Synthesis of Molybdenum and Tantalum Complexes that Contain Diamido/Donor Ligands of the Type $[(3,5\text{-}Cl_2C_6H_3NCH_2CH_2)_2NMe]^{2-}$ or $[(3,5\text{-}Cl_2C_6H_3NCH_2)_2C(2\text{-}C_5H_4N)(CH_3)]^{2-}$

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The palladium-catalyzed reaction between diethylenetriamine and 2 equiv of 3,5-dichlorobromobenzene gave $(3,5\text{-}Cl_2C_6H_3NHCH_2CH_2)_2NH$. Methylation of the central nitrogen with methyl iodide gave $(3,5\text{-}Cl_2C_6H_3NHCH_2CH_2)_2NMe$ ($H_2[Ar_{Cl}NNMe]$). The palladium-catalyzed reaction between $(H_2NCH_2)_2C(2\text{-}C_5H_4N)(CH_3)$ and 3,5-dichlorobromobenzene gave $(3,5\text{-}Cl_2C_6H_3HNCH_2)_2C(2\text{-}C_5H_4N)(CH_3)$ ($H_2[Ar_{Cl}Npy]$). Molybdenum compounds that were prepared include $[Et_3NH]\{[Ar_{Cl}NNMe]MoCl_3\}$ (**1a**), $[Ar_{Cl}NNMe]Mo(CCMe_3)(CH_2CMe_3)$ (**2**), $[Ar_{Cl}NNMe]MoCl(CH_2R)$ [R = CMe_3 (**4a**) or $SiMe_3$ (**4b**)], $[Et_3NH]\{[Ar_{Cl}Npy]MoCl_3\}$ (**5**), and $Mo[Ar_{Cl}Npy]_2$ (**6**). Tantalum complexes that were prepared include $[Ar_{Cl}NNMe]TaMe_3$ (**7**) and $[Ar_{Cl}Npy]TaMe_3$ (**8**). X-ray studies of **1a**, **4a**, **6**, and **7** are reported.

Introduction

Diamido/donor ligands in which the central donor is a nitrogen include $[(RNCH_2CH_2)_2NR']^{2-}$,[1−12] $[(RNCH_2)_2C(2\text{-}C_5H_4N)(CH_3)]^{2-}$,[13−20] and $[2,6\text{-}(CH_2NHR)_2C_6H_3N]^{2-}$.[21−24] In our group we have been interested in variations of the first two in which the amido substituent is an aryl group such as mesityl, the primary focus being the stabilization of monoalkyl cations of zirconium and hafnium and polymerization of olefins by them.[9,12,17,18,20] Recently, however, we have begun to explore the synthesis of diamido/donor complexes of more electron-rich metals, e.g., molybdenum(IV) and tungsten(IV). Two reports have appeared that deal with complexes that contain the $[(C_6F_5NCH_2CH_2)_2NMe]^{2-}$ or $[(3,4,5\text{-}C_6F_3H_2NCH_2CH_2)_2NMe]^{2-}$ ligands.[10,11] These studies suggested that electron-withdrawing groups on the amido nitrogens facilitated the synthesis of more electron-rich diamido/donor complexes. Also, in the process it became clear that at least ortho fluorides were potentially problematic. The fact that we have not yet been able to prepare any examples of simple Mo(IV) or W(IV) complexes that contain the known[17,20] mesityl-substituted ligand $[(MesNCH_2)_2C(CH_3)(2\text{-}C_5H_4N)]^{2-}$ led us to suspect that the smaller size of second and third metals in group 6 compared to group 4 combined with their lower electrophilicity may be the source of the difficulty. (Molybdenum(IV) triamido/amine complexes that contain mesityl substituents also could not be prepared.[25,26]) We felt that the 3,5-dichlorophenyl group would be a potentially useful alternative to a fluorinated phenyl group, and since 3,5-dichlorobromobenzene is commercially available, amines that contain the 3,5-dichlo-

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Table 1. Crystal Data and Structure Refinement for [Et_3NH]{[Ar_{Cl}NNMe]$MoCl_3$} (1a), {[Ar_{Cl}NNMe]MoCl(CH_2-t-Bu) (4a), and [Ar_{Cl}Npy]$_2$Mo (6)

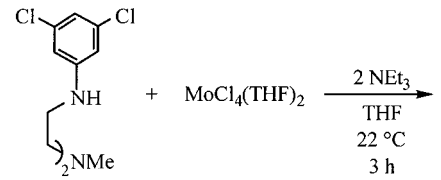
	1a	4a	6
empirical formula	$C_{54}H_{80}Cl_{14}Mo_2N_8O_2$	$C_{26}H_{36}Cl_5MoN_3O$	$C_{50}H_{34}Cl_8MoN_6$
fw	1561.44	679.77	1098.37
temp, K	293(2)	293(2	293(2)
wavelength, Å	0.71073	0.71073	0.71073
cryst syst, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	orthorhombic, *Pbca*
unit cell dimens	a = 9.0361(7) Å b = 13.8989(11) Å c = 14.0760(11) Å α = 90.6080(10)° β = 96.7660(10)° γ = 104.1260(10)°	a = 8.6227(6) Å b = 11.7787(8) Å c = 15.6400(11) Å α = 77.4370(10)° β = 80.5480(10)° γ = 79.2080(10)°	a = 14.478(4) Å b = 16.193(4) Å c = 22.068(5) Å α = 90° β = 90° γ = 90°
volume, Å^3	1701.0(2)	1510.32(18)	5174(2)
Z, calcd density, Mg/m^3	1, 1.524	2, 1.495	4, 1.410
abs coeff, mm^{-1}	0.963	0.901	0.706
F(000)	798	696	2216
θ range for data collection	2.60−23.29°	2.44−23.30°	2.10−20.00°
limiting indices	$-10 \le h \le 9$, $-15 \le k \le 10$, $-14 \le l \le 15$	$-9 \le h \le 8$, $-13 \le k \le 12$, $-17 \le l \le 12$	$-13 \le h \le 13$, $-15 \le k \le 15$, $-12 \le l \le 21$
no. of reflns collected/unique	6841/4769 [R(int) = 0.0357]	6113/ 4246 [R(int) = 0.0503]	14297/2404 [R(int) = 0.1294]
completeness to θ = 23.29	97.1%	97.0%	99.7%
abs corr	empirical	none	none
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	4769/0/361	4246/0/330	2404/0/307
goodness-of-fit on F^2	1.075	1.068	1.240
final R indices [$I>2\sigma(I)$]	R1 = 0.0420, wR2 = 0.0994	R1 = 0.0343, wR2 = 0.0891	R1 = 0.0829, wR2 = 0.1750
R indices (all data)	R1 = 0.0496, wR2 = 0.1028	R1 = 0.0363, wR2 = 0.0911	R1 = 0.1074, wR2 = 0.1854
largest diff peak and hole, e Å^{-3}	0.625 and −0.569	0.748 and −0.586	0.767 and −0.703

rophenyl group might be preparable via a palladium-catalyzed N−C coupling reaction[27,28] that we have used to prepare many other arylated amido ligands. In this paper we report two new diamines, (3,5-$C_6Cl_2H_3NHCH_2$-$CH_2)_2$NMe and (3,5-$C_6Cl_2H_3NHCH_2)_2C(CH_3)$(2-$C_5H_4N$), and several molybdenum and two tantalum complexes that contain the diamido/donor ligands derived from them.

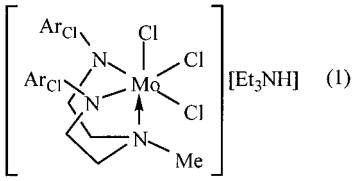
Results and Discussion

Syntheses of Molybdenum Species that Contain [(3,5-$Cl_2C_6H_3NCH_2CH_2)_2$NMe]$^{2-}$. The palladium-catalyzed reaction between diethylenetriamine and 2 equiv of 3,5-dichlorobromobenzene yields (3,5-$Cl_2C_6H_3NHCH_2$-$CH_2)_2$NH in 50% isolated yield after recrystallization from a solution of methylene chloride and pentane at 0 °C. The central nitrogen can be methylated with methyl iodide in acetonitrile in the presence of potassium carbonate at room temperature over the course of 16 h to give (3,5-$Cl_2C_6H_3NHCH_2CH_2)_2$NMe (H_2[Ar_{Cl}NNMe]) as a yellow crystalline solid in 65% yield after recrystallization from a solution of diethyl ether and pentane at 0 °C. Deprotonation of H_2[Ar_{Cl}NNMe] with *n*-butyllithium in ether gave the dilithiomonoetherate salt Li_2[Ar_{Cl}NNMe]·Et_2O as an orange powder in 59% yield.

The reaction between H_2[Ar_{Cl}NNMe] and $MoCl_4$-$(THF)_2$ in THF in the presence of 2.2 equiv of triethylamine gave paramagnetic [Et_3NH]{[Ar_{Cl}NNMe]$MoCl_3$} (**1a**) (eq 1) as a deep purple, crystalline solid in 89% yield. Resonances for the triethylammonium cation could be observed in the ^{1}H NMR spectrum at 2.31 and 1.97 ppm in CD_2Cl_2 and 1.40 ppm in C_6D_6. Salt metathesis of **1a** with tetrabutylammonium chloride in THF gave purple, crystalline [NBu_4]{[Ar_{Cl}NNMe]$MoCl_3$} (**1b**) in 86% yield. The ^{1}H NMR spectrum of **1b** in C_6D_6 showed three broad resonances at 1.46, 1.19, and 0.94 ppm for the tetrabutylammonium cation.



H_2[Ar_{Cl}NNMe]



(1)

1a

X-ray quality crystals of **1a** were grown from a 1:1 THF/diethyl ether solution at −30 °C. The X-ray crystal structure (Table 1, Figure 1) shows a near octahedral molybdenum center with the diamido/amine ligand coordinated in a *fac* arrangement. One molecule of THF is present in the unit cell. Relevant bond distances and angles can be found in Table 2. The Mo−N(amido) bond lengths (1.980(3) and 2.013(3) Å) are in the expected range, and the Mo−N(donor) bond length (2.242(3) Å) is consistent with a Mo−N dative bond. The Mo−Cl bonds trans to the amido ligands are lengthened by ∼0.1 Å compared to Mo−Cl(1) as a consequence of strong σ and π donation from the amido nitrogens. The structure is essentially the same as that of [Et_3NH]{[($C_6F_5NCH_2$-$CH_2)_2$NMe]$MoCl_3$}.[10]

Reaction of **1a** with 3 equiv of neopentylmagnesium chloride resulted in formation of the diamagnetic neo-

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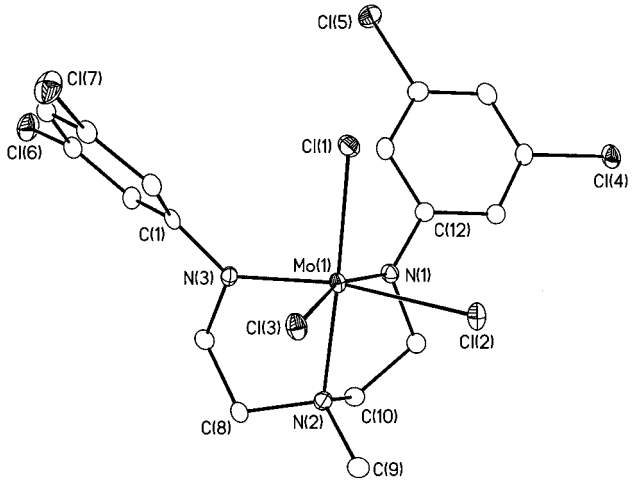
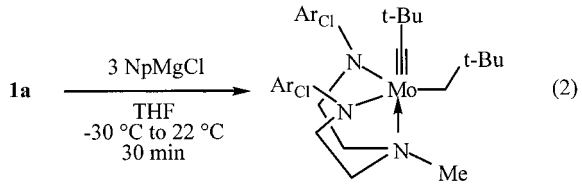


Figure 1. ORTEP drawing of the structure of $[Et_3NH]$-$\{[Ar_{Cl}NNMe]MoCl_3\}$ (**1a**). The triethylammonium cation has been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Et_3NH]\{[Ar_{Cl}NNMe]MoCl_3\}$ (1a)

Bond Lengths			
Mo−N(3)	1.980(3)	Mo−Cl(1)	2.3993(11)
Mo−N(1)	2.013(3)	Mo−Cl(2)	2.5206(11)
Mo−N(2)	2.242(3)	Mo−Cl(3)	2.4697(11)
Bond Angles			
N(3)−Mo−N(1)	101.44(14)	N(2)−Mo−N(1)	79.35(13)
N(3)−Mo−N(2)	79.35(13)	N(1)−Mo−Cl(1)	98.17(10)
N(3)−Mo−Cl(2)	169.85(10)	N(1)−Mo−Cl(2)	83.12(10)
N(3)−Mo−Cl(3)	91.58(10)	N(1)−Mo−Cl(3)	163.28(10)
N(3)−Mo−Cl(1)	95.80(10)	Cl(1)−Mo−Cl(2)	92.48(4)
N(2)−Mo−Cl(3)	163.28(10)	Cl(1)−Mo−Cl(3)	92.82(4)
N(2)−Mo−Cl(2)	91.02(9)	Cl(2)−Mo−Cl(3)	82.43(4)
N(2)−Mo−Cl(1)	175.44(9)		

pentyl/neopentylidyne molybdenum complex $[Ar_{Cl}NNMe]$-$Mo(CCMe_3)(CH_2CMe_3)$ (**2**; eq 2). We propose that this

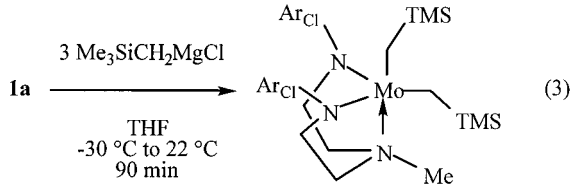


(2)

2

species is formed by loss of molecular hydrogen from putative $[Ar_{Cl}NNMe]Mo(CH_2CMe_3)_2$ (α,α-dehydrogenation).[29−32] An analogous complex that contains a $[(3,4,5\text{-}F_3C_6H_2CH_2CH_2)_2NMe]^{2-}$ ligand has been crystallographically characterized;[11] the neopentylidyne ligand was found in the axial position trans to the amine donor. Compound **2** was recrystallized from a 1:1 ether/pentane solution at −30 °C as yellow-brown crystals in 55% yield. Low yields are due in part to the compound's slight solubility in pentane. The ^1H NMR spectrum of **2** in C_6D_6 showed distinct singlet resonances for two different *tert*-butyl groups at 1.41 and 0.77 ppm and for one neopentyl methylene group at 1.58 ppm. The alkylidyne carbon resonance was found at 309.8 ppm in the $^{13}C\{^1H\}$ NMR spectrum in C_6D_6 (cf. 307.7 ppm in $[(3,4,5\text{-}F_3C_6H_2CH_2CH_2)_2NMe]Mo(CCMe_3)(CH_2CMe_3)$[11]).

A reaction analogous to that described in eq 2 was performed between **1a** and 3 equiv of trimethylsilylmethylmagnesium chloride (eq 3). The reaction mixture

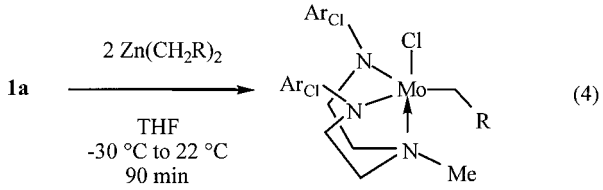


(3)

3

immediately became deep green after the addition of the Grignard reagent and gradually turned brown after being stirred for a period of 90 min at room temperature. The ether-soluble brown powder, isolated in 78% yield, was found to be the paramagnetic bis(trimethylsilylmethyl)molybdenum complex $[Ar_{Cl}NNMe]Mo(CH_2SiMe_3)_2$ (**3**). Two broad resonances at 3.57 and 1.15 ppm in the ^1H NMR spectrum in C_6D_6 were assigned to the two inequivalent trimethylsilyl groups.

Monoalkyl molybdenum complexes containing the $[Ar_{Cl}NNMe]^{2-}$ ligand can be synthesized by treating **1a** with dialkyl zinc reagents. Reaction of **1a** with either dineopentyl zinc or bistrimethylsilylmethyl zinc affords $[Ar_{Cl}NNMe]MoCl(CH_2CMe_3)$ (**4a**) in 38% yield or $[Ar_{Cl}$-$NNMe]MoCl(CH_2SiMe_3)$ (**4b**) in 68% yield, respectively (eq 4). The substantially lower yield of **4a** is partly due



(4)

4a, R = t-Bu; **4b**, R = TMS

to its higher solubility in ether. The ^1H NMR spectra of **4a** have single broad resonances at 3.85 ppm in C_6D_6 and at 3.62 ppm in CD_2Cl_2 for the methyl groups of the neopentyl ligand, while the ^1H NMR spectrum of **4b** in C_6D_6 reveals a single broad resonance at 3.05 ppm for the methyl groups of the trimethylsilyl group.

X-ray quality crystals of **4a** were obtained from a 1:2 mixture of THF and pentane at −30 °C. One molecule of THF is present in the unit cell. The X-ray crystal structure of **4a** (Table 1, Figure 2) shows the chloride to be in the apical site trans to the amine donor. Pertinent bond distances and angles are listed in Table 3. All bond distances are within the expected ranges. Steric interaction between the neopentyl group and the aryl rings is likely to be the reason the isomer with the neopentyl group in the axial position is not observed. The Mo−C(18)−C(19) angle (129.3°) is normal for a neopentyl group, as opposed to the large angle that is observed for the neopentyl group in an axial position in

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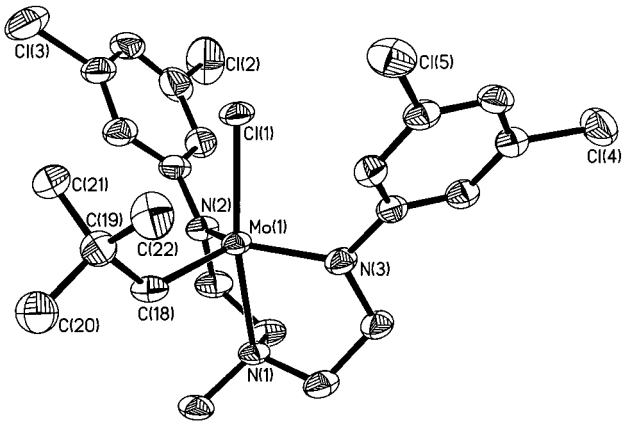


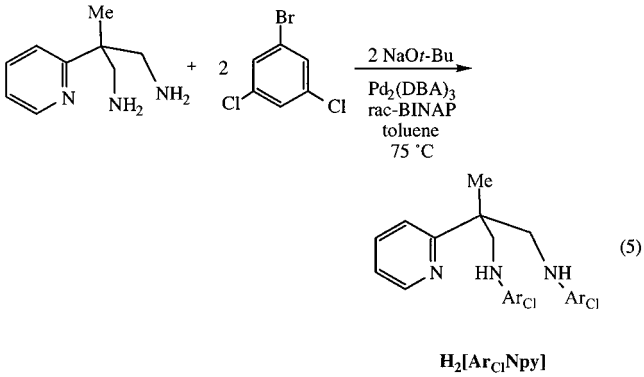
Figure 2. ORTEP drawing of the structure of [Ar_{Cl}NNMe]-MoCl(CH_2-t-Bu) (**4a**).

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for [Ar_{Cl}NNMe]MoCl(CH_2-t-Bu) (4a)

Bond Lengths			
Mo−N(1)	2.236(2)	Mo−C(18)	2.137(3)
Mo−N(2)	1.975(3)	Mo−Cl(1)	2.3881(8)
Mo−N(3)	1.994(3)		
Bond Angles			
N(2)−Mo−N(3)	129.12(11)	N(3)−Mo−N(1)	80.54(10)
N(2)−Mo−N(1)	80.15(10)	N(1)−Mo−Cl(1)	167.84(7)
N(2)−Mo−Cl(1)	94.71(8)	N(1)−Mo−C(18)	89.67(11)
N(2)−Mo−Cl(18)	112.69(12)	C(18)−Mo−Cl(1)	102.49(8)
N(3)−Mo−C(18)	113.77(12)	Mo−C(18)−C(19)	129.3(2)
N(3)−Mo−Cl(1)	94.54(8)		

[MesNNMe]Zr(CH_2CMe_3)$_2$.[18] We assume that **4b** has a structure analogous to that of **4a**.

Synthesis of Molybdenum Complexes that Contain the [(3,5-$Cl_2C_6H_3NCH_2$)$_2$C(2-C_5H_4N)(CH_3)]$^{2-}$ Ligand. The diamine, H_2[(3,5-$Cl_2C_6H_3NCH_2$)$_2$C(2-C_5H_4-N)(CH_3)], was prepared in 60% yield by treating (H_2-NCH_2)$_2$C(2-C_5H_4N)(CH_3) with 2 equiv of 3,5-dichlorobromobenzene and 2 equiv of NaO-*t*-Bu in the presence of a catalytic amount of Pd(0)/*rac*-Binap (eq 5). The

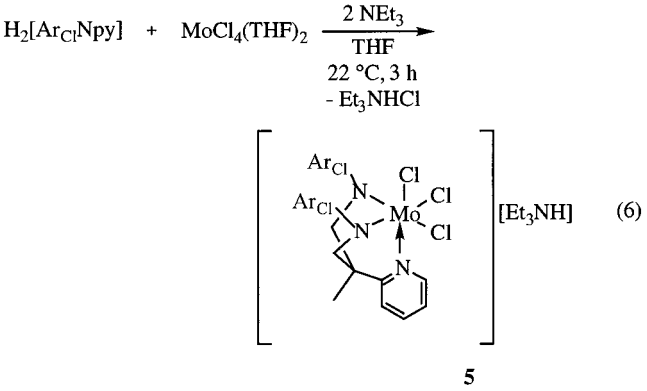


(5)

$H_2[Ar_{Cl}Npy]$

ligand is obtained as off-white analytically pure crystals after recrystallization from a mixture of pentane and ether.

The reaction between $H_2[Ar_{Cl}Npy]$ and $MoCl_4(THF)_2$ followed by addition of triethylamine produced deep purple paramagnetic [Et_3NH]{[Ar_{Cl}Npy]$MoCl_3$} (**5**; eq 6). This product is only slightly soluble in benzene, but very soluble in methylene chloride. Two broad resonances were present at 2.77 and 2.16 ppm in the ^{1}H NMR spectrum in CD_2Cl_2; they are assigned to the ethyl groups of the triethylammonium cation. Unfortunately,

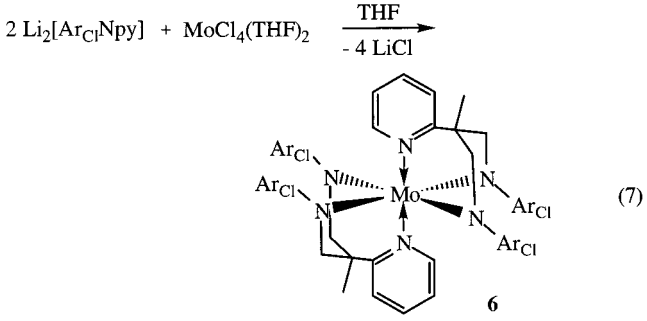


(6)

5

treatment of **5** with Grignard reagents and dialkyl zinc reagents in reactions analogous to those involving **1a** have not yet yielded isolable five-coordinate species. We suspect that the pyridine donor is more labile than the amine donor in [Ar_{Cl}NNMe]$^{2-}$ complexes and that the ligand is thereby attacked and possibly removed from the metal at some point.

In the process of exploring routes to Mo complexes we turned to reactions involving Li_2[Ar_{Cl}Npy], which was prepared readily by deprotonation of H_2[Ar_{Cl}Npy] with *n*-butyllithium. The reaction between Li_2[Ar_{Cl}Npy] in THF and $MoCl_4(THF)_2$ gave a purple paramagnetic product, the yield of which we found was optimized by employing *2* equiv of Li_2[Ar_{Cl}Npy] per Mo (eq 7). This



(7)

6

complex can be recrystallized readily from a mixture of THF and pentane at −30 °C. An X-ray study (Table 1) revealed the complex to be Mo[Ar_{Cl}Npy]$_2$ (**6**), in which two ligands are coordinated to one Mo center (Figure 3). The complex has a center of inversion at Mo. The two Mo−N(amide) bonds are the same within experimental error (Mo−N(1) = 2.058(9) Å and Mo−N(2) = 2.076(8) Å); the Mo−N(pyridine) bond (Mo−N(3) = 2.147(9) Å) is slightly shorter than the Mo−N(donor) bond in **1** (Mo−N(2) = 2.319(4) Å). All angles between cis ligands are within the range 87(5)−92(3)°.

Synthesis of Tantalum Complexes. For comparison we attempted to prepare simple six-coordinate d^0 tantalum trimethyl complexes. The reaction between Li_2[Ar_{Cl}NNMe]·Et_2O and $TaCl_2Me_3$ took place smoothly to give **7** (eq 8) in high yield. All three methyl groups coordinated to tantalum are equivalent on the ^{1}H NMR time scale at room temperature and appear as a singlet at 1.14 ppm in C_6D_6. The aryl rings rotate freely at room temperature on the basis of the appearance of a sharp doublet at 6.82 ppm. In the ^{13}C{^{1}H} NMR spectrum the resonance of the methyl groups on tantalum is seen as a broad peak at 68.8 ppm in C_6D_6 at room temperature. We assume that the fluxional behavior of **7** is the result

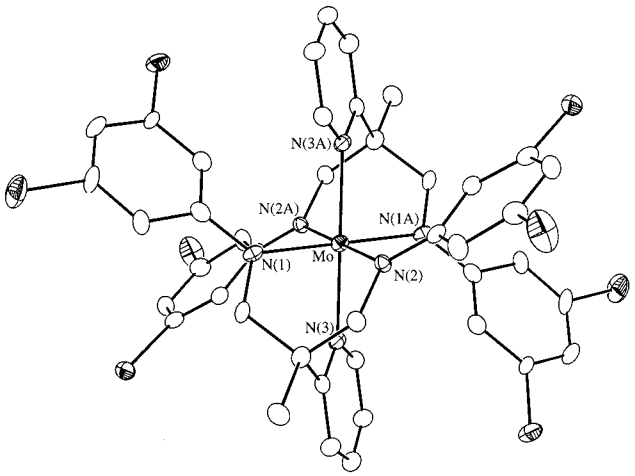


Figure 3. ORTEP drawing of the structure of Mo[Ar_{Cl}-Npy]$_2$ (**6**). Selected bond lengths (Å) and angles (deg): Mo−N(1) = 2.058(9); Mo−N(2) = 2.076(8); Mo−N(3) = 2.147(9); N(1)−Mo−N(2A) = 87.3(3); N(1)−Mo−N(2) = 92.7(3); N(1)−Mo−N(3) = 92.5(4); N(2)−Mo−N(3A) = 91.7(3); N(2)−Mo−N(3) = 88.3(3); N(1)−Mo−N(3A) = 87.5(4).

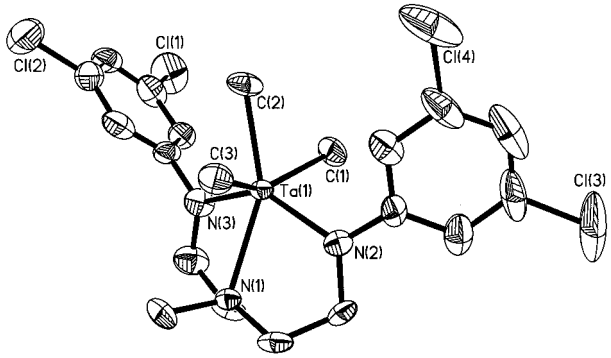
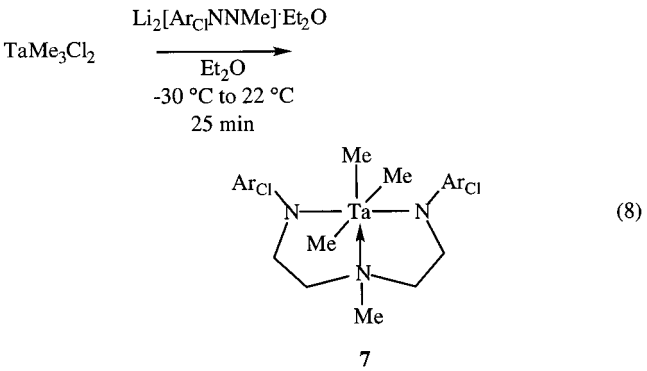


Figure 4. ORTEP drawing of the structure of [Ar_{Cl}NNMe]-$TaMe_3$ (**7**).

of an intramolecular rearrangement, although we have no definitive data that bear on that point.



(8)

7

X-ray quality crystals of **7** were obtained from a 1:1 toluene/pentane solution at −30 °C over a period of 2 days. The solid-state structure of **7** (Table 4, Figure 4) shows that the ligand is bound to the metal in a meridional geometry. Relevant bond distances and angles are listed in Table 5. The compound is a highly distorted octahedral species with a relatively long Ta−N(1) bond (2.379(7) Å). All Ta−C bond lengths are normal and approximately the same length. The long Ta−N(1) bond suggests that the three methyl groups become equivalent as a consequence of dissociation of N(1) from the metal and subsequent rearrangement of the five-cordinate bisamidotrimethyl species. The meridional geometry found for **7** contrasts with the facial geometry found for **1a**. At this point it is not clear why, even if one takes into consideration the difference in d electron count.

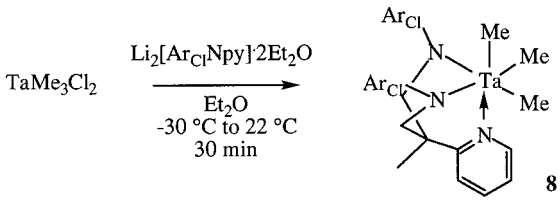
Table 4. Crystal Data and Structure Refinement for [Ar_{Cl}NNMe]$TaMe_3$ (7)

empirical formula	$C_{20}H_{26}Cl_4N_3Ta$
fw	631.19
temp	293(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	a = 12.006(3) Å, α = 90° b = 11.415(3) Å, β = 95.27(3)° c = 17.381(6) Å, γ = 90°
volume	2372.0(12) Å^3
Z	4
density(calcd)	1.767 Mg/m^3
abs coeff	5.096 mm^{-1}
F(000)	1232
cryst size	0.24 × 0.40 × 0.70 mm^3
θ range for data collection	2.47−23.28°
index ranges	$-12 \le h \le 13$, $-5 \le k \le 12$, $-19 \le l \le 19$
no. of reflns collected	9163
no. of ind reflns	3413 [R(int) = 0.1044]
completeness to θ = 23.28°	99.6%
abs corr	empirical
max. and min. transmn	0.9949 and 0.5716
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	3413/0/254
goodness-of-fit on F^2	1.122
final R indices [$I>2\sigma(I)$]	R1 = 0.0527, wR2 = 0.1456
R indices (all data)	R1 = 0.0540, wR2 = 0.1469
extinction coeff	0.0016(3)
largest diff peak and hole	2.866 and −2.055 e Å^{-3}

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for [Ar_{Cl}NNMe]$TaMe_3$ (7)

Bond Lengths			
Ta−N(1)	2.379(7)	Ta−C(1)	2.218(10)
Ta−N(2)	2.057(8)	Ta−C(2)	2.241(10)
Ta−N(3)	2.005(7)	Ta−C(3)	2.214(10)
Bond Angles			
N(3)−Ta−N(2)	135.6(3)	N(2)−Ta−C(2)	128.4(3)
N(3)−Ta−C(2)	93.8(4)	C(3)−Ta−N(1)	88.2(3)
N(3)−Ta−C(3)	113.3(4)	C(2)−Ta−N(1)	153.8(4)
N(3)−Ta−N(1)	71.2(3)	C(1)−Ta−N(1)	124.4(4)
N(3)−Ta−C(1)	94.2(4)	C(3)−Ta−C(1)	143.6(4)
N(2)−Ta−N(1)	73.2(3)	C(3)−Ta(1)−C(2)	78.0(4)
N(2)−Ta−C(1)	84.6(4)	C(1)−Ta−C(2)	76.8(4)
N(2)−Ta−C(3)	91.0(4)		

A trimethyl tantalum complex, [Ar_{Cl}Npy]$TaMe_3$ (**8**), is also formed by the reaction between Li_2[Ar_{Cl}Npy]·$2Et_2O$ and $TaCl_2Me_3$ (eq 9). The resonances for the three equivalent methyl groups are observed as a singlet at 1.31 ppm in the ^{1}H NMR spectrum in C_6D_6 and as a singlet at 72.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum in C_6D_6. We assume that the ligand in **8** must adopt a



(9)

8

facial geometry as a consequence of its tethered backbone structure. (Unfortunately, X-ray quality crystals could not be obtained.) The $[Ar_{Cl}Npy]^{2-}$ ligand also may be flexible enough to allow equilibration of the three methyl groups after dissociation of the pyridine donor.[19]

Conclusions

We conclude that the 3,5-dichlorophenyl group on the amido nitrogens in two types of diamido/donor ligands is a viable alternative to fluorinated aryl rings. The advantages of the 3,5-dichlorophenyl group are that 3,5-dichlorobromobenzene is not expensive and ligands may be prepared via C−N coupling reactions. The disadvantage of the 3,5-dichlorophenyl group relative to a fluorinated group is that there is no ready NMR handle for following reactions of paramagenetic species. The potential lability of the donor in each ligand, especially $[(3,5\text{-}Cl_2C_6H_3NCH_2)_2C(2\text{-}C_5H_4N)(CH_3)]^{2-}$, ultimately may limit the chemistry that is available for less electrophilic metal centers.

Experimental Section

General Procedures. All air-sensitive work was carried out in a Vacuum Atmospheres drybox under a nitrogen atmosphere or by standard Schlenk techniques unless otherwise noted. Diethyl ether, toluene, and pentane were sparged with nitrogen and passed through a column of activated alumina. Tetrahydrofuran, benzene, and methylene chloride were distilled from benzophenone ketyl. C_6D_6 and CD_2Cl_2 were sparged with nitrogen for 10 min. All listed solvents were stored over 4 Å molecular sieves. $MoCl_4(THF)_2$ was synthesized according to the literature preparation.[33] Me_3SiCH_2MgCl was obtained from Aldrich and used without further purification. Triethylamine was obtained from Aldrich and distilled from calcium hydride. Tetrabutylammonium chloride was obtained from Aldrich and placed under high vacuum overnight prior to use. Neopentylmagnesium chloride,[34] dineopentyl zinc,[35,36] $(Me_3SiCH_2)_2Zn$,[36] and $TaCl_2Me_3$[37] were synthesized according to their respective literature preparations. Diethylenetriamine was obtained from Aldrich and distilled from calcium hydride. $Pd_2(dba)_3$ and *rac*-BINAP were obtained from Strem and used without further purification. The diamine starting material, $H_3CC(2\text{-}C_5H_4N)(CH_2NH_2)_2$, was synthesized according to the literature preparation.[16] 1-Bromo-3,5-dichlorobenzene was obtained from Aldrich and placed under high vacuum overnight prior to use. *n*-Butyllithium was obtained from Aldrich and titrated with 1-propanol and phenanthroline before use. Silica gel 60, particle size 0.040−0.063 mm (230−400 mesh ASTM), used for column chromatography was obtained from EM Science. Elemental analyses were performed by Kolbe Microanalytical Laboratory (Mülheim an der Ruhr, Germany).

Reported NMR chemical shifts are listed in parts per million referenced to either the residual protons or carbon-13 atoms of the deuterated solvents. ^1H NMR spectra were obtained on an instrument operating at 500 MHz, while $^{13}C\{^1H\}$ NMR spectra were obtained on an instrument operating at 125 MHz. All spectra were recorded near 22 °C.

$H_2[Ar_{Cl}NNH]$. The Pd catalyst was prepared by dissolving *rac*-BINAP (0.453 g, 0.727 mmol) in toluene (50 mL) in a 100 mL round-bottom flask with heating. $Pd_2(dba)_3$ (0.333 g, 0.364 mmol) was added to the warm solution, and the solution was stirred for 20−30 min, then filtered to remove Pd(0). The resulting deep red-orange solution was transferred to a 300 mL Schlenk flask containing diethylenetriamine (5.00 g, 48.5 mmol) and 1-bromo-3,5-dichlorobenzene (21.9 g, 97.0 mmol). Sodium *tert*-butoxide (10.8 g, 112 mmol) was added, and the Schlenk flask sealed and removed from the drybox. The reaction mixture was opened to a flow of nitrogen, stirred for 36 h at 85 °C, then cooled slightly. The warm mixture was filtered to remove NaBr and then the toluene removed from the filtrate. The residue was taken up in diethyl ether (350 mL) and extracted with H_2O (300 mL). The water layer was separated and washed with diethyl ether (2 × 100 mL). The ether portions were combined and rinsed with water (2 × 100 mL), then dried with $MgSO_4$. The $MgSO_4$ was filtered off and the filtrate concentrated using the rotary evaporator to leave a red-brown oil. This oil was dissolved in methylene chloride (100 mL) and transferred to a 250 mL round-bottom flask. Pentane (100 mL) was added to the brown solution, and the flask was stored at 0 °C overnight, over which time a brown solid formed. Two crops were obtained. Yield: 9.11 g (48%). ^1H NMR ($CDCl_3$): δ 6.68 (m, 2, H_p), 6.48 (m, 4, H_o), 4.25 (s, 2, ArN*H*), 3.18 (q, 4, ArNHC*H*$_2$), 2.89 (t, 4, AlkylNHC*H*$_2$), 1.26 (s, 1, AlkylN*H*). ^1H NMR (C_6D_6): δ 6.74 (m, 2, H_p), 6.24 (m, 4, H_o), 3.55 (s, 2, ArN*H*), 2.41 (q, 4, ArNHC*H*$_2$), 2.10 (t, 4, AlkylNHC*H*$_2$), 0.18 (s, 1, AlkylN*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 150.1 135.7 117.4 111.2 48.2 43.4. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 150.7 136.3 117.6 111.6 48.0 43.2. HRMS (ESI): calcd for $C_{16}H_{17}N_3Cl_4$ $[M + H]^+$ 392.0255, found $[M + H]^+$ 392.0245.

$H_2[Ar_{Cl}NNMe]$. The acetonitrile, diethyl ether, and pentane used in this reaction were reagent grade and used as obtained from the supplier. K_2CO_3 (4.59 g, 33.2 mmol) was added to a solution of $H_2[Ar_{Cl}NNH]$ (3.57 g, 9.08 mmol) in acetonitrile (150 mL). The reaction mixture was purged with N_2 for 20 min and then opened to a flow of nitrogen. Methyl iodide (0.59 mL, 9.54 mmol) was added via syringe in three portions over 60 min, and the reaction mixture was stirred overnight. Volatile components were removed in vacuo. The remaining tan residue was taken up in diethyl ether (200 mL) and extracted with water (200 mL). The water layer was separated and extracted with ether (100 mL). The ether portions were combined, rinsed with water (100 mL), then with saturated NaCl solution (100 mL), and dried with $MgSO_4$. The $MgSO_4$ was filtered off and ether removed by the rotary evaporator, leaving a thick yellow oil. The oil was redissolved in diethyl ether (10 mL) and layered on a plug of silica gel on packed Celite, which was subsequently eluted with ether (200 mL). The pale yellow filtrate was concentrated to approximately 5 mL, and pentane (10 mL) was added. The solution became cloudy with a white precipitate. Cooling of this mixture to 0 °C overnight gave an off-white crystalline solid, yield 2.42 g (65%). ^1H NMR ($CDCl_3$): δ 6.68 (m, 2, H_p), 6.43 (m, 4, H_o), 4.26 (s, 2, ArN*H*), 3.13 (q, 4, ArNHC*H*$_2$), 2.65 (t, 4, AlkylNMeC*H*$_2$), 2.30 (s, 3, AlkylN*Me*). ^1H NMR (C_6D_6): δ 6.75 (t, 2, H_p), 6.19 (d, 4, H_o), 3.61 (t, 2, ArN*H*), 2.39 (q, 4, ArNHC*H*$_2$), 1.91 (t, 4, AlkylNHC*H*$_2$), 1.74 (s, 3, AlkylN*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 150.0 135.7 117.3 111.2 56.0 42.0 41.0. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 150.5 136.4 117.7 111.6 55.7 41.9 40.9. HRMS (ESI): calcd for $C_{17}H_{19}N_3Cl_4$ $[M + H]^+$ 406.0411, found $[M + H]^+$ 406.0405.

$Li_2[Ar_{Cl}NNMe]\cdot Et_2O$. *n*-Butyllithium (3.16 mL, 1.71 M, 5.40 mmol) was added dropwise to a solution of $H_2[Ar_{Cl}NNMe]$ (1.00 g, 2.46 mmol) in diethyl ether (25 mL) at −30 °C. A precipitate formed immediately, and the mixture was stirred for 60 min at room temperature. The solid was filtered off, rinsed with pentane (50 mL), and dried to yield an orange powder, yield 710 mg (59%). ^1H NMR (C_6D_6): δ 6.67 (s, 2, H_o), 6.28 (s, 4, H_p), 2.85 (q, 4, *Et*$_2$O), 2.60 (m, 2, C*H*$_2$ backbone), 2.52 (m, 2, C*H*$_2$ backbone), 2.17 (m, 2, C*H*$_2$ backbone), 1.97 (m, 2, C*H*$_2$ backbone), 1.69 (s, 3, N*Me*), 0.66 (t, 6, *Et*$_2$O). Anal.

(33) Dilworth, J. R.; Richards, R. L.; Chen, G. J.-J.; McDonald, J. W. *Inorg. Synth.* **1980**, *20*, 119.
(34) Schrock, R. R.; Sancho, J.; Pederson, S. F. *Inorg. Synth.* **1989**, *26*, 44.
(35) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.
(36) Moorhouse, S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1974**, 2187.
(37) Juvinall, G. L. *J. Am. Chem. Soc.* **1964**, *86*, 4202.

Calcd for $C_{21}H_{27}N_3Cl_4Li_2O$: C, 51.15; H, 5.52; N, 8.52; Cl, 28.76. Found: C, 51.24; H, 5.43; N, 8.40; Cl, 28.70.

$H_2[Ar_{Cl}Npy]$. The Pd catalyst was prepared by dissolving *rac*-BINAP (0.566 g, 0.909 mmol) in toluene (30 mL) in a 100 mL round-bottom flask with heating. $Pd_2(dba)_3$ (0.416 g, 0.455 mmol) was added to the warm solution and the solution was stirred for 20−30 min, then filtered to remove Pd(0). The resulting deep red-orange solution was transferred to a 300 mL Schlenk flask containing the diamine, $H_3CC(2\text{-}C_5H_4N)(CH_2\text{-}NH_2)_2$ (5.00 g, 30.3 mmol), and 1-bromo-3,5-dichlorobenzene (14.4 g, 63.6 mmol). Sodium *tert*-butoxide (6.70 g, 69.7 mmol) was added, and the Schlenk flask was sealed and removed from the drybox. The reaction mixture was stirred for 12 h at 85 °C, then cooled slightly. The warm mixture was filtered to remove NaBr and then the toluene removed from the filtrate. The residue was taken up in diethyl ether (200 mL) and extracted with H_2O (200 mL). The water layer was washed with diethyl ether (3 × 100 mL). The ether portions were combined and dried with $MgSO_4$. The $MgSO_4$ was filtered off and the filtrate concentrated to approximately 50 mL. Addition of pentane (50 mL) to the yellow solution followed by cooling to 0 °C gave an off-white crystalline solid in three crops, yield 6.10 g (44%). ^{1}H NMR ($CDCl_3$): δ 8.63 (d, 1, Py), 7.71 (m, 1, Py), 7.36 (d, 1, Py), 7.24 (dd, 1, Py), 6.63 (s, 2, H_p), 6.44 (s, 4, H_o), 4.63 (t, 2, CH_2NHAr), 3.55 (d, 2, CH_2NHAr), 3.38 (d, 2, CH_2NHAr), 1.50 (s, 3, CH_3). ^{1}H NMR (C_6D_6): δ 8.30 (d, 1, py), 6.99 (m, 1, py), 6.70 (s, 2, H_p), 6.67 (d, 1, py), 6.59 (m, 1, py), 6.17 (d, 4, H_o), 4.06 (t, 2, CH_2NHAr), 3.04 (dd, 2, CH_2NHAr), 2.83 (dd, 2, CH_2NHAr), 0.95 (s, 3, CH_3). $^{13}C\{^1H\}$ ($CDCl_3$): δ 163.4 150.3 149.2 137.5 135.6 122.4 121.4 117.1 111.3 51.8 45.3 22.8. $^{13}C\{^1H\}$ (C_6D_6): δ 163.9 150.8 149.3 137.2 136.2 122.4 121.7 117.6 111.7 51.6 45.6 22.4. Anal. Calcd for $C_{21}H_{19}N_3Cl_4$: C, 55.41; H, 4.21; N, 9.23. Found: C, 55.54; H, 4.30; N 9.30.

$Li_2[Ar_{Cl}Npy]\cdot 2Et_2O$. *n*-Butyllithium (2.88 mL, 1.60 M, 4.61 mmol) was added to a solution of $H_2[Ar_{Cl}Npy]$ (1.00 g, 2.20 mmol) in diethyl ether (10 mL) at −30 °C and a precipitate formed. The mixture was stirred at room temperature for 1 h. The white powder was filtered, rinsed with diethyl ether (3 × 4 mL), and dried in vacuo, yield 0.757 g (83%). ^{1}H NMR (C_6D_6): δ 7.91 (m, 1, Py), 7.19 (m, 1, Py), 6.97 (d, 1, Py), 6.59−6.56 (m, 3, Py and H_p), 6.33 (br s, 4, H_o), 3.17 (br d, 2, CH_2-NLiAr), 3.11 (q, 8, Et_2O), 3.03 (br d, 2, CH_2NLiAr), 1.19 (br s, 3, CH_3), 0.87 (t, 12, Et_2O). Anal. Calcd for $C_{29}H_{37}N_3Cl_4Li_2O_2$: C, 56.61; H, 6.06; N, 6.83. Found: C, 56.48; H, 6.15; N 6.88.

$[Et_3NH]\{[Ar_{Cl}NNMe]MoCl_3\}$ (1a). $MoCl_4(THF)_2$ (0.938 g, 2.46 mmol) was added to a stirring solution of $H_2[Ar_{Cl}NNMe]$ (1.00 g, 2.46 mmol) in THF (25 mL). A deep red solution formed and was stirred for 10 min. NEt_3 (0.75 mL, 5.40 mmol) was added dropwise. The solution became deep purple, and a white solid formed immediately. The reaction mixture was stirred for an additional 3 h and filtered. The dark purple solid was collected (a mixture of the desired product and Et_3NHCl) and rinsed with THF (100 mL). The deep purple THF filtrate was concentrated to dryness to leave a sparkling purple solid. This solid was transferred to a frit and rinsed with diethyl ether (25 mL) to remove unreacted starting material. X-ray quality crystals were obtained from a 1:1 THF/diethyl ether solution at −30 °C, yield 1.72 g (89%). ^{1}H NMR (CD_2Cl_2): δ 26.57 (br s), 19.42 (sharp s), 8.49 (br s), 2.31, 1.97 (Et_3NH), −2.36 (br s), −29.80 (br s), −96.30 (br s), −110.74 (br s). ^{1}H NMR (C_6D_6): δ 26.93 (br s), 19.58 (sharp s), 8.41 (br s), 1.40 (Et_3-NH), −2.94 (br s), −30.03 (br s), −97.75 (br s), −107.02 (br s). Anal. Calcd for $C_{23}H_{33}N_4Cl_7Mo$: C, 38.93; H, 4.69; N, 7.89; Cl, 34.97. Found: C, 39.12; H, 4.78; N, 7.74; Cl, 35.11.

$[Bu_4N]\{[Ar_{Cl}NNMe]MoCl_3\}$ (1b). Solid Bu_4NCl (0.136 g, 0.491 mmol) was added to a stirring solution of **1a** (0.500 g, 0.705 mmol) in THF (30 mL). The reaction mixture was stirred overnight and then THF removed in vacuo. The residue was extracted with benzene (5 mL) and filtered to remove Et_3NHCl and excess Bu_4NCl. The benzene was removed to leave a sparkling dark purple solid, yield 0.520 g (87%). ^{1}H NMR (C_6D_6): δ 27.40 (br s), 19.48 (sharp s), 5.83 (br s), 1.46, 1.19, 0.94 (Bu_4N), −2.15 (br s), −29.37 (br s), −94.52 (br s), −102.04 (br s). Anal. Calcd for $C_{27}H_{41}N_4Cl_7Mo$: C, 46.64; H, 6.29; N, 6.59; Cl, 29.20. Found: C, 46.74; H, 6.36; N, 6.64; Cl, 29.14.

$[Ar_{Cl}NNMe]Mo(CCMe_3)(CH_2CMe_3)$ (2). Me_3CCH_2MgCl (0.19 mL, 2.43 M, 0.462 mmol) was added dropwise to a stirring solution of **1a** (0.120 g, 0.154 mmol) in THF (5 mL) at −30 °C. The reaction immediately turned deep green and gradually became brown while stirring at room temperature for 30 min. Volatile components were removed in vacuo. Diethyl ether (5 mL) was added to the brown residue followed by 1,4-dioxane (0.13 mL, 1.54 mmol). The mixture was stirred for 10 min and filtered, and the solid was rinsed with ether (3 × 2 mL). The dark yellow-brown filtrate was concentrated to approximately 1 mL and filtered through glass filter paper. Pentane (1 mL) was added to the solution, which was then stored at −30 °C overnight to yield yellow-brown crystals, yield 55 mg (56%). ^{1}H NMR (C_6D_6): δ 7.06 (d, 4, H_o), 6.97 (t, 2, H_p), 3.13 (m, 2, backbone CH_2), 3.07 (m, 2, backbone CH_2), 2.11 (m, 2, backbone CH_2), 1.92 (s, 3, N*Me*), 1.90 (m, 2, backbone CH_2), 1.58 (s, 2, neopentyl CH_2), 1.41 (s, 9, C*Me*$_3$), 0.77 (s, 9, C*Me*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 309.8 166.7 134.7 123.7 123.5 72.8 58.7 55.1 50.9 43.9 35.21 35.15 30.0. Anal. Calcd for $C_{27}H_{37}N_3Cl_4Mo$: C, 50.56; H, 5.81; N, 6.55; Cl, 22.11. Found: C, 50.44; H, 5.92; N, 6.50; Cl, 21.98.

$[Ar_{Cl}NNMe]Mo(CH_2SiMe_3)_2$ (3). Me_3SiCH_2MgCl (1.06 mL, 1.0 M, 1.06 mmol) was added dropwise to a stirring solution of **1a** (0.250 g, 0.320 mmol) in THF (10 mL) at −30 °C. The reaction immediately turned deep green and gradually became brown while stirring at room temperature for 90 min. Volatile components were removed in vacuo. Diethyl ether (5 mL) was added to the brown residue followed by 1,4-dioxane (0.27 mL, 3.20 mmol). The mixture was stirred for 10 min and filtered, and the solid was rinsed with ether (3 × 2 mL). The brown filtrate was concentrated to dryness, and the brown residue left was triturated with pentane (5 mL) and filtered, yield 170 mg (79%). ^{1}H NMR (C_6D_6): δ 17.07 (br s), 12.24 (br s), 9.97 (br s), 6.15 (sharp s), 3.57 (br s, Si*Me*$_3$), 1.15 (br s, Si*Me*$_3$), −41.25 (br s), −57.87 (br s). Anal. Calcd for $C_{25}H_{39}N_3Cl_4Si_2Mo$: C, 44.45; H, 5.82; N, 6.22; Cl, 20.99. Found: C, 44.52; H, 5.71; N, 6.21; Cl, 21.14.

$[Ar_{Cl}NNMe]MoCl(CH_2CMe_3)$ (4a). $(Me_3CCH_2)_2Zn$ (68 mg, 0.282 mmol), diluted with THF (1 mL), was added dropwise to a stirring solution of **1a** (0.100 g, 0.128 mmol) in THF (5 mL) at −30 °C. The solution immediately turned deep green and was stirred at room temperature for 90 min. Volatile components were removed in vacuo. The remaining solid was triturated with ether (5 mL). The mixture was filtered, and the solid was rinsed with ether (5 mL) and pentane (5 mL) and dried to yield a green-gray powder. X-ray quality crystals were obtained from a 1:2 THF/pentane solution at −30 °C over 3 days, yield 30 mg (39%). ^{1}H NMR (CD_2Cl_2): δ 35.20 (br s), 25.61 (weak br s), 15.64 (br s), 10.66 (br s), 4.73 (sharp s), 3.62 (br s, C*Me*$_3$), −48.38 (br s), −86.63 (br s). ^{1}H NMR (C_6D_6): δ 35.83 (br s), 26.69 (weak br s), 15.33 (br s), 10.29 (br s), 4.07 (sharp s), 3.85 (br s, C*Me*$_3$), −46.64 (br s), −83.91 (br s). Anal. Calcd for $C_{22}H_{28}N_3Cl_5Mo$: C, 43.48; H, 4.64; N, 6.91; Cl, 29.17. Found: C, 43.58; H, 4.57; N, 7.08; Cl, 29.31.

$[Ar_{Cl}NNMe]MoCl(CH_2SiMe_3)$ (4b). $(Me_3SiCH_2)_2Zn$ (68 mg, 0.282 mmol), diluted in THF (1 mL), was added dropwise to a stirring solution of **1a** (0.100 g, 0.128 mmol) in THF (5 mL) at −30 °C. The solution immediately turned deep green and was stirred at room temperature for 90 min. Volatile components were removed in vacuo. The remaining solid was triturated with ether (5 mL). The mixture was filtered, and the solid was rinsed with ether (5 mL) and pentane (5 mL) and dried in vacuo to yield a green powder, yield 55 mg (69%). ^{1}H NMR (C_6D_6): δ 25.30 (br s), 14.05 (br s), 3.55 (sharp s), 3.05 (br s, Si*Me*$_3$), −53.78 (br s), −82.78 (br s). Anal. Calcd for $C_{21}H_{28}N_3Cl_5SiMo$: C, 40.44; H, 4.52; N, 6.74; Cl, 28.42. Found: C, 40.32; H, 4.46; N, 6.65; Cl, 28.54.

[Et_3NH]{[Ar_{Cl}Npy]$MoCl_3$} (5). $MoCl_4(THF)_2$ (0.419 g, 1.10 mmol) was added to a stirring solution of $H_2[Ar_{Cl}Npy]$ (0.500 g, 1.10 mmol) in THF (10 mL). A deep red solution formed and was stirred for 10 min. NEt_3 (0.34 mL, 2.42 mmol) was added dropwise. The solution became a deep red-purple color, and a white solid formed immediately. The reaction mixture was stirred for an additional 3 h and filtered. The dark purple solid was rinsed with THF (10 mL). The deep purple filtrate was concentrated to dryness to leave a dark red-purple foam. This foam was redissolved in THF (5 mL) and added to stirring chilled (−30 °C) pentane. The resulting purple solid was collected, rinsed with ether (5 mL) and pentane (10 mL), and dried, yield 0.645 g (78%). ^{1}H NMR (CD_2Cl_2): δ 92.85 (br s), 33.25 (sharp s), 22.55 (sharp s), 5.19 (sharp s), 2.77, 2.16 (*Et_3*-NH), −11.75 (strong sharp s), −22.14 (br s), −38.51 (sharp s), −61.81 (br s). Anal. Calcd for $C_{27}H_{33}N_4Cl_7Mo$: C, 42.80; H, 4.39; N, 7.39; Cl, 32.75. Found: C, 42.71; H, 4.47; N, 7.48; Cl, 32.63.

Mo[Ar_{Cl}Npy]$_2$. To $Li_2[Ar_{Cl}Npy]\cdot 2Et_2O$ (963 mg, 1.58 mmol) in THF (10 mL) was added solid $MoCl_4(THF)_2$ (303 mg, 0.793 mmol). The dark brown reaction mixture was stirred at room temperature for 12 h, and the solution became dark red. The solvent was removed under vacuum, and the dark residue was extracted with CH_2Cl_2 (20 mL) and filtered through a frit with Celite. The CH_2Cl_2 was removed under vacuum to give a dark purple oil. The oil was triturated with a minimum amount of ether, and the dark purple ether filtrate was pipetted from the dark residue. The residue was dissolved in THF, and the solution was filtered. The THF solution was concentrated to ∼5 mL and layered with pentane (∼2 mL). Cooling this solution to −30 °C overnight gave 257 mg (32%) of dark purple-red crystalline product. ^{1}H NMR (C_6D_6): δ 24.5, 21.4 (br), 15.2, 13.3, 4.4, −21.7, −23.7, −28.7, −30.1, −30.8, −34.9. Anal. Calcd for $C_{42}H_{34}Cl_8N_6Mo$: C, 50.33; H, 3.42; N, 8.38; Cl, 28.30. Found: C, 50.18; H, 3.51; N, 8.26; Cl 28.19.

[Ar_{Cl}NNMe]$TaMe_3$ (7). A solution of $TaCl_2Me_3$ (0.116 g, 0.391 mmol) in diethyl ether (3 mL) was added dropwise to a slurry of $Li_2[Ar_{Cl}NNMe]\cdot Et_2O$ (0.193 g, 0.391 mmol) in diethyl ether (5 mL) at −30 °C. The bright yellow mixture was stirred for 25 min at room temperature, then all solvents were removed in vacuo. The resulting yellow powder was dissolved in benzene (10 mL), and the solution was filtered through Celite to remove LiCl. All solvents were removed from the yellow filtrate in vacuo to leave a yellow powder. X-ray quality crystals were grown from a 1:1 toluene/pentane solution, yield 0.195 g (79%). ^{1}H NMR (C_6D_6): δ 6.90 (t, 2, H_p), 6.82 (d, 4, H_o), 3.09 (m, 2, arylNC*H_2*), 3.02 (m, 2, arylNC*H_2*), 2.11 (m, 2, alkylNC*H_2*), 1.90 (s, 3, N*Me*), 1.75 (m, 2, alkylNC*H_2*), 1.14 (s, 9, Ta*Me_3*). ^{13}C{^{1}H} NMR (C_6D_6): δ 155.7 135.6 123.5 121.3 68.8 56.6 54.8 45.3. Anal. Calcd for $C_{20}H_{26}N_3Cl_4Ta$: C, 38.06; H, 4.15; N, 6.66; Cl, 22.47. Found: C, 38.16; H, 4.07; N, 6.58; Cl, 22.35.

[Ar_{Cl}Npy]$TaMe_3$ (8). A solution of $TaCl_2Me_3$ (0.100 g, 0.337 mmol) in diethyl ether (3 mL) was added dropwise to a slurry of $Li_2[(Ar_{Cl})_2N_2py]\cdot 2Et_2O$ (0.205 g, 0.337 mmol) in diethyl ether (3 mL) at −30 °C. The dark orange mixture was stirred for 30 min at room temperature, then concentrated to dryness. The resulting residue was taken up in benzene (5 mL), and the solution was filtered through Celite to remove LiCl. The brown filtrate was concentrated to dryness. The resulting brown solid was triturated and rinsed with pentane (10 mL). An orange-brown powder was collected, yield 0.198 g (87%). ^{1}H NMR (C_6D_6): δ 8.23 (m, 1, py), 6.84 (m, py and H_p), 6.72 (d, 4, H_o), 6.63 (d, 1, py), 6.27 (m, 1, py), 3.06 (d, 2, backbone C*H_2*), 3.26 (d, 2, backbone C*H_2*), 1.31 (s, 9, Ta*Me_3*), 0.72 (s, 3, *Me*). ^{13}C-{^{1}H} NMR (C_6D_6): δ 160.9 155.2 147.5 138.5 135.5 122.8 122.4 120.8 120.3 72.7 63.9 44.6 23.2. Anal. Calcd for $C_{24}H_{26}N_3Cl_4Ta$: C, 42.44; H, 3.86; N, 6.19; Cl, 20.88. Found: C, 42.57; H, 3.92; N, 6.11; Cl, 20.78.

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Supporting Information Available: Fully labeled ORTEP drawing, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **1a**, **4a**, **6**, and **7** are available free of charge via the Internet at http://pubs.acs.org.

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