Synthesis of Triamidoamine Ligands of the Type $(ArylNHCH_2CH_2)_3N$ and Molybdenum and Tungsten Complexes That Contain an $[(ArylNCH_2CH_2)_3N]^{3-}$ Ligand

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Aryl bromides react with $(H_2NCH_2CH_2)_3N$ in a reaction catalyzed by $Pd_2(dba)_3$ in the presence of BINAP and NaO-t-Bu to give the arylated derivatives $(ArylNHCH_2CH_2)_3N$ [Aryl = C_6H_5 (**1a**), 4-FC_6H_4 (**1b**), 4-t-BuC_6H_4 (**1c**), 3,5-$Me_2C_6H_3$ (**1d**), 3,5-$Ph_2C_6H_3$ (**1e**), 3,5-(4-t-$BuC_6H_4)_2C_6H_3$ (**1f**), 2-MeC_6H_4 (**1g**), 2,4,6-$Me_3C_6H_2$ (**1h**)]. Reactions between $(ArNHCH_2CH_2)_3N$ (Ar = C_6H_5, 4-FC_6H_4, 3,5-$Me_2C_6H_3$, and 3,5-$Ph_2C_6H_3$) and $Mo(NMe_2)_4$ in toluene at 70 °C lead to $[(ArNHCH_2CH_2)_3N]Mo(NMe_2)$ complexes in yields ranging from 64 to 96%. Dimethylamido species (Ar = 4-FC_6H_4, 3,5-$Me_2C_6H_3$) could be converted into paramagnetic $[(ArNHCH_2CH_2)_3N]$-MoCl species by treating them with 2,6-lutidinium chloride in tetrahydrofuran (THF). The "direct reaction" between **1a**−**f** and $MoCl_4(THF)_2$ in THF followed by 3 equiv of MeMgCl yielded $[(ArNHCH_2CH_2)_3N]MoCl$ species (**3a**−**f**) in high yield. If 4 equiv of LiMe instead of MeMgCl are employed in the direct reaction, then $[(ArNHCH_2$-$CH_2)_3N]MoMe$ species are formed. Tungsten species, $[(ArNHCH_2CH_2)_3N]WCl$, could be prepared by analogous "direct" methods. Cyclic voltammetric studies reveal that MoCl complexes become more difficult to reduce as the electron donating ability of the $[(ArNHCH_2CH_2)_3N]^{3-}$ ligand increases, and the reductions become less reversible, consistent with ready loss of chloride from $\{[(ArNHCH_2CH_2)_3N]MoCl\}^-$. Tungsten complexes are more difficult to reduce, and reductions are irreversible on the CV time scale.

Introduction

Transition metal and actinide complexes that contain a triamidoamine ligand of the general formula $[(RNCH_2CH_2)_3N]^{3-}$ have been explored extensively over the past several years,[1−41] as have transition metal complexes that contain three sterically bulky monodentate amido ligands.[42−51] Triamidoamine ligands bind to transition metals in oxidation state +3 or higher in a tetradentate manner, leaving three metal orbitals (one of σ symmetry and two of π symmetry) to bind additional ligands

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in the apical pocket, an arrangement that favors the formation of metal−ligand multiple bonds. This feature of the triamidoamine ligand has led to some unusual results, e.g., the synthesis of terminal phosphido and arsenido complexes[9,35] and the discovery that some Mo alkyl complexes and many W complexes decompose by α,α-dehydrogenation to give alkylidyne complexes.[4,10] In the process of elucidating the chemistry of Mo and W alkyl complexes it was discovered that in the absence of two α hydrogens molybdenum and tungsten alkyl complexes undergo α hydride elimination as much as 6 orders of magnitude faster than β hydride elimination.[4,10,11,36] In complexes that contain a $[(RNCH_2CH_2)_3N]^{3-}$ ligand only two $M-N_{eq}$ π-bonds can form. Therefore, the $[(RNCH_2CH_2)_3N]^{3-}$ ligand can donate a maximum of 12 electrons to the metal center. However, orbital overlap is more favorable for one of the two π-bonds, so in most cases essentially only one $M-N_{eq}$ π-bond is present and the $[(RNCH_2CH_2)_3N]^{3-}$ ligand can be said to contribute only 10 electrons to the total electron count.

Before the work to be described here was begun, all transition metal chemistry involving $[(RNCH_2CH_2)_3N]^{3-}$ ligands had been carried out on complexes in which the R group was a methyl,[37−39] a trialkylsilyl,[16,40] or a pentafluorophenyl group.[41] However, during the course of our experiments on complexes in which R = $SiMe_3$ or C_6F_5, several drawbacks were revealed. The silicon−nitrogen bond is inherently weak, and several complexes were found to decompose by loss of a trimethylsilyl (TMS) group or by CH activation within a TMS group.[10,11,13,33,40] Also, low yields of Mo and W chloride complexes containing TMS substituted triamidoamine ligands were attributed to cleavage of N−Si bonds during preparation of complexes of the type $[((TMS)NCH_2CH_2)_3N]MCl$.[10,11] The primary drawback of the C_6F_5 ligand is its instability toward strong nucleophiles.[12] The C_6F_5 groups also lead to a relatively electron deficient metal center, which can be undesirable if strong π back-donation into a ligand in the coordination pocket is desired.

We believed that the chemistry of a complex containing a triamidoamine ligand substituted with ordinary aryl groups would be richer for cases that required a significant amount of π back-donation, e.g., metal dinitrogen complexes, that such complexes would not suffer the drawbacks of analogous complexes that contain C_6F_5 and TMS substituted ligands, and that some steric variation should be possible that would slow intermolecular reactions or the formation of bimolecular complexes. We first developed a route to such ligands that was based upon formation of the appropriate triamide of nitrilotriacetic acid followed by reduction with lithium aluminum hydride. This method initially was attractive to us because nitrilotriacetic acid is an inexpensive starting material, and because a wide variety of anilines is commercially available. However, we found construction of aromatic carbon−nitrogen bonds by methods pioneered by the Buchwald[52−59] and Hartwig[60−63] groups to be more convenient. Eight ligands have been synthesized by this method and are reported here along with the syntheses of several Mo and W starting materials. In view of the greater convenience of the catalytic C−N coupling method, syntheses of several of the $(ArylNHCH_2CH_2)_3N$ species reported here by the nitriloacetic acid route are provided only as Supporting Information. A portion of this work has been reported in the form of a communication.[64]

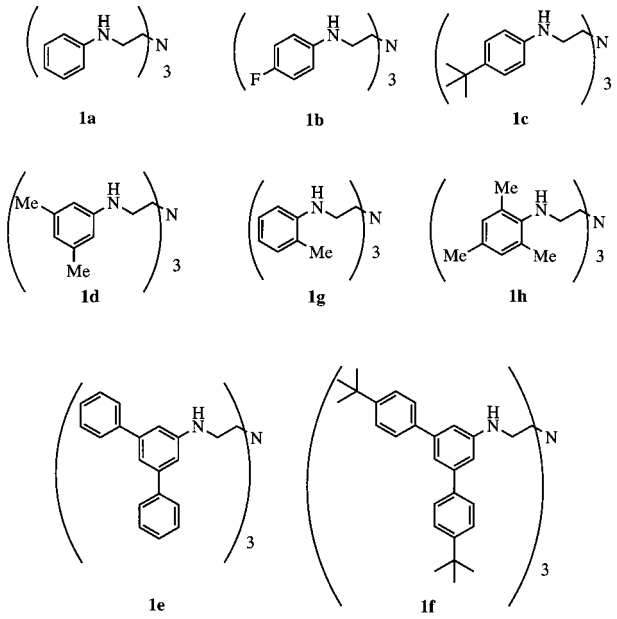

Figure 1. Arylated TREN precursors to triamidoamine ligands.

Results and Discussion

Ligand Syntheses. The aryl bromides that are required for the synthesis of **1a**−**d**, **1g**, and **1h** (Figure 1) are commercially available. Those required to prepare ligands **1e** and **1f** are not commercially available, but they can be prepared in two steps from inexpensive 2,4,6-tribromoaniline, as shown in eq 1. The literature procedure was followed in the first step,[65] except that 2,4,6-tribromoiodobenzene was recrystallized from dichloromethane instead of benzene/ethanol. 2,4,6-Tribromoiodobenzene was then coupled with 2 equiv of aryl Grignard reagent in a reaction that proceeds through two benzyne intermediates.[65]

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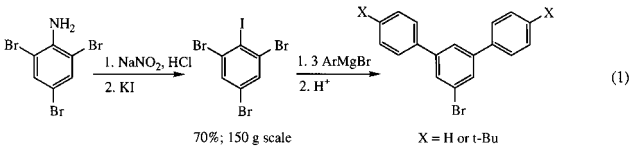
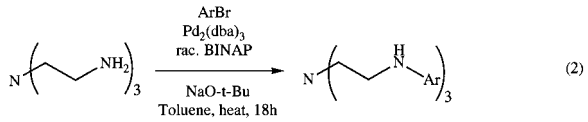
3,5-Diphenylbromobenzene is a known compound.[65] 3,5-Bis(4-*tert*-butylphenyl)bromobenzene is a new compound, but it was prepared by virtually the same method as 3,5-diphenylbromobenzene.



(1)

Arylated triethylenetetramines were synthesized via the coupling of 3 equiv of the aryl bromide in the presence of 3 equiv of sodium *tert*-butoxide per $(H_2NCH_2CH_2)_3N$ using $Pd_2(dba)_3$ (1 mol % versus ArBr) and BINAP as the catalyst (eq 2).[56,66] Yields ranged from a low of 27% for **1b** (aryl = 4-FC_6H_4) to 90% for **1g** (aryl = 2-MeC_6H_4). (The yield for **1a** (aryl = C_6H_5) was 57%, for **1c** (aryl = 4-t-BuC_6H_4) 47%, for **1d** (aryl = 3,5-$Me_2C_6H_3$) 58%, for **1h** (aryl = 2,4,6-$Me_3C_6H_2$) 79%, for **1e** (aryl = 3,5-$Ph_2C_6H_3$) 51%**,** and **for 1f** (aryl = 3,5-(4-t-$BuC_6H_4)_2C_6H_3$) 64%.) Reactions typically were run at 80 °C in toluene for 18 h. However, 100 °C was necessary for the preparation of **1g** and **1h** due to the increased steric demand of the aryl bromide. We found that if all components of the reaction were combined before heating the reaction, the yield of the desired product was highly irreproducible. We speculate that TREN competes with BINAP as a ligand for Pd based on the observation that when TREN is added to the reaction mixture, the color changes from the purple of $Pd_2(dba)_3$ to dark yellow, but no color change is observed when only $Pd_2(dba)_3$, solid racemic BINAP, aryl bromide, and toluene are present in the reaction flask. Upon heating, the reactions turn dark brown, and a large amount of gray solid, which appears to be Pd metal, is formed. The problem appears to be that racemic BINAP is not very soluble in toluene at room temperature and many equivalents of TREN are present for each Pd. Irreproducible yields are avoided if BINAP is heated in toluene (150 mL/g of BINAP) until it dissolves, and then $Pd_2(dba)_3$ is added as a solid in order to form the catalyst. This strategy has also been employed in certain circumstances by the Buchwald group.[56] A small amount of black solid forms, but after it is filtered off, the orange color persists upon addition of the catalyst to the other reaction components and throughout the course of the coupling reaction. When the catalyst is "pre-formed" in this manner, the yields of the coupling reactions are reproducible.



(2)

There is a second complication that limits the yields in some circumstances. Reactions that employ BINAP as a ligand are inherently selective for primary amines over secondary amines,[56] but a second arylation of one "arm" of the desired product cannot be completely avoided if the aryl group is small. Products in which one of the three arms of the ligand has been doubly arylated (e.g., $(PhNHCH_2CH_2)_2NCH_2CH_2NPh_2$) can be isolated during column chromatography, typically in ~15% yield. Performing the reactions at lower temperatures for longer times did not increase the isolated yield of **1a** significantly. Since exactly 3 equiv of aryl bromide are employed, the amount of "overarylated" material equals the yield of material in which one of the three arms has not been arylated at all, thereby decreasing the yield of **1a** even further.

Compounds **1a**−**d** must be purified by column chromatography on silica gel using a 3:1 mixture of hexane and ethyl acetate to which 3% (by volume) of a saturated solution of ammonia in methanol has been added. The overarylated compounds elute from these columns immediately before compounds of type **1**. The products of type **1** are often initially obtained as pale yellow oils, but colorless crystals can be grown from mixtures of ether and hexane (**1a**, **1b**, and **1d**), or pure hexane (**1c**). We speculate that the low yield of **1b** can be ascribed to the sensitivity of the fluorine atom to sodium *tert*-butoxide, but we did not attempt to optimize the reaction by using different bases. Compounds **1a**−**d** are slightly sensitive to the combination of air and light. If a vial of powder is stored on the laboratory shelf, the material on the outside of the vial will turn pale yellow over the course of several weeks, while material not exposed to the light remains white. No discoloration is observed if the compounds are stored in a glovebox under dinitrogen or in a vial covered with aluminum foil.

Yields of **1g** (Ar = *o*-tolyl) and **1h** (Ar = mesityl) are relatively high (90 and 79%, respectively) because little or no overarylated material is formed. Also **1g** and **1h** need not be purified by column chromatography. Analytically pure material can be obtained simply by recrystallization of the product from a mixture of ether and hexane. Chromatography also is unnecessary in order to purify **1e** or **1f**, even though overarylated material is formed, because the solubility of overarylated material in these cases in common organic solvents is much higher than that of **1e** and **1f**. Purification of **1f** poses a challenge as a consequence of its low solubility in organic solvents. Chloroform is the only common solvent in which it exhibits some significant solubility. Compound **1f** can be separated easily from other organic products by simple filtration, but separation of it from the NaBr produced during the coupling reaction must be accomplished by means of a chloroform/water extraction. Evidently this process is not efficient, as the low values for elemental analyses (C, H, and N) suggest that some inorganic salts are still present.

It is possible that $(ArNHCH_2CH_2)_2NCH_2CH_2NAr_2$ compounds could be employed as diamidodiamine ligands for early transition metals. Therefore the C−N coupling reactions were run until all of the aryl bromide was consumed in order to maximize the yield of tetraarylamine. Compounds in which Ar = 4-fluorophenyl, 4-*tert*-butylphenyl, and 3,5-bis(4-*tert*-butylphenyl)phenyl were isolated and fully characterized. When Ar = 4-*tert*-butylphenyl, the compound can be crystallized from hexane, while that in which Ar = 3,5-bis(4-*tert*-butylphenyl)-phenyl can be crystallized from ether. That in which Ar = 4-fluorophenyl has been obtained only as an oil.

Synthesis of Molybdenum Chloride Complexes from Mo(NMe$_2$)$_4$. The most desirable starting material in order to explore the chemistry of molybdenum(IV) triamidoamine complexes would be a monochloride species, but we would expect such a species to be paramagnetic. Therefore we found it attractive initially to prepare a diamagnetic dimethylamido complex, the synthesis of which is easily followed by NMR, and subsequently to convert the dimethylamido complex to the chloride by protonolysis. Dimethylamido complexes of Mo(IV) that contain a triamidoamine ligand are diamagnetic as a consequence of strong M−N π bonding involving one of the two π orbitals on the metal available for bonding to a ligand in the trigonal pocket, leaving the two d electrons paired up in the other π orbital.

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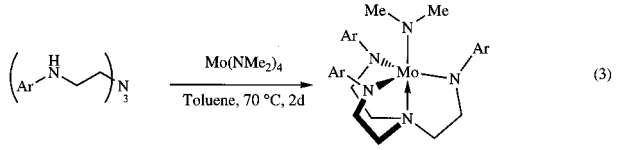
Reactions between $(ArNHCH_2CH_2)_3N$ (Ar = C_6H_5, 4-FC_6H_4, 3,5-$Me_2C_6H_3$, and 3,5-$Ph_2C_6H_3$) and $Mo(NMe_2)_4$[67] in toluene at 70 °C lead to $[(ArNHCH_2CH_2)_3N]Mo(NMe_2)$ complexes (eq 3) in yields ranging from 64 to 96%. In the case of ligands containing highly electron deficient aryl groups such as C_6F_5, dimethylamide complexes can be prepared in pentane at room temperature over the course of several hours.[41] However, more forcing conditions are required for complete reaction when the aryl group is more electron rich, but the temperature must be controlled carefully. No reaction occurs below ~65 °C, while complexes of type 2 decompose above 80 °C.

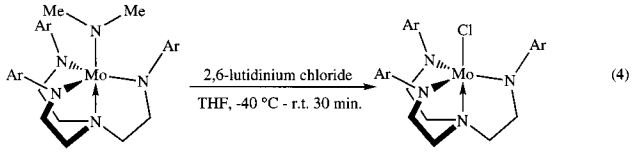


(3)

2a Ar = C_6H_5, 81%
2b Ar = 4-FC_6H_4, 93%
2d Ar = 3,5-$Me_2C_6H_3$, 64%
2e Ar = 3,5-$Ph_2C_6H_3$, 96%

Compounds **2a**, **2b**, **2d**, and **2e** are diamagnetic, dark purple crystalline solids, which are insoluble in pentane. They are extremely air, moisture, and thermally sensitive and decompose rapidly upon exposure to dichloromethane. Their ^{1}H NMR spectra are typical of trigonally symmetric diamagnetic complexes in that two triplets are observed for the methylene backbone protons and the aryl rings rotate freely about the N−C_{ipso} bond. Rotation of the dimethylamide ligand with respect to the TREN ligand is also rapid (one singlet is observed for the dimethylamide protons), which is a common feature of dimethylamido complexes of earlier transition metals. The resonance in the ^{19}F NMR spectrum for **2b** occurs at −124.4 ppm, which is in the normal range for a fluorine in the para position of an arylamine.

Reaction of **2b** or **2d** with 2,6-lutidinium chloride in THF produced **3b** or **3d** (eq 4). Compound **3d** is less soluble than the other chlorides (it will crystallize out of concentrated THF solutions), while **3b** is soluble in aromatic hydrocarbons. No reaction was observed when **2e** was treated with 2,6-lutidinium chloride, presumably for steric reasons. Compounds **3b** and **3d** are red, paramagnetic solids. (The π-bonding from the chloride ligand is not strong enough to break the degeneracy of the two π-type orbitals on the metal.) The practical consequence of the paramagnetism is that resonances in the ^{1}H NMR spectrum are broadened and shifted to a significant degree compared to the parent compounds **1**. Nevertheless, ^{1}H NMR spectroscopy is a useful diagnostic tool, since all of the compounds' resonances occur at characteristic chemical shifts and can be assigned. The resonances for the protons on the backbone of the TREN ligand always occur upfield, with one resonance around −20 ppm and the other around −75 ppm. The resonances for the ortho and meta protons on the aryl ring always occur downfield, with the meta resonance always being further downfield and sharper (16 ppm) than the ortho resonance (9 ppm).



(4)

2b Ar = 4-FC_6H_4
2d Ar = 3,5-$Me_2C_6H_3$

3b Ar = 4-FC_6H_4, 86%
3d Ar = 3,5-$Me_2C_6H_3$, 64%

^{19}F NMR spectroscopy is an especially useful probe for reactions involving paramagnetic complexes, which was the primary motivation for the preparation of complexes containing the 4-fluorophenyl ligand. Resonances in the ^{19}F NMR spectrum also are often sharper for paramagnetic complexes than those in the ^{1}H NMR spectrum, especially in the case of **3b**, where the fluorine is relatively far removed from the metal. Therefore, it is relatively easy to determine how many compounds are present in a crude reaction mixture. Furthermore, reactions can be followed by recording spectra of aliquots from the reaction mixture. The ^{19}F resonance for **3b** occurs at −110.5 ppm, slightly downfield from the normal diamagnetic position.

Direct Synthesis of Molybdenum Chloride and Methyl Complexes. Although the syntheses shown in eqs 3 and 4 are relatively foolproof, synthesis of more than a gram or two of a chloride complex by this method is not practical by virtue of the limited quantities of $Mo(NMe_2)_4$ that can be prepared and isolated at one time, at least in our hands. Monochloride complexes that contain the more sterically protective ligands derived from **1e** and **1f** also are not preparable by this route. Therefore, with our knowledge of the NMR spectra of compounds **3b** and **3d** we began a search for a more "direct" synthesis of a monochloride complex. We chose the readily available $MoCl_4(THF)_2$[68] as the starting material.

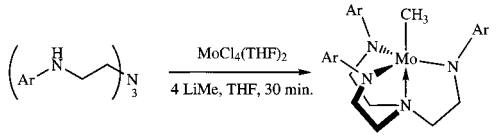
The strategy that proved to be successful was inspired by the synthesis of $[(C_6F_5NCH_2CH_2)_3N]MoCl$, where a red Mo(IV) complex of unknown type is prepared in situ by adding the free amine to $MoCl_4(THF)_2$, followed by addition of triethylamine in order to remove 3 equiv of HCl.[41] Since the amine proton in the arylamines employed here is not as acidic as that in $(C_6F_5NHCH_2CH_2)_3N$, we found that triethylamine is not a strong enough base. A number of stronger bases such as DBU, KH, proton sponge, and *n*-butyllithium were tried, but none yielded appreciable amounts of chloride. However, when 3 equiv of neopentyllithium or methyllithium were added to a mixture of the tetraamine and $MoCl_4(THF)_2$ and the mixture was allowed to stand for 24 h, chlorides **3a** (Ar = C_6H_5), **3b** (Ar = 4-FC_6H_4), **3c** (Ar = 4-t-BuC_6H_4), and **3d** (Ar = 3,5-$Me_2C_6H_3$) were produced in good yield.

The formation of chloride **3b** using 3 equiv of methyllithium as a base was monitored by ^{19}F NMR. After 24 h, the only peak present in the ^{19}F NMR spectrum other than free amine was at −110 ppm (in THF), matching that of **3b** prepared by protonolysis of **2b** (eq 4). Surprisingly, after 1 h, the major product present in the mixture had a ^{19}F NMR signal at −104 ppm. Over the course of 16 h, the signal for this product decreased in intensity as the signal for **3b** increased in intensity. When 4 equiv of methyllithium was added to a mixture of **1b** and $MoCl_4(THF)_2$, this product was the only metal containing product formed after 30 min, and it was *not* converted to **3b** after leaving it in the reaction mixture for 24 h.

Isolation and characterization of the product formed upon addition of 4 equiv of LiMe (eq 5) confirmed that it is a methyl complex, $[(4\text{-}FC_6H_4NCH_2CH_2)_3N]MoMe$ (**4b**). In addition to elemental analysis, evidence to support this formulation includes the fact that adding 1 equiv of methyllithium or methylmagnesium chloride to **3b** in THF yields **4b** quantitatively. Methyl complexes **4a** (Ar = C_6H_5), **4c** (Ar = 4-t-BuC_6H_4), and **4d** (Ar = 3,5-$Me_2C_6H_3$) also were prepared by adding 4 equiv of

(67) Bradley, D. C.; Chisholm, M. H. *J. Chem. Soc. A* **1971**, 2741.
(68) Dilworth, J. R.; L., R. R.; Chen, G. J.; McDonald, J. W. *Inorg. Synth.* **1980**, *20*, 119.

methyllithium to the initial amine adduct, as shown in eq 5.

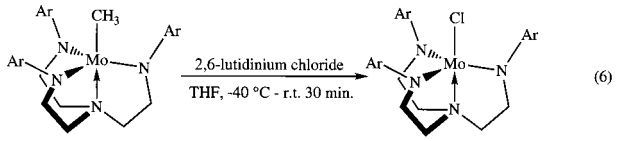


(5)

4a Ar = C_6H_5, 51%
4b Ar = 4-FC_6H_4, 63%
4c Ar = 4-t-BuC_6H_4, 69%
4d Ar = 3,5-$Me_2C_6H_3$, 63%

All of the methyl complexes shown in eq 5 are soluble in benzene or toluene, while **4c** is highly soluble in ether and somewhat soluble in pentane. All can be crystallized from mixtures of toluene and pentane. Proton NMR spectra of **4a**−**d** are similar to spectra of **3a**−**d**, but there are enough differences to allow for easy identification. Specifically, the high-field methylene resonances in compounds **4** are about 8 ppm downfield of the corresponding resonances in compounds **3**, and the resonance for the ortho hydrogens is about 5 ppm upfield. A proton or carbon resonance cannot be observed for the methyl group in **4a**−**d** using routine NMR methods. This has been true for all methyl and alkyl complexes of this general type.[11]

Methyl complexes that contain the ligands derived from **1a**−**d** could be converted to chloride complexes cleanly by treating them with 1 equiv of 2,6-lutidinium chloride (eq 6). This proved to be a more convenient and reliable synthesis of the chlorides than allowing a mixture of the Mo−ligand adduct and 3 equiv of methyllithium to stir for 24 h.

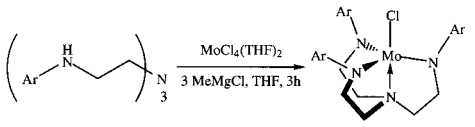


(6)

4a Ar = C_6H_5
4b Ar = 4-FC_6H_4
4c Ar = 4-t-BuC_6H_4
4d Ar = 3,5-$Me_2C_6H_3$

3a Ar = C_6H_5, 81%
3b Ar = 4-FC_6H_4, 84%
3c Ar = 4-t-BuC_6H_4, 63%
3d Ar = 3,5-$Me_2C_6H_3$, 77%

We felt that compounds **4** were formed first in a reaction involving methyllithium because of the relatively high reactivity of methyllithium and further speculated that a less aggressive alkylating agent (MeMgCl) might result in formation of compounds **3** directly. This proved to be the case, as shown in eq 7.



(7)

3a Ar = C_6H_5, 57%
3b Ar = 4-FC_6H_4, 63%
3c Ar = 4-t-BuC_6H_4, 63%
3d Ar = 3,5-$Me_2C_6H_3$, 62%
3e Ar = 3,5-$Ph_2C_6H_3$, 38%
3f Ar = 3,5-(4-t-BuC_6H_4)$_2$$C_6H_3$, 44%

Compounds **3a**−**f** can be prepared directly in high yield in less than 3 h, without significant contamination by the monomethyl complexes. It is important that methylmagnesium chloride is employed; reactions employing methylmagnesium iodide yielded a mixture of chloride and the analogous iodide complexes.[69]

The solubility of compounds **3** in various solvents differs dramatically, so several different methods had to be developed for their isolation in the reactions shown in eq 7. Chlorides **3a** and **3d** are sparingly soluble in THF, and they crystallize out of reaction mixtures as they are formed. Material that is collected by filtration of the reaction mixture is analytically pure, since the magnesium salts remain in solution. The other chlorides are highly soluble in THF, so the magnesium salts have to be removed by complexation with 1,4-dioxane. Compound **3b** crystallizes upon concentration of the THF solution. Compounds **3c** and **3f** can be isolated by removing all of the THF, washing the crude residue with ether, and collecting the ether insoluble material. Complexes **3a**−**d** and **3f** are soluble and stable in dichloromethane and chloroform, and they can be recrystallized from mixtures of dichloromethane and pentane.

The most difficult compound to isolate is **3e**; it does not crystallize readily, and once it crystallizes, it does not dissolve again readily. Storage of a crude reaction mixture at −40 °C overnight does not result in the crystallization of any product. If dioxane is added to remove magnesium salts, and the $MgCl_2$(dioxane) is filtered off within 30 min, pure product can be obtained by concentrating the THF solution of the filtrate until crystallization begins. However, if the $MgCl_2$(dioxane) is not filtered off quickly, **3e** starts to crystallize out; at this stage the crystals can no longer be separated from magnesium salts. However, from a point of view of preparing dinitrogen complexes by reduction under dinitrogen, as will be described in a subsequent paper, contamination of **3e** with $MgCl_2$(dioxane) is not a serious problem.

It was not possible to prepare compounds **3** or **4** in which the aryl group contains ortho substituents (Ar = mesityl or *o*-tolyl) using methods analogous to those described above. When **1g** or **1h** is added to $MoCl_4(THF)_2$ in THF, a red "adduct" is not formed readily at room temperature. We propose that steric inaccessibility of the ortho-substituted arylamines prevents formation of the intermediate that reacts smoothly with methyllithium, and therefore addition of methyllithium or methylmagnesium chloride to what amounts to a mixture of free ligand and $MoCl_4(THF)_2$ simply leads to decomposition. The initial red adduct that we presume to be an intermediate in all successful reactions has never been isolated or identified.

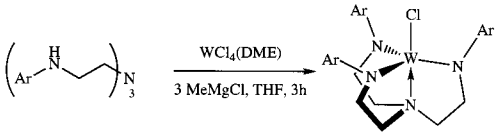
It also proved impractical to prepare compounds **3** by treating $MoCl_4(THF)_2$ with the trilithium salt of several of the ligands. A typical yield (e.g., of **3c**) by this method is only ∼10%. We suspect that reduction of Mo(IV) to Mo(III) by the trilithium salt leads to low yields of the desired Mo(IV) monochloride species. No further effort was made to prepare compounds **3** using this approach.

Direct Synthesis of Tungsten Chloride and Methyl Complexes. Since $W(NMe_2)_4$ is not known, the most convenient starting material for preparing a tungsten monochloride complex is WCl_4(DME).[70] One complication associated with the use of WCl_4(DME) in THF is that WCl_4(DME) reacts with THF to form $WCl_4(THF)_2$, and the THF ligands are much more difficult to displace than is DME.[70] Therefore, although methods analogous to the most successful described above for molybdenum can be employed for tungsten, it is imperative that WCl_4(DME) be added slowly as a solid to a warm (50 °C) THF solution of the ligand. The TREN ligand apparently is a better ligand for W than is THF, so a soluble adduct is formed readily. If WCl_4(DME) is added too quickly, or the mixture is kept at room temperature, white $WCl_4(THF)_2$ begins to precipitate out, and it does not react further. The initial W adduct is yellow. No attempt was made to isolate this adduct.

(69) George E. Greco, Ph.D. Thesis, Massachusetts Institute of Technology, 2000.

(70) Persson, C.; Andersson, C. *Inorg. Chim. Acta* **1993**, *203*, 235.

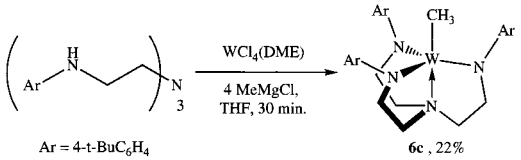
Deprotonation of the adducts with 3 equiv of methylmagnesium chloride leads to tungsten monochloride complexes (**5**) in yields ranging from 24 to 43% (eq 8). Lower yields for tungsten complexes versus molybdenum complexes also were observed in syntheses of $[(Me_3SiNCH_2CH_2)_3N]^{3-}$ [10] and $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ [41] complexes, while a yield of only 10% was reported for the synthesis of $[(i\text{-}PrNCH_2CH_2)_3N]WCl$ from $Li_3[(i\text{-}PrNCH_2CH_2)_3N]$ and $WCl_4(DME)$.[71] As was the case for Mo compounds **3**, differences in solubility between the various W complexes necessitated different workup procedures. In general, the workup procedure developed for the Mo chloride complex containing a particular ligand also was applicable for the W chloride complex. Specifically, **5a** and **5d** crystallized out of crude reaction mixtures and were collected by filtration, while **5b**, **5c**, and **5e** were isolated by removing the $MgCl_2$ as its dioxane adduct and then crystallizing the products from either THF or mixtures of THF and ether. Like **3e**, once crystals of **5e** have formed, they cannot be redissolved in any solvent, including boiling THF and boiling toluene, so a ^1H NMR spectrum of **5e** could not be obtained.



5a Ar = C_6H_5, 24%
5b Ar = 4-FC_6H_4, 28%
5c Ar = 4-t-BuC_6H_4, 43%
5d Ar = 3,5-$Me_2C_6H_3$, 41%
5e Ar = 3,5-$Ph_2C_6H_3$, 35%

Like their Mo analogues, compounds **5a**−**e** are all paramagnetic, and resonances in ^1H NMR spectra are broadened and shifted accordingly. However, resonances in the spectra of W complexes are sharper than in the spectra of the corresponding Mo complexes, presumably as a consequence of greater spin−orbit coupling in the W systems. A graphic demonstration of this fact is that coupling can be observed between the meta and para protons on the aryl ring in the spectrum of **5a**. Two notable differences in chemical shifts exist between the Mo and W complexes. The resonance for the ortho protons on the aryl rings occurs about 9 ppm further downfield in the W complexes, so that it is actually downfield of the meta resonance. More significant is the downfield shift of the upfield backbone resonance, which shifts from −75 ppm in Mo complexes to −50 ppm in W complexes.

Treatment of the adduct formed from **1c** and $WCl_4(DME)$ with 4 equiv of MeMgCl resulted in the formation of $[(4\text{-t-}BuC_6H_4NCH_2CH_2)_3N]WMe$ (**6c**) in 22% yield (eq 9). Unlike **5c**, **6c** is soluble in ether, so it was isolated by recrystallization from ether. Like **5c**, **6c** is paramagnetic, and the difference in ^1H NMR chemical shifts between **6c** and **5c** mirrors the difference between compounds **4** and compounds **3**. Specifically, the resonance for the ortho protons on the aryl ring is shifted upfield by 5 ppm (from 17.3 to 12.8 ppm), and the resonance for the low-field backbone protons is shifted downfield by 4 ppm (from −25.6 to −21.6 ppm). We did not attempt to prepare other examples of methyl complexes, although we would not expect those syntheses to be significantly different from that of **6c**.



Ar = 4-t-BuC_6H_4 **6c**, 22%

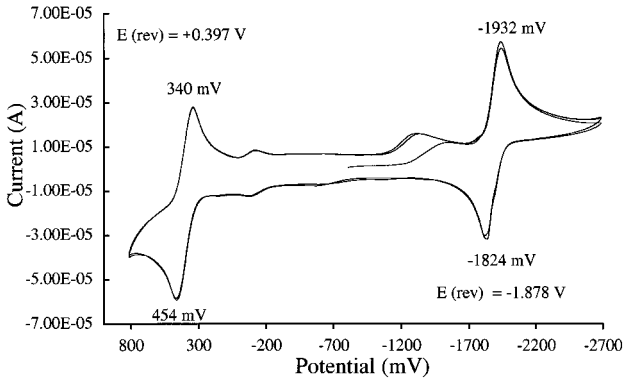


Figure 2. CV of $[(C_6F_5NCH_2CH_2)_3N]MoCl$.

One of the reasons for preparing **6c** was to determine whether it decomposes to a W(VI) methylidyne complex by α,α-dehydrogenation, which is the observed mode of reactivity for alkyl complexes containing a $[(Me_3SiNCH_2CH_2)_3N]^{3-}$ ligand.[4,10] While **6c** is an unstable compound, it decomposes in a complex fashion to unidentified species whose NMR spectra are clearly not consistent with formation of a methylidyne complex. The decomposition of **6c** appears to be accelerated in the presence of MeMgCl. The low yield of **6c** also could be explained on this basis. Due to the instability of **6c**, satisfactory elemental analysis could not be obtained. It should also be noted that attempts to prepare $[(C_6F_5NCH_2CH_2)_3N]WMe$ by alkylation of $[(C_6F_5NCH_2CH_2)_3N]WCl$ in a variety of solvents resulted in the formation of unidentified decomposition products.[12] It is certainly possible that $[(C_6F_5NCH_2CH_2)_3N]W{\equiv}CH$ and $[(4\text{-t-}BuC_6F_4NCH_2CH_2)_3N]W{\equiv}CH$ are both formed at some stage, but themselves are unstable, perhaps as a consequence of the methylidyne ligand being a sterically less well protected than in the $[(Me_3SiNCH_2CH_2)_3N]^{3-}$ complexes. Synthesis of other alkyl complexes and resolution of stability issues will be the subject of future investigations.

Cyclic Voltammetry Studies on Molybdenum and Tungsten Chloride Complexes. The primary motivation behind the synthesis of $[(ArNCH_2CH_2)_3N]MoCl$ complexes was our desire to reduce them under N_2 and prepare dinitrogen complexes. The successful preparation of dinitrogen complexes is detailed in the following paper in this issue, but we report electrochemical studies of compounds **3** and **5** here. All potentials are referenced to the ferrocene/ferrocenium couple.[72] Measurements were performed in THF using Bu_4NPF_6 as the supporting electrolyte. All data were recorded at a scan rate of 500 mV/s.

For reference the CV of $[(C_6F_5NCH_2CH_2)_3N]MoCl$ [41] is shown in Figure 2. The key features are a reversible reduction at −1.878 V and a reversible oxidation at +0.397 V. The oxidation wave is also observed upon first scanning to positive potentials, so it corresponds to a reversible oxidation of $[(C_6F_5NCH_2CH_2)_3N]MoCl$ to $[[(C_6F_5NCH_2CH_2)_3N]MoCl]^+$. The reversibility of the reduction suggests that $\{[(C_6F_5NCH_2CH_2)_3N]MoCl\}^-$ does not lose chloride readily on the time scale employed. $[(C_6F_5NCH_2CH_2)_3N]MoCl$ is not a suitable starting material for preparing complexes that contain dinitrogen, possibly for this reason.[41] $[(C_6F_5NCH_2CH_2)_3N]Mo$(triflate) is a suitable starting material, but this compound is too insoluble for CV studies under the conditions reported here.

The CV's of **3b** (Figure 1S; see Supporting Information) and **3a** (Figure 3) are similar to that of $[(C_6F_5NCH_2CH_2)_3N]MoCl$,

(71) Scheer, M.; Muller, J.; Schiffer, M.; Baum, G.; Winter, R. *Chem. Eur. J.* **2000**, *6*, 1252.
(72) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

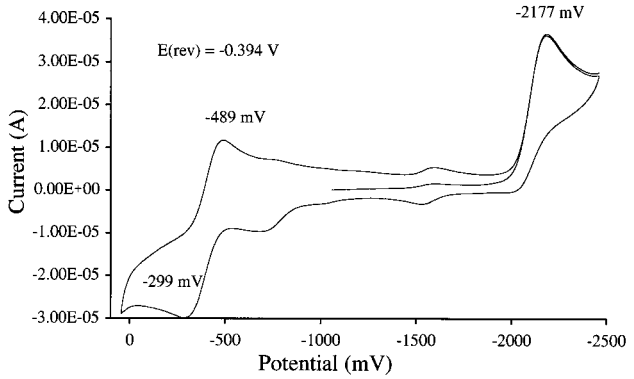


Figure 3. CV of $[(C_6H_5NCH_2CH_2)_3N]MoCl$ (**3a**).

Table 1. Reduction Potentials of $[(ArNCH_2CH_2)_3N]]MCl$ (M = Mo or W) Compounds[a]

Ar	molybdenum	tungsten
C_6F_5[b]	−1.878 (rev)	−2.39 (peak)
$4FC_6H_4$ (**3b**)[c]	−2.085 (quasi-rev)	−2.58 (peak)
C_6H_5 (**3a**)	−2.18 (peak)	−2.65 (peak)
$3,5\text{-}Me_2C_6H_3$ (**3d**)	−2.24 (peak)	−2.69 (peak)
$4\text{-}t\text{-}BuC_6H_4$ (**3c**)	−2.26 (peak)	−2.62 (peak)

[a] See Experimental Section for conditions. All potentials are relative to the ferrocene/ferrocenium couple. "Peak" refers to the peak potential of the irreversible wave. [b] Reversible oxidation potential = +0.397 V. [c] Reversible oxidation potential = −0.370 V.

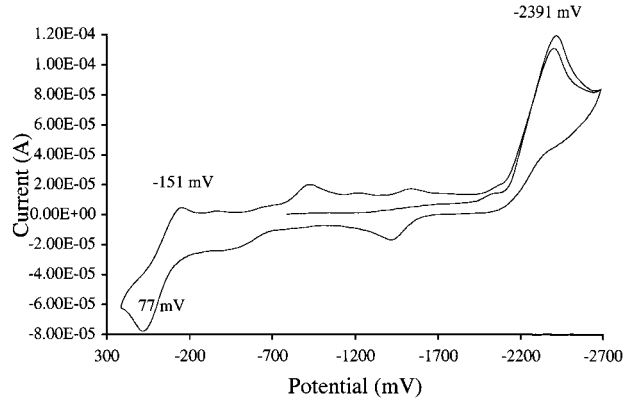


Figure 4. CV of $[(C_6F_5NCH_2CH_2)_3N]WCl$.

but only the oxidations are reversible on the 500 mV/s time scale. Compound **3b** is harder to reduce than $[(C_6F_5NCH_2CH_2)_3N]MoCl$ (by 207 mV; Table 1), while **3a** is the most difficult to reduce of the three. In short, the most difficult complex to reduce leads to a monoanion that loses chloride most readily. This is the trend that one might expect on the basis of the progressively greater electron donating ability of the three ligands involved. The CV's for **3d** and **3c** (see Supporting Information, Figures 2S and 3S, respectively) are similar to that of **3a**. The reductions are irreversible on the time scale employed, and no well-behaved oxidation is observed. Compounds **3d** and **3c** are slightly more difficult to reduce than **3a** (Table 1).

The CV of $[(C_6F_5NCH_2CH_2)_3N]WCl$ [41] is shown in Figure 4. Compared to $[(C_6F_5NCH_2CH_2)_3N]MoCl$, the reduction potential is more negative by 459 mV, and the oxidation potential is more negative by 377 mV, consistent with the expected greater difficulty of reducing W(IV) relative to Mo(IV) and greater ease of oxidizing W(IV) relative to Mo(IV). The reduction is clearly irreversible. A return wave is observed for the oxidation, but the intensity of the cathodic wave is much smaller than that of the anodic wave, indicating partial decomposition of the oxidation product on the time scale of the experiment.

Cyclic voltammograms of $[(ArNCH_2CH_2)_3N]WCl$ compounds in which Ar is C_6H_5, $4\text{-}FC_6H_4$, $3,5\text{-}Me_2C_6H_3$, or $4\text{-}t\text{-}BuC_6H_4$ are similar to the CV shown in Figure 4. The peak potentials for the irreversible reductions for these compounds are listed in Table 1. Irreversible oxidations are also observed, but no attempt was made to understand them in any detail. Two trends can be observed from the data in Table 1. First, W complexes are reduced at a potential ~0.5 V more negative than the analogous Mo complexes. Second, compounds containing the 4-F ligand are reduced at potentials ~0.1 V more positive than those containing the phenyl ligand, and compounds that contain the C_6F_5 ligand are reduced at potentials ~0.3 V more positive than those containing the phenyl ligand. These trends are consistent with what one might have predicted qualitatively.

Conclusions

We have shown that it is possible to substitute $(H_2NCH_2CH_2)_3N$ readily with a variety of aryl groups using palladium catalyzed addition of aryl bromides, a method that is more convenient than the synthesis and reduction of a triamide of nitrilotriacetic acid. Paramagnetic molybdenum and tungsten complexes of the type $[(ArNCH_2CH_2)_3N]MCl$ and $[(ArNCH_2CH_2)_3N]MMe$ could be prepared directly from MCl_4 starting materials in good yields if the aryl group does not contain an ortho methyl group. Diamagnetic complexes of the type $[(ArNCH_2CH_2)_3N]Mo(NMe_2)$ also could be prepared from the free ligand and $Mo(NMe_2)_4$. Cyclovoltammetric studies revealed both oxidation and reduction waves for the monochloride complexes at positions that reflect the expected trends.

Experimental Procedures

General Details. All reactions were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using Schlenk techniques. Ether, toluene, and pentane were sparged with nitrogen for 45 min followed by passage through a 1 gallon column of activated alumina as described in the literature.[73] Tetrahydrofuran, dimethoxyethane, and 1,4-dioxane were distilled from sodium benzophenone ketyl, and dichloromethane was distilled from CaH_2. C_6D_6 was sparged with nitrogen and stored over 4 Å molecular sieves. $CDCl_3$ was dried over CaH_2, vacuum transferred to a solvent storage flask, stored at −35 °C, and passed through a plug of alumina before use. 2,4,6-Tribromoiodobenzene,[65] 3,5-diphenylbromobenzene,[65] $MoCl_4(THF)_2$,[68] $Mo(NMe_2)_4$,[67] $WCl_4(DME)$,[70] $[(C_6F_5NCH_2CH_2)_3N]MoCl$, and $[(C_6F_5NCH_2CH_2)_3N]WCl$ [41] were prepared by published methods. 2,6-Lutidinium chloride was prepared by treating an ethereal solution of 2,6-lutidine with HCl in ether. All other starting materials are commercially available and were used as received.

^1H NMR spectra were recorded at an operating frequency of 300 or 500 MHz, and ^{13}C NMR spectra were recorded at an operating frequency of 75.5 or 125.8 MHz. The residual protons or carbon-13 atoms of the deuterated solvents were used as internal references. ^{19}F NMR spectra were recorded at an operating frequency of 282.2 MHz and were referenced externally using $CFCl_3$ (0 ppm). Chemical shifts are reported in parts per million, and coupling constants are in hertz. All spectra were acquired at ca. 22 °C. Elemental analyses (C, H, N) were performed in our laboratory using a Perkin-Elmer 2400 CHN analyzer, or by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

3,5-Bis(4-*tert*-butylphenyl)bromobenzene. In the glovebox, a 1 L round-bottom flask was charged with Mg powder (12.12 g, 507 mmol) and 300 mL of THF. 4-Bromo-*tert*-butylbenzene (97.5 g, 457 mmol)

(73) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

was dissolved in 250 mL of THF in an addition funnel. A small amount of the bromide was added to the reaction flask, and the Grignard reaction was initiated by heating. After initiation, the remainder of the bromide was added over a period of 2 h. The flask was heated with the heat gun until the THF boiled and then allowed to cool to room temperature. The solution of the Grignard reagent was decanted from the excess Mg into a 2 L flask. 2,4,6-Tribromoiodobenzene (63.9 g, 145 mmol) was dissolved in 250 mL of THF in an addition funnel and then added dropwise to the aryl Grignard solution. The reaction mixture was stirred at room temperature for 3 h and then heated under reflux (on the Schlenk line) for 2 h. The reaction was quenched by pouring it into a mixture of ice and 2 M HCl. THF was removed on the rotary evaporator, and a large amount of solid formed in the flask. The aqueous phase was extracted three times with dichloromethane, and the dichloromethane layers were dried over $MgSO_4$ and concentrated to a thick oil. *tert*-Butylbenzene and 4-*tert*-butyliodobenzene were removed by vacuum distillation. The residue was dissolved in a minimal amount of hexane, and the product was collected as colorless crystals in three crops; yield 35.12 g (83.3 mmol, 57%): ^{1}H NMR ($CDCl_3$): δ 7.71 (t, 1, para), 7.68 (t, 6, ortho), 7.55 (d, 4, aryl), 7.49 (d, 4, aryl), 1.39 (s, 18, t-Bu). ^{13}C NMR ($CDCl_3$): δ 151.24, 143.63, 137.11, 128.72, 127.05, 126.07, 124.73, 123.36, 34.81, 31.56. HRMS. Calcd for $C_{26}H_{29}Br$: 420.1453. Found (EI): 420.1445.

2, 2′, 2″-Tris(phenylamino)triethylamine (1a). The Pd catalyst was pre-formed by dissolving racemic BINAP (1.49 g, 2.40 mmol) in 150 mL of toluene with vigorous heating and stirring, adding $Pd_2(dba)_3$ (0.82 g, 0.90 mmol) as a solid, and removing unreacted Pd by filtration through Celite to yield a light orange solution. A 1 L Schlenk flask was charged with TREN (8.77 g, 60.0 mmol), bromobenzene (28.3 g, 180 mmol), sodium *tert*-butoxide (20.0 g, 208 mmol), and toluene (500 mL). The Pd catalyst solution was added last, and the reaction mixture remained light orange. The reaction mixture was heated to 80 °C under nitrogen (on the Schlenk line) for 20 h. It was then cooled to room temperature, and NaBr was removed by filtration. Toluene was removed on a rotary evaporator, and the resulting brown oil was purified by column chromatography on silica gel. The column was eluted with a 3:1 mixture of hexane and ethyl acetate to which was added 3% (by volume) of a saturated solution of NH_3(g) in methanol. A yellow oil was isolated from the column, which solidified when exposed to high vacuum. White crystals (12.82 g, 34.2 mmol, 57%) were obtained upon recrystallization from ether/pentane at −40 °C: ^{1}H NMR ($CDCl_3$): δ 7.12 (t, 6, meta), 6.70 (t, 3, para), 6.50 (d, 6, ortho), 4.09 (br s, 3, NH), 3.19 (t, 6, CH_2), 2.81 (t, 6, CH_2); ^{13}C NMR ($CDCl_3$) δ 148.72(C_{ipso}), 129.82 (C_m), 118.10 (C_p), 113.59 (C_o), 53.80 (CH_2), 42.41(CH_2); IR (Nujol; cm^{-1}): 3359, 1601, 1506, 1322, 1264, 1178, 1116, 1059, 991, 912, 866, 748, 693, 508. Anal. Calcd for $C_{24}H_{30}N_4$: C, 76.97; H, 8.07; N, 14.96. Found: C, 76.74; H, 8.20; N, 14.96.

2, 2′, 2″-Tris(4-fluorophenylamino)triethylamine (1b). This compound was synthesized in a manner similar to that used to prepare **1a** starting from TREN (7.31 g, 50.0 mmol), *p*-bromofluorobenzene (26.3 g, 150 mmol), $Pd_2(dba)_3$ (0.69 g, 0.75 mmol), *rac*-BINAP (1.25 g, 2.00 mmol), sodium *tert*-butoxide (16.8 g, 175 mmol), and toluene (400 mL). Column chromatography and recrystallization from ether/hexane gave 5.84 g (13.6 mmol, 27%) of white crystals: ^{1}H NMR ($CDCl_3$): δ 6.65 (t, 6, H_m), 6.39 (dd, 6, H_o) 4.03 (br s, 3, NH), 3.22 (t, 6, CH_2), 2.60 (t, 6, CH_2). ^{13}C NMR ($CDCl_3$): δ 156.44 (d, C_p, J_{CF} = 235), 145.05 (d, C_{ipso}, J_{CF} = 1.8), 116.20 (d, C_m, J_{CF} = 22.1), 114.27 (d, C_o, J_{CF} = 7.2), 53.78 (CH_2), 43.08 (CH_2). ^{19}F NMR ($CDCl_3$): δ −127.695 (7 lines). IR (Nujol; cm^{-1}): 3382, 1613, 1509, 1315, 1292, 1260, 1214, 1156, 1114, 1057, 917, 823, 514. HRMS. Calcd for $C_{24}H_{27}F_3N_4$: 428.2188. Found (EI): 428.2188.

2, 2′, 2″-Tris(4-*tert*-butylphenylamino)triethylamine (1c). This compound was synthesized in a manner similar to that used to prepare **1a** starting from TREN (8.77 g, 60.0 mmol), 4-bromo-*tert*-butylbenzene (38.4 g, 180 mmol), $Pd_2(dba)_3$ (0.82 g, 0.90 mmol), *rac*-BINAP (1.49 g, 2.40 mmol), sodium *tert*-butoxide (20.2 g, 210 mmol), and toluene (500 mL). Column chromatography and recrystallization from hexane at −80 °C afforded 15.91 g (29.3 mmol, 49%) of white crystals: ^{1}H NMR (C_6D_6): δ 7.26 (d, 6, H_m), 6.53 (d, 6, H_o), 3.85 (br s, 3 NH), 2.84 (t, 6, CH_2), 2.26 (t, 6, CH_2), 1.30 (s, 27, t-Bu). ^{13}C NMR ($CDCl_3$): δ 146.55 (C_{ipso}), 140.85 (C_p), 126.70 (C_m), 113.48 (C_o), 53.93 (CH_2), 42.70 (CH_2), 34.56, 32.30 (t-Bu). IR (Nujol; cm^{-1}): 3372, 1616, 1521, 1407, 1324, 1305, 1259, 1192, 1165, 1128, 1060, 920, 821, 550. HRMS. Calcd for $C_{36}H_{54}N_4$: 542.4348. Found (EI): 542.4348.

2, 2′, 2″-Tris(3,5-dimethylphenylamino)triethylamine (1d). This compound was synthesized in a manner similar to that used to prepare **1a** starting from TREN (3.66 g, 25.0 mmol), 5-bromo-*m*-xylene (13.6 g, 75 mmol), $Pd_2(dba)_3$ (0.34 g, 0.37 mmol), *rac*-BINAP (0.70 g, 1.1 mmol), sodium *tert*-butoxide (8.4 g, 88 mmol), and toluene (250 mL). Column chromatography and recrystallization from ether/hexane gave 6.64 g (14.6 mmol, 58%) of white crystals: ^{1}H NMR ($CDCl_3$): δ 6.38 (s, 3, H_p), 6.13 (s, 6, H_o) 4.03 (br s, 3, NH), 3.17 (t, 6, CH_2), 2.80 (t, 6, CH_2), 2.21 (s, 18, Ar−CH_3). ^{13}C NMR ($CDCl_3$): δ 148.49 (C_{ipso}), 138.94(C_m), 119.70 (C_p), 111.26 (C_o), 53.22 (CH_2), 41.97 (CH_2), 21.67 ($ArCH_3$). IR (Nujol; cm^{-1}): 3384, 1603, 1509, 1339, 1303, 1263, 1193, 1114, 1059, 988, 857, 819, 689. Anal. Calcd for $C_{30}H_{42}N_4$: C, 78.56; H, 9.23; N, 12.21. Found C, 78.62; H, 9.45; N, 11.97.

2, 2′, 2″-Tris[(3,5-diphenyl)phenyl]triaminotriethylamine (1e). A 100 mL Schlenk flask was charged with TREN (439 mg, 3.0 mmol), 3,5-diphenylbromobenzene (2.78 g, 9.00 mmol), $Pd_2(dba)_3$ (41 mg, 0.045 mmol), *rac*-BINAP (65 mg, 0.11 mmol), sodium *tert*-butoxide (1.01 g, 10.5 mmol), and toluene (45 mL). The reaction mixture was heated to 80 °C overnight. The reaction mixture was then cooled to room temperature and filtered to remove NaBr. The toluene was removed on the rotary evaporator, and the residue was dissolved in dichloromethane. The solution was filtered once again and concentrated to 20 mL. Hexane was added until the solution turned slightly cloudy. Colorless crystals were grown at 0 °C, collected, washed with hexane, and dried in vacuo; yield 1.28 g (1.54 mmol, 51%): ^{1}H NMR ($CDCl_3$): δ 7.41 (m, 12), 7.25 (m, 18), 7.07 (t, 3), 6.71 (d, 6), 4.5 (br s, 3), 3.38 (br s, 6, CH_2), 2.98 (br s, 6, CH_2). ^{13}C NMR ($CDCl_3$): δ 148.80 (C_{ipso}), 142.84 (C_m), 141.40 (3,5-C_{ipso}), 128.48 (3,5-C_m), 127.10 (3,5-C_o and 3,5-C_p), 116.30 (C_p), 110.67 (C_o), 53.29 (CH_2), 42.12 (CH_2). IR (Nujol; cm^{-1}): 3370, 1595, 1577, 1523, 1489, 1422, 1295, 1256, 1222, 1174, 1157, 1115, 1076, 1057, 1029, 989, 949, 913, 858, 848, 757, 701, 612, 566. Anal. Calcd for $C_{60}H_{54}N_4$: C, 86.71; H, 6.55; N, 6.74. Found: C, 86.56; H, 6.48; N, 6.70.

2, 2′, 2″-Tris[(3,5-bis(4-*tert*-butylphenyl)phenyl]triaminotriethylamine (1f). The Pd catalyst was preformed by dissolving *rac*-BINAP (109 mg, 0.175 mmol) in toluene (20 mL) with vigorous heating and stirring, adding $Pd_2(dba)_3$ (69 mg, 0.075 mmol) as a solid, and removing unreacted Pd by filtration through Celite to yield a light orange solution. A 250 mL Schlenk flask was charged with TREN (731 mg, 5.00 mmol), **5b** (6.32 g, 15.0 mmol), sodium *tert*-butoxide (1.68 g, 17.5 mmol), and toluene (75 mL). The Pd catalyst solution was added last; the reaction mixture remained light orange. The reaction was heated to 80 °C overnight and then cooled to room temperature. Most of the product precipitated from toluene and was collected by filtration; it was contaminated with NaBr. The toluene mother liquor was concentrated to dryness, and the residue was extracted with ether. Another crop of ether-insoluble product (757 mg) was collected in this manner. All of the crude white solid was partitioned between 100 mL of chloroform and 100 mL of water. It required vigorous heating for all of the product to dissolve in chloroform. The aqueous phase was extracted two more times with chloroform, and these extracts were combined, dried over $MgSO_4$, and concentrated to 70 mL. Hexane was added to precipitate out the product as a white solid; yield 3.75 g (3.21 mmol, 64%): ^{1}H NMR ($CDCl_3$): δ 7.34 (d, 12, 3,5-aryl), 7.25 (d 12, 3,5-aryl), 7.07 (t, 3, para), 6.69 (d, 6, ortho), 4.56 (br s, 3, NH), 3.35 (br s, 6, CH_2), 2.98 (br s, 6, CH_2), 1.28 (s, 54, t-Bu). ^{13}C NMR ($CDCl_3$): δ 149.68 (3,5-C_p), 148.63 (C_{ipso}), 142.44 (C_m), 138.50 (3,5-C_{ipso}), 126.65 (3,5-C_m), 125.28 (3,5 C_o), 116.04 (C_p), 110.37 (C_o), 53.52 (CH_2), 42.31 (CH_2), 34.44 (t-Bu), 31.39 (t-Bu). IR (Nujol; cm^{-1}): 3384, 1602, 1520, 1497, 1270, 1112, 1055, 1022, 990, 860, 826, 763, 699, 612, 579. HRMS. Calcd for $C_{84}H_{102}N_4$: 1166.8105. Found (FAB): 1166.8076.

2, 2′, 2″-Tris(2-methylphenylamino)triethylamine (1g). This compound was synthesized in a manner similar to that used to prepare **1a** starting from TREN (3.66 g, 25.0 mmol), 2-bromotoluene (12.8 g, 75.0 mmol), $Pd_2(dba)_3$ (0.34 g, 0.37 mmol), *rac*-BINAP (0.70 g, 1.1 mmol), sodium *tert*-butoxide (8.41 g, 175 mmol), and toluene (300 mL). However, after removing most of the toluene on the rotary

evaporator, cold hexane was added to the concentrated oily orange solution to yield pale orange crystals. No chromatography was necessary for the purification of this compound. Further recrystallization from ether/hexane gave 9.41 g (22.6 mmol, 90%) of white crystals: ^{1}H NMR ($CDCl_3$): δ 7.09 (t, 3, H_m), 7.02 (d, 3, H_m), 6.66 (t, 3, H_p), 6.57 (d, 3, H_o), 3.91 (br s, 3, NH), 3.28 (t, 6, CH_2), 2.90 (t, 6, CH_2), 2.00 (s, 9, CH_3); ^{13}C NMR ($CDCl_3$) δ 145.91 (C_{ipso}), 129.99 (C_m), 127.05 (C_m), 121.95 (C_o), 117.02 (C_p), 109.64 (C_o), 53.80 (CH_2), 41.76 (CH_2), 17.16 (Ar$-CH_3$). IR (Nujol; cm^{-1}): 3380, 1606, 1583, 1508, 1319, 1302, 1262, 1190, 1160, 1140, 1089, 1057, 1049, 1025, 981, 923, 748, 717. HRMS. Calcd for $C_{27}H_{36}N_4$: 416.2940. Found (EI): 416.2940.

2, 2′, 2″-Tris(mesitylamino)triethylamine (1h). This compound was synthesized in a manner similar to that used to prepare **1g** starting from TREN (3.66 g, 25.0 mmol), 2-bromomesitylene (14.9 g, 75.0 mmol), $Pd_2(dba)_3$ (0.343 g, 0.375 mmol), rac-BINAP (0.701 g, 1.13 mmol), sodium *tert*-butoxide (8.4 g, 88 mmol), and toluene (200 mL). Recrystallization from ether/hexane gave 9.92 g (19.96 mmol, 79%) of white crystals: ^{1}H NMR (C_6D_6) δ 6.79 (s, 6, aryl), 3.37 (br s, 3, NH), 2.94 (t, 6, CH_2), 2.51 (t, 6, CH_2), 2.24 (s, 18, Me_o), 2.18 (s, 9, Me_p). ^{13}C NMR ($CDCl_3$): δ 144.28 (C_{ipso}), 131.83 (C_p), 130.20 (C_o), 130.15 (C_m), 55.67 (CH_2), 46.81 (CH_2), 21.30, 19.19 ($ArCH_3$). Anal. Calcd for $C_{33}H_{48}N_4$: C, 79.15; H, 9.66; N, 11.19. Found C, 78.71; H, 9.47; N, 10.95.

(4-FC$_6$H$_4$NHCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$N(4-FC$_6$H$_4$)$_2$. This compound was obtained as a byproduct in the preparation of **1b** on a 44 mmol scale. It is the product immediately above **1b** on a TLC plate and was isolated as an oil by column chromatography; yield 2.80 g (5.36 mmol, 12%): ^{1}H NMR (C_6D_6): δ 6.82 (t, 4, meta), 6.73 (t, 4, meta), 6.63 (dd, 4, ortho), 6.18 (d, 6, ortho), 3.63 (br s, 2, NH), 3.34 (t, 2, tertiary CH_2), 2.60 (t, 4, secondary CH_2), 2.32 (t, 2, tertiary CH_2), 2.18 (t, 4, secondary CH_2). ^{13}C NMR ($CDCl_3$): δ 157.76 (d, C_p, $J_{CF} = 241$), 155.65 (d, C_p, $J_{CF} = 235$), 144.32 (d, C_{ipso}, $J_{CF} = 2$), 144.07 (d, C_{ipso}, $J_{CF} = 5$), 122.10 (d, C_o, $J_{CF} = 8$), 115.93 (d, C_m, $J_{CF} = 22$), 115.56 (d, C_m, $J_{CF} = 22$), 113.57 (d, C_o, $J_{CF} = 7$), 53.56 (secondary CH_2), 51.96 (tertiary CH_2), 51.44 (tertiary CH_2), 42.26 (secondary CH_2). ^{19}F NMR (C_6D_6): δ -121.76 (7 lines, 2, tertiary), -128.01 (7 lines, 2, secondary). HRMS. Calcd for $C_{30}H_{30}F_4N_4$: 522.2407. Found (FAB): 522.2424.

(4-t-BuC$_6$H$_4$NHCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$N(4-t-BuC$_6$H$_4$)$_2$. This compound was obtained as a byproduct in the preparation of **1c** in a reaction run on a 25 mmol scale. It is the product immediately above **1c** on a TLC plate. It was isolated by column chromatography and then recrystallized from cold hexane; yield 2.65 g (3.93 mmol, 16%): ^{1}H NMR (C_6D_6): δ 7.28 (d, 4, secondary meta), 7.22 (d, 4, tertiary meta), 7.08 (d, 4, tertiary ortho), 6.53 (d, 4, secondary ortho), 3.97 (br s, 2, NH), 3.71 (t, 2, tertiary CH_2), 2.86 (t, 4, secondary CH_2), 2.57 (t, 2, tertiary CH_2), 2.34 (t, 4, secondary CH_2), 1.33 (s, 18, t-Bu), 1.27 (s, 18, t-Bu). ^{13}C NMR ($CDCl_3$): δ 145.68 (C_{ipso}), 145.12 (C_{ipso}), 143.70 (C_p), 139.89 (C_p), 126.00 (C_m), 125.81 (C_m), 120.05 (C_o), 112.64 (C_o), 53.93 (secondary CH_2), 52.02 (tertiary CH_2), 50.85 (tertiary CH_2), 42.70 (secondary CH_2), 34.16, 33.85, 31.60, 31.48 (t-Bu). Anal. Calcd for $C_{46}H_{66}N_4$: C, 81.85; H, 9.85; N, 8.30. Found: C, 81.80; H, 9.93; N, 8.24.

[3,5-(4-t-BuC$_6$H$_4$)$_2$C$_6$H$_3$)NHCH$_2$CH$_2$]$_2$NCH$_2$CH$_2$N(3,5-(4-t-BuC$_6$H$_4$)$_2$C$_6$H$_3$)$_2$. This compound was obtained as a byproduct in the preparation of **1f**. It remains in toluene solution and dissolves in ether when the ether extraction is performed. It crystallizes out of ether in pure form; yield 292 mg (0.194 mmol, 4%): ^{1}H NMR ($CDCl_3$): δ 7.47 (d, 8, 3,5-aryl), 7.41 (s, 2, tertiary para), 7.38 (m, 12, 3,5-aryl and tertiary ortho), 7.34 (d, 8, 3,5-aryl), 7.31 (d, 8, 3,5-aryl), 7.03 (s, 2, secondary para), 6.65 (s, 4, secondary ortho), 4.48 (br s, 2 NH), 4.13 (t, 2, tertiary CH_2), 3.28 (br s, 4, secondary CH_2), 3.05 (t, 2, tertiary CH_2), 2.94 (t, 4, secondary CH_2), 1.31 (s, 36, t-Bu), 1.28 (s, 36, t-Bu). ^{13}C NMR ($CDCl_3$): δ 150.20 (3,5-C_p), 149.72 (3,5-C_p), 148.74 (C_{ipso}), 148.62 (C_{ipso}), 142.65 (C_m), 142.32 (C_m), 138.70 (3,5-C_{ipso}), 138.05 (3,5-C_{ipso}), 126.74 (3,5-C_m), 126.68 (3,5-C_m), 125.60 (3,5-C_o), 125.30 (3,5-C_o), 119.65 (C_p), 118.61 (C_p), 115.78 (C_o), 110.44 (C_o), 53.94 (secondary CH_2), 52.59 (tertiary CH_2), 51.33 (tertiary CH_2), 41.91 (secondary CH_2), 34.52 (t-Bu), 34.49 (t-Bu), 31.44 (t-Bu), 31.37 (t-Bu). HRMS. Calcd for $C_{110}H_{130}N_4$: 1507.0296. Found (FAB): 1507.0255.

[(C$_6$H$_5$NCH$_2$CH$_2$)$_3$N]MoNMe$_2$ (2a). A 250 mL Schlenk flask was charged with $Mo(NMe_2)_4$ (1.95 g, 7.15 mmol), $(C_6H_5NHCH_2CH_2)_3N$ (1.87 g, 5.00 mmol), and toluene (80 mL). The reaction mixture was heated under argon at 60 °C for 2 days then filtered through Celite to remove any insoluble decomposition products. The solvent was removed, and the residue was washed with pentane. The pentane-insoluble black material was collected, dried in vacuo, and found to be pure by ^{1}H NMR; yield 2.08 g (4.06 mmol, 81%): ^{1}H NMR (C_6D_6): δ 7.15 (t, 6, meta), 6.85 (t, 3, para), 6.75 (d, 6, ortho), 3.43 (t, 6, CH_2), 3.37 (s, 6, NMe_2), 2.67 (t, 6, CH_2).

[(4-FC$_6$H$_4$NCH$_2$CH$_2$)$_3$N]MoNMe$_2$ (2b). A 250 mL Schlenk flask was charged with $Mo(NMe_2)_4$ (2.84 g, 10.5 mmol), $(4\text{-}FC_6H_4NHCH_2CH_2)_3N$ (3.90 g, 9.10 mmol), and toluene (100 mL). The reaction was heated to 70 °C for 2 days on the Schlenk line. Solids which formed during the reaction were filtered off, and the solution was concentrated to dryness. The residue was washed with pentane, and dried in vacuo to yield 4.80 g (8.48 mmol, 93%) of nearly black crystals. Analytically pure material was obtained by recrystallization from mixtures of DME and pentane at -40 °C: ^{1}H NMR (C_6D_6): δ 6.76 (t, 6, H_m), 6.45 (dd, 6, H_o), 3.25 (s, 6, NCH_3), 3.23 (t, 6, CH_2), 2.60 (t, 6, CH_2). ^{13}C NMR (C_6D_6): δ 159.04 (d, C_p, $J_{CF} = 239$), 158.91 (C_{ipso}), 125.07 (d, C_o, $J_{CF} = 7$), 115.14 (d, C_m, $J_{CF} = 21$), 63.91 (br, NCH_3 and CH_2), 57.04 (CH_2). ^{19}F NMR (C_6D_6): δ -123.40. Anal. Calcd for $C_{26}H_{30}F_3N_5Mo$: C, 55.22; H, 5.35; N, 12.38. Found: C, 55.08; H, 5.35; N, 12.43.

[(3,5-Me$_2$C$_6$H$_3$NCH$_2$CH$_2$)$_3$N]MoNMe$_2$ (2d). A 250 mL Schlenk flask was charged with $Mo(NMe_2)_4$ (1.77 g, 6.50 mmol), $(3,5\text{-}Me_2C_6H_3NHCH_2CH_2)_3N$ (2.29 g, 5.00 mmol), and toluene (125 mL). The reaction was heated to 70 °C for 2 days on the Schlenk line. Toluene was removed, and the residue was washed with pentane until the pentane washings were colorless. The resulting solid was collected and recrystallized from ether/pentane to yield 1.90 g (3.18 mmol, 64%) of dark purple crystals: ^{1}H NMR (C_6D_6): δ 6.51 (s, 3, H_p), 6.44 (s, 6, H_o), 3.49 (t, 6, CH_2), 3.37 (s, 6, NCH_3), 2.69 (t, 6, CH_2). 2.21 (s, 18, $ArCH_3$). ^{13}C NMR (C_6D_6): δ 137.18, 128.80, 122.91, 121.91 (all aryl C), 63.70 (NCH_3), 62.68, 57.14 (backbone methylenes), 21.74, ($ArCH_3$). Anal. Calcd for $C_{32}H_{45}N_5Mo$: C, 64.52; H, 7.61; N, 11.76. Found: C 64.26; H, 7.64; N, 11.52.

[(3,5-Ph$_2$C$_6$H$_3$NCH$_2$CH$_2$)$_3$N]MoNMe$_2$ (2e). A 100 mL Schlenk flask was charged with $(3,5\text{-}Ph_2C_6H_3NHCH_2CH_2)_3N$ (1.45 g, 1.75 mmol), $Mo(NMe_2)_4$ (673 mg, 2.47 mmol), and toluene (50 mL). The flask was transferred to the Schlenk line and heated to 70 °C for 2 days. Toluene was removed, and the residue was dissolved in THF. Insoluble impurities were filtered off, and the solution was concentrated to give 1.87 g. (96%) of crude material. Spectroscopically pure material can be obtained by recrystallization from a mixture of THF and pentane followed by three washings of the crystals with pentane: ^{1}H NMR indicates 2 molecules of THF in the crystals: ^{1}H NMR (C_6D_6): δ 7.57$-$7.53 (m, 12), 7.47 (t, 3), 7.13 (m, 18), 7.09 (d, 6), 3.55 (t, 6, CH_2), 3.44 (s, 6, NMe_2), 2.76 (t, 6, CH_2). ^{13}C NMR (C_6D_6): δ 142.49, 142.45, 127.82, 127.69, 121.95, 120.02, 63.46, 57.15.

[(C$_6$H$_5$NCH$_2$CH$_2$)$_3$N]MoCl (3a). Solid $MoCl_4(THF)_2$ (2.41 g, 6.30 mmol) was added to a solution of $(C_6H_5NHCH_2CH_2)_3N$ (2.25 g, 6.0 mmol) in THF (120 mL) resulting in an immediate color change to dark red followed by the precipitation of a red oil. The reaction mixture was cooled to -35 °C. A solution of methylmagnesium chloride (6 mL, 3.0 M in THF, 18 mmol) was diluted to 20 mL, cooled to -35 °C, and then added dropwise to the reaction mixture. The reaction mixture was allowed to warm to room temperature with stirring overnight. The red product precipitated out in analytically pure form. It was collected, washed once with THF, twice with ether, and dried in vacuo; yield 1.71 g (3.40 mmol, 57%): ^{1}H NMR ($CDCl_3$): δ 16.36 (H_m), 9.06 (H_o), 1.47 (H_p), -19.30 (CH_2), -77.78 (CH_2). Anal. Calcd for $C_{24}H_{27}ClN_4Mo$: C, 57.32; H, 5.41; N, 11.14; Cl, 7.05. Found: C 57.08; H, 5.37; N, 11.19; Cl, 7.11.

[(4-FC$_6$H$_4$NCH$_2$CH$_2$)$_3$N]MoCl (3b). A 250 mL flask was charged with $MoCl_4(THF)_2$ (1.91 g, 5.00 mmol), THF (60 mL), and $(4\text{-}FC_6H_4NHCH_2CH_2)_3N$ (2.14 g, 2.10 mmol). The reaction mixture turned deep red immediately. It was stirred for 10 min and then cooled to -35 °C. MeMgCl (5.0 mL, 3.0 M in THF, 15 mmol) was diluted to 20 mL, cooled to -35 °C, and added dropwise to the reaction mixture. The reaction was stirred at room temperature for 2 h and then allowed to sit overnight without further stirring. 1,4-Dioxane (8 mL) was added, followed by another hour of stirring. The reaction mixture was then

filtered through Celite and concentrated to 15 mL. Red crystals formed during the process. The crystals were collected, washed with ether, and dried in vacuo; yield 1.77 g (3.17 mmol, 63%): ^{1}H NMR ($CDCl_3$): δ 15.64 (H_m), 9.41 (H_o), −17.71 (CH_2), −80.07 (CH_2). ^{19}F NMR (THF): δ −110.5. Anal. Calcd for $C_{24}H_{24}F_3ClN_4Mo$: C, 51.77; H, 4.34; N, 10.06; Cl, 6.37. Found: C, 51.86; H, 4.37; N, 9.95; Cl, 6.31.

Synthesis of 3b from 2b. A solution of **2b** (4.80 g, 8.48 mmol) in THF (50 mL) was cooled to −40 °C. 2,6-Lutidinium chloride (1.22 g, 8.48 mmol) was added as a solid, and the stirred reaction was allowed to warm to room temperature over a period of 2 h, during which time the color turned dark red. THF was removed in vacuo, and the crude residue was washed with ether, toluene, and pentane. The red product (4.08 g, 7.33 mmol, 86%) was collected on a frit and dried in vacuo.

[(4-t-Bu$C_6H_4NCH_2CH_2)_3$N]MoCl (3c). A 500 mL round-bottom flask was charged with (4-t-Bu$C_6H_4NCH_2CH_2)_3$N (7.06 g, 13.0 mmol) and $MoCl_4(THF)_2$ (4.97 g, 13.0 mmol). THF (150 mL) was added, and the reaction mixture was stirred at room temperature for 30 min to yield a dark red solution and then cooled to −40 °C for 2 h. MeMgCl (13 mL, 3.0 M in THF, 39 mmol) was diluted to 50 mL, cooled to −40 °C, transferred to a precooled addition funnel, and added dropwise to the reaction mixture over a period of 30 min. After the reaction mixture was stirred overnight at room temperature, THF was removed on the rotary evaporator. The residue was dissolved in toluene,then 4 mL of 1,4-dioxane (4.5 g, 47 mmol) was added, and the mixture was stirred for 1 h. Filtration through Celite removed $MgCl_2$(dioxane). Toluene was removed in vacuo, and the residue was extracted with ether. The ether-insoluble red product was collected on a frit and dried in vacuo; yield 5.51 g (8.21 mmol, 63%): ^{1}H NMR (C_6D_6): δ 15.66 (H_m), 9.50 (H_o), 1.48 (t-Bu), −17.74 (CH_2), −75.96 (CH_2). Anal. Calcd for $C_{36}H_{51}ClN_4Mo$: C, 64.42; H, 7.66; N, 8.35; Cl, 5.28. Found: C, 64.13; H, 7.48; N, 8.28; Cl, 5.34.

[(3,5-Me$_2C_6H_3NCH_2CH_2)_3$N]MoCl (3d). This material was prepared in a manner similar to that used to prepare **3a** starting from (3,5-$Me_2C_6H_3NHCH_2CH_2)_3$N (3.67 g, 8.00 mmol), $MoCl_4(THF)_2$ (3.06 g, 8.00 mmol), and MeMgCl (8.0 mL, 3.0 M in THF, 24 mmol). Pure product crystallized out of the reaction mixture; yield 2.89 g (4.92 mmol, 62%): ^{1}H NMR ($CDCl_3$): δ 8.99 (H_o), 1.76 (H_p), 1.66 (CH_3), −16.15 (CH_2), −73.89 (CH_2). Anal. Calcd for $C_{30}H_{39}ClN_4Mo$: C, 61.38; H, 6.70; N, 9.54; Cl, 6.04. Found: C, 61.04; H, 6.62; N, 9.33; Cl, 6.17.

Synthesis of 3d from 2d. This material was prepared in a manner similar to that described for the synthesis of **3b** from **2b**, starting from **2d** (595 mg, 1.00 mmol) and 2,6-lutidinium chloride (144 mg, 1.00 mmol). The product precipitated out of THF as it formed; yield 374 mg (0.64 mmol, 64%).

[(3,5-Ph$_2C_6H_3NCH_2CH_2)_3$N]MoCl (3e). $MoCl_4(THF)_2$ (573 mg, 1.50 mmol) was added as a solid to a solution of (3,5-$Ph_2C_6H_3NHCH_2CH_2)_3$N (1.25 g, 1.50 mmol) in THF (50 mL). All initially dissolved to give a red solution, but after stirring for 5 min a large amount of red precipitate formed. After cooling to −35 °C, the precipitate dissolved. MeMgCl (1.5 mL, 3.0 M in THF, 4.5 mmol) was diluted to 15 mL, and cooled to −35 °C. The solution of MeMgCl was then added dropwise to the reaction mixture, resulting in a color change from red to orange. After allowing the reaction to warm to room temperature with stirring, 1,4-dioxane (2 mL) was added, resulting in the precipitation of a white powder, which was filtered off. Removal of THF on the rotary evaporator yielded an orange solid, which could not be redissolved in any solvent, including THF. The product was collected, washed with THF, and dried in vacuo; yield 546 mg (0.57 mmol, 38%): ^{1}H NMR (C_6D_6): δ 9.31, 7.56, 7.19, 7.04, 2.52, 0.18, −15.26, −76.08 (all br s). Anal. Calcd for $C_{60}H_{51}ClN_4Mo$: C, 75.11; H, 5.36; N, 5.84; Cl, 3.70. Found: C, 75.13; H, 5.44; N, 5.69; Cl, 3.62.

[{3,5-(4-t-Bu$C_6H_4)_2C_6H_3NCH_2CH_2\}_3$N]MoCl (3f). A sample of {3,5-(4-t-$BuC_6H_4)_2C_6H_3NHCH_2CH_2\}_3$N (3.04 g, 2.60 mmol) was dissolved in 150 mL THF with vigorous heating. $MoCl_4(THF)_2$ (0.993 g, 2.6 mmol) was added as a solid to give a dark red solution, which was cooled to −35 °C. MeMgCl (2.6 mL, 3.0 M in THF, 7.8 mmol) was diluted to 10 mL, and also cooled to −35 °C. The solution of MeMgCl was added dropwise to the reaction mixture, resulting in a color change from red to orange. After allowing the reaction to warm to room temperature with stirring, 1,4-dioxane (2 mL) was added, resulting in the precipitation of a white powder. THF was removed on the rotary evaporator, and the residue was redissolved in toluene. $MgCl_2$(dioxane) was filtered off, and the toluene was removed. The product was suspended in ether and collected on a frit, although the finely divided nature of the product rendered this a slow process; yield 1.47 g (1.13 mmol, 44%). ^{1}H NMR (C_6D_6): δ 7.82, 7.43, 2.57, 1.22(t-Bu), −16.51(CH_2), −70.90(CH_2). Anal. Calcd for $C_{84}H_{99}ClN_4Mo$: C, 77.84; H, 7.70; N, 4.32; Cl, 2.74. Found: C, 77.91; H, 7.62; N, 4.19; Cl, 2.82.

[($C_6H_5NCH_2CH_2)_3$N]MoMe (4a). A 100 mL round-bottom flask was charged with $MoCl_4(THF)_2$ (1.07 g, 2.8 mmol), ($C_6H_5NHCH_2CH_2)_3$N (1.05 g, 2.8 mmol) and THF (30 mL). The mixture was stirred at room temperature for 15 min, during which time it turned dark red. The mixture was cooled to −40 °C, methyllithium (8 mL, 1.4 M in ether, 11.2 mmol) was added dropwise, and the reaction was allowed to warm to room temperature over a period of 1 h while being stirred. The THF was removed, and the residue was extracted with 50 mL toluene. Gentle heating was required to dissolve all of the complex. LiCl and some purple insoluble material were removed by filtration. Toluene was removed, and the residue was extracted with ether. The insoluble product was collected, washed with ether and pentane, and dried in vacuo to yield 689 mg (1.43 mmol, 51%) of dark orange powder. Analytically pure material could be obtained by recrystallization from cold toluene. ^{1}H NMR (C_6D_6): δ 16.00 (H_m), 3.94 (H_o), −1.06 (H_p), −11.02 (CH_2), −66.48 (CH_2). Anal. Calcd for $C_{25}H_{30}N_4Mo$: C, 62.24; H, 6.27; N, 11.61. Found: C 62.39; H, 6.14; N, 11.42.

Conversion of 4a to 3a. A solution of **4a** (724 mg, 1.50 mmol) in THF (50 mL) was cooled to −40 °C. 2,6-Lutidinium chloride (215 mg, 1.50 mmol) was added as a solid, and the reaction was allowed to warm to room temperature while being stirred over a period of 1 h, during which time some red product began to precipitate out of solution. The solvent was removed in vacuo, and the residue was extracted with ether. The insoluble product was collected, washed with ether and pentane, and dried in vacuo to give 609 mg (1.21 mmol, 81%) of orange solid. The product could be recrystallized from a mixture of dichloromethane and pentane at −40 °C.

[(4-F$C_6H_4NCH_2CH_2)_3$N]MoMe (4b). This complex was synthesized in a manner similar to that used to prepare **4a** starting from $MoCl_4(THF)_2$ (802 mg, 2.10 mmol), (4-$FC_6H_4NHCH_2CH_2)_3$N (900 mg, 2.10 mmol) and MeLi (6 mL). The red solid was recrystallized from toluene to yield 709 mg (1.32 mmol, 63%) of red crystals in two crops. ^{1}H NMR (C_6D_6): δ 16.28 (H_m), 4.15 (H_o), −10.50 (CH_2), −72.60 (CH_2). ^{19}F NMR (THF): δ −104.8. Anal. Calcd for $C_{25}H_{27}F_3N_4Mo$: C, 55.97; H, 5.07; N, 10.44. Found: C, 55.74; H, 5.08; N, 10.39.

Conversion of 4b to 3b. The procedure was the same as for the conversion of **4a** to **3a,** starting from **4b** (230 mg, 0.43 mmol) and 2,6-lutidinium chloride (61 mg, 0.43 mmol). The red product (200 mg, 0.36 mmol, 84%) was obtained after removal of THF and washing the crude residue with ether and pentane.

[(4-t-Bu$C_6H_4NCH_2CH_2)_3$N]MoMe (4c). This complex was synthesized in a manner similar to that used to prepare **4a** starting from $MoCl_4(THF)_2$ (802 mg, 2.10 mmol), (4-t-$BuC_6H_4NHCH_2CH_2)_3$N (1.14 g, 2.10 mmol) and MeLi (6 mL). Red crystals were collected in one crop (943 mg, 1.45 mmol, 69%) upon recrystallization from a mixture of toluene and pentane at −40 °C. ^{1}H NMR (C_6D_6): δ 16.16 (H_m), 3.88 (H_o), 1.57 (t-Bu), −11.48 (CH_2), −70.10 (CH_2). Anal. Calcd for $C_{37}H_{54}N_4Mo$: C, 68.29; H, 8.36; N, 8.61. Found: C, 68.11; H, 8.28; N, 8.44.

Conversion of 4c to 3c. The procedure was the same as for the conversion of **4a** to **3a** starting from **4c** (488 mg, 0.75 mmol) and 2,6-lutidinium chloride (108 mg, 0.75 mmol). The red solid was recrystallized from a mixture of toluene and pentane at −40 °C to yield 371 mg (0.55 mmol, 74%) of red crystals in one crop.

[(3,5-Me$_2C_6H_3NCH_2CH_2)_3$N]MoMe (4d). This complex was synthesized in a manner similar to that used to prepare **4a** starting from $MoCl_4(THF)_2$ (1.07 g, 2.80 mmol), (3,5-$Me_2C_6H_3NHCH_2CH_2)_3$N (1.28 g, 2.80 mmol) and MeLi (8 mL). An orange powder was obtained after removing toluene and washing the residue with ether and pentane (1.01 g, 1.78 mmol, 63%). Analytically pure material could be obtained by recrystallization from toluene. ^{1}H NMR (C_6D_6): δ 3.80 (H_o), 1.07

(CH_3), −0.82 (H_p), −11.59 (CH_2), −68.78 (CH_2). Anal. Calcd for $C_{31}H_{42}N_4Mo$: C, 65.71; H, 7.47; N, 9.89. Found: C, 65.76; H, 7.43; N, 9.98.

Conversion of 4d to 3d. The procedure was the same as for the conversion of **4a** to **3a** starting from **4d** (670 mg, 1.20 mmol) and 2,6-lutidinium chloride (172 mg, 1.20 mmol). The orange product crystallized out of THF, and was isolated by filtering the crude reaction mixture after cooling the mixture to −40 °C; yield 543 mg,(0.93 mmol, 77%). Analytically pure material was obtained by recrystallization from a mixture of dichloromethane and pentane at −40 °C.

[($C_6H_5NCH_2CH_2)_3N$]WCl (5a). A solution of $(C_6H_5NHCH_2CH_2)_3N$ (1.50 g, 4.00 mmol) in 50 mL THF was heated with a heat gun until the solvent was almost boiling. WCl_4(dme) (1.66 g, 4.00 mmol) was added as a solid in 200 mg portions to the stirring solution such that all dissolved before another portion was added. A yellow precipitate formed upon completion of the addition. After stirring at room temperature for 15 min, the reaction mixture was cooled to −35 °C. MeMgCl (4.0 mL, 3.0 M in THF, 12.0 mmol) was diluted to 20 mL, cooled to −35 °C, and added slowly to the reaction mixture. The yellow precipitate completely dissolved to give an orange solution. The reaction was stirred overnight at room temperature during which time the product precipitated out as an orange powder. It was collected, washed with THF and ether, and dried in vacuo; yield 570 mg (0.96 mmol, 24%). ^{1}H NMR (CD_2Cl_2): δ 18.13 (s, 6, H_o), 17.34 (d, 6, H_m), 3.12 (t, 3, H_p), −25.64 (br s, 6, CH_2), −50.97 (br s, 6, CH_2). Anal. Calcd for $C_{24}H_{27}ClN_4W$: C, 48.79; H, 4.61; N, 9.48; Cl, 6.00. Found: C, 48.85; H, 4.71; N, 9.43; Cl, 5.84.

[(4-$FC_6H_4NCH_2CH_2)_3N$]WCl (5b). A solution of $(4\text{-}FC_6H_4NHCH_2CH_2)_3N$ (1.72 g, 4.00 mmol) in 50 mL THF was heated with a heat gun until the solvent was almost boiling. WCl_4(DME) (1.66 g, 4.0 mmol) was added as a solid in 200 mg portions to the stirring solution such that all dissolved before another portion was added. No precipitate was observed. After stirring at room temperature for 15 min, the reaction mixture was cooled to −35 °C. MeMgCl (4.0 mL, 3.0 M in THF, 12.0 mmol) was diluted to 20 mL, cooled to −35 °C, and added slowly to the reaction mixture. The reaction was stirred overnight at room temperature, then 6 mL of 1,4-dioxane were added, and the reaction was stirred for another 30 min. The reaction mixture was filtered through Celite and concentrated to 15 mL, which resulted in the crystallization of the red product. The crystals were collected, washed once with THF, twice with ether, and dried in vacuo; yield 732 mg (1.13 mmol, 28%). ^{1}H NMR (CD_2Cl_2): δ 18.79 (s, 6, H_o), 16.93 (d, 6, H_m), −24.36 (br s, 6, CH_2), −52.77 (br s, 6, CH_2). ^{19}F NMR (THF): δ −108.47. Anal. Calcd for $C_{24}H_{24}ClF_3N_4W$: C, 44.71; H, 3.75; N, 8.69; Cl, 5.50. Found: C, 44.59; H, 3.81; N, 8.61; Cl, 5.43.

[(4-t-$BuC_6H_4NCH_2CH_2)_3N$]WCl (5c). This material was prepared by a method similar to that used to prepare **3c** starting from $(4\text{-t-}BuC_6H_4NCH_2CH_2)_3N$ (2.36 g, 4.35 mmol), WCl_4(DME) (1.99 g, 4.80 mmol), and MeMgCl (4.5 mL, 3.0 M in THF, 13.5 mmol). The only difference is that WCl_4(DME) was added slowly to a solution of the ligand prior to cooling and addition of MeMgCl; yield 1.41 g. (1.86 mmol, 43%). ^{1}H NMR (C_6D_6): δ 17.34 (s, 6, ortho), 17.04 (s, 6, meta), 2.03 (s, 27, t-Bu), −25.65 (br s, 6, CH_2), −49.8 (br s, 6, CH_2). Anal. Calcd for $C_{36}H_{51}N_4ClW$: C, 56.96; H, 6.77; N, 7.38; Cl, 4.67. Found: C 57.11; H, 6.72; N, 7.29; Cl, 4.61.

[(3,5-$Me_2C_6H_3NCH_2CH_2)_3N$]WCl (5d). This material was synthesized in a manner similar to that used to prepare **5a** starting from $(3,5\text{-}Me_2NHCH_2CH_2)_3N$ (2.29 g, 5.00 mmol), WCl_4(DME) (2.07 g, 5.00 mmol), and MeMgCl (5.0 mL, 3.0 M in THF, 15 mmol); yield 1.38 g (2.04 mmol, 41%). ^{1}H NMR (CD_2Cl_2): δ 18.92 (s, 6, H_o), 3.62 (s, 3, H_p), 3.05 (s, 18, 3,5-Me_2), −23.93 (br s, 6, CH_2), −50.72 (br s, 6, CH_2). Anal. Calcd for $C_{30}H_{39}ClN_4W$: C, 53.38; H, 5.82; N, 8.30; Cl, 5.25. Found: C, 53.22; H, 5.74; N, 8.19; Cl, 5.21.

[(3,5-$Ph_2C_6H_3NCH_2CH_2)_3N$]WCl (5e). This material was synthesized in a manner similar to that used to prepare **5b**, starting from $(3,5\text{-}Ph_2C_6H_3NHCH_2CH_2)_3N$ (416 mg, 0.500 mmol), WCl_4(DME) (208 mg, 0.500 mmol), and MeMgCl (0.5 mL, 3.0 M in THF diluted to 2 mL, 1.5 mmol); yield 184 mg (0.175 mmol, 35%). Anal. Calcd for $C_{60}H_{51}ClN_4W$: C, 68.81; H, 4.91; N, 5.35; Cl, 3.38. Found: C, 69.11; H, 4.92; N, 5.28; Cl, 3.43.

[(4-t-$BuC_6H_4NCH_2CH_2)_3N$]WMe (6c). WCl_4(DME) (934 mg, 2.25 mmol) was added to a solution of $(4\text{-t-}BuC_6H_4NCH_2CH_2)_3N$ (1.22 g, 2.25 mmol) in 20 mL of THF. The reaction mixture was stirred at room temperature for 30 min to yield a pale orange solution and then cooled to −35 °C for 2 h. MeMgCl (3 mL, 3.0 M in THF, 9 mmol) was diluted to 15 mL, cooled to −35 °C, and then added dropwise to the reaction mixture over 10 min. The reaction mixture was stirred 1 h at room temperature, and THF was removed on the rotary evaporator. The residue was dissolved in 30 mL of toluene, and 1.2 mL 1,4-dioxane (1.35 g, 14.0 mmol) was added. The mixture was stirred for 30 min and then filtered through Celite to remove $MgCl_2$(dioxane). Toluene was removed in vacuo, and the residue was dissolved in ether. The mixture was cooled to −35 °C to give orange crystals, which were washed with pentane and dried in vacuo; yield 275 mg (0.370 mmol, 22%). ^{1}H NMR (C_6D_6): δ 17.98 (s, 6, C_m), 12.79 (s, 6, C_o), 1.97 (s, 27, t-Bu), −21.61 (br s, 6, CH_2), −49.6 (br s, 6, CH_2).

Cyclic Voltammetry. Electrochemical measurements were performed using a Bioanalytical Systems CV-50W potentiostat interfaced to a VC-2 voltammetry cell. All measurements were performed in THF using Bu_4NPF_6 as the supporting electrolyte.

Platinum disk working and platinum wire auxiliary electrodes were employed. The nonaqueous reference electrode was assembled from the kit provided by BAS. A 0.1 M solution of Bu_4NPF_6 in acetonitrile was prepared, and 17 mg of $AgNO_3$ were added to 10 mL of this solution to produce a 0.01 M solution of Ag^+ ion. This solution was stored in the drybox freezer when not in use in order to prevent light-induced decomposition (brown color), but warmed to room temperature again before use. The reference electrode was prepared by filling the electrode body with Ag^+ ion solution and replacing the silver wire. When not in use, the reference electrode body was filled with a 0.1 M solution of Bu_4NPF_6 in CH_3CN, and the entire electrode was stored in a stoppered Schlenk tube containing electrolyte solution. The sweep rate employed was 500 mV/s.

All analyte solutions consisted of 1.00 g of Bu_4NPF_6 dissolved in 6 mL of THF (0.43 M solution). A typical sample size was 50 mg for compounds with molecular weights on the order of 1000. A standard solution of ferrocene was run at the start of each day, and the oxidation potential was measured. All other measurements were referenced to the ferrocene/ferrocenium couple as recommended by IUPAC.[72] The rest potential of every analyte solution was measured using the function of the same name under the Control menu of the BAS software. Separation between the anodic and cathodic peaks for a well-behaved process was usually ∼100 mV.

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Supporting Information Available: Text describing further details of syntheses and Figures 1S, 2S, and 3S showing CV's of **3b**, **3d**, and **3c**, respectively . This material is available free of charge via the Internet at http://pubs.acs.org.

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