−0.72	−0.87	−0.69	−0.70	−0.69	−0.69	−0.69	−0.77	−0.74	−0.74	−0.74	−0.74
Me	0.33		0.33		0.34	0.33	0.33	0.34	0.35	0.36	0.36	0.34
M−E σ bond												
Occupancy	1.871	1.869	1.837	1.831	1.840	1.835	1.849	1.918	1.898	1.900	1.899	1.905
M												
%[a]	37.13	43.16	41.35	39.77	42.19	42.96	41.49	33.98	41.20	42.84	45.48	44.22
%s	30.51	50.86	48.84	48.00	51.53	55.14	54.73	32.50	50.33	52.43	85.87	59.51
%p	0.37	0.81	0.14	0.40	0.69	1.49	1.63	0.49	0.16	0.72	1.73	1.66
%d	68.59	48.21	50.80	51.36	47.69	43.24	43.51	66.68	49.38	46.76	42.34	42.37
E												
%[a]	62.87	54.86	58.65	60.23	57.81	57.04	58.51	66.02	58.80	57.16	54.52	55.78
%s	16.86	10.29	13.10	14.22	12.42	10.96	8.82	19.08	14.63	13.66	11.73	9.78
% p	82.87	89.26	86.44	85.34	87.11	88.64	90.96	80.64	84.85	85.83	87.85	90.02
% d	0.27	0.45	0.46	0.44	0.47	0.40	0.22	0.28	0.52	0.51	0.24	0.20
M−E π bond												
Occupancy	1.988	1.975	1.981	1.969	1.981	1.981	1.978	1.983	1.975	1.975	1.974	1.882
M												
%[a]	45.81	56.06	56.13	55.09	56.42	58.12	57.13	42.49	51.03	52.03	53.00	50.28
% p	0.42	1.23	1.08	1.08	1.04	1.24	1.27	0.73	1.51	1.45	1.86	12.39
% d	99.47	98.74	98.90	98.89	98.94	98.75	98.27	99.16	98.46	98.54	98.13	87.09
E												
%[a]	54.19	43.94	43.87	44.91	43.58	41.88	42.87	57.51	48.97	47.97	47.00	49.72
% p	99.72	99.39	99.45	99.48	99.54	99.76	99.90	99.70	99.49	99.55	99.76	99.89
% d	0.28	0.61	0.55	0.52	0.46	0.24	0.10	0.30	0.51	0.45	0.24	0.11

[a] The % values give the polarization of the M−E bonds.

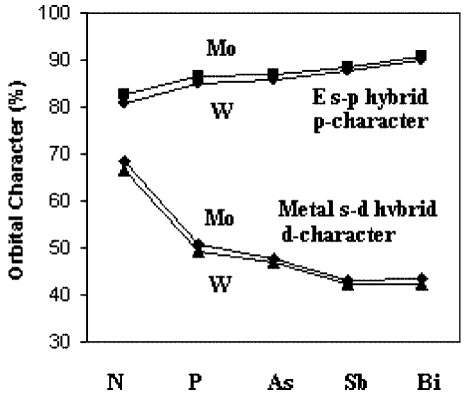

Figure 2. Metal s-d hybrid and E s-p hybrid orbitals for M≡E σ-bond in $[(MeO)_3M{\equiv}E]$ (M = Mo, W; E = N, P, As, Sb, Bi)

The latter values are approximately one third of the WBI values of the M≡E bonds. This is a first hint that the M−E bonds have a substantial degree of multiple bonding. The calculated NBO charge distribution indicates that the metal atoms always carry a large positive charge. Note that tungsten is always more positively charged than molybdenum. Nitrogen carries a significant negative charge in the nitrido complexes, while the heavier pnicogen ligands have only a small negative charge or, in cases of some molybdenum species, are slightly positive.

A more definitive picture of M≡E bonding is obtained through NBO analysis of the delocalized Kohn−Sham orbitals. The characteristics of the M≡E bonding orbitals are listed in Table 3. The M−E σ-bonding orbitals are always polarized towards the pnicogen atoms E, particularly for

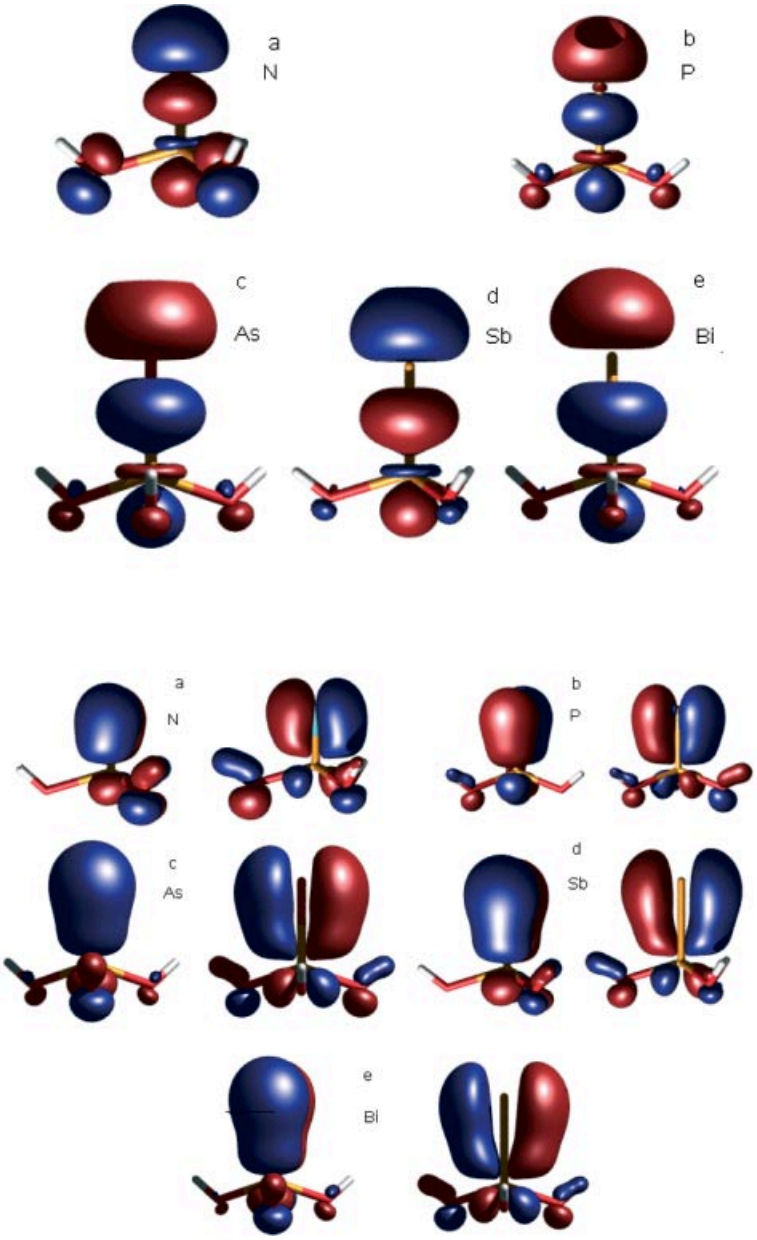

Figure 3. Plot of Mo≡E σ- (top) and π- (bottom) molecular orbitals of $[(HO)_3Mo{\equiv}E]$ (E = N, P, As, Sb, Bi)

the nitrogen complexes. The M−N π-bonds are also polarized towards nitrogen, albeit less so than the σ-bonds, while the heavier pnicogen M−E π-bonds show a small polarization towards the metal atom. The hybridization of the M−E σ-bonds at the pnicogen atoms has a large p character, which is always >80% of the total AO contribution. The hybridization of the metal atoms in the metal−nitrido bonds is approximately sd^2, while the s and d contributions in the heavier metal−pnicogen σ-bonds are more balanced. The trend of the sp^n and sd^n character of the pnicogen and metal atoms of the σ-bonds is shown in Figure 2. It becomes obvious that the %d contribution at the metal atom of the σ-bonds for the heavier pnicogens is much lower than that for nitrogen. The strong triple-bond character of the M≡E bonds becomes visible by the envelope plots of the calculated σ- and π-orbitals of the model compounds $[(HO)_3Mo{\equiv}E]$ (E = N, P, As, Sb, Bi), which are shown in Figure 3.

Besides the charge decomposition analysis using the NBO method, we also carried out an energy decomposition analysis of the metal−pnicogen bonds in $[(HO)_3M{\equiv}E]$. The results are given in Table 4.

The calculated data in Table 4 show that the M≡E bonds are rather strong. The theoretically predicted BDEs of the nitrido bonds are 163.6 kcal/mol for $[(HO)_3Mo{\equiv}N]$ and 179.2 kcal/mol for $[(HO)_3W{\equiv}N]$. The heavier pnicogen complexes have significantly weaker bonds. The calculated bond energies are between 122.6 kcal/mol for $[(HO)_3W{\equiv}P]$ and 64.3 kcal/mol for $[(HO)_3Mo{\equiv}Bi]$. The bond energies show the expected trend for the BDE of the pnicogens, N >> P > As > Sb > Bi. The tungsten complexes have stronger bonds than the molybdenum complexes.

The breakdown of the metal−pnicogen interaction energies into the different energy terms shows that the M≡N bond has a larger covalent character (about 60%) than electrostatic character (Table 4). The covalent contribution to the M≡E bonds becomes significantly smaller than the electrostatic contribution for the heavier pnicogens. The trend for the covalent character for the pnicogens is N >> P > As > Sb > Bi. The trend is graphically shown in Figure 4. The ratio of σ- to π-bonding in the covalent M≡E bond is almost 50:50.

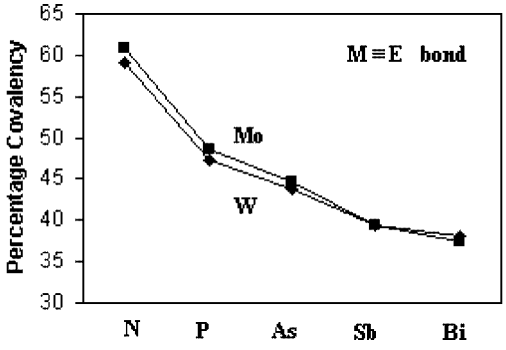

Figure 4. Trends of the covalent contributions to the M≡E bonding interactions in $[(HO)_3M{\equiv}E]$ (M = Mo, W; E = N, P, As, Sb, Bi)

Summary and Conclusion

The results of the bonding analysis of the title compounds show that the metal−pnicogen bonds are genuine triple bonds containing a σ- and a degenerate π-bond. The questions that have been addressed in the introduction can be answered as follows. (i) The M−E σ-bonds are always polarized towards the pnicogen atom E, particularly for the nitrogen complexes. The M−N π-bonds are also polarized towards nitrogen, while the π-bonds of the heavier pnicogens (P−Bi) show a small polarization towards the metal atom. The M−E σ-bonds at the pnicogen E are sp^n-hybridized; the p character is always > 80% of the total AO contribution, while the hybridization of the metal atoms in the nitrido complexes is approximately sd^2 and in the heavier homologues, approximately sd. (ii) The ratio of the energy contributions of the σ- and π-orbitals to the covalent bonding in $[(HO)_3M{\equiv}E]$ is about 50:50 for all pnicogen atoms E. (iii) The metal−nitrido bonds in $[(HO)_3M{\equiv}N]$ are more covalent than electrostatic in character. The covalent

Table 4. Energy decomposition analysis of $[(HO)_3M{\equiv}E]$ at BP86/TZ2P; energy contributions in kcal/mol

	Mo					W				
Term	N	P	As	Sb	Bi	N	P	As	Sb	Bi
ΔE_{int}	−175.2	−119.0	−106.1	−86.0	−76.5	−192.4	−136.9	−123.4	−102.2	−91.7
ΔE_{Pauli}	462.4	300.2	281.5	244.8	241.0	475.2	320.8	302.3	264.6	250.5
ΔE_{elstat}	−249.4	−215.8	−214.7	−200.2	−198.7	−272.3	−241.7	−239.4	−222.5	−212.0
ΔE_{orb} [a]	−388.3	−203.4	−172.8	−130.7	−119.1	−395.3	−215.9	−186.3	−144.3	−130.2
	(60.9%)	(48.5%)	(44.6%)	(39.5%)	(37.5%)	(59.3%)	(47.2%)	(43.8%)	(39.3%)	(38.0%)
a_1	−204.2	−101.4	−87.1	−66.9	−63.1	−205.7	−105.4	−91.2	−70.9	−66.4
a_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
e [b]	−184.1	−102.0	−85.7	−63.8	−56.0	−189.6	−110.5	−95.1	−73.4	−63.8
	(47.4%)	(50.1%)	(49.6%)	(48.8%)	(47.0%)	(48.0%)	(51.2%)	(51.0%)	(50.9%)	(49.0%)
ΔE_{prep}	11.6	12.3	12.2	11.9	12.2	13.2	14.3	14.2	14.0	14.3
$\Delta E(-D_e)$	−163.6	−106.7	−93.9	−74.1	−64.3	−179.2	−122.6	−109.2	−88.2	−83.4

[a] The values in parentheses are the percentage contribution to the total attractive interactions reflecting the covalent character of the bond. [b] The values in parentheses are the percentage π-contribution to the total orbital interactions, ΔE_{orb}.

character becomes smaller when the pnicogen atom becomes heavier, following the trend N >> P > As > Sb > Bi. (iv) The $[(HO)_3M{\equiv}E]$ tungsten complexes have stronger bonds, which are slightly less covalent than the molybdenum complexes. The π-bonding contribution in the former species is slightly larger than in the latter.

[1] F. A. Cotton, R. A. Walton, *Multiple Bonds between Metal Atoms*, 2nd ed.; Clarendon, Oxford, **1993**. M. H. Chisholm, *Acc. Chem. Res.* **1990**, *23*, 419.
[2] W. A. Nugent, J. M. Meyer, *Metal-Ligand Multiple Bonds*, John Wiley & Sons, New York, **1988**.
[3] H. Fischer, P. Hofmann, F. R. Kreisal, R. R. Schrock, U. Schubert, K. Weiss, Carbyne Complexes; VCH Publishers, New York, **1988**.
[4] *Transition Metal Carbyne Complexes*, F. R. Kreisal, Ed.; Kluwer: Dordrecht, The Netherlands, **1993**.
[5] A. M. LaPoint, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1995**, *117*, 4802.
[6] S. F. Vyboishchikov, G. Frenking, *Chem. Eur. J.* **1998**, *4*, 1439.
[7] G. Frenking, N. Fröhlich, *Chem. Rev.* **2000**, *100*, 717.
[8] S. K. Cho, Y. S. Gal, S. H. Jin, H. K. Kim, *Chem. Rev.* **2000**, *100*, 1645.
[9] J. W. Herndon, *Coord. Chem. Rev.* **2002**, *227*, 1.
[10] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed.; Wiley, New York, **1999**.
[11] K. Dehnicke, J. Strähle, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 955.
[12] M. Scheer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1947.
[13] C.-M. Ho, T.-C. Lau, H.-L. Kwong, W.-T. Wong, *J. Chem. Soc., Dalton Trans.* **1999**, 2411.
[14] [14a] A. Neuhaus, A. Veldkamp, G. Frenking, *Inorg. Chem.* **1994**, *33*, 5278. [14b] S. F. Vyboichshikov, G. Frenking, *Theor. Chem. Acc.* **1999**, *102*, 300. [14c] P. Spuhler, M. Lein, G. Frenking, *Z. Allg. Anorg. Chem.* **2003**, *629*, 803.
[15] K. L. Kunze, J. F. Harrison, *J. Am. Chem. Soc.* **1990**, *112*, 3812.
[16] J. F. Harrison, *J. Chem. Phys.* **1996**, *100*, 3513.
[17] A. Fiedler, S. Iwata, *Chem. Phys. Lett.* **1997**, *271*, 143.
[18] A. Daoudi, S. Elkhattabi, G. Berthiar, J. P. Flament, *Chem. Phys.* **1998**, *230*, 31.
[19] S. Elkhattabi, A. Daoudi, J. P. Flament, G. Berthiar, *Chem. Phys.* **1999**, *241*, 257.
[20] [20a] T. R. Cundari, *Chem. Rev.* **2000**, *100*, 807. [20b] J. F. Harrison, *Chem. Rev.* **2000**, *100*, 679 and references cited therein.
[21] R. S. Simons, P. P. Power, *J. Am. Chem. Soc.* **1996**, *118*, 11966.
[22] L. Pu, B. Twamley, S. T. Haubrich, M. M. Olmstead, B. V. Mork, R. S. Simons, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 650.
[23] A. C. Filippou, A. I. Philippoupolos, P. Portius, D. U. Neumann, *Angew. Chem. Int. Ed.* **2000**, *39*, 2778.
[24] A. C. Filippou, P. Portius, A. I. Philippoupolos, *Organometallics* **2002**, *21*, 635.
[25] K. K. Pandey, M. Lein, G. Frenking, *J. Am. Chem. Soc.* **2003**, *125*, 1660.
[26] M. Scheer, *Coord. Chem. Rev.* **1997**, *163*, 271.
[27] A. T. Termaten, H. Aktas, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Organometallics* **2003**, *22*, 1827.
[28] B. T. Sterenberg, K. A. Udachin, A. J. Carty, *Organometallics* **2003**, *22*, 3927.
[29] A. W. Ehlers, E. J. Baerends, K. Lammertsma, *J. Am. Chem. Soc.* **2002**, *124*, 2831.
[30] J. Sanchez-Nieves, B. T. Sterenberg, K. A. Udachin, A. J. Carty, *J. Am. Chem. Soc.* **2003**, *125*, 2404.
[31] F. Basuli, J. Tomaszewski, J. C. Huffman, D. J. Mindiola, *J. Am. Chem. Soc.* **2003**, *125*, 10170.
[32] F. Basuli, B. C. Bailey, J. C. Huffman, M.-H. Baik, D. J. Mindiola, *J. Am. Chem. Soc.* **2004**, *126*, 1924.
[33] G. Becker, W. Becker, R. Knebl, H. Schmidt, U. Weber, M. Westerhausen, *Nova Acta Leopoldina* **1985**, *59*, 55.
[34] M. H. Chisholm, J. C. Huffman, J. W. Pasterczyk, *Inorg. Chim. Acta* **1987**, *133*, 17.
[35] M. L. Ziegler, H.-P. Neumann, *Chem. Ber.* **1989**, *112*, 25.
[36] A. R. Arnold, D. P. Ridga, A. L. Rheingold, *J. Am. Chem. Soc.* **1995**, *117*, 4427.
[37] C. E. Laplaza, W. N. Davis, C. C. Cummins, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2042.
[38] R. R. Schrock, N. C. Zanetti, W. N. Davis, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2044.
[39] J. A. Johnson-Carr, N. C. Zanetti, R. R. Schrock, M. D. Hopkins, *J. Am. Chem. Soc.* **1996**, *118*, 11305.
[40] M. Scheer, J. Müller, M. Häser, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2492.
[41] F. H. Stephens, J. S. Figueroa, P.-L. Diaconescu, C. C. Cummins, *J. Am. Chem. Soc.* **2003**, *125*, 9264.
[42] T. Wagener, G. Frenking, *Inorg. Chem.* **1998**, *37*, 1805.
[43] G. Wu, D. Rovnyak, M. J. A. Johnson, N. C. Zanetti, D. G. Musaev, K. Morokuma, R. R. Schrock, R. G. Griffin, C. C. Cummins, *J. Am. Chem. Soc.* **1996**, *118*, 10654.
[44] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[45] D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[46] [46a] K. Raghavachari, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650. [46b] A. D. McClean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639.
[47] M. Couty, M. B. Hall, *J. Comput. Chem.* **1996**, *17*, 1359.
[48] A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 111.
[49] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
[50] W. R. Wadt, P. J. Hay, *Chem. Phys.* **1985**, *82*, 284.
[51] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.
[52] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, B. G. Zarzewski, J. A. Montgomery, R. E. Startmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels K. N. Kudin, M. C. Straiin, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochteriski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen. M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian98; Gussain, Inc., Pittsburgh PA, **1998**.
[53] G. Schaftenaar, MOLDEN3.4 CAOSCAMM Center, The Netherlands, **1998**.
[54] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
[55] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.
[56] [56a] C. Chang, M. Pelissier, Ph. Durand, *Phys. Scr.* **1986**, *34*, 394. [56b] J.-L. Heully, I. Lindgren, E. Lindroth, S. Lundquist, A.-M. Martensson-Pendrill, *J. Phys. B* **1986**, *19*, 2799. [56c] E. van Lenthe, E. J. Baerends, J. G. Snijders, *J. Chem. Phys.* **1993**, *99*, 4597. [56d] E. van Lenthe, E. J. Baerends, J. G. Snijders, *J. Chem. Phys.* **1996**, *105*, 6505. [56e] E. van Lenthe, R. van Leeuwen, E. J. Baerends, J. G. Snijders, *Int. J. Quantum Chem.* **1996**, *57*, 281. [56f] E. van Lenthe, A. W. Ehlers, E. J. Baerends, *J. Chem. Phys.* **1999**, *110*, 8943.
[57] J. G. Snijders, E. J. Baerends, P. Vernooijs, *At. Data Nucl. Data Tables* **1982**, *26*, 483.
[58] E. J. Baerends, D. E. Ellis, P. Ros, *Chem. Phys.* **1973**, *2*, 41.
[59] J. Krijn, E. J. Baerends, *Fit Functions in the HFS-Method*, Internal Report (in Dutch), Vrije University Amsterdam, The Netherlands, **1984**.
[60] E. J. Baerends, J. A. Autschbach, A. Berces, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D.

E. Ellis, L. Fan, T. H. Fischer, C. Fonseca Guerra, S. J. A. van Gisbergen, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, F. E. Harris, P. van den Hoek, H. Jacobsen, G. van Kessel, F. Kootstra, E. van Lenthe, V. P. Osinga, S. Patchkovskii, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. G. Snijders, M. Sola, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, O. Visser, E. Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, T. Ziegler, ADF **2002**−01, Scientific Computing & Modelling NV, The Netherlands.

[61] [61a] K. Morokuma, *J. Chem. Phys.* **1971**, *55*, 1236. [61b] K. Morokuma, *Acc. Chem. Res.* **1977**, *10*, 294.

[62] [62a] T. Ziegler, A. Rauk, *Theor. Chim. Acta* **1977**, *46*, 1. [62b] T. Ziegler, A. Rauk, *Inorg. Chem.* **1979**, *18*, 1558. [62c] T. Ziegler, A. Rauk, *Inorg. Chem.* **1979**, *18*, 1755.

[63] A. Diefenbach, M. B. Bickelhaupt, G. Frenking, *J. Am. Chem. Soc.* **2000**, *122*, 6449.

[64] J. Uddin, G. Frenking, *J. Am. Chem. Soc.* **2001**, *123*, 1683.

[65] K. K. Pandey, *Inorg. Chem.* **2003**, *42*, 6764.

[66] L. Pauling *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, New York, 1960, p. 239: The relationship of bond order to length is given by $d_n = d_1 - 0.71 \log n$ *where n is the bond order,* d_1 *and* d_n *are the lengths of bonds with bond order 1 and n, respectively.*

[67] [67a] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 19**84**. [67b] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, **1960**.

[68] K. A. Wiberg, *Tetrahedron* **1968**, *24*, 1083.

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