

## Formation and Calculations of the Simple Terminal Triplet Pnictinidene Molecules $N\div MF_3$ , $P\div MF_3$ , and $As\div MF_3$ ( $M = Ti, Zr, Hf$ )

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Laser-ablated Ti, Zr, and Hf atoms react with  $NF_3$ ,  $PF_3$ , or  $AsF_3$  to produce triplet state terminal pnictinidene  $N\div MF_3$ ,  $P\div MF_3$ , or  $As\div MF_3$  molecules, which are trapped in an argon matrix. Products are identified from infrared spectra and comparison to theoretically predicted vibrations. Density functional theory calculations converge to  $C_{3v}$  symmetry structures for these lowest energy products. The two unpaired electrons in nitrogen 2p, phosphorus 3p, or arsenic 4p orbitals are shared in different small amounts with empty metal  $nd$  orbitals leading to very weak degenerate  $\pi\alpha$  molecular orbitals based on bonding orbital analysis and spin density calculations. This weak  $\pi$  bonding interaction with early transition metal group 4  $nd$  orbitals is optimum for Zr with phosphorus 3p orbitals.

### Introduction

Nitrenes, compounds of the general formula R-N, are analogues of carbenes, and both generally function as reactive intermediates. The common source of nitrenes is the photolysis of azides.<sup>1</sup> Most nitrenes have triplet ground states, and  $CH_3-N$  is a simple example.<sup>2,3</sup> A characteristic reaction of alkyl nitrenes is substituent rearrangement to give the imine.<sup>1</sup> Methylene imine  $CH_2=NH$  is a well-known most stable isomer of triplet  $CH_3-N$ .<sup>4,5</sup> The more stable perfluoro analogue  $CF_2=NF$  is easier to investigate by experiment,<sup>6,7</sup> and the  $CF_3-N$  isomer has recently been observed in the triplet ground-state by matrix isolation electron spin resonance methods.<sup>8</sup> These two isomers have approximately the same energy within the error of calculations. We have been unable to find experimental evidence for phosphorus or arsenic analogues of the simple above reactive intermediates. Such terminal pnictinidenes tend to coordinate with formal double bonding to organometallic fragments,<sup>9</sup> but under matrix isolation conditions the terminal pnictinidene can be

isolated and characterized. Examples of related molecules include the phospho- and arsaalkenes  $CF_3P=CF_2$  and  $CF_3As=CF_2$ ,  $RE=C(NMe_2)_2$ , ( $E = P, As$ ) and phosphinidene complexes.<sup>10,11</sup>

Reactions of laser ablated group 4 transition metal atoms with ammonia have prepared transition metal imine analogues  $MH_2=NH$ , which were characterized by matrix infrared spectra and density functional calculations.<sup>12,13</sup> The analogous reactions of ammonia with Mo and W metal atoms produced instead the lower energy  $MH_3\equiv N$  terminal metal nitrides. However, the greater stability of metal fluoride bonds supported the formation of the Cr, Mo, and W trifluoro derivatives  $MF_3\equiv N$  and the phosphide species for Mo and W in the analogous reactions with  $NF_3$  and  $PF_3$ .<sup>14,15</sup> Reactions with arsenic trifluoride followed suit with terminal arsenides for Mo and W.<sup>16</sup> Accordingly, group 4 metal atom reactions with  $NF_3$ ,  $PF_3$ , and  $AsF_3$  were performed to seek the novel trifluorometal triplet state pnictinidenes  $MF_3-N$ ,  $MF_3-P$ , and  $MF_3-As$ , and a combined experimental and theoretical investigation is reported here. Hereafter, we will use the  $E\div MF_3$  notation to indicate these triplet ground-state product group 15 non-metal and group 4 transition metal containing molecules.

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### Experimental and Computational Methods

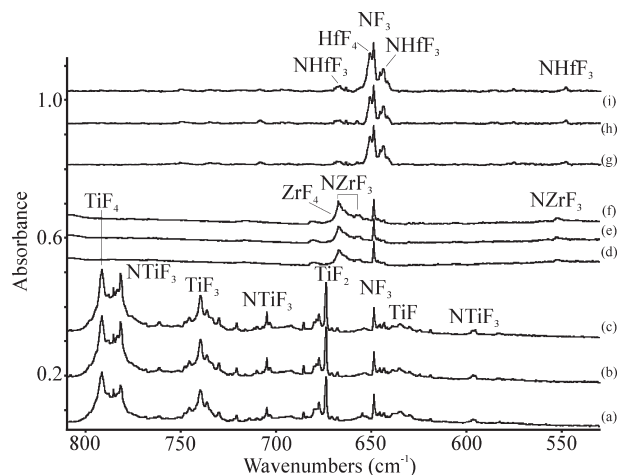
Laser ablated Ti (Goodfellow), Zr, and Hf (Johnson-Matthey) atoms were reacted with  $\text{NF}_3$  (Matheson),  $\text{PF}_3$  (PCR Research), or  $\text{AsF}_3$  (Ozark-Mahoning, vacuum distilled from dry NaF) in excess argon during condensation at 5–8 K using closed-cycle refrigerators described elsewhere.<sup>17,18</sup> Reagent gas mixtures were typically 0.5% in argon and the laser ablated metal atom concentrations were much lower. After reaction, infrared spectra were recorded at a resolution of  $0.5 \text{ cm}^{-1}$  using Nicolet 550 or 750 spectrometers with Hg–Cd–Te B range detectors. Samples were later irradiated for 15 min periods by a mercury arc street lamp (175 W) with the globe removed using a combination of optical filters, and then samples were annealed to allow reagent diffusion and further reaction.

Following our work on reactions with the isoelectronic fluoroform molecule, theoretical computations were performed using the Gaussian 03 program with the B3LYP hybrid density functional and some comparisons with the BPW91 functional.<sup>19–21</sup> The 6-311 + G(2d) basis was used to represent the electronic density of nitrogen, fluorine, phosphorus, and arsenic atoms, and SDD pseudopotentials were used for the metal atoms.<sup>22,23</sup> Frequencies were computed analytically, and all energy values reported include zero-point vibrational corrections. The calculation of vibrational frequencies is not an exact science, and density functional theory (DFT) provides a very good approximation for observed frequencies. Calculated frequencies are usually a few percent higher than observed values,<sup>24,25</sup> but that is not always the case. Finally, bonding analysis was done using the natural bond orbital method in Gaussian 03.<sup>19,26</sup>

### Results and Discussion

Infrared spectra of products formed in the reactions of laser-ablated titanium, zirconium, and hafnium atoms with  $\text{NF}_3$ ,  $\text{PF}_3$ , and  $\text{AsF}_3$  in excess argon during condensation at 5–8 K will be presented in turn. Density functional calculations were performed to support the identifications of new reaction products. Bands common to experiments using different laser ablated metals with  $\text{NF}_3$  [such as  $\text{NF}_2$  and  $\text{NF}_2^-$ ], with  $\text{PF}_3$  [ $\text{PF}_2$ ,  $\text{PF}_5$ , and  $\text{PF}_2^-$ ], and with  $\text{AsF}_3$  [ $\text{AsF}_2$  and  $\text{AsF}_3$ ] have been identified previously and will not be mentioned again here.<sup>15,27,28</sup>

**Infrared Spectra.** Sets of infrared spectra for Ti, Zr, and Hf reactions with  $\text{NF}_3$  are compared in Figure 1. The strong bands at  $791.8$  and  $740.2 \text{ cm}^{-1}$  in the Ti reaction, trace (a), have been reported previously and assigned to



**Figure 1.** Infrared spectra for group 4 metal atom reaction products with  $\text{NF}_3$  in excess argon in the  $810\text{--}530 \text{ cm}^{-1}$  region. (a) Spectrum after co-deposition of laser-ablated Ti and  $\text{NF}_3$  at 0.5% in argon at 8 K for 60 min, (b) after  $>220 \text{ nm}$  irradiation for 20 min, (c) after annealing to 30 K, and (d) spectrum after co-deposition of laser-ablated Zr and  $\text{NF}_3$  at 0.5% in argon at 8 K for 60 min, (e) after  $>290 \text{ nm}$  irradiation, and (f) after  $>220 \text{ nm}$  irradiation, and (g) spectrum after co-deposition of laser-ablated Hf and  $\text{NF}_3$  at 0.5% in argon at 8 K for 60 min, (h) after annealing to 20 K, and (i) after  $>220 \text{ nm}$  irradiation.

binary titanium fluoride species as have the weaker bands at  $677.7$ ,  $674.0$ , and  $643.6 \text{ cm}^{-1}$ .<sup>29,30</sup> The latter assignments were made to these products from the thermal Ti atom reaction with argon/fluorine samples. New bands at  $782.1$ ,  $705.1$ , and  $596.7 \text{ cm}^{-1}$  increase 30% on full arc ( $>220 \text{ nm}$ ) irradiation, and sharpen on annealing to 30 K, spectra (b) and (c). The major Zr reaction product at  $667.4 \text{ cm}^{-1}$  is joined by weaker  $658.2$  and  $553.1 \text{ cm}^{-1}$  bands, which increase in concert 10% on  $>290 \text{ nm}$  irradiation and another 30% on  $>220 \text{ nm}$  irradiation, scans (d,e,f). The shoulder absorption at  $668.6 \text{ cm}^{-1}$  is in agreement with the major product from an experiment with Zr and  $\text{F}_2$  in excess argon performed in this laboratory and is near the  $668.0 \text{ cm}^{-1}$  band observed earlier for  $\text{ZrF}_4$ .<sup>31</sup> The strongest Hf product band shifts lower to  $650.8 \text{ cm}^{-1}$  just above the  $\text{NF}_3$  absorption at  $648.9 \text{ cm}^{-1}$ , but this is in precise agreement with our major band for the Hf and  $\text{F}_2$  reaction and appropriate for  $\text{HfF}_4$ .<sup>31</sup> Comparison with the zirconium experiment suggests that there is a major product absorption at  $643.9 \text{ cm}^{-1}$  with weaker associated  $666.7$  and  $548.1 \text{ cm}^{-1}$  bands that increase together 20% on  $>20 \text{ K}$  annealing and another 20% on  $>220 \text{ nm}$  irradiation, spectra (g,h,i).

Infrared spectra for the corresponding group 4 metal atom reactions with  $\text{PF}_3$  are illustrated in Figure 2. The  $\text{TiF}_3$  and  $\text{TiF}_2$  bands were barely detected as  $\text{PF}_3$  is a more stable compound than  $\text{NF}_3$ . The major Ti reaction product at  $769.0 \text{ cm}^{-1}$  is joined by a weaker band at  $688.2 \text{ cm}^{-1}$ , and these two bands increase 30% on  $>290 \text{ nm}$  irradiation and reduce a like amount on subsequent  $>220 \text{ nm}$  irradiation, traces (a,b,c). With Zr the strong product

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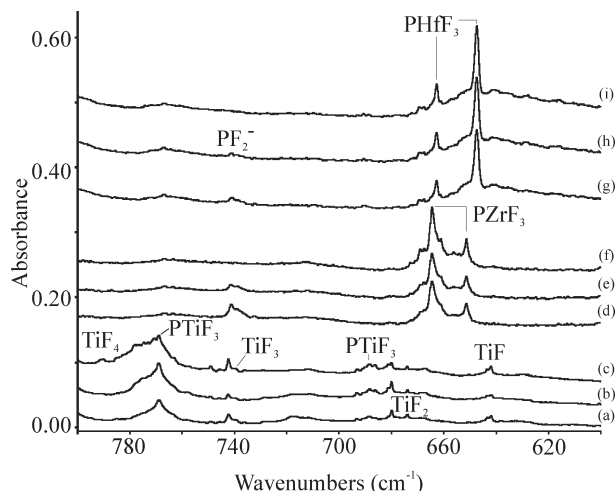
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**Table 1.** Observed and Calculated Fundamental Frequencies of the  $N \div MF_3$  Nitrene Complexes in the Ground  ${}^3A_1$  Electronic States with  $C_{3v}$  Structures<sup>a</sup>

approx. mode description	$N \div TiF_3$			$N \div ZrF_3$			$N \div HfF_3$			$N \div HfF_3$ (BPW91)	
	obs	calc	int	obs	calc	int	obs	calc	int	calc	int
M–F str, $a_1$							666.7	645	34	630	30
M–F str, e	782.1 <sup>b</sup>	796	255 × 2	667.4 <sup>c</sup>	669	208 × 2	643.9	639	156 × 2	626	142 × 2
M–F str, $a_1$	705.1 <sup>b</sup>	719	102	658.2	647	61					
$N \div M$ str, $a_1$	596.7	629	29	553.1	565	58	548.1	550	49	537	39
$MF_3$ def, e		203	15 × 2		168	22 × 2		162	3 × 2	162	4 × 2
$MF_3$ def, $a_1$		190	21		152	26		141	23	138	19
$N-M-F$ def, e		176	1 × 2		155	6 × 2		152	24 × 2	150	16 × 2

<sup>a</sup> Frequencies and intensities are in  $cm^{-1}$  and  $km/mol$ . Observed in an argon matrix. Frequencies and intensities computed with B3LYP/6-311+G(2d) in the harmonic approximation using the SDD core potential and basis set for metal atoms. Calculations using the BPW91 functional gave similar frequencies as shown for the hafnium product. <sup>b</sup> The mode symmetry notations are based on the  $C_{3v}$  structure. <sup>c</sup> Band probably over some  $ZrF_4$  absorption.

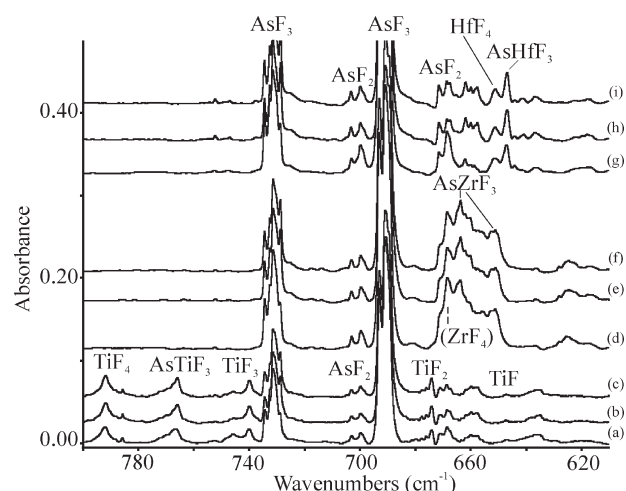


**Figure 2.** Infrared spectra for group 4 metal atom reaction products with  $PF_3$  in excess argon in the  $800\text{--}600\text{ cm}^{-1}$  region. (a) Spectrum after co-deposition of laser-ablated Ti and  $PF_3$  at 0.5% in argon at 8 K for 60 min, (b) after 290 nm irradiation for 20 min, and (c) after  $>220$  nm irradiation for 20 min. (d) Spectrum after co-deposition of laser-ablated Zr and  $PF_3$  at 0.13% in argon at 8 K for 60 min, (e) after  $>290$  nm irradiation, and (f) after  $>220$  nm irradiation. (g) Spectrum after co-deposition of laser-ablated Hf and  $PF_3$  at 0.5% in argon at 8 K for 60 min, (h) after  $>290$  nm irradiation, and (i) after  $>220$  nm irradiation.

bands at  $664.2$  and  $651.4\text{ cm}^{-1}$  were very intense (absorbance 0.2 and 0.1, respectively) using 0.5% precursor in argon, so the sample was diluted to 0.13%, and these bands with the same relative intensity are shown in Figure 2. The  $664.2$  and  $651.4\text{ cm}^{-1}$  bands were not changed on the initial  $>290$  nm irradiation but increased together 50% on the next  $>220$  nm irradiation, spectra (d,e,f). Using Hf the product band relative intensities reverse at  $662.6$  and  $647.4\text{ cm}^{-1}$ , and these bands increase 10% on  $>290$  nm irradiation and another 20% on  $>220$  nm irradiation, scans (g,h,i).

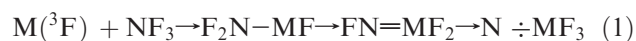
Spectra for group 4 metal reactions with  $AsF_3$  are shown in Figure 3. The bands at  $791.8$ ,  $740.2$ , and  $674.2\text{ cm}^{-1}$  in the Ti reaction for  $TiF_{4,3,2}$  are weaker than with  $NF_3$ , and a new absorption was observed at  $765.9\text{ cm}^{-1}$ . The corresponding band for Zr is  $663.6\text{ cm}^{-1}$ , and  $ZrF_4$  absorption underneath increases the  $AsF_2$  peak at  $668.6\text{ cm}^{-1}$ . Using Hf the  $HfF_4$  band is observed at  $651.0\text{ cm}^{-1}$  and the new product lower at  $646.9\text{ cm}^{-1}$ .

**Identification of the  $N \div MF_3$  molecules.** Reactions of Ti, Zr, and Hf atoms with  $NF_3$  gave new strong, medium, and weak product absorptions with each metal, which



**Figure 3.** Infrared spectra for group 4 metal atom reaction products with  $AsF_3$  in excess argon in the  $800\text{--}610\text{ cm}^{-1}$  region. (a) Spectrum after co-deposition of laser-ablated Ti and  $AsF_3$  at 0.5% in argon at 5 K for 60 min, (b) after 290 nm irradiation for 20 min, and (c) after  $>220$  nm irradiation for 20 min. (d) Spectrum after co-deposition of laser-ablated Zr and  $AsF_3$  at 0.13% in argon at 5 K for 60 min, (e) after  $>290$  nm irradiation, and (f) after  $>220$  nm irradiation. (g) Spectrum after co-deposition of laser-ablated Hf and  $AsF_3$  at 0.5% in argon at 5 K for 60 min, (h) after  $>290$  nm irradiation, and (i) after  $>220$  nm irradiation.

are compared in Table 1 with frequencies calculated for the lowest energy product molecule. The metal atom reaction with  $NF_3$  most likely proceeds through an insertion step like the halomethane reactions investigated extensively in this laboratory,<sup>32</sup> and here the reaction proceeds from the difluoroamine inserted species to the fluoroimine and then to the nitrene species. These steps in the reaction are 216, 235, and 274 kcal/mol lower in energy than the initial reactants Ti and  $NF_3$ , respectively. The zirconium fluoroimine and nitrene species are 266 and 313 kcal/mol lower energy than the combined reagents, and the analogous hafnium products are 261 and 319 kcal/mol lower than the starting materials.



Our experience with Ti–F, Zr–F, and Hf–F stretching frequencies is that the B3LYP calculated values slightly exceed the argon matrix observed values by about 5% for

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**Table 2.** Observed and Calculated Fundamental Frequencies of the P÷MF<sub>3</sub> Complexes in the Ground <sup>3</sup>A<sub>1</sub> Electronic States with C<sub>3v</sub> Structures<sup>a</sup>

approx. mode description	P÷TiF <sub>3</sub>			P÷ZrF <sub>3</sub>			P÷HfF <sub>3</sub>				P÷HfF <sub>3</sub> (BPW91)	
	obs	calc	int	obs	calc	int	obs	calc	int	calc	int	
M–F str, a <sub>1</sub>							662.6	639	10	625	67	
M–F str, e	769.0	785	219 × 2	664.2	665	181 × 2	647.4	635	138 × 2	623	124 × 2	
M–F str, a <sub>1</sub>	688.2	699	138	651.4	640	98						
P÷M str, a <sub>1</sub>		369	28		330	32		308	20	304	17	
MF <sub>3</sub> def, e		193	8 × 2		167	11 × 2		158	9 × 2	155	7 × 2	
MF <sub>3</sub> def, a <sub>1</sub>		172	11		146	15		138	16	132	13	
P–M–F def, e		133	0 × 2		115	3 × 2		111	3 × 2	107	4 × 2	

<sup>a</sup> Frequencies and intensities are in cm<sup>-1</sup> and km/mol. Observed in an argon matrix. Frequencies and intensities computed with B3LYP/6-311 + G(2d) in the harmonic approximation using the SDD core potential and basis set for metal atoms. Calculations using the BPW91 functional gave similar frequencies as shown for the hafnium product. The mode symmetry notations are based on the C<sub>3v</sub> structure.

**Table 3.** Observed and Calculated Fundamental Frequencies of the As÷MF<sub>3</sub> Complexes in the Ground <sup>3</sup>A<sub>1</sub> Electronic States with C<sub>3v</sub> Structures<sup>a</sup>

approx. mode description	As÷TiF <sub>3</sub>			As÷ZrF <sub>3</sub>			As÷HfF <sub>3</sub>			As÷HfF <sub>3</sub> (BPW91)	
	obs	calc	int	obs	calc	int	obs	calc	int	calc	int
M–F str, a <sub>1</sub>							n.o.	639	78	625	74
M–F str, e	765.9	783	209 × 2	663.6	664	173 × 2	646.9	635	133 × 2	622	120 × 2
M–F str, a <sub>1</sub>	n.o.	697	147	651.1	640	108					
As÷M str, a <sub>1</sub>		295	24		246	26		214	16	210	13
MF <sub>3</sub> def, e		192	7 × 2		167	11 × 2		162	10 × 2	155	7 × 2
MF <sub>3</sub> def, a <sub>1</sub>		148	6		132	9		133	10	125	8
As–M–F def, e		117	0 × 2		100	2 × 2		100	2 × 2	92	2 × 2

<sup>a</sup> Frequencies and intensities are in cm<sup>-1</sup> and km/mol. Observed in an argon matrix. Frequencies and intensities computed with B3LYP/6-311 + G(2d) in the harmonic approximation using the SDD core potential and basis set for metal atoms. Calculations using the BPW91 functional gave similar frequencies as shown for the hafnium product. The mode symmetry notations are based on the C<sub>3v</sub> structure.

**Table 4.** Structural Parameters and Physical Constants for Triplet State Pnictinidenes E÷MF<sub>3</sub> (E = N, P, As, M = Ti, Zr, Hf) in C<sub>3v</sub> Symmetry<sup>a</sup>

parameter	N÷TiF <sub>3</sub>	P÷TiF <sub>3</sub>	As÷TiF <sub>3</sub>	N÷ZrF <sub>3</sub>	P÷ZrF <sub>3</sub>	As÷ZrF <sub>3</sub>	N÷HfF <sub>3</sub>	P÷HfF <sub>3</sub>	As÷HfF <sub>3</sub>
r(E÷M)	1.959	2.426	2.530	2.143	2.606	2.715	2.146	2.609	2.715
r(M–F)	1.756	1.759	1.759	1.925	1.926	1.925	1.922	1.923	1.922
<(EMF)	105.8	105.4	105.2	106.8	106.8	107.0	106.5	106.8	107.0
q(E) <sup>b</sup>	-0.19/-0.19	0.06/0.14	0.003/0.16	-0.44/-0.42	-0.22/-0.08	-0.27/-0.05	-0.42/-0.45	-0.08/-0.13	-0.18/-0.09
q(M) <sup>b</sup>	1.14/1.60	0.80/1.27	0.82/1.25	1.62/2.27	1.39/1.92	1.43/1.99	1.50/2.38	1.10/2.04	1.16/2.01
q(F) <sup>b</sup>	-0.32/-0.47	-0.28/-0.47	-0.27/-0.47	-0.39/-0.62	-0.39/-0.61	-0.39/-0.61	-0.36/-0.64	-0.34/-0.64	-0.33/-0.64
E(s) <sup>c</sup>	1.89	1.90	1.92	1.91	1.91	1.93	1.91	1.91	1.92
E(p) <sup>c</sup>	3.30	2.95	2.91	3.49	3.15	3.11	3.53	3.20	3.15
M(s) <sup>c</sup>	0.16	0.28	0.29	0.15	0.27	0.28	0.21	0.33	0.35
M(d) <sup>c</sup>	1.97	2.10	2.10	1.38	1.55	1.55	1.22	1.35	1.35
M(p) <sup>c</sup>	0.73	0.31	0.32	0.18	0.25	0.26	0.19	0.26	0.27
F(s) <sup>c</sup>	1.90	1.90	1.90	1.93	1.92	1.92	1.93	1.92	1.92
F(p) <sup>c</sup>	5.56	5.57	5.57	5.68	5.68	5.68	5.71	5.71	5.71
s(E) <sup>d</sup>	1.925	1.882	2.010	1.885	1.802	1.924	1.894	1.810	1.936
s(M) <sup>d</sup>	0.008	0.077	-0.071	0.082	0.175	0.039	0.080	0.195	0.044
s(F) <sup>d</sup>	0.023	0.014	0.021	0.011	0.008	0.012	0.009	0.002	0.007
μ <sup>e</sup>	0.15	1.05	1.28	0.39	0.59	0.79	0.54	0.49	0.70
ΔE <sup>f</sup>	274	313	319	122	138	169	150	191	197

<sup>a</sup> Bond lengths and angles are in Å and degrees. All calculations performed at the B3LYP//6-311 + G(2d)/SDD level. <sup>b</sup> Mulliken atomic/Natural charges. <sup>c</sup> Natural electron configuration for valence orbitals. <sup>d</sup> Mulliken atomic spin densities: value given for only one fluorine atom. <sup>e</sup> Molecular dipole moment in D. <sup>f</sup> Binding energy in kcal/mol relative to M + EF<sub>3</sub>.

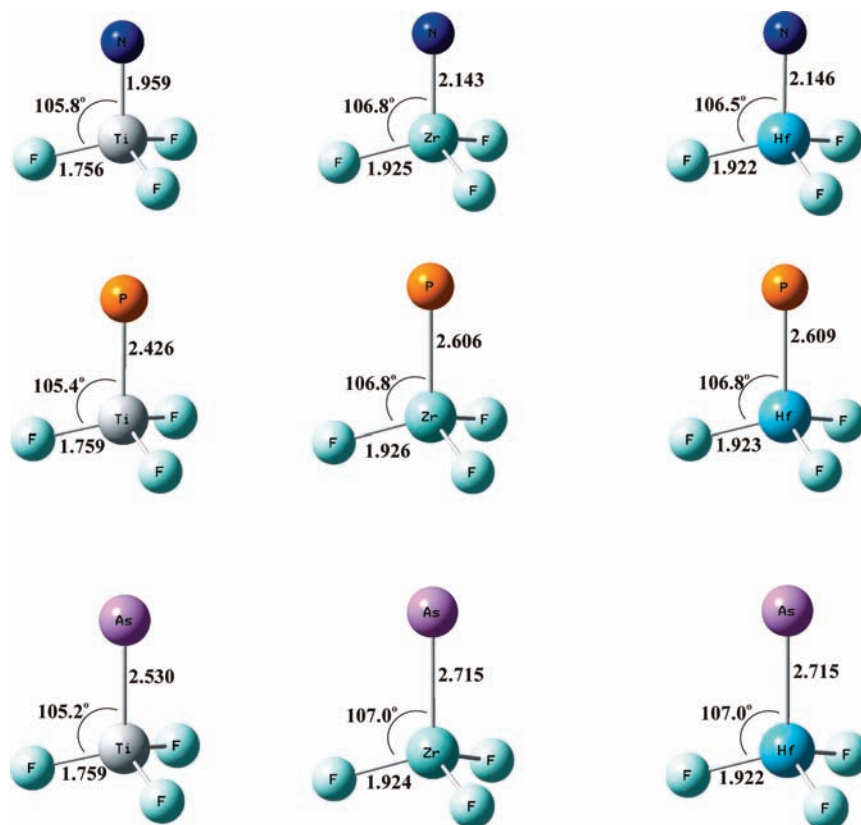
Ti–F, and within 2% on either side for Zr–F and Hf–F modes.<sup>18,32</sup> The observed and calculated frequencies in Table 1 fit even better than this relationship, which substantiates our identification of these new triplet state nitrene molecules. The observed and calculated infrared intensities are also qualitatively correct. Notice the reversal in the order of antisymmetric and symmetric M–F stretching frequencies with increasing metal mass between Zr and Hf, and this is also matched by our calculations.

Notice that the M÷N stretching frequencies for the group 4 nitrene series at 596.7, 553.1, and 548.1 cm<sup>-1</sup> are significantly lower than the M≡N stretching frequencies for the group 6 nitride series at 1015, 1075, and 1091 cm<sup>-1</sup>, respectively, although the analogous M–F stretching frequencies differ by less than 50 cm<sup>-1</sup>.<sup>15</sup> Observed frequencies for the N÷ZrF<sub>3</sub> and N÷HfF<sub>3</sub> molecules may be compared with those for the isoelectronic HC÷ZrF<sub>3</sub> [659.7, antisym; 651.7, sym; 627.6 cm<sup>-1</sup>, C–Zr str] and HC÷HfF<sub>3</sub> [648.6, sym; 642.9, antisym; 621.7 cm<sup>-1</sup>;

**Table 5.** Description of the E÷M Bonding Molecular Orbitals for Triplet State Terminal Pnictinidenes E÷MF<sub>3</sub> (E = N, P, As, M = Ti, Zr, Hf)<sup>a</sup>

m. o. <sup>b</sup>	N÷TiF <sub>3</sub>	P÷TiF <sub>3</sub>	As÷TiF <sub>3</sub>	N÷ZrF <sub>3</sub>	P÷ZrF <sub>3</sub>	As÷ZrF <sub>3</sub>	N÷HfF <sub>3</sub>	P÷HfF <sub>3</sub>	As÷HfF <sub>3</sub>
$\sigma_\alpha$	77%N,23%Ti	62%P,38%Ti	60%As,40%Ti	82%N,18%Zr	68%P,32%Zr	67%As,33%Zr	83%N,17%Hf	69%P,31%Hf	68%As,32%Hf
$\sigma_\beta$	67%N,33%Ti	54%P,46%Ti	51%As,49%Ti	77%N,23%Zr	64%P,36%Zr	62%As,38%Zr	78%N,22%Hf	66%P,34%Hf	64%As,36%Hf
$\pi_\alpha$	89%N,11%Ti	86%P,14%Ti	87%As,13%Ti	100%N,0%Zr	88%P,12%Zr	88%As,12%Zr	100%N,0%Hf	89%P,11%Hf	89%As,11%Hf
$\pi_\alpha$	89%N,11%Ti	86%P,14%Ti	87%As,13%Ti	100%N,0%Zr	88%P,12%Zr	88%As,12%Zr	100%N,0%Hf	89%P,11%Hf	89%As,11%Hf

<sup>a</sup> All calculations performed at the B3LYP//6-311+G(2d)/SDD level. Natural bond orbital analysis employed. <sup>b</sup> Bonding molecular orbital occupancies greater than 0.98 electron. Electron spins are indicated  $\alpha$  and  $\beta$ . The  $\pi$  molecular orbitals are degenerate and are dominated by pnictide p (100%) and metal d (>79%) atomic orbitals.

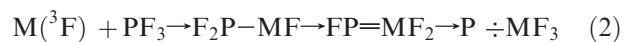
**Figure 4.** Structures calculated for nine group 4 transition metal trifluoride pnictinidenes using B3LYP/6-311+G(2d)/SDD methods.

C–Hf str] triplet state species.<sup>32</sup> The four observed M–F stretching frequencies for the N÷M nitrenes are 1–18 cm<sup>-1</sup> higher than for the C÷M species, but the C–Zr stretching frequency is 74.5 cm<sup>-1</sup> higher than the N–Zr stretching mode and the C–Hf frequency is 73.6 cm<sup>-1</sup> above the N–Hf value. These consistent frequency trends for closely related isoelectronic molecules substantiate our assignments.

A major contribution to the energy differences between the last steps of reaction 1 is the strong M–F bonds compared to weak N–F bonds. An interesting comparison can be made between the isoelectronic HN=CH<sub>2</sub> and N÷CH<sub>3</sub> reactive species. The latter is computed at the B3LYP level to be 50 kcal/mol higher in energy, and a major factor here is the single N–C bond compared to the N=C bond. However, in contrast, as mentioned above the trifluorotitanium nitrene is more stable (39 kcal/mol) than the FN=TiF<sub>2</sub> imine isomer owing to the stronger Ti–F bond.

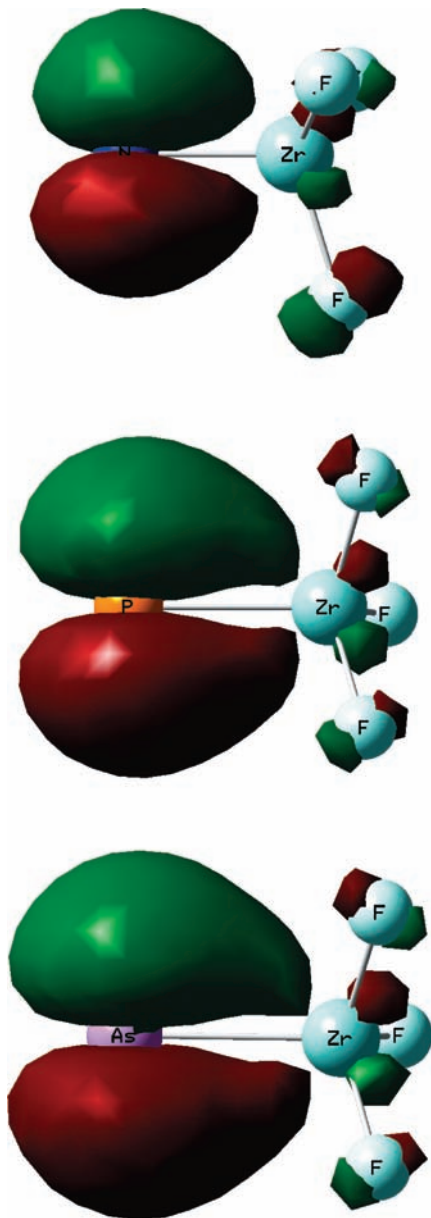
**Identification of the P÷MF<sub>3</sub> molecules.** Phosphorus trifluoride is less reactive, and the infrared spectra contain fewer absorptions. The overall reaction 2 is

less exothermic: the final products are 122, 138, and 169 kcal/mol lower in energy than the reagents.



For the Ti reaction, new Ti–F stretching absorptions at 769.0 and 688.2 cm<sup>-1</sup> fall 13–17 cm<sup>-1</sup> lower in frequency than the nitrene product, but the strong product bands with Zr are only 3–7 cm<sup>-1</sup> lower than the nitrene values as the heavier metal mediates the group 15 mass change. Notice the reversal in mode intensities for the Hf product at 662.6 and 647.4 cm<sup>-1</sup> as the symmetric and antisymmetric M–F<sub>3</sub> stretching mode positions reverse. This relationship is in accord with our vibrational frequency calculations (Table 2).

**Identification of the As÷MF<sub>3</sub> molecules.** Arsenic trifluoride is intermediate in reactivity, as attested by the intermediate yield of TiF<sub>2,3,4</sub> and HfF<sub>4</sub>, and the overall reaction energetics. Reaction (3) is 150, 191, and 197 kcal/mol exothermic for the three metals, respectively. The spectra in Figure 3 reveal one new metal dependent product band for each metal, at 765.9 cm<sup>-1</sup> for Ti, at



**Figure 5.** One of the weak degenerate  $\pi$  molecular orbitals calculated for the pnictinidene series  $N\div ZrF_3$ ,  $P\div ZrF_3$ , and  $As\div ZrF_3$  using B3LYP/6-311 + G(2d)/SDD methods and plotted with an iso-electron density of  $0.03 e/au^3$ .

$663.6\text{ cm}^{-1}$  for Zr, and at  $646.9\text{ cm}^{-1}$  for Hf. These bands fall stepwise in line below the analogous  $NMF_3$  and  $PMF_3$  product antisymmetric M–F stretching frequencies (Tables 1 and 2) as the heavier transition metal dampens the effect of pnictide substitution. Our DFT predictions for the strongest infrared absorption correlate very closely<sup>24,25</sup> with the observed absorptions (Table 3).

**Bonding in the Terminal Pnictinidenes.** Natural bond orbital analysis<sup>26</sup> was performed for the group 4 metal terminal pnictinidene series, and the results are outlined in Tables 4 and 5. The first point to notice is that the Mulliken atomic electron spin densities on the N, P, and As centers are 1.8 or greater indicating clearly that there is only a small amount of (p-d)  $\pi$  bonding interaction in these triplet ground-state molecules. Perhaps the most interesting finding is that the lowest of these group 15 spin densities, 1.802 and 1.810, are on P in the Zr and Hf phosphinidines, and the metals have spin densities of

0.175 and 0.195, respectively. This combination represents the most favorable (p-d)  $\pi$  orbital overlap. Even so the (p-d)  $\pi$  molecular orbitals are dominated by the P atom with 88 and 89% contributions from P 3p (Table 5). Both the smaller N 2p and the larger As 4p valence orbitals are less effective than the P 3p orbitals. Although (p-d)  $\pi$  bonding is more important for N than P, this is based largely on interaction with first row elements.<sup>33,34</sup> When the partner is an early transition metal  $nd$  orbital, P 3p dominates the (p-d)  $\pi$  bonding scene.

Another comparison of interest is with the isoelectronic  $HC\div MF_3$  molecules, which have been prepared by the analogous reactions with fluorocarbonyl,<sup>32</sup> where the computed  $HC\div MF_3$  and  $N\div MF_3$  bond lengths are almost the same (within 0.02 Å). The analogous calculation for  $HC\div TiF_3$  finds 1.837 and 0.123 spin densities on C and Ti, which may be compared with the 1.925 and 0.008 values given for  $N\div TiF_3$  in Table 4. In addition, natural bond orbital calculations find that the more diffuse C 2p orbital overlaps more effectively than N 2p with Ti 3d, and the  $\pi_\alpha$  molecular orbitals are 79% C and 21% Ti, which shows more interaction than the 89% N and 11% Ti  $\pi_\alpha$  molecular orbitals for  $N\div TiF_3$  (Table 5). Although the spin densities for N (1.885) and Zr (0.082) indicate electron transfer, the computed molecular orbitals are 100% N, but the bonding situation is more favorable for C with Zr as the C (1.894) and Zr (0.115) spin densities and the  $\pi_\alpha$  MO 85% C and 15% Zr indicate. Similarly, the C (1.921) and Hf (0.094) spin densities for  $HC\div HfF_3$  are near the nitrene values (Table 4), but the  $\pi_\alpha$  molecular orbitals are 86% C as compared to 100% N (Table 5, Figures 4, 5).

## Conclusions

The  $NF_3$ ,  $PF_3$ , or  $AsF_3$  molecules react with laser-ablated Ti, Zr, and Hf atoms to produce triplet state terminal pnictinidene  $N\div MF_3$ ,  $P\div MF_3$ , or  $As\div MF_3$  molecules, which are trapped in an argon matrix and identified by their infrared spectra and comparison to computed vibrational frequencies. Density functional theory calculations converge to  $C_{3v}$  symmetry triplet state structures with relatively long terminal group 15-group 4 bonds for these lowest energy reaction products. The two unpaired electrons in nitrogen 2p, phosphorus 3p, or arsenic 4p orbitals are shared to various degrees with empty metal  $nd$  orbitals leading to very weak degenerate  $\pi$  molecular orbitals based on DFT bonding orbital analysis and spin density calculations. This weak  $\pi$  bonding interaction with early transition metal group 4  $nd$  orbitals appears to work best with Zr and Hf with phosphorus 3p orbitals, and almost as well for arsenic 4p orbitals. Although there are more terminal nitride than phosphide complexes, and even fewer arsenide complexes,<sup>35</sup> our work suggests that phosphinidenes and even arseninidenes can be stabilized by early transition metal complexes in macroscopic reactions.

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