

Triamidoamine Complexes of Molybdenum and Tungsten That Contain Metal–E (E = N, P, and As) Single, Double, or Triple Bonds

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Abstract: Addition of two or more equivalents of LiPPhH to $[N_3N]MCl$ ($[N_3N]^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}$; M = Mo or W) produced $[N_3N]M\equiv P$ complexes via intermediate $[N_3N]M(PPhH)$ complexes. The reaction between $[N_3N]MoCl$ and 2 equiv of LiAsPhH in the absence of light gave a mixture of $[N_3N]Mo\equiv As$ (~30% yield) and $[N_3N]MoPh$. $[N_3N]Mo\equiv N$ and $[N_3N]W\equiv N$ were both prepared via decomposition of intermediate azide complexes. Tungsten nitrido, phosphido, or arsenido complexes react readily with methyl triflate in toluene to give the cationic methyl imido, methyl phosphinidene, and methyl arsinidene complexes, respectively. Addition of methyl triflate or trimethylsilyl triflate to $[N_3N]Mo\equiv N$ yields the cationic imido complexes $\{[N_3N]Mo=NMe\}OTf$ and $\{[N_3N]Mo=NSiMe_3\}OTf$, respectively, but $\{[N_3N]Mo=PMe\}OTf$ is not stable in solution at room temperature for more than 1–2 h. The reaction between “[Rh(CO)₂(CH₃CN)₂]PF₆” and 2 equiv of $[N_3N]Mo\equiv P$ or $[N_3N]W\equiv P$ gave red, crystalline adducts that contain two $[N_3N]M\equiv P$ “ligands”, e.g., $[Rh\{[N_3N]W\equiv P\}_2(CO)(CH_3CN)]^+$, while red, crystalline $[Rh\{[N_3N]W\equiv As\}_2(CO)(CH_3CN)]PF_6$ could be prepared by an analogous route. $\{[N_3N]Mo=NSiMe_3\}OTf$ could be reduced to “19-electron” $[N_3N]Mo=NSiMe_3$, while addition of MeMgCl to $\{[N_3N]Mo=NSiMe_3\}OTf$ or $\{[N_3N]Mo=NMe\}OTf$ yielded complexes of the type $[N_3N]Mo(NR)(Me)$. The complex in which R = Me was unstable with respect to loss of methane and formation of the iminato complex, $[N_3N]Mo(N=CH_2)$. Both $[N_3N]W(PPhH)$ and $[N_3N]Mo(PPhH)$ ($[N_3N]^{3-} = [(C_6F_5NCH_2CH_2)_3N]^{3-}$) could be prepared readily, but all attempts to prepare $[N_3N]W\equiv P$ failed. X-ray studies of $[N_3N]W\equiv P$, $[N_3N]Mo(PPhH)$, $[N_3N]Mo\equiv As$, $\{[N_3N]W=AsMe\}OTf$, $[Rh\{[N_3N]W\equiv P\}_2(CO)(CH_3CN)]^+$, and $[N_3N]Mo=NSiMe_3$ are presented and discussed.

Introduction

There has been much speculation in the literature concerning monomeric transition metal compounds that contain a multiple metal–phosphorus bond.^{1–7} In the last few years several mononuclear phosphinidene complexes in fact have been characterized crystallographically.^{8–13} Monomeric transition metal complexes that contain a double bond between the metal and the higher pnictogens are much rarer. For example, only one metal arsinidene complex, (silox)₃Ta=AsPh (silox = *t*-Bu₃SiO), has been synthesized and crystallographically character-

ized.¹² Tantalum arsinidene complexes of the type $[N_3N]Ta=AsR$ were believed to be the ultimate products of reactions between $[N_3N]Ta(C_2H_4)$ and arsines such as Me₃SiAsH₂, but these species were not isolated in pure form.¹⁴ Finally, although complexes that are believed to contain a triple bond between antimony and a metal, namely $[(CO)_{n-1}M\equiv Sb]^-$ (M = Cr, Mo, and W), had been detected in the gas phase,¹⁵ and compounds in which a terminal phosphido complex is a ligand had been prepared,⁶ no monomeric transition metal complex that contained a metal–pnictogen bond other than the well-known nitrido complexes¹⁶ had been isolated and characterized.

Transition metal–phosphorus triple bonds became a reality with the synthesis and structural characterization of two related terminal phosphido complexes of Mo and W.^{17,18} In each complex three metal–amido linkages are present. One type, trigonal bipyramidal $[(Me_3SiNCH_2CH_2)_3N]M\equiv P$ (M = Mo or W),¹⁸ contains a trimethylsilyl-substituted triamidoamine ligand ($[N_3N]^{3-}$),¹⁹ while the other, trigonal monopyramidal $[N(t-Bu)(3,5-C_6H_3)_3]Mo\equiv P$, contains monodentate *tert*-butylarylamido ligands and no ligand trans to the phosphido ligand.¹⁷ $[N_3N]M\equiv P$ compounds are especially interesting in view of the stability of

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(1) Binger, P. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Medical Publishers, Inc.: New York, 1990.

(2) Nixon, J. F. *Chem. Rev.* **1988**, *88*, 1327.

(3) Chisholm, M. H.; Folting, K.; Pasterczyk, J. W. *Inorg. Chem.* **1988**, *27*, 3057.

(4) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Hildenbrand, U.; Westerhausen, M. *Phosphorus & Sulfur* **1987**, *30*, 349.

(5) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1104.

(6) Scheer, M.; Schuster, K.; Budzichowski, T. A.; Chisholm, M. H.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1995**, 1671.

(7) Cowley, A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81.

(8) Bohra, P.; Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *Polyhedron* **1989**, *8*, 1884.

(9) Cowley, A. H.; Pellerin, B.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 6734.

(10) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 756.

(11) Hou, Z.; Breen, T. L.; Stephan, D. W. *Organometallics* **1993**, *12*, 3158.

(12) Bonanno, J. B.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1994**, *116*, 11159.

(13) Arney, D. S. J.; Schnabel, R. C.; Scott, B. C.; Burns, C. J. *J. Am. Chem. Soc.* **1996**, *118*, 6780.

(14) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3643.

(15) Arnold, F. P. J.; Ridge, D. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1995**, *117*, 4428.

(16) Nugent, W. A.; Mayer, J. M. *Metal–Ligand Multiple Bonds*; Wiley: New York, 1988.

(17) Laplaza, C. E.; Davis, W. M.; Cummins, C. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2041.

(18) Zanetti, N. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2044.

(19) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483.

Table 1. Bond Distances (Å) and Angles (deg) for $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$, $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$, $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$, and $\{[\text{N}_3\text{N}]\text{W}=\text{AsMe}\}^+$

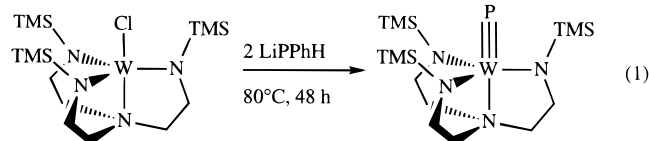
compd	M–N _{eq}	M–N _{ax}	N _{eq} –M–N _{eq}	M–N _{eq} –Si	N _{ax} –M–N–Si ^d	other
$[\text{N}_3\text{N}]\text{W}\equiv\text{P}^a$	1.975(6)	2.34(1)	115.8(1)	125.4(3)	178	2.162(4) (W≡P) 101.9(2) (P–W–N _{eq})
$[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$	1.964(8)	2.33(2)	116.3(2)	127.0(5)	178	2.252(3) (Mo≡As) 101.2(2) (As–Mo–N _{eq})
$\{[\text{N}_3\text{N}]\text{W}=\text{AsMe}\}^+$	1.940(12) ^b	2.218(11)	114.8(5) ^c	125.5(6) ^b	169 ^b	2.2494(14) (W=As) 173.3(6) (W–As–C)
	1.969(11)		116.0(5)	127.8(6)	166	101.0(3)–102.5(3) (As–W–N _{eq})
	1.949(12)		116.8(5)	126.1(7)	169	2.227(3) (Mo–P)
$[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})^a$	1.992(5) ^b	2.251(5)	115.0(2) ^c	127.3(2) ^b	167 ^b	129.7(2) (Mo–P–C) 134(1) (Mo–P–H)
	2.014(5)		124.1(2)	128.7(2)	179	100.3(2)–101.7(2) (P–Mo–N _{eq})
	2.010(5)		110.7(2)	135.6(2)	152	1.771(4) (Mo–N(5)) 172.4(2) (Mo–N(5)–Si) 172.78(12) (N(4)–Mo–N(5))
$[\text{N}_3\text{N}]\text{Mo}=\text{NSiMe}_3$	2.038(3) ^b	2.468(3)	104.89(12) ^c	131.4(2) ^b	135 ^b	
	1.969(3)		124.56(13)	128.2(2)	152	
	1.994(3)		110.48(13)	124.6(2)	163	

^a See ref 18. ^b Measurements concern N(1), then N(2), then N(3). ^c Measurements concern N(1) and N(2), then N(1) and N(3), then N(2) and N(3). ^d Dihedral angles were obtained from a Chem 3D structure.

related complexes that contain metal–carbon triple bonds^{20–22} and the “diagonal” relationship between C and P.⁵ Here we report the full details of the synthesis of complexes of the type $[\text{N}_3\text{N}]\text{M}\equiv\text{E}$ (M = Mo or W) in which E = N, P, or As, along with the imido, phosphinidene, or arsinidene products of electrophilic attack on them, some examples of metal complexes that contain phosphido or arsenido $[\text{N}_3\text{N}]\text{M}\equiv\text{E}$ “ligands”, and some chemistry of amido and phosphido complexes. Portions of this work have appeared in preliminary form.^{18,23}

Results

Preparation of Terminal Nitrido, Phosphido, and Arsenido Complexes. The attempted synthesis of a phenylphosphido complex by treating $[\text{N}_3\text{N}]\text{WCl}$ ²⁰ with 2 equiv of LiPPhH in a mixture of toluene and tetrahydrofuran (4:1) at 80 °C led instead (over a period of 48 h) to $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ (eq 1) as yellow cubes in ~50% yield. The phosphorus resonance in $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$



is found at 1080 ppm in the ³¹P NMR spectrum with ¹J_{PW} = 138 Hz. When 1.3 equiv of LiPPhH and $[\text{N}_3\text{N}]\text{WCl}$ were heated in toluene-*d*₈ at 110 °C over a period of 2 days, then $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ was formed in 88% yield versus an internal standard. $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ also has been prepared by treating $[\text{N}_3\text{N}]\text{WCl}$ with 2 equiv of LiP(SiMe₃)₂.²⁴ In all such reactions, and as has been documented more extensively in the analogous Mo system (see below), it is believed that complexes of the type “[N_3N]W–[P(R)(Li)]” are unobservable intermediates that decompose to give LiR (R = phenyl or SiMe₃²⁴) and $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$.

An X-ray study¹⁸ showed $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ to be a monomeric species in which the W≡P bond length is 2.162(4) Å. (Bond distances and angles are compared in Table 1 for $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$,¹⁸ $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$,¹⁸ and three other crystallographically characterized compounds reported here.) The W–N_{eq}–Si angle (125°) and N_{ax}–W–N–Si dihedral angle (178°) are typical of

(20) Shih, K.-Y.; Totland, K.; Seidel, S. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 12103.

(21) Schrock, R. R.; Shih, K.-Y.; Dobbs, D.; Davis, W. M. *J. Am. Chem. Soc.* **1995**, *117*, 6609.

(22) Murdzek, J. S.; Schrock, R. R. In *Carbyne Complexes*; VCH: New York, 1988.

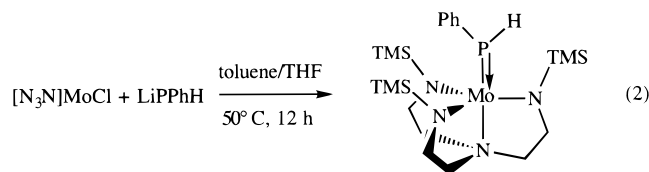
(23) Johnson-Carr, J. A.; Zanetti, N. C.; Schrock, R. R.; Hopkins, M. D. *J. Am. Chem. Soc.* **1996**, *118*, 11305.

(24) Scheer, M.; Müller, J.; Häser, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2492.

$[\text{N}_3\text{N}]\text{M}$ complexes in which there is little steric interaction between the trimethylsilyl groups and the ligand in the trigonal pocket.²⁵ Most other distances and angles are similar to what is found in $[\text{N}_3\text{N}]\text{WCl}$ ²⁴ (W–N_{eq} = 1.985(11) Å and N_{eq}–W–N_{eq} = 117.66(6)°, for example). The exception is the W–N_{ax} distance in $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ (2.34(1) Å) versus the W–N_{ax} distance in $[\text{N}_3\text{N}]\text{WCl}$ (2.182(6) Å). The relatively long W–N_{ax} distance of 2.34(1) Å is consistent with the expected greater trans influence of a triply bound element versus a chloride.

When $[\text{N}_3\text{N}]\text{WCl}$ is treated with only 1 equiv of LiPPhH, then the crude product mixture contained small quantities of what we proposed to be diamagnetic $[\text{N}_3\text{N}]\text{W}(\text{PPhH})$ on the basis of its proton and ³¹P NMR spectra ($\delta\text{P} = 91$ ppm, *J*_{PW} = 719 Hz; $\delta\text{H} = 18.68$ ppm, *J*_{HP} = 300 Hz, *J*_{HW} = 36 Hz). $[\text{N}_3\text{N}]\text{W}(\text{PPhH})$ could not be separated from $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ readily. However, $[\text{N}_3\text{N}]\text{W}(\text{PPhH})$ could be prepared and isolated in ~50% yield by adding PPhH₂ to $[\text{N}_3\text{N}]\text{W}(\text{C}_6\text{H}_5)$ ²⁶ in toluene at room temperature. On the basis of the similarity of the proton and ³¹P NMR spectrum of $[\text{N}_3\text{N}]\text{W}(\text{PPhH})$ to that of crystallographically characterized $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ (see below), we presume that $[\text{N}_3\text{N}]\text{W}(\text{PPhH})$ is structurally analogous to $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$. Its diamagnetism can be ascribed to donation of the phosphorus lone pair to the metal and consequent pairing of the two d electrons in the remaining π orbital. The proton NMR spectrum suggests that $[\text{N}_3\text{N}]\text{W}(\text{PPhH})$ is *C*_{3v} symmetric on the NMR time scale, i.e., the phenylphosphido ligand “rotates” readily with respect to the $[\text{N}_3\text{N}]$ ligand, even at –60 °C.

The reaction between $[\text{N}_3\text{N}]\text{MoCl}$ ^{27,28} and 1 equiv of LiPPhH at 50 °C in a mixture of toluene and THF yields orange, diamagnetic $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ in good yield (eq 2). Like the



tungsten analog, $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ is diamagnetic and has apparent *C*_{3v} symmetry on the NMR time scale. The proton NMR spectrum shows the phosphido proton resonance at 12.16

(25) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9.

(26) Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Dobbs, D. A.; Shih, K.-Y.; Davis, W. M. *Organometallics* In press.

(27) Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Shih, K.-Y.; O'Donoghue, M. B.; Davis, W. M.; Reiff, W. M. *J. Am. Chem. Soc.* In press.

(28) Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804.

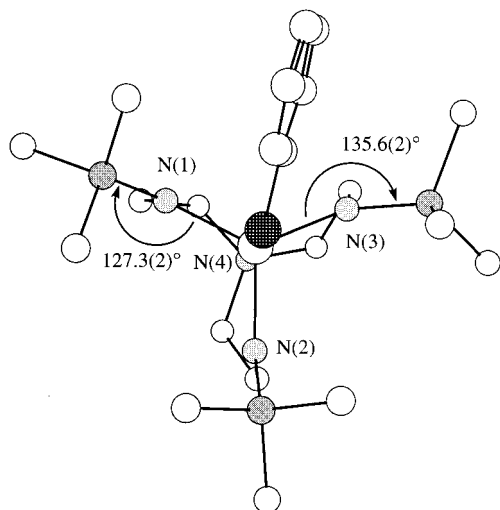


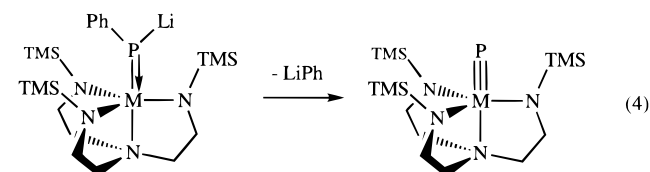
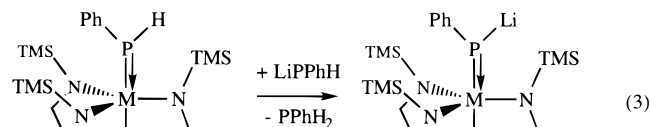
Figure 1. A top view of the structure of $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Mo}(\text{PPhH})$ (P-H proton omitted).

ppm with a coupling to phosphorus of 283 Hz (cf., 18.68 ppm and 300 Hz in $[\text{N}_3\text{N}]\text{W}(\text{PPhH})$). The phosphido phosphorus resonance (142 ppm) is found ~ 50 ppm further downfield from where it is found in $[\text{N}_3\text{N}]\text{W}(\text{PPhH})$ (91 ppm).

An X-ray structural study of $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ (Figure 1) shows that it is a trigonal bipyramidal species that contains an essentially planar phenylphosphido ligand (proton located) with $\text{Mo}=\text{P} = 2.227(3)$ Å, $\text{Mo}=\text{P}-\text{C} = 129.7(2)^\circ$, and $\text{Mo}=\text{P}-\text{H} = 134(1)^\circ$. The phosphido ligand is turned so that the phenyl ring points between N(1) and N(3). Consequently, the N(1)-Mo-N(3) angle is opened slightly (to $124.1(2)^\circ$) compared to the other two $\text{N}_{\text{eq}}-\text{Mo}-\text{N}_{\text{eq}}$ angles. The plane of the phosphido ligand does not quite coincide with the N(4)-Mo-N(2) plane, as shown by the N(2)-Mo-P- C_{ipso} dihedral angle of 168° . Therefore the SiMe_3 group attached to N(3) is tipped furthest away from the phosphido ligand ($\text{Mo}-\text{N}(3)-\text{Si} = 135.6(2)^\circ$ versus $127.3(2)^\circ$ and $128.7(2)^\circ$). The overall result is that two of the $\text{N}_{\text{ax}}-\text{Mo}-\text{N}-\text{Si}$ dihedral angles are significantly less than 180° (167° and 152°). A "twisting" of the trimethylsilyl groups and a consequent decrease in a $\text{N}_{\text{ax}}-\text{Mo}-\text{N}-\text{Si}$ dihedral angle was shown to be consistent with an increase in steric hindrance in analogous molybdenum complexes of the type $[\text{N}_3\text{N}]\text{MoR}$,²⁷ and was postulated to be the first and most facile response to an increase in steric crowding within the trigonal coordination pocket.²⁵ The Mo- N_{ax} distance in $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ is slightly shorter ($2.251(5)$ Å) than the W- N_{ax} distance in $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ ($2.34(1)$ Å), consistent with a larger trans effect for the W-P triple bond than for the Mo-P pseudo double bond. In spite of the preferred orientation of the phenyl ring between N(1) and N(3), and the generally crowded nature of the coordination environment in which the phosphido ligand is located, steric hindrance between the phenyl ring and the TMS groups is not great enough to restrict rotation of the phosphido ligand on the NMR time scale, and the molecule therefore has apparent C_{3v} symmetry.

Addition of 2 equiv of LiPPhH to $[\text{N}_3\text{N}]\text{MoCl}$ in a mixture of toluene and THF, or 1 equiv of LiPPhH to $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$, followed by heating the reaction to 70°C for 12 h, yields yellow, diamagnetic $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$ in good yield. The chemical shift of the terminal phosphido ligand in $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$ was found to be 1346 ppm, approximately 266 ppm further downfield than the phosphorus resonance in $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ (1080 ppm). No $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$ is formed upon heating a solution of $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ in toluene to 120°C for 3 days. We speculate that the phenylphosphido ligand in $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ is deprotonated to

give an unobserved lithiated (or anionic) phenylphosphinidene complex (eq 3), which then decomposes to give the terminal phosphido complex and phenyl lithium (eq 4). The phenyl

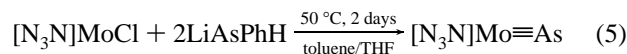


lithium then reacts with PPhH_2 that is generated in the deprotonation reaction (eq 3) to yield benzene and LiPPhH . Consistent with this proposal is the fact that when $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ was heated with 1.0 equiv of LiPh at 110°C in toluene- d_8 for 4 days, $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$ and benzene (90% relative to $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$) were produced. In a similar experiment that employed 0.5 equiv of LiPh at 65°C over a period of 4 days, $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ disappeared in a first-order manner to give benzene and $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$, consistent with LiPh -catalyzed decomposition of $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ to $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$.

The proposed mechanism of forming the terminal phosphido complexes would suggest that the reaction between Li_2PPh and $[\text{N}_3\text{N}]\text{MCl}$ should be a suitable method of preparing $[\text{N}_3\text{N}]\text{M}\equiv\text{P}$. Indeed, $[\text{N}_3\text{N}]\text{WCl}$ reacts with 1 equiv of Li_2PPh to give $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ in $\sim 50\%$ yield, presumably via decomposition of unobserved intermediate " $[\text{N}_3\text{N}]\text{W}(\text{PPhLi})$ " (eq 4). $[\text{N}_3\text{N}]\text{WPh}$ is formed in $\sim 10\%$ yield in this reaction, we presume as a consequence of a competitive, secondary reaction between $[\text{N}_3\text{N}]\text{WCl}$ and LiPh .²⁶ In contrast, the reaction between Li_2PPh and $[\text{N}_3\text{N}]\text{MoCl}$ did not produce $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$ in any significant yield.

The formation of tungsten alkylidyne complexes via α,α -dehydrogenation of alkyl complexes of the type $[\text{N}_3\text{N}]\text{WCH}_2\text{R}^{20}$ and formation of $(\text{silox})_3\text{Ta}=\text{PPh}$ by adding phenylphosphine to $(\text{silox})_3\text{Ta}^{12}$ together suggest that $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ might be the product of the reaction between $[\text{N}_3\text{N}]\text{WCl}$ and LiPH_2 . Indeed, LiPH_2 reacts with $[\text{N}_3\text{N}]\text{WCl}$ in THF over a period of 24 h to give $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ as the only observable product. It is not known whether this type of reaction involves α,α -dehydrogenation of $[\text{N}_3\text{N}]\text{W}(\text{PH}_2)$ or a catalyzed decomposition of $[\text{N}_3\text{N}]\text{W}(\text{PH}_2)$ that proceeds via intermediate $[\text{N}_3\text{N}]\text{W}(\text{PHLi})$. In contrast, the reaction between LiPH_2 and $[\text{N}_3\text{N}]\text{MoCl}$ again did not produce $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$ in any significant yield.

The reaction between $[\text{N}_3\text{N}]\text{MoCl}$ and 2 equiv of LiAsPhH in the absence of light yields orange, diamagnetic $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$ in $\sim 30\%$ yield. Another pentane-soluble, but paramagnetic, product that was produced in approximately the same yield in this reaction proved to be $[\text{N}_3\text{N}]\text{MoPh}$.²⁶ We also have seen no evidence for $[\text{N}_3\text{N}]\text{Mo}(\text{AsPhH})$ as an intermediate in this reaction. An attempt to prepare $[\text{N}_3\text{N}]\text{Mo}(\text{AsPhH})$ or $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$ by adding AsPhH_2 to $[\text{N}_3\text{N}]\text{MoPh}$ in toluene- d_8 in the absence of light yielded $\text{H}_3[\text{N}_3\text{N}]$ as the only recognizable product.



A view of the structure of $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$ is shown in Figure 2 and bond distances and angles are listed in Table 1. The

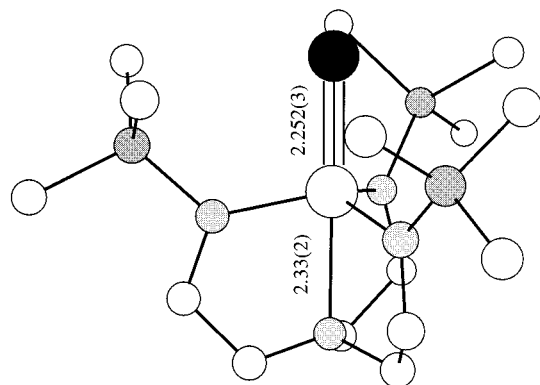


Figure 2. A view of the structure of $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Mo}\equiv\text{As}$.

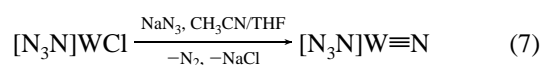
$\text{Mo}\equiv\text{As}$ bond length was found to be 2.25 Å, ~ 0.1 Å longer than the $\text{W}\equiv\text{P}$ bond in $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$, and consistent with the $\text{Mo}-\text{As}$ bond being a triple bond. The bond distance of 2.252(3) Å should be compared with a $\text{W}-\text{As}$ distance of 2.2903(11) Å in recently structurally characterized $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$.²⁴ The values for $\text{M}-\text{N}_{\text{eq}}$, $\text{M}-\text{N}_{\text{ax}}$, and $\text{N}_{\text{eq}}-\text{M}-\text{N}_{\text{eq}}$ are also similar to analogous bond distances and angles in $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$ ²⁴ ($\text{W}-\text{N}_{\text{eq}} = 1.989(4)$ Å, $\text{W}-\text{N}_{\text{ax}} = 2.336(6)$ Å, and $\text{N}_{\text{eq}}-\text{W}-\text{N}_{\text{eq}} = 115.69(8)^\circ$), as one might expect. Other distances and angles are close to what they are in $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ and deserve no further comment. It should be noted that $[\text{N}_3\text{N}]\text{WCl}$,²⁴ $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$,¹⁸ and $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$ ²⁴ all crystallize in the space group $Pa\bar{3}$, so to ensure that bond distances to P or As are accurate, it is crucial that the sample of $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ or $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$ used in an X-ray study not be contaminated with cocrystallized $[\text{N}_3\text{N}]\text{WCl}$.

An attempt to prepare $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$ by adding 2 equiv of LiAsPhH to $[\text{N}_3\text{N}]\text{WCl}$ (2 days in toluene/THF, 22 °C, absence of light) yielded $[\text{N}_3\text{N}]\text{WPh}$ as the only significant product (by NMR); only traces of $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$ were found. However, $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$ can be prepared in good yield by allowing a slight excess of phenylarsine to react with $[\text{N}_3\text{N}]\text{WPh}$ for 48 h at room temperature in the dark (eq 6). Approximately 2 equiv of



benzene are also formed, according to ^1H NMR spectra. The object of this reaction was to form intermediate $[\text{N}_3\text{N}]\text{W}(\text{AsPhH})$ via proton transfer from As to the phenyl ligand in “ $[\text{N}_3\text{N}]\text{WPh}(\text{AsPhH}_2)$ ”. However, we found no evidence that $[\text{N}_3\text{N}]\text{W}(\text{AsPhH})$ is an intermediate in this reaction. $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$ has also been prepared by treating $[\text{N}_3\text{N}]\text{WCl}$ with 2 equiv of $\text{LiAs}(\text{SiMe}_3)_2$, although higher temperatures are required than for synthesis of $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ from $[\text{N}_3\text{N}]\text{WCl}$ and $\text{LiP}(\text{SiMe}_3)_2$, and there was no evidence for formation of intermediate $[\text{N}_3\text{N}]\text{W}[\text{As}(\text{TMS})_2]$.²⁴

The tungsten nitrido complex, $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$, can be synthesized as shown in eq 7, while the analogous molybdenum complex is best prepared from $[\text{N}_3\text{N}]\text{MoCl}$ and Me_3SiN_3 in



toluene at 90 °C over a period of 24 h. Intermediate azide complexes are proposed to form in each case. Decomposition of azide complexes (from sodium azide or trimethylsilyl azide) is a relatively common method of preparing nitrido complexes, and a large number of nitrido complexes are known.¹⁶

Infrared spectra of the $[\text{N}_3\text{N}]\text{M}\equiv\text{E}$ (E = N, P, and As) complexes in the region below 1500 cm^{-1} are relatively

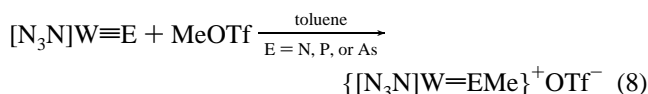
Table 2. Stretching Frequencies (cm^{-1}) for Compounds of the Type $[\text{N}_3\text{N}]\text{M}\equiv\text{E}^a$

$\text{M}\equiv\text{E}$	ν_{ME}	$\text{M}\equiv\text{E}$	ν_{ME}
$\text{W}\equiv\text{N}$	1015 (R), 1012 (IR)	$\text{Mo}\equiv\text{N}$	1001 (IR)
$\text{W}\equiv^{15}\text{N}$	987 (R)		
$\text{W}\equiv\text{P}$	516 (R), 516 (IR)	$\text{Mo}\equiv\text{P}$	521 (R)
$\text{W}\equiv\text{As}$	343 (R)	$\text{Mo}\equiv\text{As}$	374 (R)

^a (R) implies a determination by Raman spectroscopy on a solid sample.²³ (IR) implies a determination by Infrared spectroscopy on a solid sample in Nujol.

complex. However, the Raman spectra are considerably sharper, and the $\text{M}\equiv\text{E}$ stretch could be clearly identified for all compounds except $[\text{N}_3\text{N}]\text{Mo}\equiv\text{N}$, which had not yet been prepared at the time the Raman study was carried out.²³ Once the locations of the $\text{M}\equiv\text{E}$ stretches were known with certainty, it was possible to locate the $\text{W}\equiv\text{N}$ and $\text{W}\equiv\text{P}$ absorptions in the IR spectra (Nujol) at 1012 and 516 cm^{-1} , respectively. An IR spectrum of $[\text{N}_3\text{N}]\text{Mo}\equiv\text{N}$ (Nujol) shows a strong stretch at 1001 cm^{-1} analogous to that found in the spectrum of $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$. Therefore we assume that $\nu_{\text{MoN}} = 1001$ cm^{-1} . Observed stretching frequencies from both Raman and IR studies are listed in Table 2.

Electrophilic Attack on Nitrido, Phosphido, and Arsenido Complexes. Tungsten nitrido, phosphido, or arsenido complexes react readily with methyl triflate in toluene to give the imido, phosphinidene, and arsinidene complexes, respectively, in quantitative yield (eq 8). The phosphorus resonance in



$\{[\text{N}_3\text{N}]\text{W}=\text{P}\text{Me}\}^+$ is found at 339 ppm in the ^{31}P NMR spectrum with $J_{\text{PW}} = 748$ Hz. These values should be compared with 1080 ppm and $J_{\text{PW}} = 138$ Hz in $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$. Changes in the magnitude of coupling to tungsten are more dramatic than what is found in $[\text{N}_3\text{N}]\text{W}\equiv^{15}\text{N}$ and $\{[\text{N}_3\text{N}]\text{W}=\text{NMe}\}^+$. In $[\text{N}_3\text{N}]\text{W}\equiv^{15}\text{N}$ the nitrido ^{15}N resonance is found at 551.2 ppm relative to ammonia with $J_{\text{NW}} = 48$ Hz, while in $\{[\text{N}_3\text{N}]\text{W}=\text{NMe}\}^+$ the ^{15}N resonance is found at 145.3 ppm with $J_{\text{NW}} = 116$ Hz. The increase in J_{PW} from 138 Hz in $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ to 748 Hz in $\{[\text{N}_3\text{N}]\text{W}=\text{P}\text{Me}\}^+$ (a 5.4-fold increase) is consistent with a more significant degree of rehybridization of the σ portion of the $\text{W}\equiv\text{N}$ bond upon alkylation, assuming that the WE coupling constants in any set of $[\text{N}_3\text{N}]\text{W}\equiv\text{E}$ and $\{[\text{N}_3\text{N}]\text{W}=\text{ER}\}^+$ compounds are of the same sign and are dominated by the Fermi contact interaction. On the basis of the small value of J_{WP} alone the σ portion of the $\text{W}-\text{P}$ bond would appear to have largely p character, and the lone pair therefore would reside in an orbital with largely s character.

An X-ray structural study of $\{[\text{N}_3\text{N}]\text{W}=\text{AsMe}\}\text{OTf}$ (Figure 3) showed it to be overall similar to other molecules of this general type (Table 1). The most important features are the essentially linear arsinidene ligand ($\text{W}-\text{As}-\text{C} = 173.3(6)^\circ$) and a $\text{W}=\text{As}$ bond length of 2.2494(14) Å, which is virtually the same as the $\text{Mo}\equiv\text{As}$ bond length in $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$. The $\text{Mo}-\text{N}_{\text{ax}}$ distance (2.218(11) Å) is similar to what it is in $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ (2.251(5) Å) and $[\text{N}_3\text{N}]\text{WCl}$ (2.182(6) Å²⁴), consistent with the relatively poor trans effect of the arsenic atom in the linear arsinidene ligand compared to (especially) phosphorus and arsenic in the terminal phosphido and arsenido complexes, respectively. The linearity of the arsinidene ligand in this species contrasts strongly with the dramatically bent phenyl arsinidene ligand ($107.2(4)^\circ$) and longer $\text{Ta}=\text{As}$ bond length

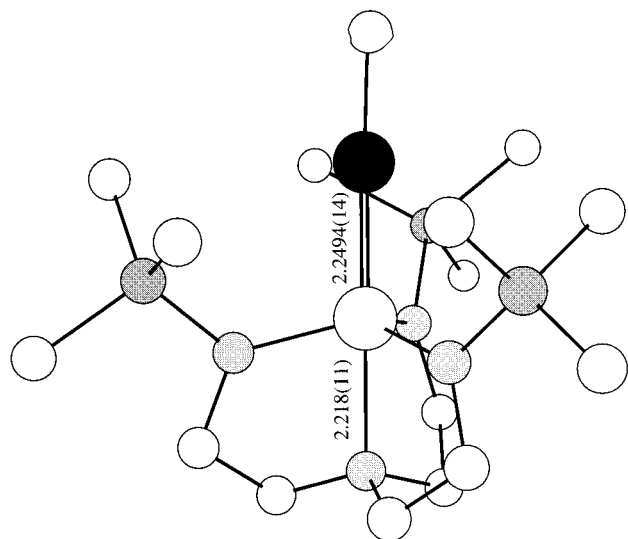


Figure 3. A view of the structure of $\{[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{W}=\text{AsMe}\}^+\text{OTf}^-$ (cation only).

(2.428(2) Å) in $(\text{silox})_3\text{Ta}=\text{AsPh}$,¹² the only other crystallographically characterized arsinidene complex. At this stage it is not known to what extent the linearity of the arsinidene ligand in $\{[\text{N}_3\text{N}]\text{W}=\text{AsMe}\}^+\text{OTf}^-$ is dictated by steric factors. Although the $\text{N}_{\text{eq}}-\text{W}-\text{N}_{\text{eq}}$ angles (166–169°) suggest that there is some “twisting” of the trimethylsilyl groups in response to steric congestion in the trigonal pocket, the arsinidene ligand would appear to be able to bend in a manner analogous to what is observed for the phosphido ligand in $\{[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})\}$. Therefore at this stage we believe the arsinidene to be linear largely for electronic reasons. In that case the “bent” nature of the arsinidene ligand in $(\text{silox})_3\text{Ta}=\text{AsPh}$ might be ascribed to relatively poor $\text{As}\rightarrow\text{Ta}$ π bonding, as a result of competitive $\text{O}\rightarrow\text{Ta}$ π bonding from the silox ligands in a pseudotetrahedral environment. In a pseudotrigonal bipyramidal $[\text{N}_3\text{N}]^{3-}$ complex π bonding to the three equatorial amido nitrogens involves primarily the $d_{x^2-y^2}$ and d_{xy} orbitals, which are virtually independent of the d_{xz} and d_{yz} orbitals that are used for π bonding to an apical ligand.

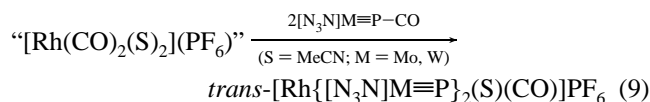
Addition of methyl triflate or trimethylsilyl triflate to $[\text{N}_3\text{N}]\text{Mo}=\text{N}$ yields the cationic imido complexes, $\{[\text{N}_3\text{N}]\text{Mo}=\text{NMe}\}^+\text{OTf}^-$ and $\{[\text{N}_3\text{N}]\text{Mo}=\text{NSiMe}_3\}^+\text{OTf}^-$, respectively, in high yield. Imido complexes are relatively common,¹⁶ and there is nothing unusual about these. However, addition of methyl triflate to $[\text{N}_3\text{N}]\text{Mo}=\text{P}$ is complex when carried out at room temperature. Only when $[\text{N}_3\text{N}]\text{Mo}=\text{P}$ and 1 equiv of methyl triflate are allowed to react slowly in ether at -30 °C over a period of several days can an insoluble orange microcrystalline solid be prepared in ~40% yield. The ^{31}P NMR spectrum shows a phosphorus resonance at 282.7 ppm, which is significantly upfield of the phosphorus resonance in $\{[\text{N}_3\text{N}]\text{W}=\text{PMe}\}^+\text{OTf}^-$ (339 ppm). In $[\text{N}_3\text{N}]\text{M}(\text{PPhH})$ and $[\text{N}_3\text{N}]\text{M}=\text{P}$ complexes the phosphorus resonance in the Mo complex is downfield from its position in the tungsten analog. Nevertheless, the ^{31}P chemical shift is at least of approximately the same magnitude as it is in $\{[\text{N}_3\text{N}]\text{W}=\text{PMe}\}^+\text{OTf}^-$. Since the compound analyzes correctly for C, H, and N, we are relatively confident that $\{[\text{N}_3\text{N}]\text{Mo}=\text{PMe}\}^+\text{OTf}^-$ has been prepared. $\{[\text{N}_3\text{N}]\text{Mo}=\text{PMe}\}^+\text{OTf}^-$ can be recrystallized from a mixture of THF and diethyl ether, but is not stable in solution at room temperature. After 1–2 h, these solutions in dichloromethane or THF darken; ^{31}P and ^1H NMR spectra suggest that $\{[\text{N}_3\text{N}]\text{Mo}=\text{PMe}\}^+\text{OTf}^-$ has largely decomposed within 2 h and the only identifiable product (in ~30% yield) is paramagnetic $[\text{N}_3\text{N}]\text{MoOTf}$.²⁶

An attempt to prepare $\{[\text{N}_3\text{N}]\text{Mo}=\text{AsMe}\}^+\text{OTf}^-$ by a method analogous to that used to prepare $\{[\text{N}_3\text{N}]\text{Mo}=\text{PMe}\}^+\text{OTf}^-$ was even less successful. What we believe is $\{[\text{N}_3\text{N}]\text{Mo}=\text{AsMe}\}^+\text{OTf}^-$ could be observed by ^1H NMR in $\text{THF}-d_8$ at -70 °C. However, this belief is based solely on a methyl resonance at 3.72 ppm, as found for $\{[\text{N}_3\text{N}]\text{Mo}=\text{PMe}\}^+\text{OTf}^-$, and typical $[\text{N}_3\text{N}]^{3-}$ resonances. However, this compound could not be isolated in pure form, and attempts to recrystallize it by ether diffusion into a THF solution at -35 °C resulted in a considerable amount of decomposition and no improvement in purity. The decomposition products could not be identified. Therefore the existence of $\{[\text{N}_3\text{N}]\text{Mo}=\text{AsMe}\}^+\text{OTf}^-$ could not be confirmed by elemental analysis, and $\{[\text{N}_3\text{N}]\text{Mo}=\text{AsMe}\}^+$ therefore must be regarded as the only missing member of the series of $\{[\text{N}_3\text{N}]\text{M}=\text{EMe}\}^+$ (E = N, P, and As) complexes.

At this stage we do not know why all $\{[\text{N}_3\text{N}]\text{W}=\text{EMe}\}^+$ complexes can be prepared, whereas the stabilities of $\{[\text{N}_3\text{N}]\text{Mo}=\text{EMe}\}^+$ complexes decline rapidly in the order E = N > P > As. The most stable compounds appear to be those in which the dative portion of the M–E pseudo triple bond is likely to be the strongest (W > Mo and N > P > As) and E sterically most protected as a consequence of the short M=E bond.

Terminal Phosphido and Arsenido Complexes as Ligands.

The reaction between “[$\text{Rh}(\text{CO})_2(\text{MeCN})_2$] PF_6 ” (which is generated from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and TIPF_6 in acetonitrile) and 2 equiv of $[\text{N}_3\text{N}]\text{Mo}=\text{P}$ or $[\text{N}_3\text{N}]\text{W}=\text{P}$ led to soluble red crystalline complexes in good yield (eq 9). The ^{31}P NMR spectra show



one resonance for the two equivalent phosphorus atoms as a doublet at 791 (M = Mo) or 643 ppm (M = W) with coupling to rhodium of 67 (M = Mo) or 79 Hz (M = W), respectively. The NMR data for the latter should be compared with that for $\text{trans-}\{[\text{N}_3\text{N}]\text{W}=\text{P}\}_2\text{W}(\text{CO})_4$, in which the terminal phosphido resonance is found at 680 ppm and $J_{\text{WP}} = 426$ (P=W) and 151 Hz (P–W).²⁴ IR spectra show absorptions at 2021 (M = Mo) and 2014 cm^{-1} (M = W) for coordinated CO, and a C≡N stretch for acetonitrile (at 2361 cm^{-1} when M = W); no absorptions corresponding to M–P stretching modes could be identified.

An X-ray study of $[\text{Rh}\{[\text{N}_3\text{N}]\text{W}=\text{P}\}_2(\text{CO})(\text{CH}_3\text{CN})]^+$ revealed the structure shown in Figure 4. (See also Table 3.) The core geometry of $[\text{Rh}\{[\text{N}_3\text{N}]\text{W}=\text{P}\}_2(\text{CO})(\text{CH}_3\text{CN})]^+$ is distorted slightly from square planar in terms of the various angles at rhodium, the $\text{trans } [\text{N}_3\text{N}]\text{W}=\text{P}$ ligands are slightly bent so as to produce a “banana-shaped” W–P–Rh–P–W arrangement, and the Rh–P–W angles are less than 180°. A cis arrangement of $[\text{N}_3\text{N}]\text{W}=\text{P}$ ligands would appear to be precluded on steric grounds. The Rh–P distances are what one would expect for a Rh–P distance in a rhodium phosphine complex, while the W–P distances (2.177(5) and 2.173(5) Å) are not lengthened to a statistically significant degree from the W–P distance in $[\text{N}_3\text{N}]\text{W}=\text{P}$ (2.162(4) Å). The observed distortions from a strictly square planar geometry are not likely to be costly energetically, and perhaps are dictated to a significant degree by crystal packing forces. This structure should be compared with that for $\text{trans-}\{[\text{N}_3\text{N}]\text{W}=\text{P}\}_2\text{W}(\text{CO})_4$,²⁴ in which the W≡P bonds are lengthened to 2.202(2) Å, while the dative P–W bond lengths are 2.459(2) and 2.460(2) Å.

Red, crystalline $[\text{Rh}\{[\text{N}_3\text{N}]\text{W}=\text{As}\}_2(\text{CO})(\text{CH}_3\text{CN})]\text{PF}_6$ was prepared by adding $[\text{N}_3\text{N}]\text{W}=\text{As}$ to “[$\text{Rh}(\text{CO})_2(\text{MeCN})_2$] PF_6 ” (generated from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and TIPF_6 in acetonitrile). The

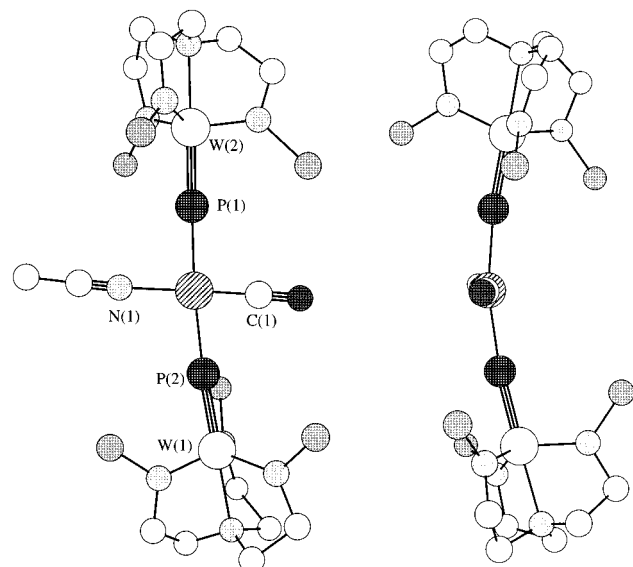


Figure 4. Drawing of the structure of $[\text{Rh}\{[\text{N}_3\text{N}]\text{W}\equiv\text{P}\}_2(\text{CO})(\text{CH}_3\text{CN})]^+$.

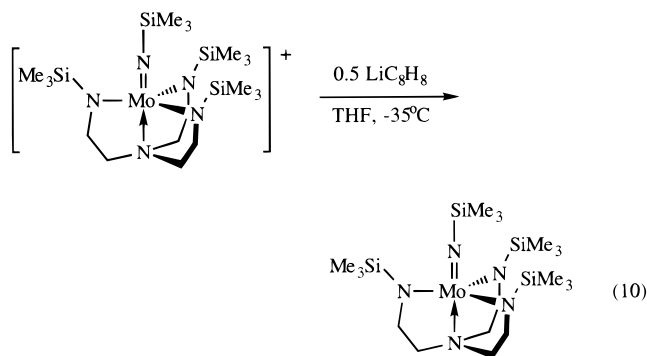
Table 3. Selected Bond Distances (Å) and Angles (deg) in $[\text{Rh}\{[\text{N}_3\text{N}]\text{W}\equiv\text{P}\}_2(\text{CO})(\text{CH}_3\text{CN})]^+$

Distances (Å)					
Rh–C(1)	1.81(3)	Rh–P(1)	2.316(5)	W(2)–P(1)	2.177(5)
Rh–N(2)	2.09(2)	Rh–P(2)	2.305(5)	W(1)–P(2)	2.173(5)
Angles (deg)					
C(1)–Rh–P(2)	86.8(7)	P(2)–Rh–P(1)	166.7(2)		
C(1)–Rh–N(1)	173.8(8)	P(1)–Rh–N(1)	92.4(4)		
C(1)–Rh–P(1)	89.2(7)	W(1)–P(2)–Rh	172.3(3)		
P(2)–Rh–N(1)	93.0(4)	W(2)–P(1)–Rh	173.3(3)		

physical properties, IR data, and NMR data for $[\text{Rh}\{[\text{N}_3\text{N}]\text{W}\equiv\text{As}\}_2(\text{CO})(\text{CH}_3\text{CN})\text{PF}_6$ are analogous to those for $[\text{Rh}\{[\text{N}_3\text{N}]\text{W}\equiv\text{P}\}_2(\text{CO})(\text{CH}_3\text{CN})\text{PF}_6$. Therefore there is no reason to suspect that the structure of $[\text{Rh}\{[\text{N}_3\text{N}]\text{W}\equiv\text{As}\}_2(\text{CO})(\text{CH}_3\text{CN})\text{PF}_6$ is not analogous to that of $[\text{Rh}\{[\text{N}_3\text{N}]\text{W}\equiv\text{P}\}_2(\text{CO})(\text{CH}_3\text{CN})\text{PF}_6$.

Further Reactions of Mo Imido Complexes. In a reaction in which dinitrogen is bound to Mo and reduced in a stepwise manner, a terminal nitrido complex is a possible intermediate.^{29–32} To be in a position to reduce dinitrogen catalytically it would be necessary to remove the nitrido ligand in a well-defined and controlled manner. Therefore we explored some reactions that bear on removing the nitrido ligand.

We have shown that the nitrido ligand in $[\text{N}_3\text{N}]\text{Mo}\equiv\text{N}$ is readily attacked by electrophiles, a process that is relatively common, at least for electrophiles other than a proton.¹⁶ A plausible next step would be reduction by one electron. $\{[\text{N}_3\text{N}]\text{Mo}\equiv\text{NSiMe}_3\}\text{OTf}$ can be reduced cleanly with either $\text{Li}_2\text{C}_8\text{H}_8$ or sodium naphthalenide to a Mo(V) amido complex. No reduction is observed over several days when magnesium is employed as the reducing agent in THF. $[\text{N}_3\text{N}]\text{Mo}\equiv\text{NSiMe}_3$ is a blue paramagnetic compound with a proton NMR spectrum that reveals only three shifted, broad resonances (at room temperature) for the two types of TMS groups and a resonance for one of the two backbone methylene groups. Temperature-dependent magnetic susceptibility (SQUID) measurements



confirm that $[\text{N}_3\text{N}]\text{Mo}\equiv\text{NSiMe}_3$ is a d^1 Curie paramagnet down to 5 K in the solid state with a magnetic moment of $1.64 \mu_B$. Attempts to prepare the analogous $[\text{N}_3\text{N}]\text{Mo}\equiv\text{NMe}$ compound so far have failed. Isolation of the iminato complex, $[\text{N}_3\text{N}]\text{Mo}(\text{N}=\text{CH}_2)$ (see below), would suggest that $[\text{N}_3\text{N}]\text{Mo}\equiv\text{NMe}$ might be susceptible to loss of a hydrogen radical from the imido methyl group at some point during its attempted synthesis.

An X-ray study revealed that $[\text{N}_3\text{N}]\text{Mo}\equiv\text{NSiMe}_3$ is a C_3 -symmetric species that contains a nearly linear imido ligand ($\text{Mo}-\text{N}_{\text{imido}}-\text{Si} = 172.4^\circ$; Figure 5, Table 1). The $\text{Mo}=\text{N}$ bond length ($1.771(4) \text{ \AA}$) is also typical of Mo–nitrogen pseudo triple bonds in amido complexes.¹⁶ The imido TMS group is tipped between N(1) and N(3), which accounts for the larger N(1)–Mo–N(3) angle. The $[\text{N}_3\text{N}]^{3-}$ ligand backbone is distorted to a significant degree in response to the bulk of the TMS group on the imido ligand, as shown by the $\text{N}_{\text{ax}}-\text{Mo}-\text{N}-\text{Si}$ dihedral angles being considerably less than 180° (135° for the N(4)–Mo–N(1)–Si(1) dihedral angle; Table 1). “Tipping” of the TMS groups away from the “upright” position (dihedral angle $\sim 180^\circ$) appears to be the most facile response of the ligand backbone to steric congestion in the trigonal coordination pocket.^{25,27} The Mo–N(4) bond ($2.468(3) \text{ \AA}$) is long compared to other Mo– N_{ax} bonds in the $[\text{N}_3\text{N}]\text{Mo}$ complexes reported here. Therefore it seems possible the “19-electron” $[\text{N}_3\text{N}]\text{Mo}\equiv\text{NSiMe}_3$ has a pseudo triple Mo–N(5) bond and an unpaired electron in an orbital with a significant degree of Mo– N_{ax} σ antibonding character. Alternatively, the imido ligand may be forced into nearly a linear Mo–N(5)–Si arrangement for steric reasons, but the amount of Mo–N(5) dative π bonding is minimal, and either the d_{xz} or the d_{yz} orbital contains the single electron. The long Mo–N(4) bond would seem to suggest the former, but the slight bending of the Mo–N–Si linkage away from 180° also would be consistent with the latter. At this point it is not possible to choose between these two explanations.

A next logical step toward removing a nitrogen-containing product would be to add an electrophile to the imido nitrogen in $[\text{N}_3\text{N}]\text{Mo}\equiv\text{NSiMe}_3$ to form a cationic Mo(V) amido complex. Reactions were attempted with MeOTf , Me_3SiOTf , pyridinium chloride, acetyl chloride, Me_3SiCl , or methyl iodide. All apparently failed. Only oxidation to $[\text{N}_3\text{N}]\text{Mo}\equiv\text{N}$ or $\{[\text{N}_3\text{N}]\text{Mo}\equiv\text{NSiMe}_3\}^+$ was observed, or the $[\text{N}_3\text{N}]^{3-}$ ligand was lost from the metal as $\text{H}_3[\text{N}_3\text{N}]$. Further reduction of $[\text{N}_3\text{N}]\text{Mo}\equiv\text{NSiMe}_3$ also failed. No reaction occurred with sodium naphthalenide or sodium amalgam in THF, while an attempted reduction with sodium sand in THF led only to decomposition. The failure to reduce “19-electron” $[\text{N}_3\text{N}]\text{Mo}\equiv\text{NSiMe}_3$ is not surprising in view of the likely high energy of the orbital into which the electron must be placed.

In view of the existence of $[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2\text{N})_3\text{N}]\text{Mo}(\text{NMe}_2)$,³³ we attempted to prepare $[\text{N}_3\text{N}]\text{Mo}(\text{NMe}_2)$. This

(29) Richards, R. L. *Chem. Br.* **1988**, 24, 133.

(30) Dilworth, J. R.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982.

(31) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, 95, 1115.

(32) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, 78, 589.

(33) Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, 116, 4382.

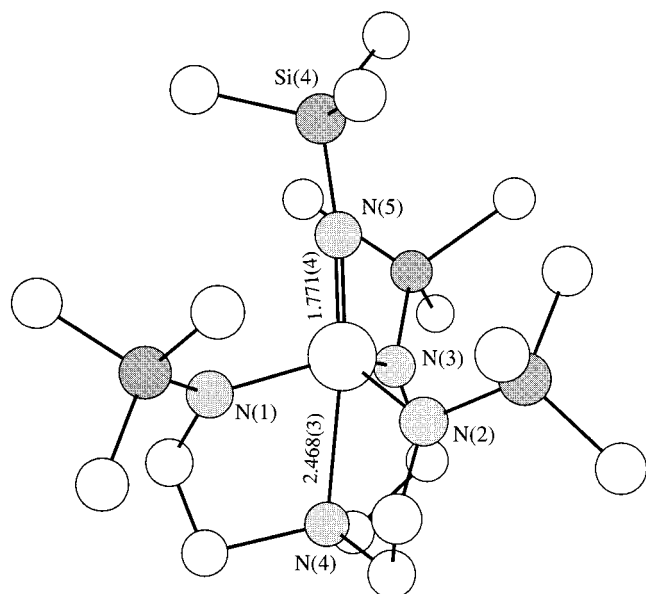


Figure 5. A drawing of the structure of $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Mo}=\text{NSiMe}_3$.

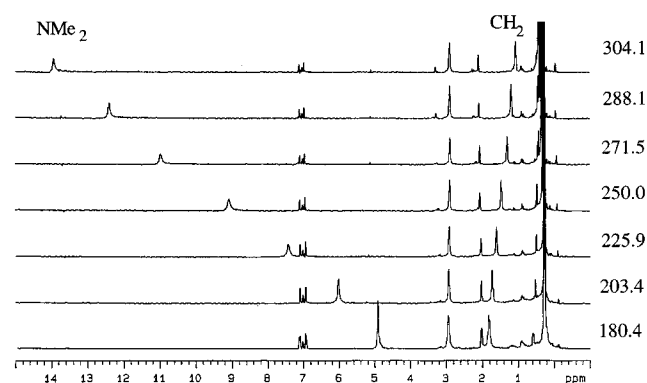
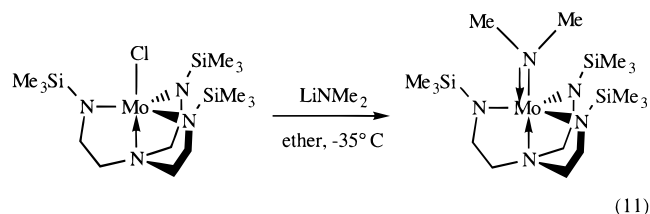


Figure 6. Temperature-dependent proton NMR spectrum of $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Mo}(\text{NMe}_2)$.

complex can be prepared virtually quantitatively (according to proton NMR spectra) as shown in eq 11. $[\text{N}_3\text{N}]\text{Mo}(\text{NMe}_2)$ is



extremely soluble in pentane and usually could be isolated only as a blue-purple oil. It has been crystallized by diffusing acetonitrile into an ether solution. The d^2 dimethylamido complex appears to be diamagnetic at first glance, as one would expect, since the pseudo doubly bound dimethylamido ligand has local C_{2v} symmetry and the metal has local C_{3v} symmetry. Therefore the two d electrons are paired up in a d_{xz} or d_{yz} orbital. (If the axial ligand has cylindrical symmetry then the d_{xz} and d_{yz} orbitals remain degenerate and the complex is high spin.^{25,27}) However, the resonance for the methyl group appears as a broad singlet with unusually large chemical shift in the ^1H NMR spectrum near room temperature (Figure 6), and the chemical shift of this resonance, to a larger extent than any other, depends upon temperature. At 180 K the dimethylamido resonance appears near 5 ppm, while it appears near 14 ppm at 304 K.

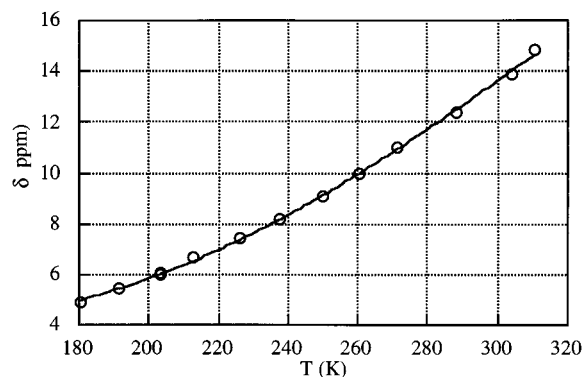


Figure 7. Temperature-dependent shift of the NMe_2 group in $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Mo}(\text{NMe}_2)$ fit to eq 12.

One of the methylene proton resonances also shifts, to a less significant degree, from near 2 ppm at 180 K to closer to 1 ppm at 304 K, but the other methylene resonance (near 3 ppm) does not shift appreciably in this temperature range. To explain the temperature-dependent behavior of the dimethylamido and backbone methylene resonances we propose that the diamagnetic form of $[\text{N}_3\text{N}]\text{Mo}(\text{NMe}_2)$ is in rapid equilibrium with a high spin form and that the dimethylamido resonance is contact shifted by the paramagnetic form. The high spin form is likely to follow Curie–Weiss behavior in the temperature range 180–304 K, as do $[\text{N}_3\text{N}]\text{MoCl}$ and $[\text{N}_3\text{N}]\text{Mo}(\text{alkyl})$ complexes.²⁷ If we assume the rate of interconversion of the high spin and low spin forms is fast at all temperatures here, we can employ the expression shown in eq 12^{34–36} to determine the enthalpy and

$$\delta = \delta_{\text{dia}} + \frac{C}{T(1 + \exp(\frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R}))} \quad (12)$$

entropy difference between the high spin and low spin states. (In eq 12 δ is the observed chemical shift at temperature T , δ_{dia} is the chemical shift of the diamagnetic form, which is assumed to be independent of temperature, and C is a constant. Situations of this general type also have been analyzed with use of a slightly different expression.^{37–44}) The temperature dependence of the chemical shift of the NMe_2 group is shown in Figure 7. A fit to eq 12 yields $\delta_{\text{dia}} = 3.8(4)$ ppm, $\Delta H^\circ = 9.9(1.3)$ kJ mol^{-1} , and $\Delta S^\circ = -40$ J K^{-1} mol^{-1} . The error of ΔS° is estimated to be at least ± 20 J K^{-1} mol^{-1} . A chemical shift of 3.8 ppm is in the expected range for a metal amide complex (cf. ~ 3.9 ppm in $[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2\text{N})_3\text{N}]\text{Mo}(\text{NMe}_2)$ ³³ at 22 °C). A similar treatment of the chemical shift of the upfield backbone methylene resonance yielded $\delta_{\text{dia}} = 1.91(3)$ ppm, $\Delta H^\circ = 10.2(1.4)$ kJ mol^{-1} , and $\Delta S^\circ = -50$ J K^{-1} mol^{-1} , in agreement with the previously obtained values for ΔH° and ΔS° . Therefore

(34) Gütllich, P.; McGarvey, B. R.; Kläui, W. *Inorg. Chem.* **1980**, *19*, 3704.

(35) Kläui, W.; Eberspach, W.; Gütllich, P. *Inorg. Chem.* **1987**, *26*, 3977.

(36) Smith, M. E.; Andersen, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 1119.

(37) LaMar, G. N.; Horrocks, W. D., Jr.; Holm, R. H., Eds. *NMR of Paramagnetic Molecules*; Academic: New York, 1973.

(38) Kriley, C. E.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1994**, *116*, 5225.

(39) Saillant, R.; Wentworth, R. A. D. *Inorg. Chem.* **1969**, *8*, 1226.

(40) Cotton, F. A.; Eglin, J. L.; Hong, B.; James, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 4915.

(41) Cotton, F. A.; Chen, H. C.; Daniels, L. M.; Feng, X. *J. Am. Chem. Soc.* **1992**, *114*, 89980.

(42) Fettinger, J. C.; Keogh, D. W.; Kraatz, H.-B.; Poli, R. *Organometallics* **1996**, *15*, 5489.

(43) Campbell, G. C.; Reibenspies, J. H.; Haw, J. F. *Inorg. Chem.* **1991**, *30*, 171.

(44) Boersma, A. D.; Phillipi, M. A.; Goff, H. M. *J. Magn. Reson.* **1984**, *57*, 197.

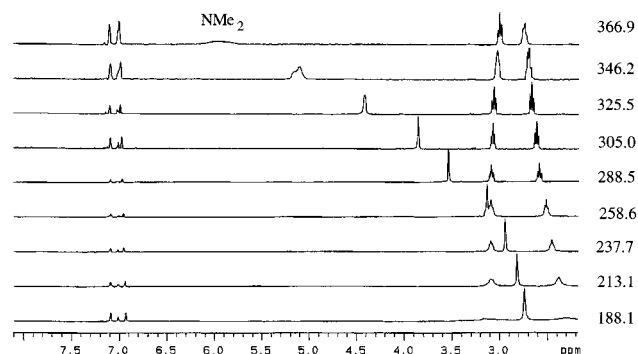


Figure 8. Temperature-dependent proton NMR spectrum of $[(C_6F_5NCH_2CH_2N)_3N]Mo(NMe_2)$.

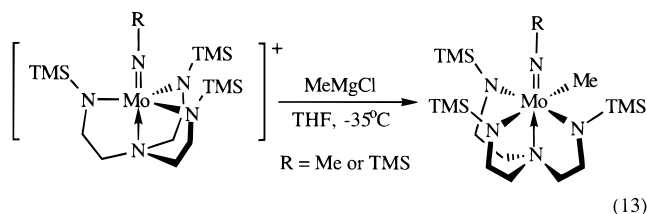
we feel relatively confident that the high spin form of $[N_3N]Mo(NMe_2)$ is only ~ 2.5 kcal mol $^{-1}$ higher in energy than the low spin form. At room temperature the equilibrium constant is of the order of 10^{-3} , i.e., only $\sim 0.1\%$ of $[N_3N]Mo(NMe_2)$ is in the high spin form. We can only speculate as to the nature of the high spin form. An interesting possibility is that the amido ligand in the high spin form is not planar, i.e., the electron count in metal-based orbitals is 16 and an electron pair is present in an orbital that is largely centered on nitrogen.

The temperature dependence of the proton NMR spectrum of $[N_3N]Mo(NMe_2)$ contrasts with the apparently “normal” spectrum observed for $[(C_6F_5NCH_2CH_2N)_3N]Mo(NMe_2)$.³³ In fact, the spectrum of $[(C_6F_5NCH_2CH_2N)_3N]Mo(NMe_2)$ is also temperature dependent (Figure 8), with the dimethylamido resonance shifting from 2.75 ppm at 188 K to 6 ppm at 357 K (with concomitant broadening almost into the baseline). If the chemical shift of the dimethylamido ligand is plotted versus temperature and fit to eq 12 we obtain $\delta_{dia} = 2.74(1)$ ppm, $\Delta H^\circ = 18.2(0.7)$ kJ mol $^{-1}$, and $\Delta S^\circ = -20$ J K $^{-1}$ mol $^{-1}$. The much higher value for ΔH° is consistent with the much less dramatic shift for the dimethylamido resonance from ~ 2.8 to 6 ppm as the temperature is raised from 188 to 367 K, and with a complex in which the π bond is stronger than it is in $[N_3N]Mo(NMe_2)$ as a consequence of the electron-withdrawing ability of the C_6F_5 substituents relative to TMS substituents.

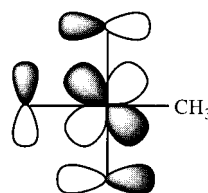
The chemical shifts for the phosphido protons in $[N_3N]Mo(PPhH)$ (12.16 ppm) and $[N_3N]W(PPhH)$ (18.68 ppm) led us to question as to whether these too depend dramatically upon temperature. However, variable-temperature proton NMR spectra of $[N_3N]Mo(PPhH)$ between 22 and 80 °C show only small, “normal” shifts for the phosphido proton. We conclude that the high spin form of $[N_3N]Mo(PPhH)$ is so high in energy that it cannot be accessed to any significant extent in this temperature range. Since the precise nature of the high spin form is not known, we cannot provide any quantifiable explanation as to why the difference in energy of the high spin (HS) and low spin (LS) forms of $[N_3N]Mo(PPhH)$ is so much greater than the high and low spin forms of $[N_3N]Mo(NMe_2)$. However, in the complexes examined so far, one could correlate the LS/HS gap with the degree of π bonding in the LS complex, i.e., π bonding of the phosphido ligand in $[N_3N]Mo(PPhH)$ most efficiently “locks” the complex in the relatively low energy, low spin state.

The failure to attack $[N_3N]Mo=N(SiMe_3)$ with electrophiles led us to attempt to treat $\{[N_3N]Mo=NR\}^+$ complexes with carbon nucleophiles. For example, the reaction between $\{[N_3N]Mo=NMe\}^+$ and MeMgCl might yield known $[N_3N]Mo(NMe_2)$. However, both $\{[N_3N]Mo=NR\}^+$ complexes (R = Me and SiMe $_3$) react with MeMgCl to yield dark purple diamagnetic crystalline products in virtually quantitative yield that analyze as $[N_3N]Mo(NR)(Me)$ species. Since NMR spectra

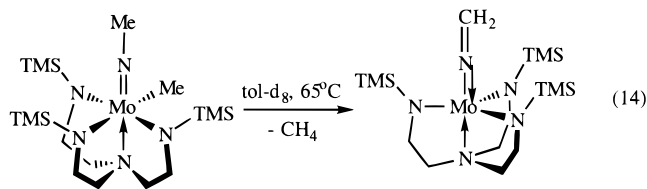
of these species suggest that they have mirror symmetry, we propose that the methyl group has attacked the metal to give a Mo(VI) species, as shown in eq 13. (The results of an X-ray



study of $[N_3N]Mo(NTMS)(Me)$ were of sufficiently high quality to confirm the pseudooctahedral core and the Mo-CH $_3$ linkage, but the structure could not be refined to an acceptable level.) The Mo(CH $_3$) resonance appears at 0.43 ppm in $[N_3N]Mo(NTMS)(Me)$ and 0.19 ppm in $[N_3N]Mo(NMe)(Me)$ in proton NMR spectra, and 20.7 and 18.8 ppm, respectively, in carbon NMR spectra. $[N_3N]Mo(NMe)(CD_3)$ has the same spectrum as $[N_3N]Mo(NMe)(Me)$ except the resonance at 0.19 ppm is absent. The relatively small chemical shift of the added methyl group in the proton NMR spectrum is consistent with its being bound to the metal, not to a nitrogen atom. If we assume that the imido ligand is bound to the metal through a pseudo triple bond, then only a single additional π bond can be formed if an 18-electron count in metal-ligand bonding orbitals is to be maintained. A suitable π bonding orbital of this general type would be the combination in the MoN $_3$ C plane shown below.



$[N_3N]Mo(NTMS)(Me)$ is thermally quite stable. After heating a solution of $[N_3N]Mo(NTMS)(Me)$ to 100 °C for 3 days, it decomposes to yield $[N_3N]Mo=N$ as the major product. $[N_3N]Mo(NMe)(Me)$ is much less thermally stable than $[N_3N]Mo(NTMS)(Me)$, decomposing in solution slowly even at room temperature to give methane and what we propose to be the diamagnetic iminato complex, $[N_3N]Mo(N=CH_2)$ (eq 14). After 48 h at 65 °C $[N_3N]Mo(N=CH_2)$ is formed in



quantitative yield, according to NMR spectra. However, its high solubility limits its isolated yield to 34% on a small scale (~ 100 mg). The methylene group of the iminato ligand appears as a singlet at 5.19 ppm.⁴⁵

Attempts to Prepare $[C_6F_5NCH_2CH_2N]_3N^3-$ ($[N_3NF]^{3-}$) Complexes. The next most common type of triamidoamine ligand is the $[C_6F_5NCH_2CH_2N]_3N^3-$ ($[N_3NF]^{3-}$) ligand.²⁵ Therefore we became interested in whether we could prepare $[N_3NF]M=$ P complexes by the same techniques used to prepare $[N_3N]M=$ P complexes.

(45) For other examples of iminato complexes see: Shapley, P. A.; Shusta, J. M.; Hunt, J. L. *Organometallics* **1996**, *15*, 1622, and references therein.

Lithium phenylphosphide reacts readily with $[\text{N}_3\text{N}_F]\text{WCl}^{33}$ in toluene to give brown, crystalline, diamagnetic $[\text{N}_3\text{N}_F]\text{W}(\text{PPhH})$ in high yield. The phosphido proton resonance was located at 17.50 ppm in the proton NMR spectrum ($J_{\text{HP}} = 295$ Hz, $J_{\text{HW}} = 22$ Hz) and the phosphorus resonance at 118.1 ppm ($J_{\text{PW}} = 742$ Hz). Brown, crystalline $[\text{N}_3\text{N}_F]\text{Mo}(\text{PPhH})$ was synthesized by the same method ($\delta_{\text{HP}} = 11.20$ ppm; $J_{\text{HP}} = 281$ Hz; $\delta_{\text{P}} = 189.6$ ppm). These data are analogous to those found for $[\text{N}_3\text{N}]\text{W}(\text{PPhH})$ and $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$. Many attempts were made to convert $[\text{N}_3\text{N}_F]\text{W}(\text{PPhH})$ into $[\text{N}_3\text{N}_F]\text{W}\equiv\text{P}$ employing various lithium reagents (LiPPhH , LiBu , LiMe , and LiPh) under a variety of conditions, but in all cases either no reaction occurred or no products could be identified. Chemical oxidation ($[\text{Cp}_2\text{Fe}]\text{OTf}$) followed by addition of triethylamine also did not yield a clean product. Attempts to cleave the phosphorus–phenyl linkage photochemically or with lithium metal also were unsuccessful, as was the reaction between $[\text{N}_3\text{N}_F]\text{WCl}$ and Li_2PPh . We conclude that if $[\text{N}_3\text{N}_F]\text{W}\equiv\text{P}$ is formed in some of these reactions it is unstable under the reaction conditions. More likely $[\text{N}_3\text{N}_F]\text{W}\equiv\text{P}$ simply is not formed as readily as $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$. The electron withdrawing nature of the C_6F_5 rings renders the metal more electron poor and therefore less susceptible to oxidation to the 6+ oxidation state. The C_6F_5 rings might also be subject to electron transfer from or nucleophilic attack by a lithium reagent. Other results also suggest that $[\text{N}_3\text{N}_F]^{3-}$ complexes are more difficult to oxidize than $[\text{N}_3\text{N}]^{3-}$ analogs. For example, $[\text{N}_3\text{N}_F]\text{W}(\text{CH}_2\text{-SiMe}_3)$ loses hydrogen relatively slowly while the reaction between $[\text{N}_3\text{N}]\text{WCl}$ and $\text{LiCH}_2\text{SiMe}_3$ yields $[\text{N}_3\text{N}]\text{W}\equiv\text{CSiMe}_3$ rapidly,⁴⁶ presumably via intermediate $[\text{N}_3\text{N}]\text{W}(\text{CH}_2\text{SiMe}_3)$, as has been observed for other $[\text{N}_3\text{N}]\text{W}(\text{CH}_2\text{R})$ complexes.²⁰ Since $[\text{N}_3\text{N}_F]\text{M}$ complexes are also less sterically crowded in the trigonal pocket than are $[\text{N}_3\text{N}]\text{M}$ complexes,²⁵ there also would be less steric pressure on phosphorus substituents to be lost to give $[\text{N}_3\text{N}_F]\text{M}\equiv\text{P}$ species. Of course, none of these results constitutes evidence that $[\text{N}_3\text{N}_F]\text{M}\equiv\text{P}$ species are not stable, only that they cannot be made by the methods employed so far. It should be noted that $[\text{N}_3\text{N}_F]\text{M}\equiv\text{N}$ ($\text{M} = \text{Mo}$ or W) complexes have been prepared by treating $[\text{N}_3\text{N}_F]\text{MCl}$ complexes with sodium azide.³³

Discussion

It is perhaps not surprising that Mo and W terminal phosphido and arsenido complexes can be prepared when three amido ligands are present as supporting ligands, since 18-electron complexes of this general type appear to form strong $\text{M}\equiv\text{E}$ bonds ($\text{E} = \text{CR}$ or N , for example).²⁵ Although no thermodynamic data are yet available, some evidence for strong $\text{M}\equiv\text{E}$ bonds consists of the homolytic cleavage of dinitrogen by $\text{Mo}[\text{N}(t\text{-Bu})(\text{aryl})]_3$ complexes,^{47,48} and the spontaneous loss of molecular hydrogen from $[\text{N}_3\text{N}]\text{W}(\text{CH}_2\text{R})$ complexes²⁰ (and $[\text{N}_3\text{N}]\text{Mo}(\text{CH}_2\text{CMe}_3)$ ²⁷), to give $[\text{N}_3\text{N}]\text{M}\equiv\text{CR}$ complexes. It is also almost certainly important that $\text{Mo}[\text{N}(t\text{-Bu})(\text{aryl})]_3$ and $[\text{N}_3\text{N}]\text{M}$ complexes are sterically protected against bimetallic reactions by the trigonal arrangement of amido ligand substituents surrounding the terminal phosphido or arsenido ligand. The simplest consequence of a bimetallic reaction would be binding of the phosphido ligand to another metal center to form a polymer. Although $(t\text{-BuO})_3\text{W}\equiv\text{P}$ has been observed to function as a ligand,⁶ it seems plausible that free $(t\text{-BuO})_3\text{W}\equiv\text{P}$

would have a polymeric structure analogous to that of $[(t\text{-BuO})_3\text{W}\equiv\text{N}]_x$.⁴⁹

The mechanism of formation of terminal phosphido and arsenido complexes from substituted phosphides or arsenides remains relatively obscure. Observations concerning the formation of terminal phosphido complexes are consistent with formation and decomposition of intermediate “lithiophosphido” complexes, $\text{M}[\text{P}(\text{R})(\text{Li})]$ (where $\text{R} = \text{Ph}$ or SiMe_3 ²⁴). In the case of terminal arsenido complexes, however, there is no evidence that $\text{M}(\text{IV})$ arsenido complexes are in fact intermediates. The most straightforward formation of a terminal phosphido complex is the reaction between $\text{Mo}[\text{N}(t\text{-Bu})(\text{aryl})]_3$ and P_4 ,¹⁷ although there are important questions that remain to be answered even in that circumstance. The synthesis of other types of triamidoamine or other triamido/donor Mo and W complexes should help answer many of these questions, as the only two types of $[(\text{RNCH}_2\text{CH}_2)_3\text{N}]\text{M}$ complexes for which general syntheses have been reported are where $\text{R} = \text{SiMe}_3$ or C_6F_5 .²⁵ A molybdenum nitrido complex in which $\text{R} = \text{Me}$ has been reported,⁵⁰ but no direct entry into $[(\text{MeNCH}_2\text{CH}_2)_3\text{N}]\text{M}$ complexes has yet appeared.

There are now several complexes known, in addition to those reported here, that contain terminal phosphido complexes as ligands. $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{M}\equiv\text{P}$ complexes would appear to have some potential as “ancillary” phosphorus ligands, i.e., alternatives to phosphine ligands, should they become more readily available, since even a casual inspection suggests that the cone angle of a $[\text{N}_3\text{N}]\text{M}\equiv\text{P}$ “ligand” is well over 180° . The electronic characteristics of a $[\text{N}_3\text{N}]\text{M}\equiv\text{P}$ “ligand” also could prove to be beneficial toward chemistry at the metal center to which phosphorus is bound, although exactly what that benefit might be is not predictable at this stage.

Some of the chemistry reported here provides a glimpse into the possibility of employing a $[\text{N}_3\text{N}]\text{M}$ unit as a relatively inert, nonlabile “platform” for carrying out chemistry at E in $[\text{N}_3\text{N}]\text{M}\equiv\text{E}$ complexes. At this stage we are most interested in the possibility of removing a nitrido ligand, for example as an amine, and forming triamidoamine complexes that could be employed for binding and reducing dinitrogen.⁵¹ The development of triamido donor ligands that are more stable to a variety of reaction conditions we believe also will be a key to the ultimate success of employing a $[\text{N}_3\text{N}]\text{M}$ unit as an inert “platform”, and work toward these goals is currently under way.

Experimental Section

General Procedures. All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox, using standard Schlenk techniques, or on a high-vacuum line ($<10^{-4}$ Torr). Pentane was washed with $\text{HNO}_3/\text{H}_2\text{SO}_4$ (5/95 v/v), sodium bicarbonate, and H_2O , stored over CaCl_2 , and then distilled from sodium benzophenone under nitrogen. Regent grade ether, tetrahydrofuran, and benzene were distilled from sodium benzophenone under nitrogen. Toluene was distilled from molten sodium. Methylene chloride was distilled from CaH_2 . All solvents were stored in the drybox over activated 4 Å molecular sieves. Deuterated solvents were freeze–pump–thaw degassed and vacuum transferred from an appropriate drying agent, or sparged with argon and stored over sieves. NMR spectra are recorded in C_6D_6 unless noted otherwise. ^1H and ^{13}C data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protonated solvent peak. ^{19}F NMR are listed in parts per million downfield of CFCl_3 as an external standard. ^{15}N NMR chemical shifts are quoted versus ammonia and ^{31}P NMR chemical shifts versus

(46) Seidel, S. W. Unpublished observations.

(47) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861.

(48) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623.

(49) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1986**, *22*, 2903.

(50) Plass, W.; Verkade, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 2275.

(51) O'Donoghue, M. B.; Zanetti, N. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1997**, *119*, 2753.

H_3PO_4 . Coupling constants are given in hertz, but routine couplings are not listed. Numerical values of integrals of proton NMR resonances usually are not listed, unless some clarification is required, and should be assumed to be consistent with the proposed assignment. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer in our own laboratory.

All organic compounds were received from commercial suppliers and were used as received. $[\text{N}_3\text{N}]\text{MoCl}_2$,²⁷ $[\text{N}_3\text{N}]\text{WCl}_2$,²⁶ $[\text{N}_3\text{N}_F]\text{MoCl}_2$,³³ $[\text{N}_3\text{N}_F]\text{WCl}_2$,³³ and LiPH_2 ⁵² were prepared according to published procedures. $[\text{N}_3\text{N}]\text{MoPh}$ and $[\text{N}_3\text{N}]\text{WPh}$ were prepared by adding LiPh to $[\text{N}_3\text{N}]\text{MCl}$ in diethyl ether.²⁶

$[\text{N}_3\text{N}]\text{Mo}\equiv\text{N}$. $[\text{N}_3\text{N}]\text{MoCl}$ (106 mg, 0.22 mmol) was dissolved in 10 mL of toluene and placed in a bomb. TMSN_3 (120 μL , 0.90 mmol) was added by syringe and the bomb was sealed. The solution was heated at 90 °C for 24 h during which time the color of the reaction mixture changed to brown/yellow. The solvent was removed and the residue was extracted into pentane and filtered. The filtrate was reduced in volume and cooled to -30 °C to give the product as a yellow crystalline compound; yield 89 mg (88%): ^1H NMR δ 3.23 (t, CH_2), 2.14 (t, CH_2), 0.56 (s, SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 52.2 (CH_2), 51.6 (CH_2), 3.1 (SiMe_3); IR (Nujol) cm^{-1} 1001 (ν_{MoN}). Anal. Calcd for $\text{C}_{15}\text{H}_{39}\text{N}_5\text{Si}_3\text{Mo}$: C, 38.36; H, 8.37; N, 14.91. Found: C, 37.99; H, 8.17; N, 14.65.

$[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$. $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$ was prepared as described in an earlier publication.¹⁸

$[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$. LiAsPhH (295 mg, 1.84 mmol) was added to a solution of 431 mg (0.88 mmol) of $[\text{N}_3\text{N}]\text{MoCl}$ in a mixture of toluene and THF (30 mL/3 mL). The clear orange solution was stirred at 50 °C for 40 h. The solvents were removed, and the resulting brown oil was extracted twice with 60 mL of pentane. Evaporation of the solvent yielded an orange powder that was recrystallized from cold ether; yield 140 mg (30 %) of orange cubes: ^1H NMR 3.39 (t, CH_2), 1.66 (t, CH_2), 0.79 (s, TMS); $^{13}\text{C}\{^1\text{H}\}$ NMR 54.57 (s, CH_2), 51.85 (s, CH_2), 5.59 (s, TMS). Anal. Calcd for $\text{C}_{15}\text{H}_{39}\text{N}_4\text{AsSi}_3\text{Mo}$: C, 33.95; H, 7.41; N, 10.56. Found: C, 34.05; H, 7.60; N, 10.32.

$[\text{N}_3\text{N}]\text{W}\equiv\text{N}$. A suspension of $[\text{N}_3\text{N}]\text{WCl}$ (136 mg, 0.23 mmol) and NaN_3 (38 mg, 0.58 mmol) in a mixture of acetonitrile (10 mL) and tetrahydrofuran (10 mL) was stirred for 2 days at room temperature. The color changed from orange to nearly colorless. The solvent was removed in vacuo, and the residue was taken up in pentane (100 mL). Insoluble salts were removed by filtration, and the solvent was evaporated in vacuo. The white residue was recrystallized from ether at -40 °C; yield 93 mg (71%) of white needles: ^1H NMR δ 3.37 (t, CH_2), 2.00 (t, CH_2), 0.59 (s, TMS); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 51.59 (s, CH_2), 50.71 (s, CH_2), 3.12 (s, TMS). Anal. Calcd for $\text{C}_{15}\text{H}_{39}\text{N}_5\text{Si}_3\text{W}$: C, 32.31; H, 7.05; N, 12.56. Found: C, 32.68; H, 6.82; N, 12.28.

A 1:1 mixture of $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$ and $[\text{N}_3\text{N}]\text{W}\equiv^{15}\text{N}$ was prepared in an analogous fashion with $\text{Na}^{15}\text{NN}_2$: ^{15}N NMR (toluene- d_8 , versus NH_3) 551.2 ($J_{\text{NW}} = 48$ Hz).

$[\text{N}_3\text{N}]\text{W}\equiv\text{P}$. $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ was prepared as described in an earlier publication.¹⁸ It also could be prepared under similar conditions and in similar yields employing Li_2PPh or LiPH_2 .

$[\text{N}_3\text{N}]\text{W}\equiv\text{As}$. An orange solution of $[\text{N}_3\text{N}]\text{WPh}$ (50 mg, 0.81 mmol) and 50 mg (3.2 mmol) of phenylarsine in 10 mL of toluene were stirred for 48 h at room temperature in the dark. The solvent was removed in vacuo, and the brown solid was extracted with 40 mL of pentane. The pentane extract was filtered, and the pentane was removed in vacuo to give a yellow solid that was recrystallized from cold diethyl ether to yield 30 mg (61%) of yellow crystals: ^1H NMR (toluene- d_8) δ 3.55 (t, CH_2), 1.61 (t, CH_2), 0.75 (s, TMS); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 54.84 (CH_2), 52.11 (CH_2), 6.46 (TMS). Anal. Calcd for $\text{C}_{15}\text{H}_{39}\text{N}_4\text{AsSi}_3\text{W}$: C, 29.13; H, 6.36; N, 9.06. Found: C, 29.00; H, 6.58; N, 8.99.

$[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$. A mixture of $[\text{N}_3\text{N}]\text{MoCl}$ (135 mg, 0.27 mmol) and LiPPhH (38 mg, 0.33 mmol) in a mixture of toluene (15 mL) and tetrahydrofuran (5 mL) was heated for 12 h at 50 °C. The solvent was removed and the residue was taken up in pentane (50 mL). The extract was filtered and the pentane removed from the filtrate in vacuo. The orange residue was recrystallized from ether by cooling a solution to -40 °C; yield 109 mg (70%): ^1H NMR δ 12.16 (d, $J_{\text{HP}} = 283$, PH),

7.76 (m, Ar), 7.22 (t, Ar), 7.03 (m, Ar), 3.38 (t, CH_2), 2.35 (t, CH_2), 0.28 (s, TMS); $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8) δ 133.13 (d, C_{ipso}), 128.33, 128.25, 127.71, 55.86 (s, CH_2), 54.82 (s, CH_2), 4.15 (s, SiMe_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_8) δ 142.03. Anal. Calcd for $\text{C}_{21}\text{H}_{45}\text{N}_4\text{P}\text{Si}_3\text{Mo}$: C, 44.66; H, 8.03; N, 9.92. Found: C, 44.57; H, 8.05; N, 9.90.

$[\text{N}_3\text{N}]\text{W}(\text{PPhH})$. Phenylphosphine (40 mg) was added to a solution of 40 mg of $[\text{N}_3\text{N}]\text{WPh}$ in 1 mL of toluene. The orange solution was stirred for 48 h at room temperature. The solvent was removed in vacuo, and the solid was extracted with pentane. The solvent was reduced to 1 mL and stored at -40 °C overnight to yield 20 mg of orange crystalline product: ^1H NMR 18.68 (d, $J_{\text{HP}} = 300$; $J_{\text{HW}} = 36$, PPhH), 3.37 (t, CH_2), 2.21 (t, CH_2), 0.33 (s, TMS); ^{31}P NMR δ 91 (s, $J_{\text{PW}} = 719$).

$\{[\text{N}_3\text{N}]\text{Mo}\equiv\text{NMe}\}\text{OTf}$. $[\text{N}_3\text{N}]\text{Mo}\equiv\text{N}$ (104 mg, 0.22 mmol) was dissolved in 3 mL of toluene, and MeOTf (30 μL , 0.27 mmol) was added by syringe. The reaction mixture immediately deepened in color and a yellow solid precipitated. After 1 h the solvent was removed in vacuo and the resulting solid was dissolved in the minimum volume of THF. The solution was cooled to -30 °C to give the product as yellow needles; yield 129 mg (93%): ^1H NMR (CD_2Cl_2) 4.45 (s, NCH_3), 4.00 (t, CH_2), 3.24 (t, CH_2), 0.30 (s, SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) 57.0 (NCH_3), 56.2 (CH_2), 54.5 (CH_2), 3.2 (TMS). Anal. Calcd for $\text{C}_{17}\text{H}_{42}\text{N}_5\text{Si}_3\text{F}_3\text{SO}_3\text{Mo}$: C, 32.22; H, 6.68; N, 11.05. Found: C, 32.07; H, 6.61; N, 11.17.

$\{[\text{N}_3\text{N}]\text{Mo}\equiv\text{NSiMe}_3\}\text{OTf}$. $[\text{N}_3\text{N}]\text{Mo}\equiv\text{N}$ (75 mg, 0.16 mmol) was dissolved in 3 mL of toluene and TMSOTf (40 μL , 0.21 mmol) was added by syringe. The reaction mixture immediately deepened in color and a yellow solid precipitated. After 2 h the solvent was removed in vacuo and the resulting solid was dissolved in the minimum volume of THF. The solution was cooled to -30 °C to give the product as yellow needles; yield 92 mg (83%): ^1H NMR (CD_2Cl_2) 3.85 (t, CH_2), 3.11 (t, CH_2), 0.58 (s, 9, SiMe_3), 0.33 (s, 27, SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 58.2 (CH_2), 57.1 (CH_2), 3.9 (SiMe_3), 2.4 (SiMe_3). Anal. Calcd for $\text{C}_{19}\text{H}_{48}\text{N}_5\text{Si}_4\text{F}_3\text{SO}_3\text{Mo}$: C, 32.98; H, 6.99; N, 10.12. Found: C, 32.84; H, 6.47; N, 9.58.

$\{[\text{N}_3\text{N}]\text{Mo}\equiv\text{PMe}\}\text{OTf}$. Methyl triflate (35 μL , 51 mg, 0.31 mmol) was added at -35 °C to a solution of 142 mg (0.29 mmol) of $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$ in 12 mL of ether. This cold solution was stored at -35 °C for 5 days, during which time orange-red crystals grew at the wall of the vial. The solvent was decanted and the crystals washed with cold ether. $\{[\text{N}_3\text{N}]\text{Mo}\equiv\text{PMe}\}\text{OTf}$ can be recrystallized from THF by diffusion of ether into the THF solution at -35 °C; yield 104 mg (55%): ^1H NMR (THF- d_6 , -40 °C) δ 4.13 (t, CH_2), 3.72 (d, $J_{\text{PH}} = 26$, PCH_3), 3.39 (t, CH_2), 0.36 (s, SiMe_3); ^{31}P -NMR (THF- d_6 , -40 °C) δ 282.7. Anal. Calcd for $\text{MoSi}_3\text{N}_4\text{PF}_3\text{SO}_3\text{C}_7\text{H}_{17}$: C, 31.38; H, 6.51; N, 8.61. Found: C, 31.13; H, 6.69; N, 8.27.

$\{[\text{N}_3\text{N}]\text{Mo}\equiv\text{PMe}\}\text{OTf}$ decomposes slowly in solution at 22 °C.

$\{[\text{N}_3\text{N}]\text{Mo}\equiv\text{AsMe}\}\text{OTf}$ (proposed). Methyl triflate (35 μL , 33 mg, 0.20 mmol) was added at -35 °C to a solution of 98 mg (0.18 mmol) of $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$ in 12 mL of ether. This cold solution was stored at -35 °C for 6 days, during which time red crystals grew on the wall of the vial. The solution was decanted, and the crystals were washed with cold ether. The compound is relatively unstable in solution or the solid state: ^1H NMR (THF- d_6 , -70 °C) δ 4.13 (br, 6, CH_2), 3.72 (s, 3, AsCH_3), 3.36 (br, 6, CH_2), 0.36 (s, 27, SiMe_3). No pure compound could be isolated and in any case appeared to be too unstable for elemental analysis.

Reaction of $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$ with MeOTf To Yield $[\text{N}_3\text{N}]\text{Mo}(\text{OSO}_2\text{CF}_3)$. To a solution of 30 mg (0.05 mmol) of $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$ in 2 mL of toluene was added 14 μL of methyl triflate. The color changed from orange to deep red. The solution was filtered and upon evaporation red crystals of $[\text{N}_3\text{N}]\text{Mo}(\text{OTf})$ appeared; yield 33 mg (97%): ^1H NMR δ 11.0 (s, TMS), -42 (br s), -60 (br s).²⁶

$[\text{N}_3\text{N}]\text{W}\equiv\text{NMe}\}\text{OTf}$. Methyl triflate (24 μL , 0.2 mmol) was added to a solution of 100 mg (0.18 mmol) of $[\text{N}_3\text{N}]\text{W}\equiv\text{N}$ in 3 mL of diethyl ether. A white precipitate appeared immediately. After the suspension was stirred for 2 h the white residue was filtered off and recrystallized from a mixture of tetrahydrofuran and pentane; yield 102 mg (79%) of white crystals: ^1H NMR (CDCl_3) δ 4.54 (s, NCH_3), 4.18 (t, CH_2), 3.36 (t, CH_2), 0.28 (s, TMS); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 54.46 (s, CH_2), 53.34 (s, CH_2), 52.53 (s, NCH_3), 2.99 (s, TMS). Anal. Calcd for

(52) Baudler, M.; Glinka, K. *Inorg. Synth.* **1990**, 27, 228.

(53) Rosenberger, C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1997**, 36, 123.

$C_{17}H_{42}N_5F_3O_3SSi_3W$: C, 28.29; H, 5.87; N, 9.70. Found: C, 28.24; H, 6.08; N, 9.51.

^{15}N -labeled (50%) $\{[N_3N]W=^{15}NMe\}OTf$ was prepared in an analogous fashion: ^{15}N NMR (toluene- d_8) δ 145.3 ppm ($J_{NW} = 116$ Hz).

$\{[N_3N]W=PMe\}OTf$. A yellow suspension appeared upon addition of methyl triflate (8.7 μ L, 0.08 mmol) to a solution of 40 mg (0.07 mmol) of $[N_3N]W=P$ in toluene. After 1 h the solvent was evaporated and the yellow residue was recrystallized from a mixture of tetrahydrofuran and pentane; yield 50 mg (97%) of yellow needles: 1H NMR δ 3.87 (t, CH_2), 3.18 (t, CH_2), 2.57 (d, $^2J_{HP} = 25$, PMe), 0.2 (s, TMS); ^{31}P NMR δ 338.6 (s, $J_{PW} = 748$); ^{13}C NMR (CD_2Cl_2) δ 55.59 (d, $^3J_{CP} = 7.4$, CH_2), 54.91 (s, CH_2), 37.82 (d, $J_{CP} = 33.5$, PCH_3), 5.16 (s, TMS). Anal. Calcd for $C_{17}H_{42}N_5F_3O_3PSSi_3W$: C, 27.64; H, 5.73; N, 7.58. Found: C, 27.79; H, 5.81; N, 7.57.

$\{[N_3N]W=AsMe\}OTf$. Methyl triflate (8.0 μ L, 0.07 mmol) was added to a solution of $[N_3N]W=As$ (41 mg, 0.07 mmol) in toluene. After 1 h the yellow product was isolated as described for $\{[N_3N]W=PMe\}OTf$; yield 50 mg (97%) of yellow clusters: 1H NMR δ 3.95 (t, CH_2), 3.25 (t, CH_2), 2.73 (s, $AsMe$), 0.23 (s, TMS); ^{13}C NMR ($CDCl_3$) δ 54.82 (s, CH_2), 54.50 (s, CH_2), 43.29 (s, $AsCH_3$), 5.42 (s, TMS). Anal. Calcd for $C_{17}H_{42}N_5F_3O_3SSi_3W$: C, 26.09; H, 5.41; N, 7.16. Found: C, 26.38; H, 5.37; N, 7.28.

trans- $[Rh\{[N_3N]Mo=P\}_2(CO)(CH_3CN)]PF_6$. To a solution of 20 mg (0.05 mmol) of $[RhCl(CO)_2]_2$ was added 38 mg (0.11 mmol) of $TIPF_6$ in 2 mL of acetonitrile. The mixture was stirred for 2 h during which time a white precipitate was formed. The suspension was filtered through Celite. A solution of 0.1 g (0.21 mmol) of $[N_3N]Mo=P$ in 2 mL of CH_2Cl_2 was added to the yellow filtrate. The solution turned deep red immediately and after 1 h was filtered again through Celite. The solvent was removed from the filtrate in vacuo and the red residue was recrystallized at -40 °C from a mixture of CH_2Cl_2 and diethyl ether; yield 100 mg (75%) of red needles: 1H NMR (CD_2Cl_2) δ 3.34 (t, CH_2), 2.73 (t, CH_2), 2.23 (s, CH_3CN), 0.44 (s, TMS); ^{31}P NMR (CD_2Cl_2) δ 791.1 ppm (d, $J_{PRh} = 67$ Hz); IR (Nujol) cm^{-1} 2021 (ν_{CO}). Anal. Calcd for $C_{33}H_{81}N_9F_6OP_3RhSi_6Mo_2$: C, 30.72; H, 6.33; N, 9.77. Found: C, 30.38; H, 6.33; N, 9.38.

trans- $[Rh\{[N_3N]W=P\}_2(CO)(CH_3CN)]PF_6$. This compound was synthesized in an analogous fashion as above using 13.5 mg (0.035 mmol) of $[RhCl(CO)_2]_2$, 27 mg (0.077 mmol) of $TIPF_6$, and 80 mg (0.14 mmol) of $[N_3N]W=P$; yield 75 mg (73%): 1H NMR (CD_2Cl_2) δ 4.05 (t, CH_2), 2.75 (t, CH_2), 2.26 (s, CH_3CN), 0.47 (s, TMS); ^{31}P NMR (CD_2Cl_2) δ 642.57 (d, $J_{PRh} = 79$); IR (Nujol) cm^{-1} 2014 (ν_{CO}), 2361 (ν_{CN}). Anal. Calcd for $C_{33}H_{81}N_9F_6OP_3RhSi_6W_2$: C, 27.04; H, 5.57; N, 8.60. Found: C, 26.98; H, 5.22; N, 8.21.

trans- $[Rh\{[N_3N]W=As\}_2(CO)(CH_3CN)]PF_6$. This compound was synthesized in an analogous fashion as above by using 7.9 mg (0.02 mmol) of $[RhCl(CO)_2]_2$, 14.1 mg (0.04 mmol) of $Tl(PF_6)_3$, and 50 mg (0.08 mmol) of $[N_3N]W=As$; yield 50 mg (80%): 1H NMR (CD_2Cl_2) δ 4.1 (t, CH_2), 3.75 (t, CH_2), 2.27 (s, CH_3CN), 0.5 (s, TMS); IR (Nujol) cm^{-1} 2001 (ν_{CO}), 2360 (ν_{CN}).

$[N_3N]Mo(NSiMe_3)Me$. A sample of $\{[N_3N]Mo=NSiMe_3\}[CF_3SO_3]$ (151 mg, 0.218 mmol) was dissolved in 5 mL of THF. The solution was cooled to -35 °C and $MeMgCl$ (72 μ L, 0.23 mmol) was added. The color changed to deep purple. The mixture was stirred for 30 min and allowed to warm to room temperature. The solvent was removed in vacuo, and the mixture was extracted with pentane. The extract was filtered through a glasswool filter, and the solvent was removed to yield 109 mg of dark purple product (90% yield). This essentially pure sample was recrystallized from a minimal amount of pentane; yield 0.18 g (45%): 1H NMR δ 3.63 (ddd, 2, CH_2), 3.47 (m, 2, CH_2), 3.34 (t, 2, CH_2), 2.66 (dt, 2, CH_2), 2.33 (t, 2, CH_2), 2.23 (ddd, 2, CH_2), 0.46 (s, 9, $SiMe_3$), 0.45 (s, 3, $MoCH_3$), 0.38 (s, 18, $SiMe_3$), 0.32 (s, 9, $SiMe_3$); ^{13}C NMR δ 64.3 (CH_2), 62.6 (CH_2), 59.5 (CH_2), 56.7 (CH_2), 20.7 ($MoCH_3$), 3.1 ($SiMe_3$), 3.2 ($SiMe_3$), 2.8 ($SiMe_3$). Anal. Calcd for $MoSi_4N_5C_{19}H_{51}$: C, 40.90; H, 9.21; N, 12.55. Found: C, 41.28; H, 9.37; N, 12.68.

$[N_3N]Mo(NMe)Me$. This compound was prepared in a manner similar to that used to prepare $[N_3N]Mo(NSiMe_3)Me$ from $\{[N_3N]Mo(NMe)\}[CF_3SO_3]$ (142 mg, 0.224 mmol) and 75 μ L of a 3.2 M solution of $MeMgCl$. The essentially pure product was obtained quantitatively (110 mg), but could be crystallized from a minimal

amount of pentane: 1H NMR δ 3.61 (s, 3, NCH_3), 3.54 (m, 4, CH_2), 3.36 (t, 2, CH_2), 2.82 (dt, 2, CH_2), 2.47 (t, 2, CH_2), 2.25 (ddd, 2, CH_2), 0.29 (s, 18, $SiMe_3$), 0.23 (s, 9, $SiMe_3$), 0.19 (s, 3, $MoCH_3$); ^{13}C NMR δ 65.1 (CH_2), 63.3 (CH_2), 58.5 (CH_2), 55.3 (CH_2), 52.4 (NCH_3), 18.8 ($MoCH_3$), 3.8 ($SiMe_3$), 2.4 ($SiMe_3$). Anal. Calcd for $MoSi_3N_5C_{17}H_{45}$: C, 40.86; H, 9.08; N, 14.01. Found: C, 40.85; H, 8.67; N, 14.18.

$[N_3N]Mo(N=CH_2)$. $[N_3N]Mo(NMe)Me$ (91 mg, 0.182 mmol) was dissolved in 1 mL of C_6D_6 , and the solution was heated in a closed NMR tube to 65 °C for 40–48 h. The solution turned from purple to deep red during this time. The solvent was removed in vacuo to give 85 mg (95%) of essentially pure product that can be recrystallized from a minimal amount of pentane. The yield of recrystallized product (30 mg, 34%) is limited by the high solubility of the compound in pentane: 1H NMR δ 5.19 (s, 2, NCH_2), 3.29 (t, 6, CH_2), 2.22 (t, 6, CH_2), 0.47 (s, 27, $SiMe_3$); ^{13}C NMR δ 122.8 (NCH_2), 54.7 (CH_2), 53.29 (CH_2), 3.8 ($SiMe_3$). Anal. Calcd for $MoSi_3N_5C_{16}H_{44}$: C, 39.72; H, 8.54; N, 14.48. Found: C, 39.37; H, 8.85; N, 14.01.

$[N_3N]Mo=NSiMe_3$. A sample of $\{[N_3N]Mo(NSiMe_3)\}OTf$ (203 mg, 0.293 mmol) was dissolved in 8 mL of THF, and the solution was cooled to -35 °C. A freshly prepared solution of $Li_2C_8H_8$ in ether (0.183 M, 1.6 mL) was added in one portion. The solution turned deep blue. The mixture was stirred for 10 min and allowed to reach room temperature. The solvent was removed in vacuo, and the residue was extracted with 10 mL of pentane. The extract was filtered through a glass wool filter and concentrated to 1 mL. The product crystallized upon storing this solution at -35 °C; yield 125 mg (79%): 1H NMR δ 5.6 (br, $SiMe_3$), 1.15 (br, $SiMe_3$), -4.5 (br, CH_2). Anal. Calcd for $MoSi_4N_5C_{18}H_{48}$: C, 39.82; H, 8.91; N, 12.90. Found: C, 40.11; H, 9.39; N, 12.79.

$[N_3N]Mo(NMe_2)$. A sample of $[N_3N]MoCl$ (600 mg, 1.22 mmol) was dissolved in 30 mL of ether, and the solution was cooled to -35 °C. $LiNMe_2$ (66 mg, 1.3 mmol) was added to this cold solution, and the mixture was allowed to reach room temperature while being stirred over a period of a total of 3 h. The solvent was removed from the dark purple solution in vacuo and the residue was extracted with 5 mL of pentane. The extract was filtered through a glasswool filter, and the pentane was removed from the filtrate in vacuo to give a blue-purple oil (478 mg, 78%). The product was obtained as fine needles from ether by diffusion of acetonitrile into the solution in a closed, two vial, system: 1H NMR (toluene- d_8 , 30 °C) δ 13.91 (s, 6, NMe_2), 2.88 (t, 6, CH_2), 1.05 (t, 6, CH_2), 0.41 (s, 27, $SiMe_3$). Anal. Calcd for $MoSi_3N_5C_{17}H_{45}$: C, 40.86; H, 9.08; N, 14.01. Found: C, 40.54; H, 9.22; N, 13.66.

$[N_3N]W(PPhH)$. To a stirred slurry of $[N_3N]WCl$ (500 mg, 0.581 mmol) in 30 mL of toluene was added solid $LiPPhH$ (67 mg, 0.58 mmol) followed by 20 drops of THF. Addition of THF caused the reaction to become homogeneous. After 30 min, a second portion of $LiPPhH$ (20 mg, 0.17 mmol) was added. The reaction was stirred for another 30 min, at which point ^{19}F NMR showed it was complete. The solution was filtered through Celite and the volatiles removed in vacuo. The brown solid was recrystallized from CH_2Cl_2 layered with pentane at -40 °C, and 469 mg (86%) brown crystals were isolated in three crops: 1H NMR δ 17.5 (dd, $J_{PH} = 295$ Hz, $^2J_{WH} = 22$, 1, $PPhH$), 6.97 (t, 4, phenyl), 6.82 (m, 1, phenyl), 3.23 (t, 6, CH_2), 2.35 (t, 6, CH_2); ^{19}F NMR δ -150.4 (s, 6, F_{ortho}), -164.0 (t, 3, F_{para}), -165.1 (s, 6, F_{meta}); ^{31}P NMR δ 118.1 (2, $J_{PW} = 742$, $PPhH$). Anal. Calcd for $C_{30}H_{18}N_4F_{15}PW$: C, 38.57; H, 1.94; N, 6.00. Found: C, 38.57; H, 2.11; N, 5.55.

$[N_3N]Mo(PPhH)$. Solid $LiPPhH$ (45 mg, 0.39 mmol) was added to a stirred slurry of $[N_3N]MoCl$ (300 mg, 0.388 mmol) in 20 mL of toluene. Ten drops of THF was then added, which caused the mixture to become homogeneous. After 1 h, more $LiPPhH$ (14 mg, 0.12 mmol) was added and the mixture was stirred for 3 h. An ^{19}F NMR spectrum showed the reaction to be complete. The reaction was filtered through Celite, and the solvent was removed in vacuo. The brown residue was recrystallized from CH_2Cl_2 layered with pentane at -40 °C. The product was obtained as a brown microcrystalline solid, 263 mg in two crops (80%): 1H NMR δ 11.2 (d, $J_{PH} = 281$, $MoPPhH$), 6.99 (m, Ph), 6.87 (m, Ph), 3.29 (t, CH_2), 2.44 (t, CH_2); ^{19}F NMR δ -150.1 (d, 6, F_{ortho}), -164.5 (t, 3, F_{para}), -165.3 (t, 6, F_{meta}); ^{31}P NMR δ 189.6 (d). Anal. Calcd for $C_{30}H_{18}N_4F_{15}PMo$: C, 42.57; H, 2.14; N, 6.62. Found: C, 42.57; H, 2.32; N, 6.37.

X-ray Structure of $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$. The structure was solved at 188 K with use of a Siemens SMART/CCD diffractometer. (A typical procedure can be found elsewhere.⁵³) Empirical formula $\text{C}_{17}\text{H}_{42}\text{AsF}_3\text{N}_4\text{O}_5\text{SSi}_3\text{W}$, FW = 782.63, space group $P2_12_12_1$, $a = 11.647(3)$ Å, $b = 14.061(4)$ Å, $c = 18.876(6)$ Å, $V = 3091.3(14)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.682$ Mg/m³. Full details can be found in the Supporting Information.

X-ray Structure of $\{[\text{N}_3\text{N}]\text{W}=\text{AsMe}\}\text{OTf}$. The structure was solved by direct methods at 188 K with use of an Enraf-Nonius CAD-4 diffractometer. (A typical procedure can be found elsewhere.⁵⁴) Empirical formula $\text{C}_{15}\text{H}_{39}\text{N}_4\text{Si}_3\text{AsMo}$, FW = 530.62, space group $Pa\bar{3}$, $a = 17.197(2)$ Å, $V = 5085.4(4)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.386$ Mg/m³. Full details can be found in the Supporting Information.

X-ray Structure of *trans*- $[\text{Rh}\{[\text{N}_3\text{N}]\text{W}\equiv\text{P}\}_2(\text{CO})(\text{CH}_3\text{CN})]\text{PF}_6$. The structure was solved at 293 K with use of a Siemens SMART/CCD diffractometer. Empirical formula $\text{C}_{33}\text{H}_{66}\text{F}_6\text{N}_9\text{OP}_3\text{RhSi}_6\text{W}_2$, FW = 1450.98, space group $P2_1/n$, $a = 17.2988(12)$ Å, $b = 16.7599(11)$ Å, $c = 19.7912(13)$ Å, $\beta = 99.8960(10)^\circ$, $V = 5652.6(7)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.705$ Mg/m³. Full details can be found in the Supporting Information.

X-ray Structure of $[\text{N}_3\text{N}]\text{Mo}=\text{NSiMe}_3$. The structure was solved at 293 K with use of a Siemens SMART/CCD diffractometer. Empirical formula $\text{C}_{18}\text{H}_{48}\text{N}_5\text{Si}_4\text{Mo}$, FW = 542.91, space group $P2_1$, a

$= 10.8639(4)$ Å, $b = 11.9376(5)$ Å, $c = 11.3007(5)$ Å, $\beta = 90.0910(10)^\circ$, $V = 1465.57(10)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.230$ Mg/m³. Full details can be found in the Supporting Information.

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Supporting Information Available: A detailed description of X-ray data collection, structure solution, and refinement, labeled ORTEP diagrams, tables of fractional coordinates, anisotropic thermal parameters, and selected bond distances and angles for $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$, $\{[\text{N}_3\text{N}]\text{W}=\text{AsMe}\}^+$, *trans*- $[\text{Rh}\{[\text{N}_3\text{N}]\text{W}\equiv\text{P}\}_2(\text{CO})(\text{NCCCH}_3)]\text{PF}_6$, and $[\text{N}_3\text{N}]\text{Mo}(\text{NSiMe}_3)$ (34 pages). See any current masthead page for ordering and Internet access instructions. Supporting information for the structural studies of $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ and $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ can be found in an earlier publication.¹⁸

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