

## Force Constants of Molybdenum– and Tungsten–Pnictogen Triple Bonds

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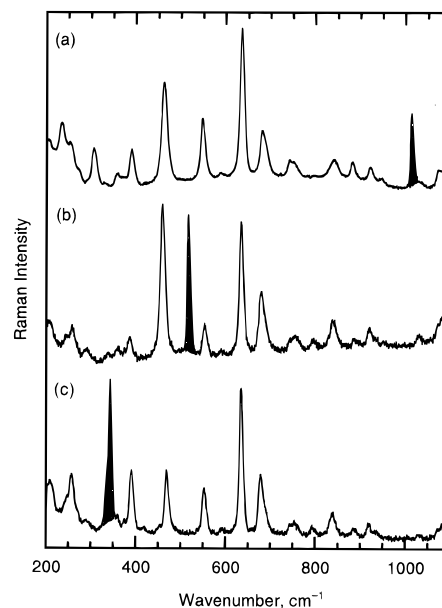
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Recently, the first examples of transition-metal complexes that contain terminal phosphido ligands,  $[\text{N}_3\text{N}]\text{M}\equiv\text{P}$  ( $[\text{N}_3\text{N}]^{3-} = [(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]^{3-}$ ;  $\text{M} = \text{Mo}$  or  $\text{W}$ )<sup>1</sup> and  $[\text{N}(t\text{-Bu})\text{-}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_3\text{Mo}\equiv\text{P}$ ,<sup>2</sup> were reported. The valence–isoelectronic relationship between the nitrido and phosphido ligands, coupled with the observation that the compounds possess short  $\text{M}–\text{P}$  bonds ( $d(\text{W}–\text{P}) = 2.162(4) \text{ \AA}$ ,  $d(\text{Mo}–\text{P}) = 2.119(4) \text{ \AA}$ ), suggests that a formal bond order of 3 be attributed to the  $\text{M}\equiv\text{P}$  linkages. We have now extended the class of  $[\text{N}_3\text{N}]\text{M}\equiv\text{E}$  compounds to include those that contain terminal arsenido ligands,  $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$  and  $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$ ,<sup>3</sup> and therefore are in a position to compare metal–pnictogen triple bonds ( $\text{E} = \text{N}$ ,  $\text{P}$ ,  $\text{As}$ ) by experimental methods. Herein we report Raman-spectroscopic measurements of  $[\text{N}_3\text{N}]\text{M}\equiv\text{E}$  compounds, which provide  $\text{M}\equiv\text{E}$  stretching frequencies and force constants.

Orange  $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$  can be isolated in  $\sim 30\%$  yield by a reaction analogous to that employed to prepare  $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$ ,<sup>1</sup> namely, addition of  $\sim 2$  equiv of  $\text{LiAsHPh}$  to  $[\text{N}_3\text{N}]\text{MoCl}$  in a mixture of toluene and THF. (See Supporting Information for all experimental details.)  $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$ , on the other hand, is best prepared ( $\sim 60\%$  yield) by reacting  $\sim 4$  equiv of  $\text{AsPh}_2$  with  $[\text{N}_3\text{N}]\text{WPh}$  in toluene over a period of 48 h in the dark. An X-ray structure of  $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$  showed it to be closely analogous to the structure of  $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ , with a  $\text{Mo}\equiv\text{As}$  bond length of  $2.252(3) \text{ \AA}$ .<sup>4</sup> White  $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$  and a 1:1 mixture of  $[\text{N}_3\text{N}]\text{W}\equiv^{14}\text{N}$  and  $[\text{N}_3\text{N}]\text{W}\equiv^{15}\text{N}$  were prepared from the reaction between sodium azide and  $[\text{N}_3\text{N}]\text{WCl}$  in  $\sim 70\%$  yield.

The Raman spectrum of  $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$  is complex, consisting of over 35 distinct bands and shoulders in the  $200\text{--}1500 \text{ cm}^{-1}$  frequency range and a cluster of intense bands in the  $\text{C}–\text{H}$  stretching region ( $2800\text{--}3000 \text{ cm}^{-1}$ ).<sup>5</sup> The  $200\text{--}1100 \text{ cm}^{-1}$  region is shown in Figure 1. Partial labeling (50%) of the terminal nitrido ligand in  $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$  with  $^{15}\text{N}$  results in a 50% reduction in the intensity of the medium-intensity band at  $1015 \text{ cm}^{-1}$  and the appearance of a new band of equal intensity at  $987 \text{ cm}^{-1}$ , thus allowing these two bands to be assigned unambiguously to the  $\text{W}\equiv^{14}\text{N}$  and  $\text{W}\equiv^{15}\text{N}$  stretching modes, respectively. The other Raman bands do not differ in frequency by more than  $2 \text{ cm}^{-1}$  or in intensity between  $[\text{N}_3\text{N}]\text{W}\equiv^{14}\text{N}$  and  $[\text{N}_3\text{N}]\text{W}\equiv^{15}\text{N}$ . The  $28 \text{ cm}^{-1}$  difference between the  $\nu(\text{W}\equiv\text{N})$



**Figure 1.** Raman spectra of microcrystalline  $[\text{N}_3\text{N}]\text{W}\equiv\text{E}$  in the  $200\text{--}1100 \text{ cm}^{-1}$  frequency range: (a)  $\text{E} = \text{N}$ ; (b)  $\text{E} = \text{P}$ ; (c)  $\text{E} = \text{As}$ . Bands assigned to  $\nu(\text{W}\equiv\text{E})$  are shaded.

frequencies for these isotopomers is close to that predicted from the diatomic oscillator approximation ( $32 \text{ cm}^{-1}$ ).

Most other bands in the Raman spectrum of  $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$  cannot be assigned to specific vibrational modes at this point because  $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$  possesses 183 vibrational degrees of freedom ( $35A_1 + 26A_2 + 61E$  under idealized  $C_{3v}$  symmetry), of which 157 ( $A_1$  and  $E$ ) are Raman allowed. Independent of their assignments, however, many of the bands in the Raman spectrum of  $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$  are expected to be conserved in the spectra of other  $[\text{N}_3\text{N}]\text{M}\equiv\text{E}$  derivatives within narrow frequency ranges because the majority of the vibrational modes in these compounds are associated with the  $\text{SiMe}_3$  groups. Consistent with this proposal, we find that the Raman spectra of  $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$  and  $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$  are qualitatively similar to that of  $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$  (Figure 1), with nearly all bands in the spectrum of  $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$  exhibiting counterparts (based on their relative intensities) in the spectra of  $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$  and  $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$  within  $10 \text{ cm}^{-1}$  of their positions in the spectrum of  $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$ . The strong band at  $635 \text{ cm}^{-1}$ , which is assigned to  $\nu(\text{Si}–\text{C})$ , is representative of the  $\text{SiMe}_3$ -localized modes, exhibiting a constant intensity and frequency ( $\pm 1 \text{ cm}^{-1}$ ) as a function of  $\text{E}$ . Because of the similarities among the spectra, the band attributable to  $\nu(\text{W}\equiv\text{P})$  can be readily identified at  $516 \text{ cm}^{-1}$  and that to  $\nu(\text{W}\equiv\text{As})$  at  $343 \text{ cm}^{-1}$ . Likewise, the most significant differences between the Raman spectra of  $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$  and  $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$  are the  $\nu(\text{Mo}\equiv\text{P})$  band at  $521 \text{ cm}^{-1}$  and the  $\nu(\text{Mo}\equiv\text{As})$  band at  $374 \text{ cm}^{-1}$ . Stretching frequencies and force constants of the  $\text{M}\equiv\text{E}$  oscillators of  $[\text{N}_3\text{N}]\text{M}\equiv\text{E}$  complexes are listed in Table 1.<sup>6</sup>

The general trends among the  $\text{M}\equiv\text{E}$  force constants can be rationalized straightforwardly. The reduction in  $\text{W}\equiv\text{E}$  force constant [ $k(\text{W}\equiv\text{N}) \gg k(\text{W}\equiv\text{P}) > k(\text{W}\equiv\text{As})$ ] with increasing  $\text{W}\equiv\text{E}$  bond length [ $d(\text{W}\equiv\text{N}) = 1.70\text{--}1.75 \text{ \AA}$ <sup>7,8</sup>  $\ll d(\text{W}\equiv\text{P}) =$

(6) The lack of stable phosphorus and arsenic isotopes prevents us from determining whether the nominal  $\nu(\text{M}\equiv\text{P})$  and  $\nu(\text{M}\equiv\text{As})$  modes to which these bands are assigned are as uncoupled from other vibrational coordinates as is  $\nu(\text{W}\equiv\text{N})$ . The frequency and relative intensity of the band at  $\sim 460 \text{ cm}^{-1}$ , which is in the vicinity of  $\nu(\text{M}\equiv\text{P})$  and  $\nu(\text{M}\equiv\text{As})$ , are, in fact, more strongly dependent on the nature of  $\text{E}$  ( $\text{WN}$ ,  $462 \text{ cm}^{-1}$ ;  $\text{WP}$ ,  $458 \text{ cm}^{-1}$ ;  $\text{WAs}$ ,  $469 \text{ cm}^{-1}$ ;  $\text{MoP}$ ,  $449 \text{ cm}^{-1}$ ;  $\text{MoAs}$ ,  $469 \text{ cm}^{-1}$ ) than are those for other bands, but these differences are sufficiently small that mixing of  $\nu(\text{M}\equiv\text{E})$  is inferred to be slight. Small structural differences between the  $[\text{N}_3\text{N}]\text{M}\equiv\text{E}$  compounds could account for the shifts in the  $460 \text{ cm}^{-1}$  band.

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(4) Orange  $\text{C}_{15}\text{H}_{39}\text{N}_4\text{Si}_3\text{AsMo}$ ,  $\text{FW} = 530.62$ , space group  $Pa\bar{3}$  (No. 205),  $a = b = c = 17.197(2) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 5085.4(4) \text{ \AA}^3$ ,  $Z = 8$ ,  $d_{\text{calcd}} = 1.386 \text{ g cm}^{-3}$ . Details will be reported fully in a future publication.

(5) FT Raman spectra of microcrystalline samples were recorded under nonresonance conditions at  $1 \text{ cm}^{-1}$  resolution using a Nicolet Raman 950 spectrometer (Nd:YVO<sub>4</sub> laser,  $\lambda_{\text{ex}} = 1064 \text{ nm}$ , power =  $0.2\text{--}0.4 \text{ W}$ ) that employed a liquid nitrogen cooled germanium diode detector (Applied Detector Corp. model 203NR).

**Table 1.** M≡E Stretching Frequencies and Force Constants for [N<sub>3</sub>N]M≡E Complexes

oscillator	$\nu(\text{M}\equiv\text{E}), \text{cm}^{-1}$	$k(\text{M}\equiv\text{E}), \text{mdyne } \text{\AA}^{-1} \text{ }^a$
W≡ <sup>14</sup> N	1015	7.90
W≡ <sup>15</sup> N	987	7.96
W≡P	516	4.16
W≡As	343	3.69
Mo≡P	521	3.74
Mo≡As	374	3.47

<sup>a</sup> Diatomic oscillator approximation.

2.162(4) Å<sup>1</sup> <  $d(\text{W}\equiv\text{As}) = 2.25\text{--}2.30$  Å (see [N<sub>3</sub>N]Mo≡As above<sup>3</sup>) is expected from empirical bond distance/force constant relationships.<sup>9–11</sup> Moreover, the observation that  $k(\text{W}\equiv\text{E}) > k(\text{Mo}\equiv\text{E})$  for a given E is consistent with data for transition-metal–oxo compounds, for which force constants involving a second transition series metal atom are typically smaller than those for the third transition series.<sup>12,13</sup> The value of  $k(\text{W}\equiv\text{N})$  is comparable to previously reported metal–nitrido force constants.<sup>12</sup> However, interpreting the magnitudes of the M≡P and M≡As force constants is less straightforward. Assigning quantitative M≡E bond orders from the force constants, as has been done for metal–oxo compounds,<sup>13</sup> is hindered by the absence of force constants for group 6 phosphine or arsine compounds, which would provide reference values for M–P or M–As single bonds, and of detailed vibrational spectroscopic studies of d<sup>0</sup> metal–phosphinidene and metal–arsinidene compounds. Therefore, we turned to the series HC≡N, HC≡P, and (hypothetical) HC≡As.<sup>14</sup> Interestingly, the relative force constants for W≡E ( $k(\text{W}\equiv\text{N}):k(\text{W}\equiv\text{P}):k(\text{W}\equiv\text{As}) = 1.91:1:0.89$ ) are virtually identical to the relative force constants for HC≡E ( $k(\text{C}\equiv\text{N}):k(\text{C}\equiv\text{P}):k(\text{C}\equiv\text{As}) = 2.06:1:0.82$ ). These data suggest, at least qualitatively, that the differences between the W≡E

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(11) The W≡E bond distances calculated from the W≡E force constants (Table 1) using the Woodruff equations ( $d(\text{W}\equiv\text{N}) = 1.70$  Å,  $d(\text{W}\equiv\text{P}) = 2.20$  Å; ref 10) are in excellent agreement with the observed (or estimated) distances, while those calculated from Badger's rule (eq 7 and Table 1 in ref 9) and from the Herschbach–Laurie relationship (eq 8 and Table 2 in ref 9) are in poorer agreement. The disagreement for the latter two relationships undoubtedly reflects the limitations of the parameters available for heteronuclear diatomic compounds, as illustrated by a recent reparameterization for homonuclear species (Harvey, P. D. *Coord. Chem. Rev.* **1996**, *153*, 175).

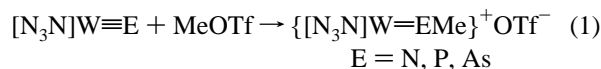
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bonds as a function of E parallel those between C≡E bonds, and provide support for attribution of a bond order of 3 to the M≡E linkages of [N<sub>3</sub>N]M≡E compounds.

An important issue which force constants do not resolve is the nature of the  $\sigma$  component of the M≡E bonds. We noted<sup>1</sup> that <sup>1</sup>J<sub>PW</sub> in [N<sub>3</sub>N]W≡P is surprisingly low (138 Hz) compared to <sup>1</sup>J<sub>PW</sub> in [N<sub>3</sub>N]W(PHPh) (719 Hz) (for example) and consequently proposed that the  $\sigma$  portion of the W≡P bond has a low s character (i.e., that the triple bond is constructed from nearly pure p orbitals, leaving the lone pair in an almost pure s orbital). (This proposal assumes the W–P coupling constants are of the same sign and dominated by the Fermi contact interaction.<sup>15,16</sup>) All [N<sub>3</sub>N]W≡E compounds can be methylated quantitatively (eq 1). In {[N<sub>3</sub>N]W=PMe}(OTf), <sup>1</sup>J<sub>PW</sub> was found



to be 748 Hz, consistent with a significant degree of rehybridization of the  $\sigma$  portion of the W–P bond to approximately sp. In contrast, the value of <sup>1</sup>J<sub>NW</sub> in [N<sub>3</sub>N]W≡<sup>15</sup>N was found to be 48 Hz ( $\delta = 551.2$  ppm), while that in {[N<sub>3</sub>N]W=NMe}OTf was found to be 116 Hz ( $\delta = 145.3$  ppm); these data may indicate a more modest degree of rehybridization of the  $\sigma$  portion of the W≡N bond upon alkylation. The scarcity of theoretical or experimental data in the literature that address such issues prevent any firm conclusions to be drawn at this stage.

In summary, we have found that the triple-bond force constants for [N<sub>3</sub>N]W≡E (E = N, P, or As) complexes scale with those of HC≡E and that the degree of increase in <sup>1</sup>J<sub>PW</sub> upon alkylation is consistent with the  $\sigma$  portion of the W≡P bond having relatively low s character.

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**Supporting Information Available:** A listing of synthetic procedures and NMR spectroscopic data for [N<sub>3</sub>N]M≡E and {[N<sub>3</sub>N]W=EMe}(OTf) complexes (3 pages). See any current masthead page for ordering and Internet access instructions.

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