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Synthesis of Aryl-Substituted Triamidoamine Ligands and Molybdenum(IV) Complexes that Contain Them

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*Summary: Compounds of the type [(ArNHCH$_2$CH$_2$)$_3$N] (Ar = phenyl (H$_3$[**1a**]), 4-fluorophenyl (H$_3$[**1b**]), 4-tert-butylphenyl (H$_3$[**1c**]), 3,5-dimethylphenyl (H$_3$[**1d**]), 2-methylphenyl (H$_3$[**1e**]), and mesityl (H$_3$[**1f**])) have been synthesized by the Pd-catalyzed coupling of (H$_2$NCH$_2$CH$_2$)$_3$N with aryl bromides. Molybdenum methyl complexes containing [**1a**−**d**]$^{3-}$ can be prepared by adding 4 equiv of methyllithium to a mixture of the ligand and MoCl$_4$(THF)$_2$; the corresponding chloride complexes are obtained upon addition of 2,6-lutidinium chloride to the methyl complexes.*

In the past several years we have prepared a large variety of transition metal complexes that contain triamidoamine ligands, [(RNCH$_2$CH$_2$)$_3$N]$^{3-}$ (R = SiMe$_3$[1] or C$_6$F$_5$[2]), and explored their chemistry.[3] Ligands of this type have proven useful for stabilizing trigonal bipyramidal species in which the apical position is sterically protected against bimolecular decomposition reactions and have given rise to a number of unusual species (e.g., molybdenum or tungsten terminal phosphido and arsenido complexes[4]) or reactions (e.g., a demonstration that certain molybdenum and tungsten alkyl complexes decompose via α-elimination by as much as 6 orders of magnitude faster than via β-elimination[5,6]). We have been particularly interested in the ability of triamidoamine molybdenum complexes to bind and activate dinitrogen.[2,7−10] Unfortunately, both [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]$^{3-}$ and [(C$_6$F$_5$NCH$_2$CH$_2$)$_3$N]$^{3-}$ suffer from some disadvantages in certain circumstances. For example, we have begun to encounter chemistry at the amido nitrogen in [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]$^{3-}$ complexes, e.g., exchange of the trimethylsilyl group for a methyl group.[8] The perfluorophenyl group, on the other hand, we believe tends to be attacked by strong nucleophiles. Therefore we have been looking for a method of preparing ligands that contain ordinary aryl substituents. We report here a potentially general approach to such ligands using a palladium-catalyzed coupling reaction between an aryl halide and an amine.[11−17]

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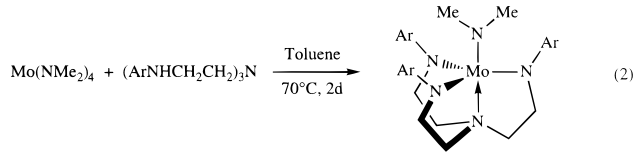
The generic form of the reaction is shown in eq 1.

$$N(CH_2CH_2NH_2)_3 + 3ArBr \xrightarrow[NaO\text{-}t\text{-}Bu,\ toluene,\ heat]{Pd_2(dba)_3,\ rac\text{-}BINAP} N(CH_2CH_2NHAr)_3 \quad (1)$$

Under the reaction conditions reported by Buchwald,[15] an excess of amine is used and the catalyst loading is 0.5 mol %. We use 3 equiv of ArBr and a catalyst loading of 3% per mole of $N(CH_2CH_2NH_2)_3$. The $(ArNHCH_2CH_2)_3N$ species that have been prepared on a scale of ~5−15 g include those in which the Ar group is phenyl itself (H_3[**1a**]; 57% yield),[18] 4-fluorophenyl (H_3[**1b**]; 27% yield), 4-*tert*-butylphenyl (H_3[**1c**]; 49% yield), 3,5-dimethylphenyl (H_3[**1d**]; 58% yield), 2-methylphenyl (H_3[**1e**]; 90% yield), and 2,4,6-trimethylphenyl (H_3[**1f**]; 79% yield). The major byproduct when the Ar group is relatively small is that in which one of the arms is doubly arylated; for example, $(PhNHCH_2CH_2)_2N(CH_2CH_2NPh_2)$ usually comprises ~15% of the total product mass. The desired $(ArNHCH_2CH_2)_3N$ product can be separated from $(ArNHCH_2CH_2)_2N(CH_2CH_2NAr_2)$ by column chromatography on silica gel. The product mixture in the case of H_3[**1b**] contains numerous other unidentified side products besides $(ArNHCH_2CH_2)_2N(CH_2CH_2NAr_2)$. Diarylation is *not* observed in the case of H_3[**1e**] and H_3[**1f**], even though higher temperatures are required (100 °C), presumably as a consequence of the greater steric demands of the 2-methylphenyl and mesityl substituents. The white products can be crystallized from mixtures of ether and pentane at −35 °C. They all dissolve readily in ether and, in the case of H_3[**1c**], also in pentane. During the course of this work the arylation of mono- and diamines (e.g., diethylenetriamine) under conditions similar to those reported here appeared in the literature.[19]

We have found that the most certain method of placing a $[(ArNCH_2CH_2)_3N]^{3-}$ ligand on Mo is the reaction between the free ligand and $Mo(NMe_2)_4$[20] (eq 2). The reaction between H_3[**1b**] or H_3[**1d**] and $Mo(NMe_2)_4$ requires 2 days at 70 °C. [**1b**]$Mo(NMe_2)$ (**2b**; 93% yield) and [**1d**]$Mo(NMe_2)$ (**2d**; 64% yield)[21] are obtained as purple-black diamagnetic crystalline solids (cf. $[(C_6F_5NCH_2CH_2)_3N]Mo(NMe_2)$[2]). They each react with 2,6-lutidinium chloride in THF to yield the respective chloride derivatives, [**1b**]MoCl (**4b**) and [**1d**]MoCl (**4d**) (see below). Compounds **4b** and **4d** are paramagnetic, red crystalline species with proton and (in the case of **4b**) fluorine NMR resonances that are shifted (generally to high field) and broadened. Nevertheless, NMR spectra are useful for diagnostic purposes. (See Supporting Information for details.)



Ar = 4-fluorophenyl (**2b**) or 3,5-dimethylphenyl (**2d**)

We felt that it should be possible to prepare $[(ArNCH_2CH_2)_3N]MoCl$ derivatives from the free ligand, $MoCl_4(THF)_2$, and triethylamine, as is the case for $[(C_6F_5NCH_2CH_2)_3N]MoCl$.[2] However, using NMR spectra of **4b** and **4d** as analytical probes, only low yields of the monochlorides were observed, and yields were not improved using DBU, KH, or proton sponge as the base. The direct reaction between $MoCl_4(THF)_2$ in THF or ether with $Li_3[(ArNCH_2CH_2)_3N]$ (prepared from the parent ligand and 3 equiv of an alkyllithium reagent) also did not yield significant quantities of the chloride derivatives. However, when the free ligands (H_3[**1a**], H_3[**1b**], H_3[**1c**], or H_3[**1d**]) were added to $MoCl_4(THF)_2$ in THF followed by 3 equiv of LiMe, the paramagnetic monochloride derivatives (**4a**−**4d**) were found to be formed in good yields after a period of 24 h. However, a second product was present in comparable amounts in each case after 1 h that was slowly converted in the reaction mixture to the monochloride over time. The second product was formed virtually exclusively after ~1 h in each case when 4 equiv of LiMe was employed. Analytical data are consistent with compounds **4** being the monochloride complexes, and with the products formed upon addition of 4 equiv of LiMe being the monomethyl derivatives, **3a**−**3d** (equation 3).[22] A more

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(18) A 1 L Schlenk flask was charged with $N(CH_2CH_2NH_2)_3$ (8.77 g, 60 mmol), bromobenzene (28.26 g, 180 mmol), $Pd_2(dba)_3$ (0.82 g, 0.9 mmol), *rac*-BINAP (1.49 g, 2.4 mmol), sodium *tert*-butoxide (19.97 g, 208 mmol), and toluene (500 mL). The reaction mixture was heated to 80 °C under dinitrogen for 20 h. It was then cooled to room temperature, and NaBr was removed by filtration. Toluene was removed in vacuo, 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.

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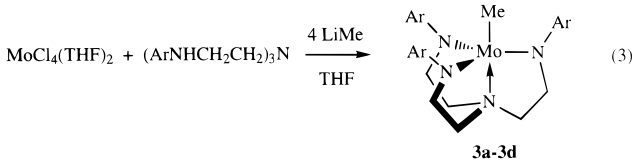
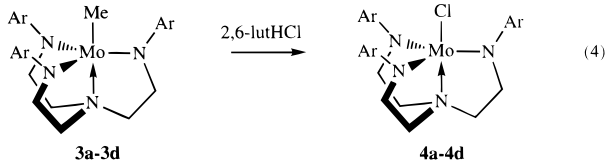
(21) A 250 mL Schlenk flask was charged with $Mo(NMe_2)_4$ (1.77 g, 6.5 mmol), **H_3[1d]** (2.29 g, 5.0 mmol), and toluene (125 mL). The reaction was heated to 70 °C for 2 days on the Schlenk line. Toluene was removed on the Rotovap, and the residue was washed with pentane until the pentane washings were colorless. The resulting solid was collected and recrystallized from ether/pentane to yield 1.9 g (3.18 mmol, 64%) of dark purple crystals.

(22) The synthesis of **3a** will be used as the example. A 100 mL round-bottom flask was charged with $MoCl_4(THF)_2$ (1.07 g, 2.8 mmol), **H_3[1a]** (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 of a 1.4 M solution in ether) 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 of toluene. Gentle heating was required to dissolve all of the complex. LiCl and some purple insoluble material were removed by filtration. Toluene 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 yield 689 mg (1.43 mmol, 51%) of dark orange powder.



(3)



(4)

reliable synthesis of **4a**−**4d** consists of addition of 2,6-lutidinium chloride to **3a**−**3d** in THF (eq 4).[23] A resonance cannot be observed for the methyl group in compounds **4**, as was also the case for related Mo(IV) triamidoamine methyl and alkyl complexes.[5,24] Addition of methyllithium to compounds **4** gives compounds **3** immediately.

The sequence of reactions that leads to **3** is not clear. A red solution is formed upon addition of the free ligands to $MoCl_4(THF)_2$, which suggests that some adduct is formed initially. We assume that at least partial binding of the potentially tetradentate ligands to Mo then allows smooth deprotonation of the amine nitrogens and alkylation of the metal by methyllithium without destructive reduction of the metal. At this stage it is not known how compounds **3** are converted into compounds **4** under the reaction conditions with time.

So far, we have not been able to prepare compounds of type **3** or **4** that contain the bulkier aryl-substituted ligands, [**1e**]$^{3-}$ or [**1f**]$^{3-}$, using methods analogous to those described above for compounds that contain [**1a**−**d**]$^{3-}$. When H_3[**1e**] or H_3[**1f**] is added to $MoCl_4(THF)_2$ in THF, a red "adduct" is not formed readily at room temperature. We propose that in the case of H_3[**1e**] and H_3[**1f**] steric inaccessibility of the aryl-substituted amines prevents formation of the required intermediate that reacts smoothly with methyllithium, and therefore addition of methyllithium to what amounts to a mixture of free ligand and $MoCl_4(THF)_2$ simply leads to decomposition.

Since we are especially interested in dinitrogen activation, we were pleased to find that when a solution of [**1b**]MoCl is added dropwise to a solution of sodium naphthalenide at −40 °C in THF under dinitrogen followed by addition of 1 equiv of Me_3SiCl, diamagnetic [**1b**]Mo−N═NSiMe_3 (**5b**) can be isolated in 56% yield (eq 5).[25] We presume that an intermediate in this

$$[\mathbf{1b}]\mathrm{MoCl} \xrightarrow[2.\ Me_3SiCl]{1.\ 2e,\ N_2,\ THF} [\mathbf{1b}]\mathrm{Mo{-}N{=}NSiMe_3} \quad (5)$$

reaction is the sodium salt of {[**1b**]Mo−N═N}$^-$ on the basis of literature precedent in the related reductions of compounds containing the $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ and $[(Me_3SiCH_2CH_2)_3N]^{3-}$ ligands.[2,9] A stretch at 1674 cm^{-1} in the infrared spectrum is characteristic of the diazenido functionality in complexes of this general type, and proton, carbon, and fluorine NMR are all consistent with the formulation of [**1b**]Mo−N═NSiMe_3.

We conclude that $(ArNHCH_2CH_2)_3N$ compounds are readily prepared using the palladium-catalyzed amine arylation reaction and that several analogues of known molybdenum triamidoamine complexes can be prepared under the right circumstances. "Direct" routes to alkyl complexes analogous to the methods disclosed here (eq 3) may prove to be a useful and short method of accessing other early transition metal alkyl complexes that contain a multidentate amido ligand. We will be exploring the utility of $[(ArNCH_2CH_2)_3N]^{3-}$ ligands in triamidoamine molybdenum chemistry, in particular with respect to binding and reducing dinitrogen. We also expect that these new ligands will be useful for a variety of other reactions involving triamidoamine transition metal complexes, and we will be especially interested in the extent to which the steric and electronic properties of the aryl substituents can be manipulated in order to control the chemistry at the apical site in pseudotrigonal bipyramidal species.

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Supporting Information Available: Experimental procedures and spectroscopic information for the reported compounds (8 pages). Ordering information is given on any current masthead page.

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(23) Synthesis of **4a**. A solution of **3a** (724 mg, 1.5 mmol) in THF (50 mL) was cooled to −40 °C, 2,6-lutidinium chloride (215 mg, 1.5 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. Some red product began to precipitate out of solution after 1 h. 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.

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(25) A solution of sodium naphthalenide (7.5 mL of a 0.17 M solution) was diluted to 20 mL and cooled to −40 °C. A separate solution of **4b** (278 mg, 0.5 mmol) was also dissolved in 10 mL of THF and cooled to −40 °C. The solution of **4b** was added dropwise to the naphthalenide solution, causing a color change from green to red. The reaction was allowed to warm to room temperature with stirring for 30 min, and then it was cooled back down to −40 °C and added slowly to a solution of Me_3SiCl (87 mg, 0.8 mmol) in THF (5 mL). The reaction mixture was allowed to warm to room temperature with stirring for 30 min, and then the THF was removed in vacuo. The residue was extracted with ether and filtered. The dark yellow filtrate was concentrated to dryness, and the resulting residue was washed with pentane and dried in vacuo; yield 175 mg (0.28 mmol, 56%).