Dioxo-, Oxo-imido-, and Bis-imido-Molybdenum(VI) Complexes with a Bis-phenolate-NHC Ligand

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S Supporting Information

ABSTRACT: We report the facile synthesis of five rare high-valent Mo(VI)-NHC complexes with a dianionic OCO-pincer benzimidazolylidene ligand (L^1) with the general formula L^1MoO_2 (1), $L^1Mo(O)(N^tBu)(THF)$ (2), $L^1Mo(N^tBu)(NH^tBu)Cl$ (3), $L^1Mo(N^tBu)_2$ (4), and $L^1 Mo(NMes)_2$ (5). These complexes represent a complete series of high-valent molybdenum(VI) complexes, obtained by consecutive exchange of the oxo for imido ligands from the dioxo complex (1) to the bis-imido complexes (4)and 5). The complexes can be synthesized in high yields following a simple deprotonation protocol, using either triethylamine or lithium diisopropylamide (LDA) as a base. All complexes have been characterized by various techniques, including ¹H, ¹³C(¹H), and ¹⁵N NMR spectroscopy, IR spectroscopy, and X-ray diffraction analysis. Except for the dioxo complex 1, all complexes adopt monomeric structures in the solid state. Compounds 1, 4, and 5 are rare examples of five-coordinated molybdenum(VI)



complexes in the solid state, while 2 is six-coordinated, having a weakly bound THF ligand in the axial position. The dioxo complex 1 was found to be stable under air and moisture in the solid state as well as in solution for several days. Furthermore, preliminary reactivity studies and an approximate determination of the pK_a value of the imido ligands in 4 are presented.

INTRODUCTION

High-valent molybdenum-oxo complexes as catalysts are of considerable interest for a large variety of reactions, including oxidative or reductive transformations¹⁻⁴ via oxygen atom transfer reactions (OATR), arene coupling reactions,⁵ oxygen activation,⁶⁻⁸ and polymerizations.⁹⁻¹³ One big advantage of molybdenum compared with many other 4d and 5d metals (e.g., rhenium, tungsten, tantalum, or niobium) is its low toxicity, biocompatibility, and low price.¹⁴ In this context, a large variety of ligands have been explored in recent years for the synthesis of high-valent molybdenum complexes.^{3,15-21} However, searching through the library of ligands explored, it becomes obvious that examples of one of the most prominent ligands in catalysis are rare and that, despite the ongoing interest in N-heterocyclic carbenes (NHCs), high-valent dioxomolybdenum complexes with NHC ligands are scarce. Pioneering work performed by Herrmann et al. in 1996 showed that NHC ligands are in principle well suited for the use in high-valent molybdenum chemistry; however, the resulting complexes were extremely sensitive toward air, moisture, and "acidic" solvents (e.g., chloroform), resulting in fast hydrolysis of the complexes.²² The sensitivity of these complexes was further probed by Royo et al., showing that the substituents on the nitrogen atoms as well as on the NHC backbone have a major influence on the stability of the complexes toward hydrolysis.²³ According to the authors, the high sensitivity of molybdenum NHC complexes toward hydrolysis renders their application in chemical catalysis rather

dim. However, in 2010, Hor and co-workers showed that in situ generated (NHC)CpMoO2 complexes are indeed potent catalysts for the epoxidation of cyclooctene.²⁴ Two years later, the same work group also structurally characterized the first example of a cationic Mo(VI)Cp(NHC) complex.²⁵ However, the structure was found to have the Lindqvist-type²⁶ anion [Mo₆O₂₄]²⁻, which most likely resulted from the decomposition of the synthesized tetrafluoroborate salt (Figure 1).



Figure 1. Previously reported attempts to isolate stable molybdenum-(VI)-NHC complexes.

Inspired by the work of Buchmeiser et al.²⁷ who showed that NHC complexes of high-valent molybdenum alkylidene and alkylidyne complexes are valuable catalysts in metathesis reactions and polymerizations, $^{10,28-40}$ we were interested in exploring the coordination chemistry of other high-valent molybdenum(VI) units, especially the above-mentioned dioxo

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Scheme 1. Synthesis of the Four Molybdenum Complexes 1-4 Featuring a Dianionic Bis-phenolate-NHC Ligand

Figure 2. ORTEP plot of 1-mono (left) and 1-dimer (right). ^tBu groups have been truncated and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at a probability level of 50%.

and the bis-imido frameworks. However, since previous studies showed that these complexes can be quite challenging in their synthesis, we sought for NHC ligands with anionic linker atoms, which facilitate the metal binding of the NHC ligand and enforce a stronger bonding of the NHC to the metal center. Employing this strategy has led to the isolation of various unusual main group, $^{41-45}$ early transition metal, $^{45-52}$ late transition metal $^{43,53-56}$ and f-element NHC complexes⁵⁷⁻⁷³ with unique reactivity patterns and spectroscopic as well as electrochemical properties. In our search for a NHC ligand that is capable of forcing the metal center to bind to the NHC moiety by using anionic linker groups, we came across the bis-phenol benzimidazolium chloride $[H_3L^1]Cl$ introduced by Bercaw et al.⁷⁴ and by Bellemin-Lapponnaz.⁷⁵ Besides forcing the NHC moiety in a close proximity to the molybdenum center, this ligand also holds two phenolates, which already have independently shown to be valuable coligands in molybdenum chemistry. $^{76-85}$ Additionally, L¹ as well as other structurally related bis-phenolate imidazolylidene ligands have been shown to be excellent supporting ligands for the synthesis and design of main group complexes such as aluminum,⁸⁶ and high-valent early transition metal complexes including titanium,^{87,88} zirconium,^{88–91} hafnium,^{88,91} vanadium,⁹² and manganese.⁹² Only recently Buchmeiser et al. have been able to stabilize a molybdenum alkylidine complex using this ligand.93

RESULTS AND DISCUSSION

Treatment of a THF solution of the ligand precursor $[H_3L^1]Cl$ with triethylamine at room temperature, followed by the addition of (DME)MoO₂Cl₂,⁹⁴ resulted in the formation of an orange solution, from which the desired dioxo molybdenum

complex 1 can be isolated. After the removal of triethylammonium chloride by filtration and subsequent precipitation with *n*-hexane, 1 is isolated in good yields of 75% as a faint yellow solid (Scheme 1). The ¹H NMR spectrum showed the presence of a single, $C_{2\nu}$ symmetric species, and the absence of the OH as well as of the benzimidazolium-2H proton indicated the formation of a NHC complex. The assignment of the new compound as a carbene complex was further supported by the presence of a NHC carbene resonance at δ 183.1 ppm in the ¹³C{¹H} NMR spectrum. Additionally, the presence of stretching frequencies at $\tilde{\nu}$ 914 and 939 cm⁻¹ in the IR spectrum, corresponding to the asymmetric and symmetric Mo-O vibrations, confirmed the presence of the MoO₂ unit.^{15–18,20} Ultimate proof for the successful formation of the desired complex was given by X-ray structure analysis. Single crystals of 1 were obtained by diffusion of pentane into a concentrated solution of 1 in THF. The complex crystallizes in the triclinic space group P-1 and was found to crystallize with two different molecules in the asymmetric unit, a molybdenum(VI)-dimer (1-dimer) with two six-coordinate molybdenum atoms in a strongly distorted octahedral environment and a molybdenum(VI) monomer (1-mono) with the molybdenum atom being five-coordinate lying in between a square pyramidal and a trigonal bipyramidal coordination environment displaying a τ_5 -value of 0.462 (Figure 2). $^{95-98}$ The main differences between the monomeric and the dimeric form can be found in the conformation of the phenolate linkers of the NHC ligand. While in the dimeric structure, the phenolate rings are both twisted into the same direction in reference to the benzimidazolylidene plane by 39.6(1) and 29.7(1) $^{\circ}$, the phenolate rings are twisted into opposite directions by 30.7(1) and -37.4(2) ° in the

monomeric structure. Because of the strong distortion of the ligand in the dimer, the benzimidazolylidene plane is also strongly bent out of the Mo-C bond line by 29.1(1) °. However, in solution, we only observe a single set of resonances for the ligand and one resonance for the carbene atom C1, indicating a high flexibility of the phenolate linkers in solution. The Mo-O distances for the terminally bound oxo ligands are 1.706(3) Å (for Mo1-O10) and 1.702(3) Å (for Mo1-O11) in 1-mono and compare well to other previously reported MoO₂ complexes.^{15,16,18} For 1-dimer, the Mo2–O20 distance with nonbridging oxo ligand was found to be 1.695(3)Å. The bridging oxygen atom O21 is asymmetrically bound to the two molybdenum centers displaying a distance of 1.761(2)Å and 2.439(3) Å to the two molybdenum atoms, respectively. The Mo-C1 distance was found to be 2.260(4) Å in 1-dimer and 2.193(4) Å in 1-mono. To further probe the structural identity of the complex in solution and to see if there is a temperature-dependent equilibrium between the complexes 1mono and 1-dimer in solution, we investigated the complexes by variable-temperature ¹H NMR spectroscopy in toluene-d₈ as well as in THF-d₈ (Figures S13 and S14). However, we did not observe any changes in the ¹H NMR spectra over a temperature range from -30 °C to +60 °C, indicating that the observation of the dimerization of 1 in the solid state is most likely related to packing effects, influencing the ligand geometry and thus leading to the formation of 1-mono and 1-dimer. Notably, opening a NMR sample of 1 in C_6D_6 to air and moisture, we have not observed any signs of decomposition of 1 in solution over 5 days, rendering the dioxo complex 1 as fairly air stable (compare Figure S12).

Having established such a simple route to molybdenum dioxo complexes, we were curious whether this route would also be applicable for the formation of oxo-imido or bis-tertbutyl-imido complexes 2 and 4. Following the same reaction protocol and workup conditions used for 1 and employing the oxo-imido-Mo(VI) precursor (DME)Mo(O)(N^tBu)Cl₂⁹⁹ resulted in the clean formation of a new yellow compound. Again, the absence of the OH resonances as well as the characteristic benzimidazolium-2H resonance in its ¹H NMR spectrum indicated successful formation of the desired oxoimido complex 2. The presence of a carbene complex was furthermore supported by the presence of a low-field resonance at δ 191.6 ppm in the ¹³C{¹H} NMR spectrum. The presence of the imido-ligand was verified by a cross peak in the ¹H-¹⁵N HMBC spectrum at δ 1.38/102.9 ppm (Table 1/Figure S19). Additionally, the presence of the oxo-ligand was indicated by the presence of a single IR stretch at $\tilde{\nu}$ 910 cm⁻¹, which lies in the range for other, previously reported

Table 1. List of the ${}^{1}H{-}{}^{15}N$ HMBC Data of 2, 3, and 4 (in ppm), Showing the Chemical Shifts of the Benzimidazole Nitrogen, as well as the Amido and the Imido Nitrogen Atoms of the Corresponding Complexes^{*a*}

complex	N ^{NHC}	NH ^t Bu	N ^t Bu
2	7.66/177.9	-	1.38/102.9
3	7.88/176.1	12.15/337.6	0.75/82.3
		12.24/337.6	
		1.52/337.6	
4	7.84/179.5	-	1.48/83.8
	7.67/179.5		

^aSee also Figures S19 (for 2), S25 (for 3), and S30 (for 4).

molybdenum(VI) oxo-imido complexes.^{2,8} We have been able to grow crystals of the complex from a concentrated THF solution at -40 °C over 2 days. Unfortunately, this method and all other attempts yielded only low quality crystals of the desired complex 2. Nevertheless, the connectivity could be confirmed and the molecular structure of 2 showed the formation of the desired NHC-oxo-imido complex (Figure 3, left). The molybdenum center in 2 can be best described as six coordinate with a weakly coordinating THF ligand occupying the sixth coordination site. It is noteworthy that the THF ligand is only present because of the crystallization from pure THF. The material isolated after the workup as described above does not contain any ligated THF, which was also verified by ¹H NMR spectroscopy (compare Figure S15). Because of the low quality of the crystals, bond lengths and angles cannot be discussed at this point.

Switching to the bis-imido precursor $(DME)Mo-(N^tBu)_2Cl_2^{100,101}$ and applying triethylamine as a base again, we were not able to isolate the desired bis-imido complex 4 from the reaction mixture, but instead the imido-amido complex 3 was obtained in high purity and yield (85%) as orange crystals after crystallization from THF. The formation of the imido-amido complex was indicated by several spectroscopic features: (i) the presence of more than three tert-butyl resonances in both the ¹H and ¹³C {¹H}NMR spectrum; (ii) the presence of a very low-field shifted resonance at δ 12.20 ppm corresponding to the proton of the amido ligand in the ¹H NMR spectrum; (iii) the presence of two different ^tBuN resonances in the ¹H-¹⁵N HMBC NMR spectrum at δ 82.5 and 337.6 ppm corresponding to the imido and the amido group (Table 1); (iv) the presence of a doublet in the ¹H–¹⁵N HMBC spectrum at δ 12.15/337.6 ppm and δ 12.24/337.6 ppm (J = 63 Hz) characteristic for NH protons (Table 1 and Figure S25); and (v) the presence of an IR stretch at $\tilde{\nu}$ 3234 cm⁻¹, which is characteristic for NH protons. The carbene resonance for this complex was found to be at δ 191.1 ppm in the ${}^{13}C{}^{1}H$ NMR spectrum. It is noteworthy that only one of three possible isomers was obtained in which the amido function is *trans* to the carbon (3-trans, Figure S45, middle), while we have not seen the formation of any *cis*-coordinated product with the amido ligand being *cis* to the carbene ligand (3-cis, Figure S45, left). The third isomer, 3-Cl (Figure S45, right) where the imido and the amido ligand are trans to each other is most likely unfavored due to the competitive π -bonding between the imido and the amido ligand in this arrangement. The assignment of complex 3 as the trans isomer is also obvious by the presence of a cross peak in the ${}^{1}\text{H}-{}^{13}\text{C}$ HMBC spectrum at δ 12.20/191.1 ppm. Such a coupling is favorably seen in a trans orientation of the carbene carbon and the NH function of the amido ligand (compare Figure S24). The *trans* conformation was also proven by X-ray crystallography (vide infra). Single crystals of 3 were obtained from a concentrated THF solution at room temperature over the course of several days. The complex crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The molybdenum atom in 3 was found to be six-coordinate in a distorted octahedral fashion (Figure 3, middle), coordinated by the three atoms of the carbene ligand, the imido, the amido, and additionally by one chlorido ligand. The Mo-N distances were found to be 1.711(3) Å for Mo1-N40 (imido ligand) and 1.954(3) Å for Mo1-N50 (amido ligand). In addition, the Mo1-N40-C40 bond angle was found to be nearly linear with 168.6(2) °, while the



Figure 3. Ball and stick representation of 2 (left). ORTEP plot of 3 (middle) and 4 (right). ^tBu groups have been partly truncated and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at a probability level of 50%.

corresponding Mo1–N50–C50 bond angle was found to be strongly bent with 142.4(2) °. These pronounced differences in bond distances and angles, in combination with the spectroscopic data, clearly support the assignment of N40 as the imido nitrogen and N50 as the amido nitrogen and therefore unambiguously prove the isolation of the (NHC)-Mo(VI)-imido-amido complex 3. The structure also unambiguously confirms the amido group being *trans* to the carbene as already inferred from NMR spectroscopy.

Probing the acidity of the NH proton in 3, we found that the complex can be easily deprotonated using either lithium diisopropylamide (LDA) or potassium hexamethyldisilazide (KHMDS), resulting in the clean formation of the originally targeted bis-imido complex 4. The ¹H NMR spectrum shows the clean formation of a single product exhibiting $C_{2\nu}$ symmetry and disappearance of the NH resonance at δ 12.20 ppm in 3 as well as the merging of the two ^tBu signals at δ 0.75 ppm and δ 1.52 ppm to a single resonance at δ 1.46 ppm in 4. Additionally, only a single cross peak was observed in the ¹H-¹⁵N HMBC spectrum of 4 at δ 1.48/83.8 ppm (Table 1/Figure S30). The assignment of 4 still being a NHC complex was furthermore supported by the observation of a low-field shifted resonance in its ¹³C{¹H} NMR spectrum shifting from δ 191.1 ppm in 3 to δ 199.3 ppm in 4. Single crystals of 4 were grown by slow evaporation of a concentrated *n*-hexane solution of 4 at room temperature. The complex crystallizes in the triclinic space group P-1 as n-hexane solvate with one equivalent of *n*-hexane in the asymmetric unit. The molybdenum atom was found to be five-coordinate in a slightly distorted square pyramidal coordination environment (Figure 3, right; $\tau_5 = 0.167$). The Mo–N distances were found to be 1.745(2) Å and 1.754(2) Å for Mo1-N40 and Mo1-N50 respectively, lying in the range of previously reported examples of molybdenum bis-imido complexes.^{17,102} While the two Mo-N distances are fairly similar, there is a big difference in the bond angle between the two imido ligands; that is, the Mo1-N50-C50 angle is close to linear with 173.1(2) ° compared to the Mo1-N40-C40 angle, which is strongly bent with 154.9(2) °.

Notably, the bis imido complex 4 can also be synthesized directly from the corresponding bis-imido molybdenum precursor $(DME)Mo(N^tBu)_2Cl_2$ and the ligand precursor $[H_3L^1]Cl$ if a stronger base than triethylamine was used (e.g., LDA or LiHMDS) and the reaction is initiated at -40 °C.¹⁰³ However, the reaction does not proceed as cleanly as

compared to that of the two-step procedure via the amidoimido complex **3**, resulting in much lower yields. It is also noteworthy at this point that lithium bases need to be used. Applying KHMDS under the same conditions, we have not observed the formation of the desired complex **4** at all, but instead, complicated mixtures have been obtained. Additionally, the oxo-imido complex **2** can also be synthesized via a ligand exchange reaction between the dioxo complex **1** and the bis-imido complex **4** at elevated temperatures (Scheme 1).

Because it is well-known that aryl-imido ligands are less reactive compared with their alkyl congeners,^{104–107} we assumed that the use of electron-deficient imido ligands (e.g., mesityl-imido) might result in the direct formation of the bis-imido complex 5 using weaker bases than LDA. Following our general protocol using (DME)Mo(NMes)₂Cl₂^{108,109} as a molybdenum source, we indeed isolated the desired bis-imido complex 5 in good yields of 79% as a dark orange microcrystalline powder (compare Scheme 2). Formation of

Scheme 2. Synthesis of the Mesityl-Substituted Bis-imido Complex 5



the desired bis-imido NHC complex was indicated by the absence of the benzimidazolium-2H resonance in the ¹H NMR spectrum as well as by the observation of a low-field resonance at δ 193.2 ppm in the ¹³C{¹H} NMR spectrum of the complex. Unfortunately, in the case of the mesityl-imido ligands, it is not possible to have an efficient polarization transfer from the six protons on the ortho-methyl groups on the mesityl ligand to the nitrogen atom, and thus, we have not been able to prove the assignment as a bis-imido complex by ¹H-¹⁵N HMBC spectroscopy. However, we have been able to grow X-ray quality single crystals by the slow evaporation of a concentrated THF solution at -40 °C. The complex crystallized in the triclinic space group P-1 with one molecule of 5 and three formula units of THF in the asymmetric unit of which one needed to be removed using the SQUEEZE operation.¹¹³ The molybdenum atom in 5 is five-coordinate in a strongly distorted trigonal bipyramidal fashion (Figure 4, left;



Figure 4. ORTEP plot of 5 (left), 6 (middle), and 7 (right). 'Bu groups have been partly truncated, and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at a probability level of 50%.





 $\tau_5 = 0.53$), with the two phenolate ligands occupying the axial coordination sites, while the imido ligands as well as the carbene unit are in the equatorial plane. The bond distances of Mo1–N40 and Mo1–N50 are 1.762(4) Å and 1.745(4) Å, thus unambiguously confirming the assignment of **5** as a bisimido complex of high-valent Mo(VI). The molybdenum carbene distance of 2.171(5) Å for Mo1–C1 lies within the range of the distances of complexes **1–4**. Further structural details regarding the molecular structure of **5** can be found in the SI. To the best of our knowledge, the bis-imido complexes **4** and **5** are only the second examples of molybdenum bisimido complexes ligated by a NHC ligand. We have recently reported a similar complex coordinated by a structurally related MIC ligand.¹⁰³

Having these new complexes in hand, we next turned our interest toward their chemical properties. Especially the bisimido complex 4 caught our attention. We believe that the isolation of the imido-amido complex 3 results from the initial formation of 4 in the presence of triethylammonium chloride, which is then protonated by triethylammonium chloride to give the observed complex 3. To probe this hypothesis, we have conducted a NMR experiment adding a suspension of triethylammonium chloride to complex 4 in C_6D_6 , which indeed resulted in the clean protonation of complex 4 to give complex 3 within an hour (compare Figure S35). Thus, we have been interested in the reactivity of 4 towards dihydrogen and if it is a potential catalyst for the hydrogenation of unactivated alkynes. Arnold and Toste et al. have recently presented a cationic bis-imido vanadium complex, which is an effective catalyst for the hydrogenation of alkynes.¹¹⁰ However, we found that complex 4 does not react with dihydrogen at all and is also not catalytically active for the hydrogenation of alkynes at mild conditions comparable to Arnold's work. To probe the basicity of the bis-imido complex 4, we subsequently reacted the complex with mesitole $(pK_a = 9)$, benzimidazole $(pK_a = 16)$, and carbazole $(pK_a = 20)$. While the reactions for mesitole and for benzimidazole proceeded very messily, along with the formation of a characteristic singlet above δ 11 ppm corresponding to the NH^tBu moiety, for carbazole no reaction was observed (compare Scheme 3 and Figures S36–S38). This states that the pK_a value of complex 4 is somewhere between 16 and 20, which proves that the complex is not basic enough to activate dihydrogen having a pK_a value of 36. Even though the reaction between 4 and mesitole was very messy leading to a myriad of products, we were able to crystallize dark red and dark purple blocks from a concentrated pentane solution. Unfortunately, it was not possible to further segregate these two products to obtain NMR spectra of the pure compounds. Nevertheless, we have been able to investigate both of these crystals by X-ray crystallography. X-ray diffraction analysis of the red crystals revealed the successful formation of the desired imido-amido complex 7 (Figure 4, right), while the purple

crystals were found to be the twofold activated product 6 (Figure 4, middle), in which one imido ligand deprotonated two equivalents of mesitole, resulting in a bis-mesitole-imido complex. In both complexes 6 and 7, the coordination environment of the molybdenum atom is distorted octahedral. Interestingly, in 6, the bis-phenolate benzimidazolylidene ligand does not coordinate in a mer-fashion, as it would be expected for a tridentate pincer type ligand, but in a facconformation. This underlines the high flexibility of this ligand and its ability to stabilize various metal cations of different sizes and steric demands. The bond lengths between the molybdenum atom to the carbene carbon was found to be 2.159(6) Å in 6 and 2.185(4) Å in 7 being in the normal range as in the complexes 1-5 (vide supra). The bond lengths between the molybdenum atom and the imido ligand in 6 and 7 were found to be 1.704(4) Å and 1.715(4) Å and are comparable to those found in the imido complexes 3, 4, and 5 (vide supra). Strikingly, none of the above-mentioned reagents were able to protonate the mesityl-imido ligands in 5, rendering this complex to be much less reactive.

CONCLUSIONS

In conclusion, we have presented a simple yet very efficient route to prepare NHC complexes of high-valent molybdenum-(VI), featuring oxo and imido ligands. We have been able to show that the outcome of the reactions leading to bis-imido complexes featuring dianionic bis-phenolate NHC ligands strongly depends on the nature (and the basicity) of the corresponding imido ligand. Electron-rich (^tBu) imido complexes have additionally been shown to react with protic substances up to a pK_a value of 16, while electron-deficient (mesityl) imido ligands are barely reactive. Additionally, we have been able to show that the rare NHC dioxo complex 1 is (in contrast to previously reported (NHC)MoO₂ complexes) stable toward air and moisture even in solution, making these complexes ideal candidates for chemical catalysis. We are currently exploring the catalytic potential of the new complexes in oxygen-transfer reactions as well as trying to find strategies to make them more reactive towards molecular hydrogen.

EXPERIMENTAL SECTION

General Remarks. If not otherwise mentioned, all transformations were carried out in an argon-filled glovebox under inert conditions. Solvents were dried by a MBraun SPS system and stored over activated molecular sieves (3 Å) for at least 1 day. Prior to use, deuterated C6D6, THF-d8 and toluene-d8 were dried over sodium/ benzophenone and CDCl3 and CD2Cl2 over calcium hydride, followed by vacuum transfer and three freeze–pump–thaw cycles. Starting materials $[H_3L^1]Cl_7^{74,75}$ (DME)MoO₂Cl₂,⁹⁴ (DME)Mo(O)-(N^tBu)Cl₂,⁹⁹ (DME)Mo(N^tBu)₂Cl₂,^{100,101} and (DME)Mo-(NMes)₂Cl₂¹⁰⁸ have been synthesized following known procedures found in the literature. If not otherwise stated, triethylamine (NEt_3) and all other chemicals have been used as received. IR spectra were recorded using a Bruker Vertex 70 with ATR equipment. NMR spectra were collected at ambient temperature on a Bruker AV-500 or an Ascent 700 spectrometer using a J-Young NMR tube. ¹H and ¹³C NMR chemical shifts (δ) are reported in ppm and were calibrated to residual solvent peaks.¹⁵N spectra were referenced vs liquid ammonia (NH₃). Elemental analysis was performed using an Elementar vario microcube instrument.

Synthetic Procedures. $L^1 MOO_2$ (1). In an argon-filled glovebox, $[H_3L^1]Cl$ (1 equiv, 0.5 mmol, 281 mg) was dissolved in 8 mL of THF and stirred for 5 min at room temperature. To the colorless solution, triethylamine (3.5 equiv, 1.75 mmol, 186 mg) dissolved in 3 mL of THF was added, resulting in a fast color change to bright yellow. The

yellow suspension was stirred for 30 min at room temperature before it was added dropwise to a stirred solution of (DME)MoO₂Cl₂ (1 equiv, 0.5 mmol, 145 mg) in THF (5 mL), resulting in the formation of a brownish yellow suspension. The reaction mixture was stirred for 16 h, before it was filtered to remove triethylammonium chloride. The solution was concentrated to about 1 mL, and n-hexane was slowly added while swirling the vial to induce precipitation of a yellow solid. The yellow solids were isolated by decanting of the solvent and washed multiple times with *n*-hexane $(4 \times 5 \text{ mL})$ to give pure complex 1 in moderate yields of 75% (238 mg, 0.375 mmol). X-ray quality crystals were grown by slow diffusion of pentane into a concentrated THF solution of 1 at room temperature. ¹H NMR $(C_6 D_6, 700 \text{ MHz}, 25 \text{ °C}): \delta \text{ (ppm)} = 7.87 \text{ (m, 2H, Aryl-H)}, 7.64 \text{ (m, })$ 4H, Aryl-H), 7.00 (m, 2H, Aryl-H), 1.70 (s, 18H, C(CH₃)₃), 1.37 (s, 18H, $C(CH_3)_3$; ¹³C{¹H} NMR (C_6D_6 , 175 MHz, 25 °C): δ (ppm) = 183.1 (Carbene-C), 150.9 (Aryl-C-O), 141.5, 141.3, 132.5, 126.1 (Aryl-C), 125.0, 123.2, 115.5, 114.2 (Aryl-CH), 35.9, 34.5 $(C(CH_3)_3)$, 31.4, 30.0 $(C(CH_3)_3)$; IR: $\tilde{\nu}$ (cm⁻¹) = 913 (O = = Mo=O, asymmetric), 939 (O=Mo=O, symmetric); elemental analysis (%) calcd for $C_{35}H_{44}N_2O_4Mo$: C, 64.41; H, 6.80; N, 4.29; found: C, 64.62; H, 7.11; N, 4.20.

 L^1 Mo(O)(N^tBu) (2). Method A. In an argon-filled glovebox, $[H_3L^1]Cl$ (1 equiv, 0.5 mmol, 281 mg) was dissolved in 8 mL of THF and stirred for 5 min at room temperature. To the colorless solution, triethylamine (3.5 equiv, 1.75 mmol, 186 mg) dissolved in 3 mL of THF was added, resulting in a fast color change to bright yellow. The yellow suspension was stirred for 30 min at room temperature before it was added dropwise to a stirred solution of (DME)MoO(N^tBu)Cl₂ (1 equiv, 0.5 mmol, 172 mg) in THF (5 mL), resulting in the formation of a brownish yellow suspension. The reaction mixture was stirred for 16 h, before it was filtered to remove triethylammonium chloride. The solution was concentrated to about 1 mL, and *n*-hexane was slowly added while swirling the vial to induce precipitation of a yellow solid. The yellow solids were isolated by decanting of the solvent and washed multiple times with *n*-hexane (4 × 5 mL) to give pure complex 2 in moderate yields of 67% (237 mg, 0.335 mmol).

Method B. Complex 1 (1 equiv, 0.025 mmol, 16 mg) and complex 4 (1 equiv, 0.025 mmol, 19 mg) were dissolved in C_6D_6 (0.65 mL) and heated to 80 °C overnight. The resulting NMR spectra was identical to the NMR obtained from the isolated complexes 2 (*vide infra*). Crystals suitable for X-ray diffraction analysis were grown from a concentrated THF solution (0.15g in 1 mL) of 2 at -40 °C over 2 days. ¹H NMR (C_6D_6 , 700 MHz, 25 °C): δ (ppm) = 7.83 (m, 2H, Aryl-H), 7.65 (d, J = 2.3 Hz, 2H, Aryl-H), 7.61 (d, J = 2.3 Hz, 2H, Aryl-H), 7.65 (m, 2H, Aryl-H), 1.78 (s, 18H, C(CH₃)₃), 1.38 (s, 27H, C(CH₃)₃ and Mo = NC(CH₃)₃); ¹³C{¹H} NMR (C_6D_6 , 175 MHz, 25 °C): δ (ppm) = 191.6 (Carbene-C), 154.6 (Aryl-C-O), 141.3, 140.6, 133.7, 127.4 (Aryl-C), 125.0, 123.0 116.4, 114.4 (Aryl-CH), 72.2 (Mo=NC(CH₃)₃), 36.7, 35.0 (C(CH₃)₃), 32.1 (C(CH₃)₃), 30.9 (Mo=NC(CH₃)₃), 30.8 (C(CH₃)₃). IR: $\tilde{\nu}$ (cm⁻¹) = 911 (Mo= O); elemental analysis (%) calcd for C₃₉H₅₃N₃O₃Mo: C, 66.18; H, 7.55; N, 5.94; found: C, 66.48; H, 7.41; N, 5.74.

 L^1 Mo(N^tBu)(NH^tBu)Cl (3). In an argon-filled glovebox, NEt₃ (3.5) equiv, 1.75 mmol, 186 mg) diluted in THF (2 mL) was slowly added dropwise to a stirring solution of the benzimidazolium salt $[H_3L^1]Cl$ (1 equiv, 0.5 mmol, 281 mg) in THF (4 mL). The color changed to pale yellow and a colorless precipitate formed. The suspension was stirred for 30 min and added at once to a solution of (DME)Mo-(N^tBu)₂Cl₂ (1 equiv, 0.5 mmol, 199 mg) in THF (2 mL). The color changed to dark red, and the reaction was stirred for another 16 h. The mixture was subsequently filtered and the solvent was concentrated to about 2 mL. Over the course of 1 day, a large mass of crystals formed which was isolated by decanting of the solvent and washing the crystals with n-hexane (5 mL) to give pure 3 in good yields of 85% (0.425 mmol, 340 mg) as an orange solid. X-ray quality crystals were grown form a concentrated solution of 3 in THF (0.1 g in 1 mL) over the course of 4 days at room temperature. ¹H NMR $(C_6 D_{6}, 700 \text{ MHz}, 25 \text{ °C}): \delta$ (ppm) = 12.20 (s, 1H, Mo- $NH(C(CH_3)_3))$, 7.91 (m, 2H, Aryl-H), 7.88 (d, J = 2.3 Hz, 2H,

Aryl-H), 7.60 (d, J = 2.3 Hz, 2H, Aryl-H), 6.96 (m, 2H, Aryl-H), 1.71 (s, 18H, C(CH₃)₃), 1.52 (s, 9H, Mo-NH(C(CH₃)₃)), 1.38 (s, 18H, C(CH₃)₃), 0.75 (s, 9H, Mo=NC(CH₃)₃); ¹³C{¹H} NMR (C₆D₆, 175 MHz, 25 °C): δ (ppm) 191.1 (Carbene-C), 156.8 (Aryl-C-O), 140.0, 139.8, 134.0, 127.4 (Aryl-C), 124.7, 122.2, 116.6, 114.9 (Aryl-CH), 73.8 (Mo=NC(CH₃)₃), 61.9 (Mo-NH(C(CH₃)₃)), 36.6, 35.0 (C(CH₃)₃), 33.6 (Mo-NH(C(CH₃)₃)), 32.2, 31.1 (C(CH₃)₃), 30.5 (Mo=NC(CH₃)₃); ¹⁵N NMR (C₆D₆, 71 MHz, 25 °C): δ (ppm) = 337.6 (Mo-NH(C(CH₃)₃)), 176.1 (Benzimidazole-N), 82.5 (Mo=NC(CH₃)₃). IR: $\tilde{\nu}$ (cm⁻¹) = 3254 (Mo-NH–C(CH₃)₃); elemental analysis (%) calcd for C₄₃H₆₃N₄O₂ClMo: C, 64.61; H, 7.94; N, 7.01; found: C, 64.25; H, 7.71; N, 7.13.

 L^1 Mo(N^tBu)₂ (4). Method A. In an argon-filled glovebox, to a solution of 3 (1 equiv, 0.5 mmol, 400 mg) in toluene (10 mL) was added dropwise a solution of KHMDS (1.1 equiv, 0.55 mmol, 110 mg) diluted in toluene (2 mL). The color changed immediately from orange to bright yellow, and the reaction mixture was stirred for another 2 h at room temperature to ensure complete deprotonation of 3. The reaction mixture was filtered and evaporated to dryness. The yellow residue was then redissolved in dichloromethane (5 mL), filtered again, and concentrated to 0.5 mL. Addition of *n*-hexane while swirling around the vial induced precipitation of the clean complex 4 which was isolated by decanting of the solution and drying under high vacuum in very good yields of 92% (0.460 mmol, 351 mg). Depending on the amount of dichloromethane left in the solution, it has been observed that precipitation of 4 starts with a short delay. If the precipitation is not starting right away, we recommend stirring the mixture of *n*-hexane and dichloromethane overnight.

Method B. The proligand [H₃L]Cl (1 equiv, 0.3 mmol, 168 mg) was dissolved in a 1:1 mixture of Et₂O/THF (5 mL) and cooled to -40 °C. To the mixture was added a cold solution of LDA (3 equiv, 0.9 mmol, 90 mg) in Et_2O (3 mL), and the mixture was stirred for 2 min and added dropwise to a -40 °C cold solution of (DME)Mo- $(N^{t}Bu)_{2}Cl_{2}(1 \text{ equiv, } 0.3 \text{ mmol, } 120 \text{ mg})$ in THF/Et₂O (1:1). The resulting bright yellow mixture was stirred for 18 h, and the cloudy yellow suspension was filtered and evaporated to dryness. The yellow residue was redissolved in toluene (10 mL), filtered again, and concentrated to about 1 mL. Pentane was added dropwise to this solution to induce precipitation of the desired complex. The complex was isolated as a yellow powder in moderate yields of 42% (96 mg, 0.126 mmol). X-ray quality crystals were grown by slow evaporation of a saturated *n*-hexane solution of 4 at room temperature. ¹H NMR $(C_6 D_{67}, 700 \text{ MHz}, 25 \text{ °C}): \delta (\text{ppm}) = 7.77 (\text{m}, 2\text{H}, \text{Aryl-H}), 7.65 (\text{d}, J)$ = 2.3 Hz, 2H, Aryl-H), 7.59 (d, J = 2.3 Hz, 2H, Aryl-H), 6.89 (m, 2H, Aryl-H), 1.80 (s, 18H, $C(CH_3)_3$), 1.46 (s, 18H, Mo=NC(CH₃)₃), 1.37 (s, 18H, C(CH₃)₃); ¹³C{¹H} NMR (C₆D₆, 175 MHz, 25 °C): δ (ppm) = 199.3 (Carbene-C), 155.8 (Aryl-C-O), 141.0, 139.3, 134.4, 127.9 (Aryl-C), 124.5, 122.5, 117.2, 114.4 (Aryl-CH), 70.1 (Mo= $NC(CH_3)_3$), 36.8, 34.9 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 32.2 (Mo= NC(CH₃)₃), 30.8 (C(CH₃)₃); ¹⁵N NMR (C₆D₆, 71 MHz, 25 °C): δ (ppm) = 179.5 (Benzimidazole-N), 83.4 (Mo=NC(CH₃)₃); elemental analysis (%) calcd for C43H62N4O2MO.0.3 C6H14: C, 68.22; H, 8.46; N, 7.10; found: C, 68.33; H, 8.15; N, 6.82.

 L^1 Mo(NMes)₂ (5). In an argon-filled glovebox, triethylamine (3.5) equiv, 1.75 mmol, 186 mg) diluted in THF (2 mL) was slowly added dropwise to a stirring solution of the benzimidazolium salt $[H_3L^1]Cl$ (1 equiv, 0.5 mmol, 281 mg) in THF (4 mL). The color changed to pale yellow, and a colorless precipitate formed. The suspension was stirred for 30 minutes and added dropwise to a solution of (DME)Mo(NMes)₂Cl₂ (1 equiv, 0.5 mmol, 262 mg) in THF (2 mL) at room temperature. The color changed to dark red, and the reaction was stirred for another 16 h. The mixture was subsequently filtered, and the filtrate was evaporated to dryness. The orange red residue was extracted with pentane, filtered again, and dried under high vacuum to give the desired bis-imido complex 5 as a red orange powder in good yields of 79% (0.395 mmol, 350 mg). X-ray quality crystals of 5 could be grown from a concentrated THF solution (100 mg in 1 mL) at -40 °C overnight. ¹H NMR (C₆D₆, 700 MHz, 25 °C): δ (ppm) = 7.89 (m, 2H, Aryl-H), 7.74 (d, J = 2.3 Hz, 2H, Aryl-H), 7.61 (d, J = 2.3 Hz, 2H, Aryl-H), 7.00 (m, 2H, Aryl-H), 6.72 (s,

4H, *m*-CH), 2.42 (s, 12H, *o*-CH₃), 2.09 (s, 6H, *p*-CH₃), 1.64 (s, 18H, C(CH₃)₃), 1.43 (s, 18H, C(CH₃)₃); ${}^{13}C{}^{1H}$ NMR (C₆D₆, 175 MHz, 25 °C): δ (ppm) = 193.2 (Carbene-C), 156.2 (Aryl-C-O), 155.1 (N-C_{ipso}), 140.7, 139,7, 135.3, 133.7, 133.6, 127.4 (Aryl-C), 124.5, 122.7, 116.5, 114.0 (Aryl-CH), 36.3, 34.7 (C(CH₃)₃), 31.8 (C(CH₃)₃), 30.3 (C(CH₃)₃), 21.1 (*p*-CH₃), 19.3 (*o*-CH₃); elemental analysis (%) calcd for C₅₃H₆₆N₄O₂Mo: C, 71.76; H, 7.50; N, 6.32; found: C, 71.55; H, 7.63; N, 6.42.

 L^1 Mo(N^tBu)(OMes)₂ (6) and L^1 Mo(N^tBu)(NH^tBu)(OMes) (7). In an argon-filled glovebox, complex 4 (1 equiv, 0.05 mmol, 38 mg) was dissolved in C₆D₆ (0.55 mL) in a J-Young NMR tube. To this was added mesitole (1.05 equiv, 0.0525 mmol, 7.5 mg) dissolved in C₆D₆ (0.1 mL). The color changed initially from bright yellow to deep orange. The resulting mixture was left to stand for 24 h at room temperature during which the color changed to dark purple. ¹H NMR spectroscopy indicated a wild mixture of compounds being formed (Figure S36). The C₆D₆ was evaporated, and the resulting purple solid was dissolved in pentane, filtered, and concentrated to 1 mL. After 5 days, a mixture of purple and dark red blocks formed at room temperature. Despite extensive efforts, we found no conditions to selectively crystallize only one species. The purple blocks have been found to be complex 6, while the dark red blocks were found to be complex 7 by X-ray crystallography.

X-ray Crystallography. Single crystals for X-ray diffraction experiments were measured at the analytical facility of the Paderborn University, the Free University of Berlin and the University of Duisburg-Essen using a Bruker Smart AXS (Paderborn). All crystals were kept at 130(2) K throughout data collection. Data collection was performed using either the APEXIII or the Smart software package. Data refinement and reduction were performed with Bruker Saint (V8.34A). All structures were solved with SHELXT and refined using the OLEX 2 software package.^{111,112} A strongly disordered THF solvent molecule in 5 was removed using the SQUEEZE operation.¹¹³ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at the geometrically calculated positions and refined using a riding model. The quality of the data obtained for 2 was very poor. Problems during the integration led to high R_{int} values and an incomplete data set. Many atomic displacement parameters refine to negative values, and R1 will not improve to less than about 25%. The model as such cannot be considered reliable; however, it matches well with other analytical means, suggesting that at least the connectivity and overall conformation of the molecule are correctly described. CCDC 1936967-1936972 contain the CIF files for complexes 1 and 3-7, respectively. For further crystallographic details, please check Tables S1 and S2 in the Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.9b00472.

Synthetic details, NMR spectra, IR spectra, UV-vis spectra, and crystallographic details for all compounds (PDF)

Accession Codes

CCDC 1936967–1936972 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The project was designed by S.H. Experimental work has been carried out by M.B., F.A.W., and S.H. IR spectra have been recorded by F.A.W. UV-vis data have been recorded by S.H. X-ray structure analyses have been performed by S.H. and R.S. The manuscript was written by S.H., F.A.W., and M.B.

Notes

The authors declare no competing financial interest.

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