

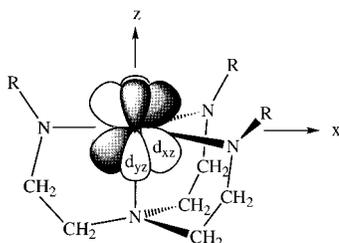
Transition Metal Complexes That Contain a Triamidoamine Ligand

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Triamidoamine ligands $[(RNCH_2CH_2)_3N]^{3-}$ in which R is a bulky substituent, can bind to a variety of transition metals (or main group elements¹) in oxidation states 3+ or higher. They usually bind to a transition metal in a tetradentate manner, thereby creating a sterically protected, 3-fold-symmetric "pocket" in which only three orbitals are available to bond to additional ligands in that pocket, two π orbitals (approximately d_{xz} and d_{yz}) and a σ orbital (approximately d_z). This frontier orbital picture



contrasts sharply with that for the ubiquitous bent metallocene in which all three orbitals (two with A_1 symmetry and one with B_2 symmetry in the C_{2v} point group) lie in the plane passing between the two Cp rings.² The fact that the two frontier π orbitals are strictly degenerate in a C_3 symmetric triamidoamine complex creates a favorable environment for forming a metal–ligand triple bond. The syntheses of $(Me_3SiNHCH_2CH_2)_3N^{3-}$ and its pentane-soluble trilitium salt,⁴ straightforwardly and on a large scale from inexpensive tris(2-aminoethyl)amine (tren), made the rapid development of transition metal triamidoamine chemistry possible. White, crystalline $(C_6F_5-NHCH_2CH_2)_3N$ is another substituted tren that can be prepared in excellent yield by nucleophilic attack on hexafluorobenzene.⁵ In this Account I discuss the highlights of the transition metal chemistry of compounds containing these two triamidoamine ligands that has

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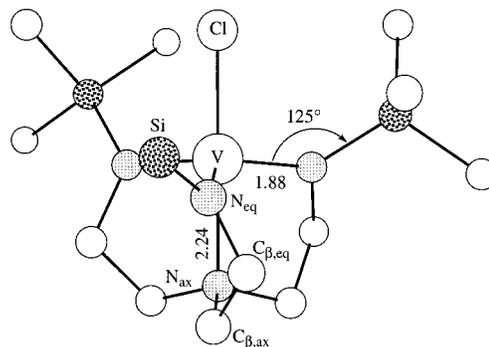


FIGURE 1. A drawing of the structure of $[(Me_3SiNCH_2CH_2)_3N]VCl$ with the methyl groups omitted on one silicon.

developed in the last several years. Complexes that contain a $[(RNCH_2CH_2)_3N]^{3-}$ ligand should be compared with those that contain three $[N(SiMe_3)_2]^-$ ligands that were developed some years ago,^{6–14} recently prepared trigonal planar complexes that contain three $[N(t-Bu)(aryl)]^-$ ligands,^{15–17} and complexes that contain tridentate triamido ligands that enforce a tetrahedral coordination geometry.^{18–20} The tetradentate triamidoamine ligands described here are closely related to neutral tren ligands, or more distantly to other trigonally symmetric neutral or monoanionic ligands (e.g., tripyrazolylborates,^{21,22} $(Ph_2PCH_2CH_2)_3N$,²³ etc.) that have been employed for decades in chemistry of (usually later) transition metals.

Silyl-Substituted tren Complexes

Vanadium and titanium complexes of the type $[N_3N]MCl$ ($[N_3N]^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}$) were synthesized by adding $Li_3[N_3N]$ to MCl_4L_2 ($M = Ti$, $L = THF$; $M = V$, $L_2 = DME$).⁴ The molecular structure of $[N_3N]VCl$ (Figure 1) is typical of pseudo-trigonal-bipyramidal complexes that contain the $[N_3N]^{3-}$ ligand. The vanadium atom is

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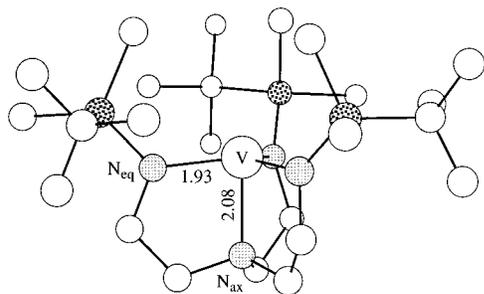


FIGURE 2. A drawing of the structure of $[(t\text{-BuMe}_2\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{V}$.

displaced from the plane of the three amide nitrogen atoms by 0.310 Å in the direction of the chloride ligand. The $\text{V}-\text{N}_{\text{ax}}$ distance (2.24 Å) is consistent with it being a somewhat long dative bond while the $\text{V}-\text{N}_{\text{eq}}$ distances (average 1.88 Å) are consistent with some multiple bond character. Only two metal- N_{eq} π bonds are possible in C_{3v} symmetry since one linear combination of the three “in-plane” 2p orbitals on the three equatorial nitrogen atoms (A_2 in C_{3v} symmetry) is a ligand-centered nonbonding orbital. Therefore, $[\text{N}_3\text{N}]^{3-}$ can be viewed as contributing a maximum of 12 electrons to the metal in a C_3 -symmetric species. In $[\text{N}_3\text{N}]\text{VCl}$ each VN_2C_2 ring can be said to have an envelope shape in which $\text{C}_{\beta,\text{eq}}$ serves as the “flap” of the envelope. Consequently, the $\text{Si}-\text{N}_{\text{eq}}-\text{C}_{\beta,\text{eq}}$ plane is “tipped” out of the $\text{N}_{\text{ax}}-\text{M}-\text{N}_{\text{eq}}$ plane by $\sim 35^\circ$, thereby altering the “depth” of the apical pocket and the nature of the π bonding between the metal and equatorial nitrogens. The $\text{M}-\text{N}_{\text{eq}}-\text{Si}$ angles in this and a variety of other structures are usually $\sim 125^\circ$ regardless of the $\text{N}_{\text{ax}}-\text{M}-\text{N}_{\text{eq}}-\text{Si}$ dihedral angle.

It is possible to prepare high-spin first-row-metal complexes (Ti–Fe) that do not contain any axial ligand, so-called “trigonal monopyramidal” complexes.²⁴ An X-ray study of $[(t\text{-BuMe}_2\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{V}$ (Figure 2) revealed slightly longer $\text{V}-\text{N}_{\text{eq}}$ bonds (average 1.93 Å) and a shorter $\text{V}-\text{N}_{\text{ax}}$ bond (2.083 Å) than in $[\text{N}_3\text{N}]\text{VCl}$. The latter is probably largely a consequence of no ligand being present in the apical pocket, and results in the vanadium lying almost in the $\text{V}(\text{N}_{\text{eq}})_3$ plane. Trigonal monopyramidal $[\text{N}_3\text{N}]\text{V}$ can be employed to form complexes of the type $[\text{N}_3\text{N}]\text{V}=\text{E}$ where $\text{E} = \text{O}, \text{S}, \text{Se},$ and Te (unstable), or NR ($\text{R} = \text{H}$ and several other groups) via atom transfer reactions.²⁵ When the E ligand is a good π donor, the $[\text{N}_3\text{N}]\text{V}=\text{E}$ complexes may be regarded as 18-electron species.

A variety of $[\text{N}_3\text{N}]^{3-}$ complexes that contain second- or third-row metals have been prepared, although yields of starting materials currently are only moderate to poor. For example, $[\text{N}_3\text{N}]\text{TaCl}_2$ can be prepared readily in $\sim 30\%$ yield from TaCl_5 and $\text{Li}_3[\text{N}_3\text{N}]$ in ether.^{26,27} Addition of 2 equiv of LiEHR' ($\text{E} = \text{N}, \text{P}$) to $[\text{N}_3\text{N}]\text{TaCl}_2$ yields d^0 species of the type $[\text{N}_3\text{N}]\text{Ta}=\text{ER}'$ and $\text{R}'\text{EH}_2$. Those containing PR' ($\text{R}' \neq \text{H}$) are rare examples of terminal d^0 phosphinidene

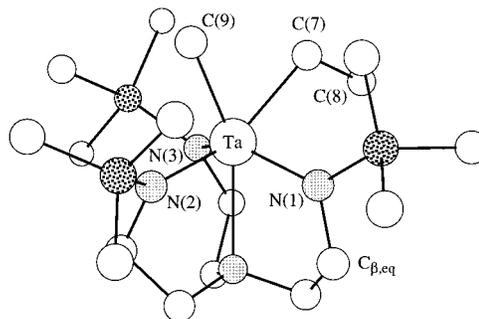
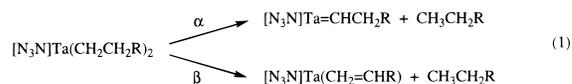


FIGURE 3. A drawing of the structure of $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Ta}(\text{Me})\text{Et}$.

complexes.^{28–30} An X-ray study of $[\text{N}_3\text{N}]\text{Ta}=\text{PCy}$ showed that the $\text{Ta}=\text{P}-\text{C}$ bond angle is almost 180° and that the $\text{Ta}=\text{P}$ bond length is 2.145(7) Å. Although these phosphinidene complexes are 18-electron species (if the axial nitrogen atom remains bound and π bonding from P is included), they react with aldehydes readily to yield $[\text{N}_3\text{N}]\text{Ta}=\text{O}$ and the corresponding phosphalkene.

What might be called “steric pressure” in the coordination pocket in tantalum complexes can be demonstrated qualitatively. Although only $[\text{N}_3\text{N}]\text{Ta}(\text{C}_2\text{H}_4)$ is formed upon adding 2 equiv of ethylmagnesium chloride to $[\text{N}_3\text{N}]\text{TaCl}_2$, intermediate $[\text{N}_3\text{N}]\text{Ta}(\text{CH}_2\text{CH}_2\text{R})_2$ complexes ($\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{CHMe}_2, \text{CMe}_3$) were found to undergo competitive α hydrogen abstraction to give an alkylidene complex or β hydrogen abstraction to give an unstable olefin complex (eq 1). Upon alkylation of $[\text{N}_3\text{N}]\text{TaCl}_2$ with



2 equiv of $\text{Me}_3\text{CCH}_2\text{CH}_2\text{MgCl}$, only an alkylidene complex is formed as a consequence of the β hydride abstraction process being so disfavored sterically.³¹ An X-ray structure of $[\text{N}_3\text{N}]\text{Ta}(\text{Me})\text{Et}$ (Figure 3) revealed a significant degree of distortion of the TaN_4 core that is caused by even the two relatively small (methyl and ethyl) ligands in the coordination pocket. The smaller methyl group ($\text{C}(9)$) is pointed toward $\text{N}(2)$. All $\text{Ta}-\text{N}-\text{Si}$ angles ($129-136^\circ$) are larger than the usual values of $125-126^\circ$ in crystallographically characterized $\text{M}[\text{N}_3\text{N}]$ species, and the $\text{N}(1)-\text{Ta}-\text{N}(3)$ angle opens to 133° (compared to 104° and 100° for the other two $\text{N}-\text{Ta}-\text{N}$ angles) in order to accommodate the ethyl ligand ($\text{C}(7)$ and $\text{C}(8)$). Activation of a $\text{C}-\text{H}_\alpha$ bond through an agostic interaction³² with the metal would require less movement of the ethyl ligand than activation of a $\text{C}-\text{H}_\beta$ bond. In “ d^0 ” $[\text{N}_3\text{N}]\text{Ta}=\text{CHCH}_2\text{R}$ complexes there is a strong agostic interaction between the CH_α bond and the metal, as judged from the low value for J_{CH_α} (~ 70 Hz), consistent with formation of a pseudo-

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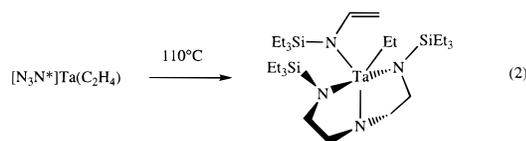
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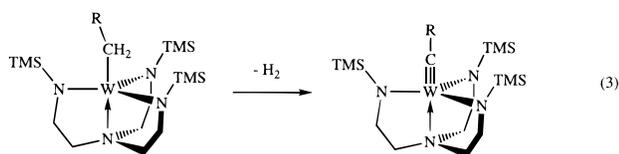
triple Ta–carbon bond and distortion of the Ta–C_α–C_β bond toward linearity. Increasing the size of the trialkylsilyl groups also increases steric pressure in the pocket; i.e., decomposition of unobservable [N₃N*]Ta(CH₂R)₂ species ([N₃N*]³⁻ = [(Et₃SiNCH₂CH₂)₃N]³⁻) yields *only* the alkylidene complexes [N₃N*]Ta=CHR.³³

Of the [N₃N]Ta(olefin) complexes, only ethylene complexes are observable. However, even they will decompose when heated to give compounds in which a C–N_{ax} bond in the original tren backbone has been cleaved (e.g., eq 2). It is believed that abstraction of a proton from C_{β,eq}



(see Figure 3) precedes C–N_{ax} bond cleavage, but details of this first-order decomposition reaction are still obscure. This type of decomposition reaction may limit the successful synthesis of aggressively reactive second- or third-row-metal complexes that contain silylated tren ligands.

Useful tungsten and molybdenum starting materials, d² complexes of the type [N₃N]MCl (M = Mo or W), can be prepared by adding some form of MCl₄ to Li₃[N₃N], although the yields again are relatively poor (between ~20% and 40%). The [N₃N]MCl complexes are paramagnetic presumably as a consequence of the two electrons being in the degenerate d_{xz} and d_{yz} orbitals. Initial exploratory reactions consisted of simple alkylations. For example, [N₃N]MoCl complexes can be alkylated to form high-spin paramagnetic *n*-alkyl complexes that are relatively stable at room temperature (R = Me, Et, etc.). However, tungsten alkyl complexes readily lose dihydrogen from the α carbon atom (eq 3), even when β protons



are present in the RCH₂ group. [N₃N]WMe can be isolated, but it decomposes slowly at 25 °C in a first-order reaction in which ΔH[‡] = 19.2 kcal mol⁻¹ and ΔS[‡] = -16 eu. The value for k_H/k_D (5–6), which is similar to what has been found for α hydrogen abstraction in d⁰ tantalum alkylidene complexes,³⁴ suggests that the rate-limiting step of this reaction may be loss of dihydrogen from an intermediate alkylidene hydride species. The M≡C bond must be extraordinarily stable in order for loss of dihydrogen to be thermodynamically favorable.

Paramagnetic cyclopropyl and cyclobutyl complexes of Mo decompose readily upon being heated via intramolecular C–C bond cleavages, as do the (unobserved) analogous tungsten cyclopropyl and cyclobutyl species,

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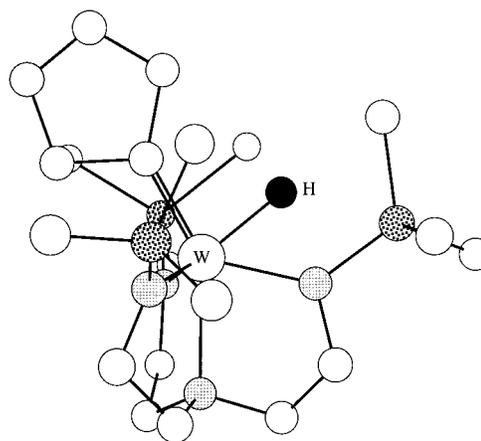
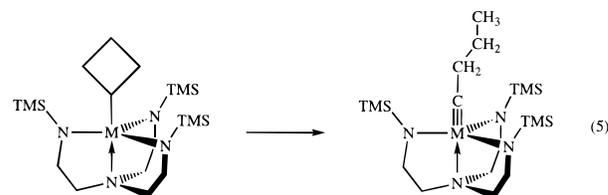
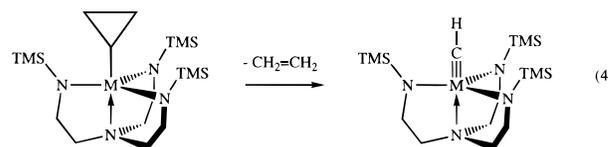
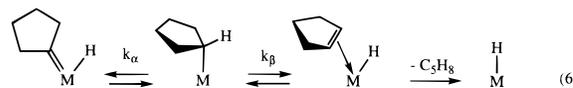


FIGURE 4. A drawing of the structure of [(Me₃SiNCH₂CH₂)₃N]W(C₅H₈)H.

as shown in eqs 4 and 5.³⁵ Paramagnetic [N₃N]Mo-



(cyclopentyl) is formed readily, but the attempted synthesis of [N₃N]W(cyclopentyl) produced the alkylidene hydride complex [N₃N]W(H)(cyclopentylidene). An X-ray study (Figure 4) revealed that the cyclopentylidene and hydride ligands lie (approximately) in a plane that passes through one of the “arms” of the N₃N ligand, as expected on the basis of the symmetries of the three frontier orbitals that are available for bonding to the alkylidene and hydride ligands. Upon heating a solution of [N₃N]Mo(cyclopentyl) or [N₃N]W(C₅H₈)(H) in C₆D₆ to 45 °C, 1 equiv of cyclopentene is evolved and pentane-soluble, sublimable, paramagnetic [N₃N]MH complexes are formed (eq 6). Formation of [N₃N]W(C₅H₈)(D) first (at low temper-



ature) upon adding LiC₅H₈D_α to [N₃N]WCl suggests that k_α is larger than k_β in d² tungsten alkyl complexes of this type. α elimination might be faster in the systems described here as a consequence of steric factors that hinder β elimination,³¹ as found in the [N₃N]Ta dialkyl complexes described earlier. Loss of cyclopentene from intermediate tungsten cyclopentene hydride complexes is the slowest of the five reactions shown in eq 6.

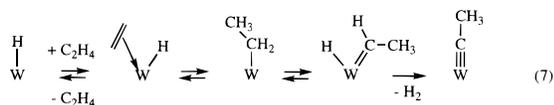
Paramagnetic [N₃N]M(C≡CR') complexes (R' = Me or Ph) can be prepared in high yield, but attempts to prepare

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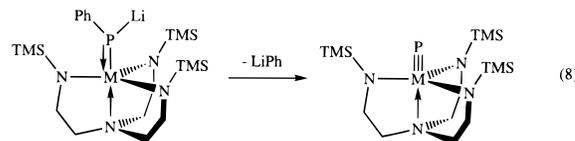
the analogous $[\text{N}_3\text{N}]\text{M}(\text{C}\equiv\text{CH})$ complexes led to diamagnetic dimers of the type $[\text{N}_3\text{N}]\text{M}\equiv\text{C}-\text{CH}=\text{CH}-\text{C}\equiv\text{M}[\text{N}_3\text{N}]$ ($\text{M} = \text{Mo}$ or W).³⁶ Formation of the coupled product (when $\text{R} = \text{H}$) can be viewed as another example of how favorable formation of a triple metal-carbon bond in $[\text{N}_3\text{N}]^{3-}$ complexes of this general type can be. Preliminary evidence suggests that the singlet carbene $[\text{N}_3\text{N}]\text{M}\equiv\text{C}-\text{CH}$: is in equilibrium with $[\text{N}_3\text{N}]\text{M}-\text{C}\equiv\text{CH}$, and is the species from which the coupled products arise.

$[\text{N}_3\text{N}]\text{WH}$ appears to be far more reactive than $[\text{N}_3\text{N}]-\text{MoH}$. For example, $[\text{N}_3\text{N}]\text{WH}$ reacts with H_2 (1 atm) over a period of 1 day to give diamagnetic, white $[\text{N}_3\text{N}]\text{WH}_3$,³⁷ but $[\text{N}_3\text{N}]\text{MoH}_3$ so far has not been observed. Reactions between $[\text{N}_3\text{N}]\text{WH}$ and CO , isocyanides, and acetylenes yield products that have precedent in the literature, although some reactions are sluggish.³⁸ In contrast, the reaction between ethylene and $[\text{N}_3\text{N}]\text{WH}$ proceeds rapidly to give the ethylidyne complex, presumably as shown in eq 7.



Since $\text{M}\equiv\text{C}$ bonds are so favorable in $[\text{N}_3\text{N}]\text{Mo}$ and $[\text{N}_3\text{N}]\text{W}$ complexes, and since certain $\text{M}\equiv\text{E}$ bonds had never been observed before (e.g., $\text{E} = \text{P}, \text{As}$), speculation arose that $[\text{N}_3\text{N}]\text{M}\equiv\text{E}$ complexes ($\text{M} = \text{Mo}$ or W) might be preparable. (Arguments in favor of and evidence for forming a transition metal-phosphorus triple bond in the right circumstances have been put forth in the literature for several years.³⁹⁻⁴⁴) The first of these turned up unexpectedly. An attempt to prepare $[\text{N}_3\text{N}]\text{W}(\text{PPhH})$ by treating $[\text{N}_3\text{N}]\text{WCl}$ with LiPPhH instead produced yellow, crystalline, pentane-soluble, diamagnetic $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$ in approximately 50% yield, as confirmed in an X-ray study ($\text{W}\equiv\text{P} = 2.162(4) \text{ \AA}$).⁴⁵ Addition of 2 equiv of LiPPhH to $[\text{N}_3\text{N}]\text{MoCl}$ gave yellow crystalline $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$ in ~75% yield. Intermediate $[\text{N}_3\text{N}]\text{Mo}(\text{PPhH})$ could be isolated and shown to react further with LiPPhH (or alkyllithium reagents) to yield $[\text{N}_3\text{N}]\text{Mo}\equiv\text{P}$. An unstable lithiated phenyl phosphide is proposed to be the precursor to the terminal phosphido product in reactions of this type (eq 8). A related terminal phosphidomolybdenum complex was prepared by the Cummins group by treating a $\text{Mo}(\text{NRR}')_3$ complex with white phosphorus, and also was structurally characterized ($\text{Mo}\equiv\text{P} = 2.119(4) \text{ \AA}$).¹⁶

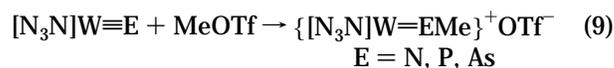
Terminal arsenido complexes have been prepared by techniques that are related to those used to prepare terminal phosphido complexes.⁴⁶ Orange $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$ can be isolated in ~30% yield by adding ~2 equiv of



LiAsHPh to $[\text{N}_3\text{N}]\text{MoCl}$ in a mixture of toluene and THF. $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$, on the other hand, is best prepared (~60% yield) by standing a mixture of ~4 equiv of AsPhH_2 and $[\text{N}_3\text{N}]\text{WPh}$ in toluene for ~48 h in the dark. These are the only known terminal arsenido complexes.⁴⁷ 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 $2.252(3) \text{ \AA}$.

The availability of a series of $\text{M}\equiv\text{E}$ complexes of Mo and W ($\text{E} = \text{N}, \text{P}, \text{As}$) allowed a comparison of the stretching frequencies and force constants for the $\text{M}\equiv\text{E}$ oscillators through Raman spectroscopy.⁴⁶ Although the Raman spectra contain many peaks, the $\text{M}\equiv\text{E}$ stretching absorptions could be located and the force constants calculated using the diatomic oscillator approximation: $\text{W}\equiv^{14}\text{N}$, 1015 cm^{-1} , $7.90 \text{ mdyne \AA}^{-1}$; $\text{W}\equiv^{15}\text{N}$, 987 cm^{-1} , $7.96 \text{ mdyne \AA}^{-1}$; $\text{W}\equiv\text{P}$, 516 cm^{-1} , $4.16 \text{ mdyne \AA}^{-1}$; $\text{W}\equiv\text{As}$, 343 cm^{-1} , $3.69 \text{ mdyne \AA}^{-1}$; $\text{Mo}\equiv\text{P}$, 521 cm^{-1} , $3.74 \text{ mdyne \AA}^{-1}$; $\text{Mo}\equiv\text{As}$, 374 cm^{-1} , $3.47 \text{ mdyne \AA}^{-1}$. The observed reduction in the $\text{W}\equiv\text{E}$ force constant [$k(\text{W}\equiv\text{N}) \gg k(\text{W}\equiv\text{P}) > k(\text{W}\equiv\text{As})$] and the observation that $k(\text{W}\equiv\text{E}) > k(\text{Mo}\equiv\text{E})$ for a given E are consistent with literature data for transition metal oxo and nitrido compounds. Interestingly, the relative force constants for $\text{W}\equiv\text{E}$ ($k(\text{W}\equiv\text{N}):k(\text{W}\equiv\text{P}):k(\text{W}\equiv\text{As}) = 1.91:1:0.89$) vary with E in almost the same manner as do those for $\text{HC}\equiv\text{E}$ ($k(\text{C}\equiv\text{N}):k(\text{C}\equiv\text{P}):k(\text{C}\equiv\text{As}) = 2.06:1:0.82$),⁴⁸ suggesting, qualitatively at least, that differences between the $\text{W}\equiv\text{E}$ bonds parallel differences between $\text{C}\equiv\text{E}$ bonds.

An alkyl group can be added to E in all $[\text{N}_3\text{N}]\text{W}\equiv\text{E}$ compounds (eq 9). In $\{[\text{N}_3\text{N}]\text{W}\equiv\text{PMe}\}(\text{OTf})$ $^1J_{\text{PW}}$ was found to be 748 Hz, compared with $^1J_{\text{PW}} = 138 \text{ Hz}$ in



$[\text{N}_3\text{N}]\text{W}\equiv\text{P}$, consistent with a considerable increase in the s character of the σ portion of the $\text{W}\equiv\text{P}$ bond. An X-ray structure of $\{[\text{N}_3\text{N}]\text{W}\equiv\text{AsMe}\}^+\text{OTf}^-$ confirms that the arsinidene is linear ($\text{W}=\text{As}-\text{Me} = 173^\circ$) and that the $\text{W}=\text{As}$ bond length (2.25 \AA) is approximately the same as the $\text{Mo}\equiv\text{As}$ bond length in $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$ and the $\text{W}\equiv\text{As}$ bond length⁴⁷ in $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$. Arsinidene complexes are extremely rare, the only other known one being $(\text{silox})_3\text{-Ta}=\text{AsPh}$.^{28,49} In $(\text{silox})_3\text{Ta}=\text{AsPh}$ ($\text{silox} = \text{OSi}(t\text{-Bu})_3$) the $\text{Ta}=\text{As}-\text{Ph}$ angle is only $107.2(4)^\circ$ and $\text{Ta}=\text{As} = 2.428(2) \text{ \AA}$, as if there were no π bonding from As to Ta . Donation of some π electron density from the silox oxygens into the orbital that would receive the lone pair from As appears to "block" π donation from As to Ta in this case.

(47) These arsenido complexes also have been prepared by treating $[\text{N}_3\text{N}]\text{MCl}$ with $\text{LiAs}(\text{SiMe}_3)_2$: Scheer, M.; Müller, J.; Häser, M. *Angew. Chem.*, in press. An X-ray structure of $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$ showed the $\text{W}\equiv\text{As}$ bond length to be $2.290(1) \text{ \AA}$.

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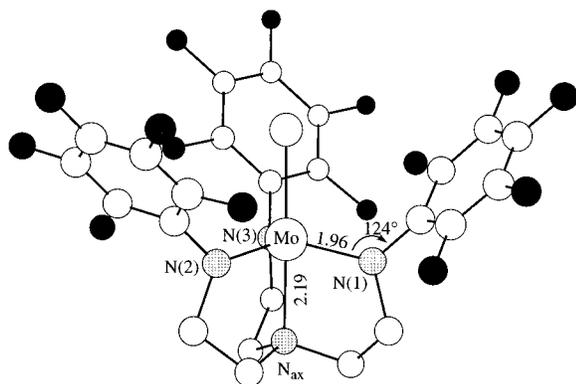


FIGURE 5. A drawing of one of the two independent molecules of $[(C_6F_5NCH_2CH_2)_3N]MoCl$.

One of the initial reasons for exploring the chemistry of triamidoamine complexes of Mo and W was to understand how dinitrogen might be bound and reduced in a C_3 -symmetric environment. A preliminary reaction between $MoCl_3(THF)_3$ and $Li_3[(t-BuMe_2SiNCH_2CH_2)_3N]$ under dinitrogen gave paramagnetic, pentane-soluble, purple $\{[(t-BuMe_2SiNCH_2CH_2)_3N]Mo\}_2(\mu-N_2)$ in very low ($\sim 10\%$) yield.³⁶ An X-ray study showed that this species can be described as a $[Mo(IV)]_2[\text{diazenido}(2-)]$ complex ($Mo-N=N-Mo$) in which $Mo-N_{\alpha} = 1.907(8)$ Å, $N=N = 1.20(2)$ Å, and $Mo-N=N = 178(1)^\circ$. It is surprising that this molecule can form, in view of the severe steric interaction between $t-BuMe_2Si$ groups at one end of the molecule and those at the other end of the molecule, as evidenced by the unusually large $Mo-N_{eq}-Si$ angles of $\sim 140^\circ$. It is interesting to note that this species apparently does not decompose readily to give $[(t-BuMe_2SiNCH_2CH_2)_3N]Mo\equiv N$, a type of symmetric cleavage reaction that has been observed upon addition of dinitrogen to certain trigonal triamido molybdenum(III) complexes.¹⁷ Calculations suggest that $N-N$ cleavage is endothermic when a donor is present in trigonal triamido molybdenum(III) complexes.⁵⁰ Recent results suggest that the dinitrogen chemistry of $[N_3N]Mo$ complexes is more extensive than indicated by the above result⁵¹ and resembles that published for $[N_3N_F]Mo$ complexes (see the next section). For example, both paramagnetic $[N_3N]Mo(N_2)$ and its one-electron (per Mo) reduction product, diamagnetic $\{[N_3N]Mo(N_2)\}_2Mg(THF)_2$, have now been isolated and structurally characterized.

Pentafluorophenyl-Substituted tren Complexes

Nucleophilic attack by tren on hexafluorobenzene produces $(C_6F_5NHCH_2CH_2)_3N$ ($H_3[N_3N_F]$) in high yield.⁵ One advantage of the $[N_3N_F]^{3-}$ ligand becomes apparent immediately; unlike syntheses of $[N_3N]MCl$ complexes ($M = Mo$ or W), $[N_3N_F]MCl$ complexes can be synthesized from MCl_4 , the parent ligand, and Et_3N in high yield. An X-ray study of $Mo[N_3N_F]Cl$ (Figure 5) showed it to be similar to structures of $[N_3N]^{3-}$ complexes, and that the planes of the three C_6F_5 rings are oriented approximately perpendicular to the $Mo-N-C_{ipso}$ plane, thereby creating a kind of "bowl" around the apical chloride.

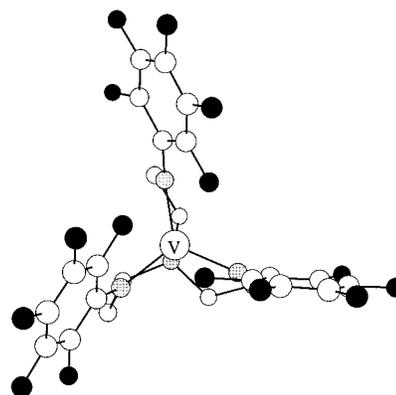
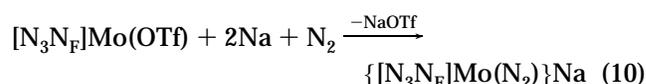
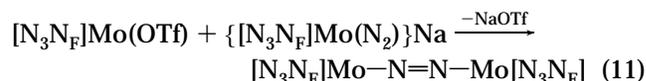


FIGURE 6. A top view of the structure of $[(C_6F_5NCH_2CH_2)_3N]V$.

Reduction of $[N_3N_F]Mo(OTf)$ with 2 equiv of sodium amalgam yields what can be viewed as the sodium salt of $\{[N_3N_F]Mo(N_2)\}^-$ (eq 10), while reduction with 1 equiv of



sodium amalgam yields the dinuclear bridging "diazenido(2-)" species $[N_3N_F]Mo-N=N-Mo[N_3N_F]$. $[N_3N_F]Mo-N=N-Mo[N_3N_F]$ is proposed to form via the reaction shown in eq 11. $[N_3N_F]Mo-N=N-Mo[N_3N_F]$ apparently does not



readily cleave homolytically to give $[N_3N_F]Mo\equiv N$, but can be reduced readily by sodium to give $\{[N_3N_F]Mo(N_2)\}Na$. The key (fast) reaction is believed to be that between dinitrogen and the *low-spin* form of d^4 $\{[N_3N_F]Mo\}^-$ to give $\{[N_3N_F]Mo(N_2)\}Na$.

Reduction of $[N_3N_F]W(OTf)$ with sodium amalgam in THF produces only a paramagnetic, and as yet unidentified, product. However, if better traps than dinitrogen are present ($L = CO$, $CN-t-Bu$, NO , or ethylene), then paramagnetic $[N_3N_F]W(L)$ complexes can be isolated in good to excellent yields.⁵²

A few titanium complexes that contain the $[N_3N_F]$ ligand ($[N_3N_F]TiX$ where $X = Br$, I , or OTf ⁵³) have been prepared, but the chemistry of $[N_3N_F]V$ complexes is more developed.⁵⁴ Vanadium complexes that have been prepared include the $V(V)$ complexes $[N_3N_F]V=O$ and several $[N_3N_F]V=N$ aryl complexes and $V(III)$ complexes $[HNEt_3]\{[N_3N_F]VCl\}$, $[N_3N_F]V(CH_3CN)$, $[N_3N_F]V(t-BuNC)$, and $[N_3N_F]V(THF)$. Oxidation of $[HNEt_3]\{[N_3N_F]VCl\}$ by ferrocenium triflate yields $[N_3N_F]VCl$, a species that can be reduced by sodium amalgam in toluene to give trigonal monopyramidal $[N_3N_F]V$.⁵⁵ An X-ray structural study of $[N_3N_F]V$ (Figure 6) reveals that the three C_6F_5 rings no longer create a bowl-shaped apical cavity, but are turned so that the ortho fluorines approximately fill the apical cavity. This orientation may be encouraged by weak $V\cdots F$ interactions ($V\cdots F_{ortho} = 2.652$ Å), with the C_3 -symmetric

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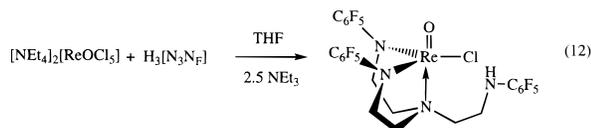
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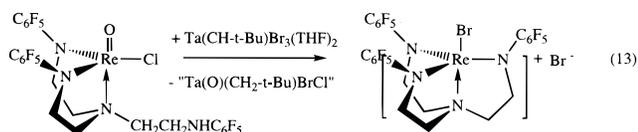
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set of σ orbitals pointing out of the VN_3 face.⁵⁶ This work suggests that dinitrogen is not activated by d^2 V(III) in $[\text{N}_3\text{N}_\text{F}]\text{V}$ to give an observable product, in contrast to the proposed activation of dinitrogen by d^3 $[\text{N}_3\text{N}]\text{Mo}$ and d^4 $\{[\text{N}_3\text{N}_\text{F}]\text{Mo}\}^-$ (see above).

The only entry into rhenium triamidoamine chemistry that has been discovered so far is the reaction between $[\text{Et}_4\text{N}]_2[\text{ReOCl}_5]$ and $(\text{C}_6\text{F}_5\text{NHCH}_2\text{CH}_2)_3\text{N}$ in THF at room temperature in the presence of NEt_3 to give the emerald green diamagnetic oxo chloride complex in which one arm of the ligand has not lost its proton (eq 12).⁵⁷ We



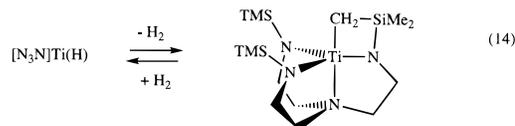
speculated that d^2 $[\text{N}_3\text{N}_\text{F}]\text{Re}=\text{O}$ may be a high-energy species, since no π donation from the oxo ligand would be possible in this trigonally symmetric species as a consequence of two d electrons being present in the second π type orbital. An attempt to exchange the oxo ligand in the rhenium oxo chloride complex with the neopentylidene ligand in $\text{Ta}(\text{CH}-t\text{-Bu})(\text{THF})_2\text{Br}_3$ gave olive green, paramagnetic $\{[\text{N}_3\text{N}_\text{F}]\text{ReBr}\}^+\text{Br}^-$ instead (eq 13).



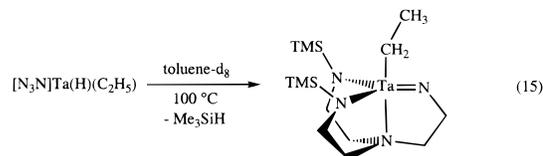
This complex reaction formally is an exchange of the oxo ligand and HCl in the rhenium oxo chloride complex with Br_2 on tantalum. All efforts to prepare $[\text{N}_3\text{N}_\text{F}]\text{ReBr}_2$ by more direct and obvious routes so far have failed. Reduction of $[\text{N}_3\text{N}_\text{F}]\text{ReBr}_2$ under dinitrogen yielded sparingly soluble, diamagnetic, orange, crystalline $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{N}_2)$ in which dinitrogen is end-on bound in the usual manner. Reduction of $[\text{N}_3\text{N}_\text{F}]\text{ReBr}_2$ in the presence of a variety of other potential ligands led to complexes that contain CO , dihydrogen, ethylene or propylene, several silanes, various phosphines, including PH_3 itself, and nitriles.⁵⁸ It is worth noting that rhenium amido complexes are rare^{59–61} and the formation of $[\text{N}_3\text{N}_\text{F}]\text{Re}$ complexes is therefore all the more surprising.

Side Reactions and Other trens

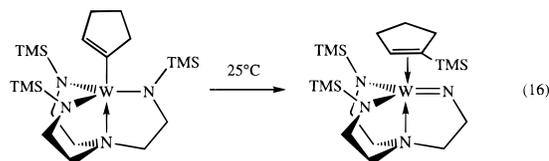
Several examples of what may be viewed as limitations in the use of the trimethylsilyl-substituted tren ligand have appeared in the course of exploring the chemistry described so far. These include decomposition of $[\text{N}_3\text{N}]\text{TiR}$ complexes by β elimination to give incipient $[\text{N}_3\text{N}]\text{TiH}$, which subsequently reacts with a CH bond in one of the TMS groups (eq 14),⁴ abstraction of a $\text{N}_{\text{eq}}\text{CH}_2$ proton and



cleavage of the $\text{C}-\text{N}_{\text{ax}}$ bond in the original tren backbone (eq 2), loss of Me_3SiH from $[\text{N}_3\text{N}]\text{Ta}(\text{C}_2\text{H}_5)(\text{H})$ (eq 15),³⁰



and migration of a TMS group to the α carbon atom of a cyclopentyl ring (eq 16).³⁸ Many of these decompositions might be avoided by employing new types of tren ligands.



So far complexes have been reported that contain *tert*-butyldimethylsilyl,²⁴ triethylsilyl,^{33,53} dimethylphenylsilyl,³⁶ or diphenylmethylsilyl³⁶ substituents. In contrast, relatively few reports of complexes that contain alkyl-substituted triamidoamine ligands have appeared. So far complexes have been reported that contain methyl-,^{62–65} ethyl-,⁶⁵ isopropyl-,⁶⁵ or benzyl-substituted⁶² trens, e.g., $[(\text{MeNCH}_2\text{CH}_2)_3\text{N}]\text{Mo}\equiv\text{N}$,⁶³ $[(i\text{-PrNCH}_2\text{CH}_2)_3\text{N}]\text{TiCl}$,⁶⁵ or $[(\text{EtNCH}_2\text{CH}_2)_3\text{N}]\text{Ti}(\text{triflate})$.⁶⁵ An alkyl-substituted tren should be considerably more electron donating overall than a silyl-substituted tren, which might lead to facile reduction of the metal in the initial synthesis. Small alkyl substituents also may not be able to prevent facile distortion of the equatorial amides away from a trigonal arrangement, and the presence of one or more protons in the substituent α to nitrogen also may allow deprotonation and formation of imine complexes. Two other aryl-substituted trens have been prepared by nucleophilic attack on fluorinated arenes⁵ ($[3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\text{NHCH}_2\text{CH}_2]_3\text{N}$ and $[2\text{-C}_6\text{H}_4(\text{CF}_3)\text{NHCH}_2\text{CH}_2]_3\text{N}$), but little chemistry involving them has been reported.

The possibility of lengthening all three arms in substituted tren complexes by one carbon atom, i.e., preparing $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{CH}_2)_3\text{N}]^{3-}$ derivatives, has been explored briefly.⁵³ The room temperature proton NMR spectrum of $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{CH}_2)_3\text{N}]\text{TiCl}$ in C_6D_6 is consistent with a ligand framework that is skewed and "rigid" on the NMR time scale, as confirmed through an X-ray structure of $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{CH}_2)_3\text{N}]\text{TiCl}$ (Figure 7). The three TiN_2C_3

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 (66) Actinide (U and Th)^{67,68} and lanthanide (Y and La)⁶⁹ complexes that contain the $[\text{N}_3\text{N}]^{3-}$ ligand have been reported.
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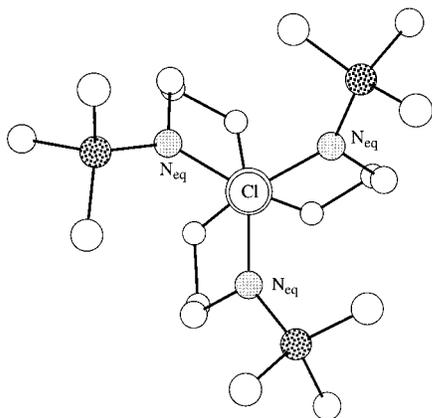


FIGURE 7. A top view of the structure of $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{CH}_2)_3\text{N}]\text{TiCl}$.

rings indeed have “chair” conformations, which produce the relatively exaggerated “tilt” to the silyl groups. Other $[(\text{R}_3\text{SiNCH}_2\text{CH}_2\text{CH}_2)_3\text{N}]^{3-}$ ligands might prove to be more compatible with larger second- or third-row metals, actinides, or early lanthanides, especially if R_3Si groups larger than TMS (e.g., Et_3Si or $i\text{-Pr}_3\text{Si}$) are employed.^{66–69}

Conclusions and the Future

There are several issues that are relevant to the chemistry of triamidoamine complexes. One is the potential direct involvement of the equatorial nitrogen atoms of the triamidoamine ligand in reactions that take place in the apical pocket, e.g., proton migrations. (So far it has been assumed that the triamidoamine ligand is not directly involved.) A second important issue is whether the axial donor nitrogen atom “dissociates” from the metal to any significant degree and thereby significantly alters the geometry of intermediates and the electronic characteristics of frontier metal orbitals. (See, for example, the structure of $[\text{N}_3\text{N}]\text{Ta}(\text{Me})(\text{triflate})$,⁷⁰ in which the $\text{Ta}-\text{N}_{\text{ax}}$ distance is 2.54 Å.) Finally, the fact that the ground state of trigonally symmetric 16-electron d^2 complexes is high spin could lead to a significant retardation of the rate of certain reactions, *if* the mechanism of the reaction requires the presence of one empty and one filled orbital. For example, two arms could open to a relatively large $\text{N}_{\text{eq}}-\text{M}-\text{N}_{\text{eq}}$ angle in order to accommodate a filled orbital between them, i.e., to give a pseudooctahedral arrangement. If the ground state high-spin form and excited state low-spin form are in rapid equilibrium, then the overall rate could be slowed significantly as a consequence of the miniscule amount of low-spin form that is present. Several attempts to determine whether spin state alone can alter the rate of an organometallic reaction have been reported in the literature.^{71–75} A circumstance such as that described here does not seem to have been described

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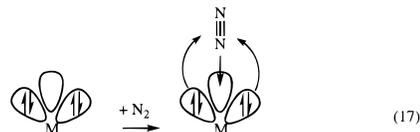
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before, perhaps in part because of what may be special features of C_3 -symmetric d^2 complexes.

The chemistry of molybdenum triamidoamine complexes that involves activation of dinitrogen may help to focus on some important issues. The great stability of $[\text{N}_3\text{N}_F]\text{Re}(\text{N}_2)$ and the ability of “ $\{[\text{N}_3\text{N}_F]\text{Mo}\}^-$ ” to bind and reduce dinitrogen to give “ $[\text{N}_3\text{N}_F]\text{Mo}-\text{N}=\text{N}-\text{NaL}_x$ ” (e.g., $\text{L} = \text{ether}$) suggest that activation of one end of dinitrogen by *low-spin* d^4 $[\text{N}_3\text{N}]\text{M}$ complexes, i.e., those with the $a_1^0e^4$ frontier orbital configuration (in C_{3v} , shown schematically in eq 17), is extraordinarily facile. Since



dinitrogen is cleaved by three-coordinate, high-spin, trigonally symmetric complexes of the type $\text{Mo}(\text{NR}_1\text{R}_2)_3$,¹⁷ the initial d^3 dinitrogen complex $\text{Mo}(\text{NR}_1\text{R}_2)_3(\text{N}_2)$ must form in some significant concentration. However, such a species has not yet been observed.⁷⁶ Therefore, it is especially interesting to note that d^3 $[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)$ is stable,⁵¹ but that the trigonal monopyramid $[\text{N}_3\text{N}]\text{Mo}$ has not yet been observed. Although studies concerning the reduction of dinitrogen are not being pursued in order to “model” the nitrogenase enzyme, and in any case it is not yet known how dinitrogen is actually reduced in nitrogenases, it is at least worth noting that the molybdenum nitrogenase^{77,78} contains a trigonally symmetric MoS_3 arrangement at one end of the MoFe_7S_9 cluster.

The construction of new tren-type ligands is an important direction in the development of triamidoamine complexes. For example, the length and flexibility of the three arms of the triamidoamine ligand, as well as its overall electronic characteristics, should significantly alter the chemistry within the pocket. Triamine ligands have now been prepared that contain some combination of arms with two and three methylenes in them.⁷⁹ Although $\text{N}(\text{o}-\text{C}_6\text{H}_4\text{OH})_3$ has been known for 30 years,⁸⁰ $\text{N}(\text{o}-\text{C}_6\text{H}_4\text{NH}_2)_3$ has been prepared only recently.⁸¹ Changing the apical nitrogen donor atom to P or As (for example) is a synthetic challenge, but significant new chemistry could be expected. One can also envision the construction of “hybrids” of the ligands described here and traditional neutral analogs such as $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_3\text{N}^{23}$ (for example, $[(\text{Ph}_2\text{PCH}_2\text{CH}_2)_3\text{N}(\text{CH}_2\text{CH}_2\text{NR})_2]^{2-}$). The potential interest in the hybrid ligands initially would revolve around the fact that they would no longer be C_3 -symmetric and a more reactive low-spin form therefore would be more accessible, or even the ground state configuration.

The trianionic and tetradentate nature of triamidoamine ligands described here makes them especially suitable for stabilizing and sterically protecting transition metals with relatively low d electron counts. It already has been

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demonstrated that some of the chemistry they support is unique, and that metal–ligand triple or pseudotriple bonds are especially stable. Over the next several years it seems likely that more unique features and capabilities of triamidoamine and related multidentate amido ligands will be uncovered.

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