Molybdenum(VI) Bis(imidoaryl) Complexes Containing the Bis(aminomethyl)aryl "Pincer" Ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (NCN): Structures of $[MoCl(\eta^2\text{-}C,N\text{-NCN})(NAr)_2]$, $[Mo(\eta^2\text{-}C,N\text{-NCN})(Me)(NAr)_2]$, and $[MoCl_2\{\eta^2\text{-}C,N\text{-NC(NH)}\}(NAr)_2]$

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The synthesis and characterization of new, five-coordinate molybdenum bis(imido) chloride complexes $[MoCl(NCN)(N\text{-}t\text{-}Bu)_2]$ (**2**) and $[MoCl(\eta^2\text{-}C,N\text{-NCN})(NAr)_2]$ (**3**) and the methylated derivative $[Mo(\eta^2\text{-}C,N\text{-NCN})(Me)(NAr)_2]$ (**5**) (NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$, Ar = $C_6H_3\text{-}i\text{-}Pr_2\text{-}2,6$) are reported. Compounds **3** and **5** react with HCl to yield the corresponding air-stable salts $[MoCl_2\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(CH_2NHMe_2)\text{-}6\}(NAr)_2]$ (**4**) and $[MoCl\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(CH_2NHMe_2)\text{-}6\}(Me)(NAr)_2]$ (**6**), respectively, of which **3**−**5** have been characterized by X-ray analysis. X-ray structure determination of **4** shows an additional chloride anion bonded to the molybdenum metal center while one of the *ortho*-(dimethylamino)methyl substituents of the NCN ligand has been selectively protonated. This proton is hydrogen bonded to one of the chloride ligands (N−H···Cl 166.2°; H···Cl 1.94 Å). Because the spectroscopic data (NMR, IR) of **6** are very similar to those found for **4**, complex **6** is believed to have structural characteristics (both in solution and in the solid state) similar to **4**. The proton on the *ortho*-(dimethylamino)methyl group of the NCN ligand in **4** and **6** reacts immediately with an alkyl-Grignard or lithium reagents with formation of the corresponding alkane, the magnesium or lithium salt, and **3** and **5**, respectively. Further reactions of **2**, **4**, and **6** with an excess of HCl, aimed at cleaving one of the imido groups, yielded unidentifiable reaction mixtures instead.

Introduction

Molybdenum and tungsten alkylidenes have proven to be excellent metathesis catalysts and to show rigid control over ring-opening metathesis polymerization (ROMP) reactions with cyclic alkenes.[1] Tungsten(VI) alkylidene complexes containing monoanionic *C*,*N*- or *O*,*N*-chelating ligands show temperature-dependent ROMP activity toward norbornene.[2] Although complexes such as $[W({=}CHSiMe_3)(CH_2SiMe_3)\{OCPh_2(2\text{-py})\}(NPh)]$ (**1**) are unreactive in the polymerization of norbornene at room temperature, heating to 70 °C in benzene produces catalytic turnovers of more than 2×10^4/hour.[3] Apparently, **1** is a "latent" ROMP catalyst at room temperature. We were interested to study the catalytic properties of the corresponding molybdenum complexes.

Useful precursors for the synthesis of Mo analogs of **1** might be the molybdenum(VI) bis(imidoaryl) or -alkyl) dichloride complexes,[4,5] which are easily accessible and in high yields. The synthesis requires that one of the two imidoaryl groups is removed at some stage to produce the desired monoimido molybdenum complex. There are several examples known where a single imido group is protonated off by strong acids or acidic alcohols. Schrock and co-workers have developed a general entry into this field involving the reaction of $[Mo(CH_2R)_2(NAr)_2]$ complexes with trifluoromethanesulfonic acid (HOTf) in 1,2-dimethoxyethane (DME) to yield $[Mo({=}CHR)(OTf)_2(NAr)(DME)]$ and $[ArNH_3^+][OTf^-]$.[4] Similarly, Radius and Sundermeyer reacted $[CpMoCl(N\text{-}t\text{-}Bu)_2]$ or $[Cp^*MoCl(N\text{-}t\text{-}Bu)_2]$ with HCl to give the corresponding monoimido molybdenum compounds by

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removing the imido ligand as the ammonium chloride salt.[6] Independently, Osborn[7] et al. and Bell[8] and coworkers have used weak organic acids (HOC_6F_5 and $HOCH(CF_3)_2$, respectively) to remove one of the *t*-Bu-imido ligands.

Since we were interested in synthesizing molybdenum alkylidene compounds that contain monoanionic chelating ligands (cf. **1**), we have tested a two-step route to the molybdenum analogous of **1** starting from complexes containing two imidoaryl or -alkyl groups. This is then followed by the selective removal of one of the imido groups with HCl to give the target compound of general formula $[MoCl_3(NCN)(NR)]$ ($NCN = [C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$, R = *t*-Bu or $C_6H_3i\text{-}Pr_2\text{-}2,6$) (see eq 1).

$$\mathrm{MoCl_2(NR)_2(DME)} \xrightarrow[\text{-LiCl}]{\text{Li(NCN)}} \mathrm{MoCl(NCN)(NR)_2}$$
$$\xrightarrow{\text{HCl}} \mathrm{MoCl_3(NCN)(NR)}$$

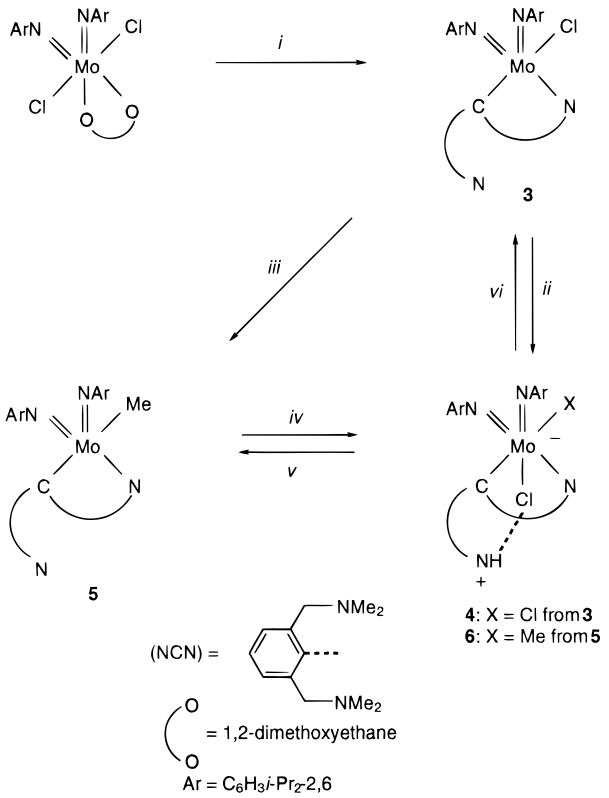
We were further interested in introducing the monoanionic, bis(aminomethyl)aryl "pincer" ligand 2,6-bis[(dimethylamino)methyl]phenyl (NCN).[9] This aryl carbanion has the ability to coordinate to a metal center in a variety of different binding modes.[10] This aspect may provide enhanced stability of the resulting catalysts, when compared to the bidentate analogs.

We here report the synthesis and reactivity of the bis(imido-*t*-Bu) precursor complex [MoCl(NCN)(N-*t*-Bu)$_2$] (**2**) and the synthesis, reactivity, and structural aspects of the bis(imidoaryl) precursor complexes [MoCl(NCN)(NAr)$_2$] (**3**) (Ar = $C_6H_3\text{-}i\text{-}Pr_2\text{-}2,6$) and its methylated derivative [Mo(NCN)(Me)(NAr)$_2$] (**5**). Moreover, we show that, in attempts to remove one of the imido ligands, the reaction of these complexes with HCl results in the formation of the corresponding chloro ammonium molybdates $[MoCl_2\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(CH_2NHMe_2)\text{-}6\}(NAr)_2]$ (**4**) and $[MoCl\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(CH_2NHMe_2)\text{-}6\}(Me)(NAr)_2]$ (**6**), respectively, via protonation of one of the *ortho*-CH_2NMe_2 groups. Remarkably, complexes **4** and **6** are air and thermally stable in the solid state.

Results and Discussion

Synthesis and Reactivity of [MoCl(NCN)(N-*t*-Bu)$_2$] (2). The reaction of [MoCl$_2$(N-*t*-Bu)$_2$(DME)] with 0.5 equiv of [Li(NCN)]$_2$[10,11] yielded [MoCl(NCN)(N-*t*-Bu)$_2$] (**2**) as a brown oil. Unfortunately, it was contaminated with small amounts of protonated NCN ligand ("pincerH"). Attempts to purify this compound were in vain. Reactions in which gaseous HCl was bubbled through a CH_2Cl_2 solution of **2** yielded a mixture of products, which also included paramagnetic compounds and additional "pincerH". None of the products formed in the early or final stages of the reaction could be isolated and identified (except "pincerH"). No formation of [MoCl$_3$(NCN)(N-*t*-Bu)] was observed.

Scheme 1[a]



Synthesis of Compounds 3–6. The reaction of 0.5 equiv of [Li(NCN)]$_2$ with [MoCl$_2$(NAr)$_2$(DME)][5] at −78 °C in Et$_2$O afforded the molybdenum(VI) compound [MoCl(NCN)(NAr)$_2$] (**3**) in 75% yield (see Scheme 1).

Complex **3** is a yellow solid that is thermally stable (<186 °C) in an inert atmosphere but decomposes in air within several hours. This material is soluble in most polar and aromatic solvents but has limited solubility in pentane and hexanes.

Reaction of 1 equiv of MeMgCl with **3** in THF at ambient temperature affords the corresponding methylated compound [Mo(NCN)(Me)(NAr)$_2$] (**5**) in 93% yield (see Scheme 1). Complex **5** is a yellow solid and is stable in air for several hours without any noticeable decomposition.

The treatment of a solution of both **3** and **5** (in CH_2Cl_2) with 1 equiv of anhydrous HCl at −20 °C (see Scheme 1) results in an immediate color change from orange to a dark red color. After workup, red air-stable solids were obtained, e.g. [MoCl$_2$\{η^2-C,N−NC(NH)\}(NAr)$_2$] (**4**) (yield > 95%) and [MoCl\{NC(NH)\}(Me)(NAr)$_2$] (**6**) (yield: 87%), which were further analyzed by elemental analysis and NMR and IR spectroscopy. Elemental analysis pointed to the presence of an extra chloride in both **4** and **6**, i.e. to a Mo:Cl stoichiometry of 1:2 in **4** and 1:1 in **6**, respectively.

Attempts to displace the chloride(s) in **4** and **6** with alkylmagnesium or alkyllithium reagents were unsuccessful. For example, addition of 1 equiv of *n*-BuLi to an Et$_2$O solution of 1 equiv of **4** and **6** resulted in deprotonation of **4** and **6** and afforded **3** and **5** and LiCl, respectively (see Scheme 1). A similar result was obtained when a nonnucleophilic organic base, e.g. N(*i*-Pr)$_2$Et, was used.

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(9) (NCN) is also referred to as "pincer".

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When compounds **4** and **6** were reacted with a second 1 equiv of anhydrous HCl (or with an excess of gaseous HCl in CH_2Cl_2) to obtain the corresponding monoimido derivatives, mixtures of products, including paramagnetic molybdenum compounds, were obtained from which no pure products could be isolated.

NMR and IR Spectroscopy. The ^1H NMR spectrum of **3** (C_6D_6) shows sharp singlet resonances for both the benzylic and the dimethylamino groups (3.77 and 2.30 ppm, respectively, at 300 K). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **5** (C_6D_6) show similar resonances but exhibit an auxiliary Me resonance at 1.03 ppm (^1H) and 22.6 ppm ($^{13}C\{^1H\}$ NMR), respectively. The NMR spectra of **3** and **5** indicate the presence of a molecular symmetry plane in the complexes (in the range of 220−300 K) that renders both *ortho*-CH_2NMe_2 substituents equivalent on the NMR time scale but give no further information about the actual coordination mode of the NCN ligand. As the single-crystal X-ray determination of **3** has shown that the NCN ligand is η^2-*C,N* bonded in the solid state (vide infra), the apparent molecular symmetry plane present in solution must arise from fluxional processes involving alternating reversible N−Mo breaking and formation and η^1-*C*-NCN aryl rotation around the C_{ipso}−Cl1 axis. Similar fluxional processes have also been observed for tantalum[12] and rhenium[13] NCN complexes.

The ^1H NMR spectra of **4** and **6** ($CDCl_3$) show two different sets for the benzylic and dimethylamino signals of which one set appears as two doublets. Moreover, a broad singlet is observed at 12 ppm. When this signal is irradiated, the pair of doublets decouple and become singlet resonances. These observations point to the protonation of one *ortho*-CH_2NMe_2 substituent while the other amino substituent is still coordinated to the Mo center; i.e., the pincer ligand is still η^2-*C,N*-bidentate coordinated as has been the case in complexes **3** and **5**. These conclusions are corroborated by the IR spectra of **4** and **6**, which clearly show a broad absorption band at 2500 cm^{-1} for the N−H bond in **4** and at 2390 cm^{-1} for the corresponding bond in **6** (these absorptions are absent in **3** and **5**). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **6** ($CDCl_3$) display an additional Me resonance at 1.10 ppm (^1H) and 26.0 ppm ($^{13}C\{^1H\}$), respectively, which shows that not only the Mo−aryl bond but also the Mo−Me bond remains intact after reaction with HCl.

Finally, both the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4** and **6** show broad signals for one set of methyl groups assigned to the isopropyl moiety, probably due to hindered rotation around the aryl−(*i*-Pr)carbon bond. These sharpen upon heating the sample to 330 K.

Solid-State Structures. Conclusive information concerning the (ground state) structures of compounds **3**−**5** and **6**, in particular concerning the actual coordination mode of the NCN ligands, came from the results of single-crystal X-ray structure determinations of **3**−**5**. These molecular structures with the adopted numbering schemes are depicted in Figures 1−3, respectively.

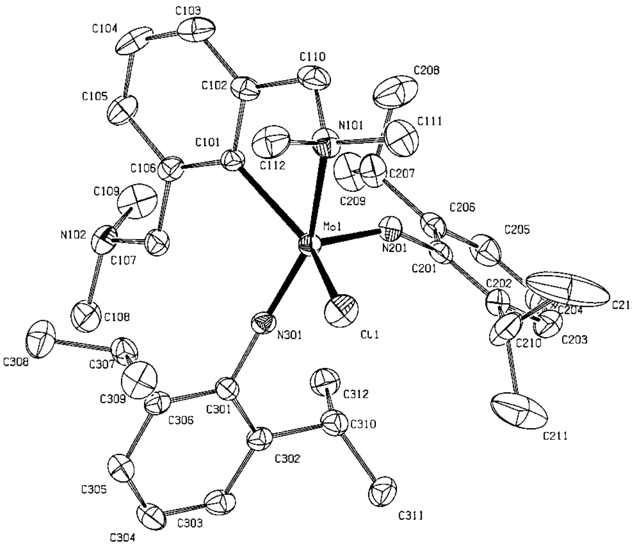

Figure 1. ORTEP drawing (50% probability atomic displacement ellipsoids) of **3**. Hydrogen atoms have been omitted for clarity.

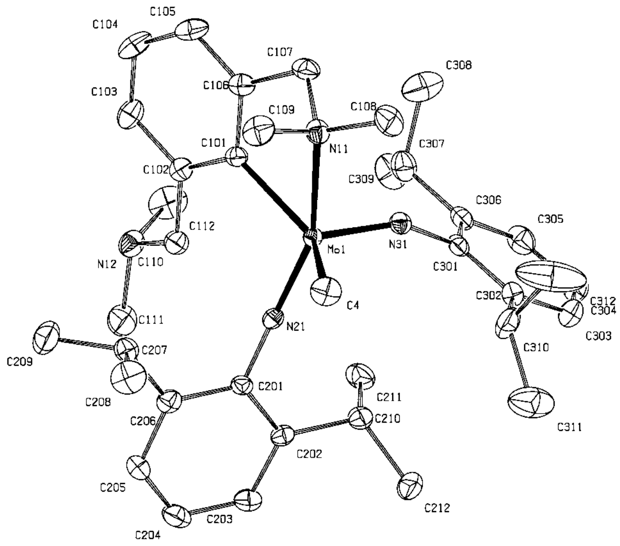

Figure 2. ORTEP drawing (50% probability atomic displacement ellipsoids) of **4**. Hydrogen atoms (except H1) and a Et_2O solvent molecule have been omitted for clarity.

The geometry around the molybdenum metal center of **3** can be best described as distorted square pyramidal (81.3% along the Berry-pseudorotation coordinate from trigonal bipyramid to square pyramid) in which the imido ligand (connected via N201) occupies the apical position. The metal lies slightly above the basal plane defined by C101, N101 of the η^2-coordinated NCN ligand, N301 of the second imido ligand, and the chloride ligand. The amino-N (N102) of the second *ortho*-(dimethylamino)methyl substituent is not coordinated to the molybdenum atom.

Compound **5** has the ligands arrayed similarly to what was found for the solid-state structure of **3** (73.5% along the Berry-pseudorotation coordinate from trigonal bipyramid to square pyramid). The metal−carbon bond distance (Mo1−C4) observed for compound **5** is in the upper part of the range for those found for other molybdenum alkyl complexes (2.08−2.20 Å).[8,14] No agostic M−H interactions were found.

Complex **4** is indeed the HCl adduct of **3** in which one (dimethylamino)methyl substituent has been selectively

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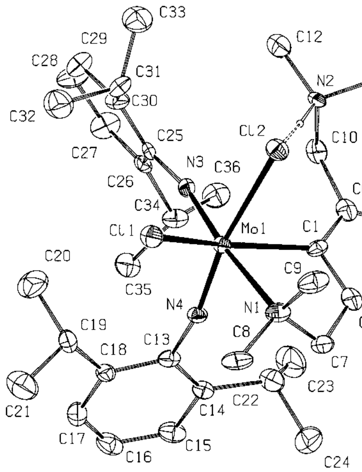

Figure 3. ORTEP drawing (50% probability atomic displacement ellipsoids) of **5**. Hydrogen atoms have been omitted for clarity.

protonated and the chloride ligand is bonded to the molybdenum metal center, i.e., [MoCl$_2$\{C$_6$H$_3$(CH$_2$NMe$_2$)-2-(CH$_2$NHMe$_2$)-6\}(NAr)$_2$]. It is therefore a six-coordinate species as a result of the coordination of a second chloride ligand; the NCN ligand is η^2-*C,N*-bidentate coordinated. Two factors determine the rather large differences in bond lengths of especially Mo1−Cl1 and Mo1−Cl2 ($\Delta \sim 0.3$ Å): (i) the stereochemistry at the molybdenum center in which each chloride has a different trans-ligand, i.e. the aryl C_{ipso} and NAr, respectively, and (ii) the presence of the hydrogen bond to Cl2 which causes lengthening of the Mo1−Cl2 bond. The proton of the ammonium moiety is pointing toward a metal-bonded chloride atom, and the nitrogen and chloride atoms are thus connected via a H-bridge (N2−H1···Cl2 166.2 °; H1···Cl2 1.94 Å). The intramolecular N−H···Cl formation further appears from the IR absoptions of **4** and **6**, which are at lower frequencies than the N−H absorptions of free tertiary ammonium salts (ca. 2700 cm^{-1}).[15] The IR data suggest that the H−N bond is weaker in **6** than in **4** (and consequently the H−Cl hydrogen bond in **6** is stronger than in **4**), a fact which is confirmed by the ^{1}H and ^{13}C\{^{1}H\} NMR HNMe_2 chemical shift values of both compounds (**4**, $\delta = 2.25$ and 42.0 ppm; **6**, $\delta = 2.17$ and 41.7 ppm, respectively). Because **6** shows spectroscopic features very similar to those of **4**, we believe that **6** has similar structural characteristics in the solid state.

In the reactions of **3** and **5** with anhydrous HCl no protonation of a NAr moiety takes place but instead one of the *ortho*-(dimethylamino)methyl substituents is quarternized. Apparently, the free *ortho*-(dimethylamino)methyl substituent acts as an intramolecular Lewis base. The second chloride ligand is bonded to the molybdenum center with formation of the chloro ammonium molybdates **4** and **6** (which shows the high Lewis acidity of the Mo center in the neutral compounds **3** and **5**). Similar protonation reactions which resulted in intramolecular hydrogen bond formation have been reported earlier by our group and by others.[16]

The difference in Lewis acidity of the molybdenum(VI) centers in **3** (formally a 14 electron species) and **4** (formally a 16 electron species) is reflected in the Mo−C and Mo−N bond distances of the η^2-*C,N*-bonded pincer ligand. This comparison is valid because the trans influences of the ligands in both complexes are almost the same. The Mo1−N101 and Mo1−C101 distances for the chloride compound **3** are significantly shorter than these distances (Mo1−N1 and Mo1−C1) in the ammonium molybdate derivative **4**. The protonated nitrogen of the second *ortho*-(dimethylamino)methyl substituent forms an intramolecular hydrogen bond with the second chloride ligand in **4**. Moreover, this chloride is stabilized by the hydrogen bond. Apparently, the extra negative charge in molybdenum center of **4** is distributed over the anionic ligands, resulting in overall longer bond distances. Although the imido Mo−N distances in **3** (Mo1−N201 and Mo1−N301) and **4** (Mo1−N3 and Mo1−N4) are almost identical, the Mo−N−C bond angles are substantially different as a result of the change in the overall coordination number (i.e. orbital occupancy) of the molybdenum center. For **3** the apical imido nitrogen (N201) has an angle of 150.2(3)° whereas this angle in the second imido nitrogen (N301) is 172.0(3)°. In the molybdate compound **4**, both imido ligands are slightly bent, 163.9(5)° vs 168.9(6)°. It must be noted, however, that the bond angles at a terminal imido NR ligand often are influenced by interligand steric interactions and crystal packing forces. Therefore, conclusions concerning the electron deficiency of the metal drawn from the bond angle of the imido ligand have to be used with caution.[17]

Reactivity of [MoCl\{C$_6$H$_2$Me$_3$-2,4,6\}(NAr)$_2$] (7). To investigate whether removal of an imido ligand was possible in the case of a related aryl−molybdenum complex, we reacted [MoCl\{C$_6$H$_2$Me$_3$-2,4,6\}(NAr)$_2$] (**7**) (Ar = C$_6$H$_3$-*i*-Pr$_2$-2,6), which has hindering, but not potentially coordinating, *ortho*-methyl substituents, with HCl (in Et$_2$O) and observed protonation of the *mesityl* fragment. The same reaction in DME results in the isolation of *mesitylene* and the starting compound [MoCl$_2$(NAr)$_2$(DME)]. No 2,6-diisopropylaniline or the corresponding ammonium salt was observed. This shows that the (C$_6$H$_2$Me$_3$-2,4,6) ligand is protonated rather than the imidoaryl nitrogen, and moreover, it demonstrates the ability of the "pincer" ligand to form stable molybdates by accommodating HCl in the complexes rather than Mo−C bond cleavage taking place.[18]

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(18) When compounds **3** and **5** were reacted with anhydrous HCl in DME (instead of CH$_2$Cl$_2$ or Et$_2$O as a solvent), compounds **4** and **6** were formed, respectively. No "pincerH" was found.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry and deoxygenated dinitrogen using standard Schlenk techniques unless otherwise stated. All solvents were carefully dried and distilled from sodium under nitrogen, prior to use, except CH_2Cl_2, which was distilled from CaH_2. The ^1H (300 MHz) and $^{13}C\{^1H\}$ (75 MHz) NMR spectra were recorded in benzene-d_6 at room temperature unless otherwise indicated. Chemical shifts (in ppm) are referenced to Me_4Si. Reflectance infrared spectra were recorded in KBr. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Commercially available reagents were used as supplied. $[MoCl_2(NAr)_2(DME)]$,[5] $[MoCl_2(N\text{-}t\text{-}Bu)_2(DME)]$,[5] $[Mg\{C_6H_2Me_3\text{-}2,4,6\}]$,[19] and $[Li(NCN)]_2$[11] were synthesized according to literature procedures.

$[MoCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(N\text{-}t\text{-}Bu)_2]$ (2). A solution of $[Li(NCN)]_2$ (0.21 g, 1.08 mmol) in Et_2O (20 mL) was slowly added to an Et_2O solution (80 mL) of $[MoCl_2(N\text{-}t\text{-}Bu)_2(DME)]$ (0.43 g, 1.08 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The color of the reaction mixture changed from dark red to yellow/brown. After 18 h, all volatiles were removed in vacuo and the residual solids were suspended in pentane (80 mL). The off-white precipitates were removed by centrifugation, and the pentane layer was collected. The solvent was then evaporated from the pentane layer leaving a yellow/brown oil (compound **2**; yield 0.44 g (88%)) which was analyzed by NMR. ^1H NMR (δ): 7.40 (d, 2, *m*-aryl-H); 7.23 (t, 1, *p*-aryl-H); 3.84 (s, 4, CH_2); 2.39 (s, 12, NMe_2); 1.44 (s, 18, $NC\mathit{Me}_3$). ^{13}C NMR (δ): 174.5 (C_{ipso}), 146.7 (C_{ortho}), 127.7 (C_{para}), 124.3 (C_{meta}), 70.7 (CH_2), 70.0 ($N\mathit{C}Me_3$), 47.5 (NMe_2), 31.2 ($NC\mathit{Me}_3$). No satisfactory elemental analysis was obtained because the yellow/brown oil (**2**) always contained small amounts (10−20%) of protonated NCN ligand $[C_6H_4(CH_2NMe_2)_2\text{-}2,6]$ which was very difficult to remove.

$[MoCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(NAr)_2]$ (3). A solution of $[Li(NCN)]_2$ (1.02 g, 5.14 mmol) in Et_2O (20 mL) was slowly added to a Et_2O/benzene solution (60 mL/20 mL) of $[MoCl_2(NAr)_2(DME)]$ (3.12 g, 5.14 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The color of the reaction mixture changed from dark red to orange/brown. After 18 h, all volatiles were then removed in vacuo and the residual solids were suspended in benzene (80 mL). The off-white precipitates were removed by centrifugation, and the benzene layer was collected. The solvent was then evaporated from the benzene layer, and the residual solids were suspended in Et_2O (20 mL). Pentane was added (50 mL), and the orange precipitate was collected and washed with pentane (3 × 30 mL). All volatiles were removed in vacuo (3 h, 70 °C) leaving a yellow solid (compound **3**; yield 2.59 g (75%)) which was pure by NMR and elemental analysis. Crystals suitable for X-ray analysis were obtained by cooling an Et_2O solution to −30 °C. ^1H NMR (δ): 7.40 (d, 2, *m*-ArH−NCN); 7.25 (t, 1, *p*-ArH−NCN); 7.00 (m, 6, NAr−H); 3.78 (sept, 4, $C\mathit{H}Me_2$), 3.77 (s, 4, CH_2); 2.30 (s, 12, NMe_2); 1.12 (d, 12, $CH\mathit{Me}_2$); 1.09 (d, 12, $CH\mathit{Me}_2$). ^{13}C NMR (δ): 177.4 (C_{ipso}), 153.7 (C_{ipso} NAr), 148.7, 145.6, 128.7, 127.8 (aryl-C), 70.6 (CH_2), 47.5 (NMe_2), 28.6 ($\mathit{C}HMe_2$), 24.6 ($CH\mathit{Me}_2$), 23.7 ($CH\mathit{Me}_2$). T_{decomp} = 186 °C. Anal. Found (calcd) for $C_{36}H_{53}ClMoN_4$: C, 64.38 (64.23); H, 7.88 (7.94); N, 8.36 (8.32).

$[MoCl_2\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(CH_2NHMe_2)\text{-}6\}(NAr)_2]$ (4). A solution of anhydrous HCl (320 μL, 3.72 M) in Et_2O was added dropwisely to a solution of **3** (0.80 g, 1.19 mmol) in CH_2Cl_2 (40 mL) at −20 °C. The solution immediately turned from orange to deep red. After the solution was warmed to room temperature and stirred for 1 h, the solvents were removed in vacuo leaving a residual dark red solid. This material was washed with Et_2O (3 × 20 mL). The volatiles were then removed from the residual material in vacuo leaving a dark red solid which was washed with pentane (2 × 20 mL). The red product (compound **4**) was dried in vacuo (2 h, 60 °C) and was pure by NMR and elemental analysis. Yield: 0.84 g (100%). Crystals suitable for X-ray analysis were obtained by cooling an Et_2O solution to −30 °C. Crystals obtained this way contain one Et_2O solvent molecule per molecule of **4**. ^1H NMR (δ, $CDCl_3$): 12.09 (b, 1, $N\mathit{H}Me_2$), 7.49 (t, 1, *p*-ArH−NCN), 7.29 (d, 2, *m*-ArH−NCN), 7.01 (m, 6, ArH), 4.29 (s, 2, $C\mathit{H}_2NMe_2$), 4.08 (d, 2, $C\mathit{H}_2NHMe_2$), 3.58 (b, 4, $C\mathit{H}Me_2$), 2.84 (s, 6, NMe_2), 2.25 (d, 6, $NH\mathit{Me}_2$), 0.99 (d, 12, $CH\mathit{Me}_2$), 0.91 (b, 12, $CH\mathit{Me}_2$). ^{13}C NMR (δ, $CDCl_3$): 181.7 (C_{ipso}), 153.5 (C_{ipso} NAr), 147.9, 144.1, 136.7, 128.9, 127.7, 126.4, 125.7, 123.1 (aryl-C), 72.4 ($\mathit{C}H_2NMe_2$), 67.1 ($\mathit{C}H_2NHMe_2$), 50.4 ($N\mathit{Me}_2$), 42.0 ($NH\mathit{Me}_2$), 27.6 ($\mathit{C}HMe_2$), 26.5 and 23.4 (b, $CH\mathit{Me}_2$). T_{decomp} = 185 °C. Anal. Found (calcd) for $C_{36}H_{54}Cl_2MoN_4$: C, 60.75 (60.93); H, 7.58 (7.67); N, 7.84 (7.87). Infrared spectrum of **4** in KBr: ν(N−H) 2500 cm^{-1} (broad).

Table 1. Selected Geometrical Details for 3−5[a]

	$[MoCl(\eta^2\text{-}C,N\text{-}NCN)(NAr)_2]$ (**3**)	$[MoCl_2\{\eta^2\text{-}C,N\text{-}NC(NH)\}(NAr)_2]$ (**4**)	$[Mo(\eta^2\text{-}C,N\text{-}NCN)(Me)(NAr)_2]$ (**5**)
	Bond Lengths (Å)		
Mo1−Cl1	2.413(2)	2.4350(17)	
Mo1−Cl2		2.721(2)	
Mo1−C101	2.184(5)		2.205(3)
Mo1−N101	2.335(4)		
Mo1−N201	1.759(3)		
Mo1−N301	1.744(4)		
N2−H1		1.0789	
Cl2−H1		1.9414	
Mo1−C1		2.198(7)	
Mo1−N1		2.430(5)	
Mo1−N3		1.771(5)	
Mo1−N4		1.768(6)	
Mo1−C4			2.194(3)
Mo1−N11			2.376(4)
Mo1−N21			1.749(3)
Mo1−N31			1.758(2)
N21−C201			1.387(4)
N31−C301			1.400(4)
	Bond Angles (deg)		
Mo1−N201−C201	150.2(3)		
Mo1−N301−C301	172.0(3)		
Cl1−Mo1−C101	141.1(9)		
Cl1−Mo1−Cl2		79.70(6)	
Cl2−H1−N2		166.18	
Mo1−N4−C13		163.9(5)	
Mo1−N3−C25		168.9(6)	
C4−Mo1−C101			136.90(12)
Mo1−N21−C201			174.5(2)
Mo1−N31−C301			151.4(2)
N11−Mo1−C4			80.05(12)

[a] The estimated standard deviations of the last significant digits are shown in parentheses.

$[Mo(C_6H_3(CH_2NMe_2)_2\text{-}2,6)(Me)(NAr)_2]$ (5). To a solution of **3** (0.85 g, 1.26 mmol) in THF (100 mL) was carefully added 0.42 mL (1.26 mmol) of a 3.0 M MeMgCl solution in THF at −30 °C. After the addition was completed, the reaction mixture was warmed to room temperature. After 4 h all volatiles were removed in vacuo (1 h, 50 °C), and 100 mL of Et_2O was added. The precipitate was separated from the clear solution by centrifugation and was washed with Et_2O (30 mL) again. The clear yellow Et_2O layers were combined, and all volatiles were removed in vacuo leaving 0.76 g (93%) of a yellow product which was pure by NMR and elemental analysis. Crystals suitable for X-ray analysis were obtained by cooling an Et_2O solution to −30 °C. ^1H NMR (δ): 7.45 (d, 2, *m*-ArH−NCN), 7.29 (t, 1, *p*-ArH−NCN), 7.05 (m, 6, NAr−H), 3.83 (s, 4, CH_2), 3.77 (sept, 4, $C\mathit{H}Me_2$), 2.18 (s, 6, NMe_2), 1.13 (d, 6, $CH\mathit{Me}_2$), 1.09 (d, 6, $CH\mathit{Me}_2$), 1.03 (s, 3, Mo−Me), ^{13}C NMR (δ): 179.6 (C_{ipso}), 153.1 (C_{ipso} NAr), 148.6, 144.6, 128.3, 127.7, 126.0, 123.6, 122.7 (aryl-C), 71.8 (CH_2), 47.6 (NMe2), 28.4 ($\mathit{C}HMe_2$), 24.6 ($CH\mathit{Me}_2$), 23.7 ($CH\mathit{Me}_2$), 22.6 (Mo-Me). T_{decomp} = 153 °C. Anal.

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Table 2. Experimental Data for the X-ray Diffraction Studies of 3−5

	3	**4**	**5**
formula	$C_{36}H_{53}N_4ClMo$	$C_{36}H_{54}N_4Cl_2Mo(Et_2O)$	$C_{37}H_{56}N_4Mo$
fw	673.24	783.79	652.82
T (K)	150	150	150
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.960(2)	10.907(1)	10.0551(8)
b (Å)	34.617(3)	23.979(2)	34.149(3)
c (Å)	11.909(3)	18.774(2)	11.9901(3)
β (deg)	121.177(15)	124.04(1)	121.299(6)
V (Å^3)	3513.0(13)	4068.8(8)	3517.9(5)
Z	4	4	4
d_{calcd} (g·cm^{-3})	1.273	1.280	1.233
F(000) (e)	1424	1664	1392
μ (Mo Kα) (cm^{-1})	4.8	4.9	4.0
cryst size (mm)	0.15 × 0.20 × 0.75	0.05 × 0.35 × 0.45	0.15 × 0.63 × 0.70
radiation (Å)	Mo Kα (0.710 73)[a]	Mo Kα (0.710 73)[a]	Mo Kα (0.710 73)[a]
θ^{min}, θ^{max} (deg)	1.2, 27.5	1.6, 27.2	1.2, 26.5
scan (ω-mode) (deg)	$0.72 + 0.35\tan(\theta)$	$0.80 + 0.35\tan(\theta)$	$0.94 + 0.35\tan(\theta)$
$h;k;l$ (min, max)	−12,12;−44,0;−12,15	0,11;−25,0;−19,20	−12,11;−41,0;−15,11
tot/unique reflcns	8727, 8032	5299, 4984	7330, 6972
obsd reflcns	5088 ($I > 2.0\sigma(I)$)	3302 ($I > 2.0\sigma(I)$)	5586 ($I > 2.0\ \sigma(I)$)
N_{ref}, N_{par}	8031, 391	4984, 448	6972, 392
R; wR; S[b]	0.0571;0.1160;1.01	0.0514;0.0981;1.02	0.0377;0.0801;1.13
weight (w^{-1})[c]	$\sigma^2(F_o^2) + (0.0273P)^2 + 2.9916P)$	$\sigma^2(F_o2) + (0.0110P)^2 + 11.2264P$	$\sigma^2(F_o2) + (0.0073P)^2 + 6.3894P$
min, max resd dens (e/Å^3)	−0.67, 0.61	−0.51, 0.86	−0.63, 0.76

[a] Graphite monochromated. [b] $R = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $P = (\mathrm{Max}(F_o^2, 0) + 2 F_c^2)/3$.

Found (calcd) for $C_{37}H_{56}MoN_4$: C, 67.24 (68.07); H, 8.44 (8.65); N, 8.37 (8.58).

[MoCl{$C_6H_3(CH_2NMe_2)$-2-(CH_2NHMe_2)-6}(Me)(NAr)$_2$] (6). A solution of anhydrous HCl (280 μL, 3.72 M) in Et_2O was added dropwisely to a solution of **5** (0.67 g, 1.03 mmol) in Et_2O (50 mL) at −20 °C. The solution immediately turned from orange to red. After 10 min, the volatiles were removed in vacuo leaving a residual red solid. This material was dissolved in CH_2Cl_2, and the small amount of solid was removed by centrifugation. The clear upper layer was collected, and the solvent was evaporated in vacuo. The residual red solid was washed with pentane (3 × 30 mL); the remaining red solid was dried in vacuo and dissolved in CH_2Cl_2 (30 mL), and pentane (20 mL) was added. The solution was cooled to −30 °C, and after 2 days bright red crystals could be isolated. Yield: 0.62 g (87%, in three crops). ^{1}H NMR (δ, $CDCl_3$): 12.03 (b, 1, NHMe$_2$), 7.86 (d, 1, m-ArH−NCN), 7.35 (t, 1, p-ArH−NCN), 7.27 (d, 1, m-ArH−NCN), 7.03 (m, 6, ArH), 4.31 (s, 2, CH_2NMe$_2$), 4.27 (d, 2, CH_2NHMe$_2$), 3.47 (sept, 4, CHMe$_2$), 2.73 (s, 6, NMe$_2$), 2.17 (d, 6, NHMe_2), 1.10 (s, 3, Mo-Me), 0.98 (d, 12, CHMe_2), 0.91 (b, 12, CHMe_2). ^{13}C NMR (δ, $CDCl_3$): 181.9 (C$_{ipso}$), 152.4 (C$_{ipso}$ NAr), 147.9, 144.1, 139.0, 128.6, 127.8, 125.9, 124.8, 122.8 (aryl-C), 74.3 (CH$_2$NMe$_2$), 65.9 (CH$_2$NHMe$_2$), 49.9 (NMe_2), 41.7 (NHMe_2), 27.8 (CHMe$_2$), 26.0 (Mo−Me), 23.4 (b, CHMe_2). T_{decomp} = 131 °C. Anal. Found (calcd) for $C_{37}H_{57}ClMoN_4(C_5H_{12})$: C, 66.61 (66.25); H, 9.29 (9.13); N, 7.56 (7.36). The compound contains a pentane solvent molecule which was confirmed by NMR. Infrared spectrum of **6** in KBr: ν(N−H) 2390 cm^{-1} (broad).

[MoCl{$C_6H_2Me_3$-2,4,6}(NAr)$_2$] (7). A solution of [Mg{$C_6H_2Me_3$-2,4,6}] (0.69 g, 2.34 mmol) in Et_2O (20 mL) was added slowly to a solution of [Mo(NAr)$_2$Cl$_2$(DME)] (1.42 g, 2.34 mmol) in Et_2O (80 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature. After 18 h the color had changed from dark red to red. The off-white precipitate was then removed by centrifugation, and the Et_2O layer was collected. The volume of the Et_2O was reduced to 40 mL, and after 4 days at −30 °C, 0.84 g (1.40 mmol, 60% yield) of dark red crystals of **7** were collected. ^{1}H NMR (δ): 6.97 (s, 6, NAr-H); 6.67 (s, 2, mes-H); 3.81 (sept, 4, CHMe$_2$), 2.75 (s, 6, o-Me); 2.01 (s, 3, p-Me); 1.08 (d, 24, CHMe_2). ^{13}C NMR (δ): 185.3 (C$_{ipso}$), 154.2 (C$_{ipso}$ NAr), 144.0 (C$_{para}$ NAr), 142.6 (C$_{ortho}$ NAr), 141.1 (C$_{para}$), 128.8 (C$_{meta}$), 128.0 (C$_{meta}$ NAr), 123.1 (C$_{ortho}$ NAr), 29.0 (CHMe$_2$), 25.2 (o-Me), 24.1 (CHMe_2), 23.3 (CHMe_2), 21.3 (p-Me). T_{decomp} = 157 °C. Anal. Found (calcd) for $C_{33}H_{45}ClMoN_2$: C, 61.56 (65.94); H, 7.06 (7.55); N, 4.30 (4.66).[20]

Reaction of [MoCl{$C_6H_2Me_3$-2,4,6}(NAr)$_2$] (7) with HCl. A solution of anhydrous HCl (290 μL, 3.72 M) in Et_2O was added dropwisely a solution of **7** (0.65 g, 1.08 mmol) in Et_2O (or DME) (50 mL) at −20 °C. The reaction was allowed to warm to room temperture (15 min). After 1 h, the volatiles were removed in vacuo leaving a residual sticky red solid which was analyzed by NMR as a mixture of imidoaryl-containing molybdenum compounds ([MoCl$_2$(NAr)$_2$(DME)] when the reaction was performed in DME) and *mesitylene*.

Structure Determination and Refinement of 3−5. X-ray data were collected on an Enraf-Nonius CAD4-T rotating anode diffractometer for a transparent, yellowish (**3** and **5**) or red (**4**) crystal glued on top of a glass fiber. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of the setting angles of a set of 25 well-centered reflections (SET4).[21] The unit-cell parameters were checked for the presence of higher lattice symmetry. An empirical absorption correction was applied (PLATON/DELABS).[22] The structures were solved by direct methods and subsequent difference Fourier techniques (SHELXS86).[23] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL93)[24] using no observance criterion. Hydrogen atoms were included on calculated positions, riding on their carrier atoms except for H1 in **4** which was found in the difference Fourier map. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. All hydrogen atoms were refined with a fixed isotropic atomic displacement parameter related to the value of the equivalent isotropic atomic displacement parameter of their carrier atom. Weights

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(20) The constant relative differences (7 ± 1%) between the calculated and found percentages in the elemental analysis of **7** might be caused by a contamination of ∼30% MgClBr. Since the material, which was sent away for analysis, was crystalline, this seems an unlikely explanation, and moreover, solutions of **7** in C_6D_6 did not contain precipitates. A likely explanation of this systematic error is that a weighing mistake took place.

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were optimized in the final refinement cycles. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography.[25] Geometrical calculations and illustrations were performed with PLATON.[22] All calculations were performed on a DECstation 5000 cluster. Crystal data and numerical details of the structure determinations and refinements are collected in Table 2. Selected geometrical details of the structures of **3**−**5** are listed in Table 1.

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Supporting Information Available: Tables of the structure determination, atomic coordinates, bond lengths and angles, and thermal parameters for **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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