Multiple-Imido Complexes of Molybdenum: Synthesis and Reactivity of the d^0 $Mo(=NR)_3$ Functional Group

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Red-orange crystals of the tris(imido) anion of molybdenum, $[Mo(NAr)_3Cl]^-$ (**3**, Ar = 2,6-C_6H_3-*i*-Pr_2) are isolated as the $[Li(THF)_4]^+$ salt from the rapid workup of the reaction between $Mo(NAr)_2Cl_2(THF)_2$ (**1**) and 2 equiv of LiNHAr (in THF). $[Li(THF)_4][Mo(NAr)_3Cl]$ (**3**) constitutes the kinetic product of this reaction since it readily reacts with byproduct H_2NAr to afford stable $Mo(NAr)_2(NHAr)_2$ (**4**). Complex **3** undergoes nucleophilic attack by PMe_3, MeLi, Me_3CCH_2Li, or Br^- to form $Mo(NAr)_3(PMe_3)$ (**5**), $[Li(THF)_4][Mo(NAr)_3Me]$ (**6**), $[Li(THF)_4][Mo(NAr)_3(CH_2CMe_3)]$ (**7**), and $[n\text{-}Bu_4N][Mo(NAr)_3Br]$ (**8**), respectively. The imido ligands in these tris(imido) complexes are also subject to electrophilic attack by a range of electrophiles to afford four- or five-coordinate bis(imido) complexes of Mo(VI). Thus, $Mo(NAr)_2(OCMe_3)_2$ (**9**) is prepared from $Mo(NAr)_3(PMe_3)$ (**5**) and Me_3COH, while metallacyclic $Mo[NArC(O)NPh](NAr)_2(PMe_3)$ (**10**) arises from $Mo(NAr)_3(PMe_3)$ (**5**) and PhNCO. $[Li(THF)_4][Mo(NAr)_3Cl]$ (**3**) is readily protonated by cyclopentadiene C_5H_6 to provide $CpMo(NAr)_2(NHAr)$ (**11**, Cp = $[\eta^5\text{-}C_5H_5]^-$). The reaction of $[HNMe_3]BPh_4$ with $[Li(THF)_4][Mo(NAr)_3(CH_2CMe_3)]$ (**7**) protonates an imido ligand rather than the alkyl to give $Mo(NAr)_2(NHAr)(CH_2CMe_3)$ (**12**). The electronic structure of the d^0 $Mo(=NR)_3$ functional group is described in terms of related $M(\sigma+2\pi)_3$ complexes with 3-fold symmetry.

Introduction

Organoimido complexes[1,2] have come under considerable scrutiny recently, in part, because of their presumed involvement in industrial processes such as propylene ammoxidation,[3] nitrile reduction,[4] and hydrodenitrogenation catalysis.[5] Although traditionally considered inert, highly reactive $L_nM{=}NR$ species have been generated that can engage in cycloaddition chemistry,[6] function as [NR] transfer reagents,[7] and even activate methane.[8] Of particular interest are recent examples of carbodiimide metathesis[9] and imine metathesis[10] catalyzed by imido complexes. One conventional feature of these reactive compounds is a coordination sphere containing multiple π donor ligands, a feature that has aroused interest in "π-loaded", multiple-imido complexes.[11−17]

We recently reported the preparation and properties of various d^0 tris(imido) complexes of tungsten,[13] thereby completing the series of d^0 $W(NR)_n$ functional groups for $n = 1-4$.[1] However, despite well-established mono $Mo(NR)$,[1,2] bis $Mo(NR)_2$,[1,18−20] and tetrakis $[Mo(NR)_4]^{2-}$ [21] imido complexes of molybdenum(VI), no d^0 tris(imido) complexes of molybdenum have been

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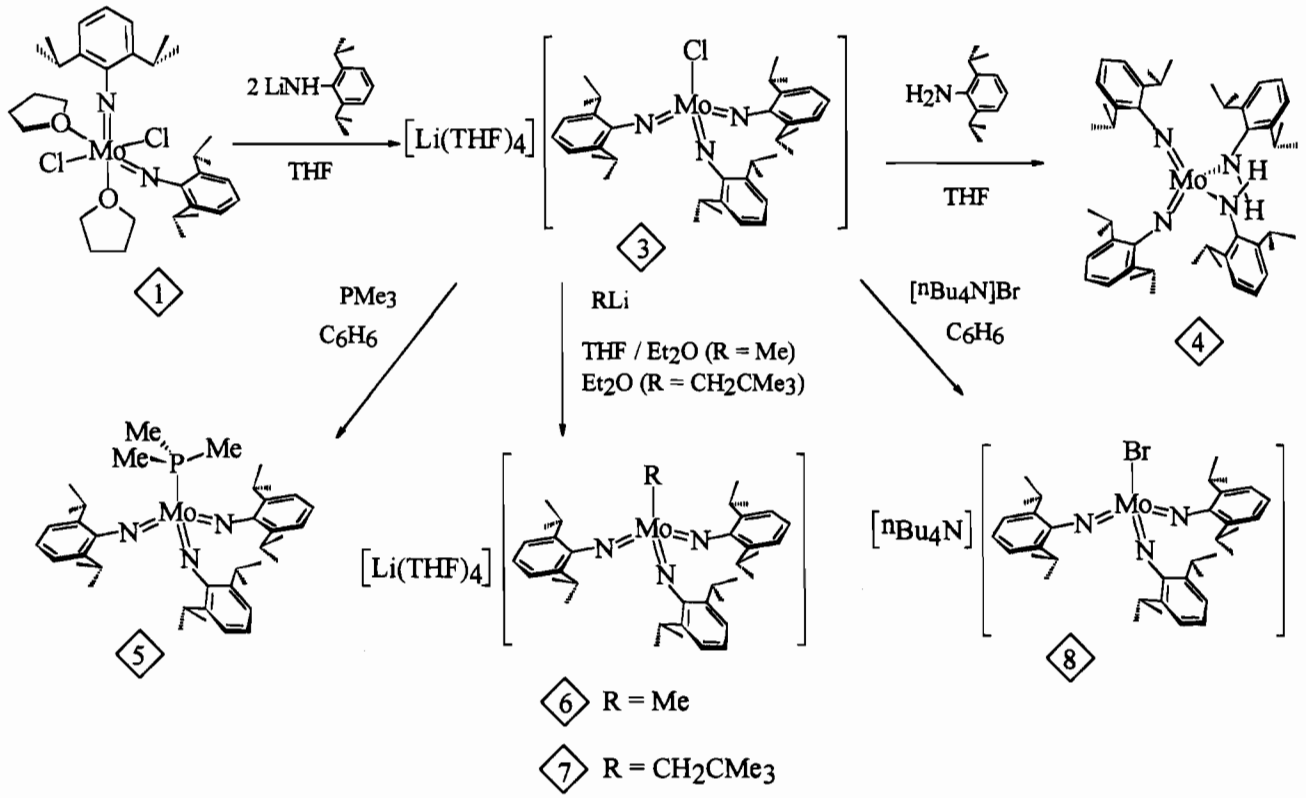
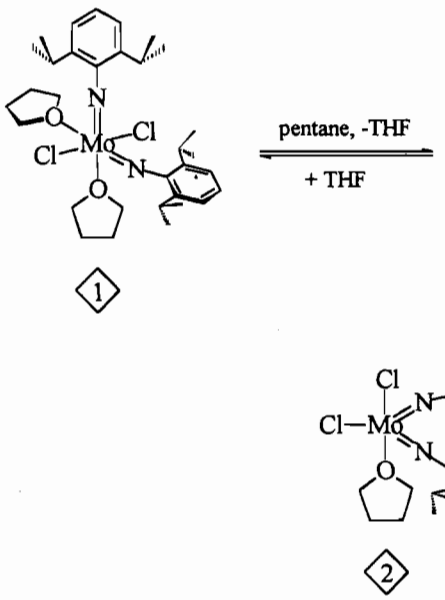
Scheme 1



characterized. In this report, we describe the kinetic accessibility of complexes containing the d^0 $Mo(NR)_3$ functional group, demonstrate their reactivity toward both nucleophiles and electrophiles, and present a qualitative molecular orbital basis for their reactivity. A portion of these results have been communicated.[22]

Results

The bis(imido) complex $Mo(NAr)_2Cl_2(THF)_2$ (**1**, Ar = 2,6-C_6H_3-*i*-Pr_2) can be prepared in 95% yield from $(NH_4)_2Mo_2O_7$, H_2NAr, NEt_3, and Me_3SiCl by a modification of the method developed by Schrock and co-workers.[18] The ^1H and ^{13}C NMR spectra of **1** indicate equivalent imido and THF ligands; therefore a structure analogous to related d^0 bis(imido) complexes of group 6, viz. with *cis*-imido and *trans*-chloride ligands, is proposed.[23-28] Osborn and co-workers prepared[20] the mono THF adduct $Mo(NAr)_2Cl_2(THF)$ (**2**) from MoO_2Cl_2 and ArNCO in THF, but by our procedure a bis THF complex is consistently obtained. However, we have found that $Mo(NAr)_2Cl_2(THF)_2$ (**1**) can be converted to $Mo(NAr)_2Cl_2(THF)$ (**2**) upon extensive washing with pentane and then readily re-formed from **2** in the presence of THF, eq 1.



(1)

Upon reacting *extremely pure* $Mo(NAr)_2Cl_2(THF)_2$ (**1**) with 2 equiv of LiNHAr in THF (for only 15 min), we isolated bright red-orange crystals of $[Li(THF)_4][Mo(NAr)_3Cl]$ (**3**) after appropriate workup, Scheme 1. Prolonged exposure of **3** to vacuum induces the slow loss of THF; therefore $[Li(THF)_4]^+$ is considered the maximum THF coordination in this complex. We have found this reaction to be extraordinarily sensitive to solvent (THF must be present at all times), reagent purity (impure **1** can give *no* **3**), and reaction time. The tris(imido) anion $[Li(THF)_4][Mo(NAr)_3Cl]$ (**3**) constitutes the *kinetic* product of this reaction, since byproduct H_2NAr reacts with $[Mo(NAr)_3Cl]^-$ over a period of hours (in THF) to completely

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convert it to more stable $Mo(NAr)_2(NHAr)_2$ (**4**) and LiCl. This reactivity feature is confirmed by reacting isolated $[Li(THF)_4][Mo(NAr)_3Cl]$ with 1 equiv of H_2NAr, which affords golden-yellow $Mo(NAr)_2(NHAr)_2$ (**4**) in nearly quantitative yield; therefore reaction time is crucial for the successful isolation of complex **3**. $Mo(NAr)_2(NHAr)_2$ (**4**) has previously been prepared and structurally characterized by Osborn and co-workers.[20]

The observation of the reaction $[Li(THF)_4][Mo(NAr)_3Cl]$ (**3**) + $H_2NAr \rightarrow Mo(NAr)_2(NHAr)_2$ (**4**) allows us to address the question of how the tris(imido) complex **3** itself arises from $Mo(NAr)_2Cl_2(THF)_2$ (**1**) and LiNHAr. One can envision the **1** + 2LiNHAr → **3** reaction proceeding either by: (i) the formation of intermediate $Mo(NAr)_2(NHAr)_2$ that transfers an amido α-H *intra*molecularly to afford $Mo(NAr)_3(NH_2Ar)$, followed by displacement of the aniline by Cl^-, or (ii) by the intermediacy of nascent $Mo(NAr)_2(NHAr)Cl$ (cf. $W(NAr)_2(NEt_2)Cl$[13]) that undergoes an *inter*molecular deprotonation by the second equivalent of $[NHAr]^-$. Clearly, thermodynamics dictate that the reaction $[Mo(NAr)_3Cl]^- + H_2NAr \rightarrow Mo(NAr)_2(NHAr)_2 + Cl^-$ is strongly favored *to the right*, rather than in the opposite direction as suggested in pathway i above. Consistent with this view is the observation that prolonged heating of solutions of $Mo(NAr)_2(NHAr)_2$ in the presence of excess PR_3 (viz. PMe_2Ph) does *not* produce any detectable amounts of either H_2NAr or a tris(imido) complex $Mo(NAr)_3(PR_3)$ (vide infra). These experiments support the notion that $[Mo(NAr)_3Cl]^-$ arises via an intermolecular deprotonation of "$Mo(NAr)_2(NHAr)Cl$" as suggested above in pathway ii. (A similar proposal has been made regarding the origin of the d^0 $W(NR)_3$ functional group.[13]) These results, along with the nucleophilic displacement of Cl^- from **3** (vide infra), provide precedent for the steps illustrated in eqs 2−5 for the formation

$$Mo(NAr)_2Cl_2(THF)_2 + [NHAr]^- \rightarrow Mo(NAr)_2(NHAr)Cl + Cl^- \quad (2)$$

$$Mo(NAr)_2(NHAr)Cl + [NHAr]^- \rightarrow [Mo(NAr)_3Cl]^- + H_2NAr \quad (3)$$

$$[Mo(NAr)_3Cl]^- + H_2NAr \rightarrow Mo(NAr)_3(NH_2Ar) + Cl^- \quad (4)$$

$$Mo(NAr)_3(NH_2Ar) \rightarrow Mo(NAr)_2(NHAr)_2 \quad (5)$$

of the kinetic product $[Mo(NAr)_3Cl]^-$ (**3**) and its conversion to the thermodynamic product $Mo(NAr)_2(NHAr)_2$ (**4**). Note that the proposed intermediate $Mo(NAr)_3(NH_2Ar)$ is not observed; thus the presumed intramolecular α-H transfer must be very fast.

Several unsuccessful attempts were made to obtain crystals of $[Li(THF)_4][Mo(NAr)_3Cl]$ suitable for an X-ray structure determination. Although a structure determination was undertaken on a marginal sample of $[Li(THF)_4][Mo(NAr)_3Cl]$, poor crystal quality limited the precision of the analysis. However, overall C_{3v} symmetry analogous to the structure of the tungsten analogs $[W(NAr)_3Cl]^-$ [13] and $W(NAr)_3(PMe_3)$[1,29] is apparent. The bonding description in C_{3v} symmetry of complexes of the type $Mo(NR)_3L$ (where L is a σ donor only) is illustrated by considering the symmetries of the ligand and metal orbitals of such a complex: ligand σ ($2a_1 + e$), ligand π ($a_1 + 2e + a_2$), metal s+p ($2a_1 + e$), and metal d ($a_1 + 2e$).[1,30] Under 3-fold symmetry, one combination of the imido nitrogen pπ orbitals

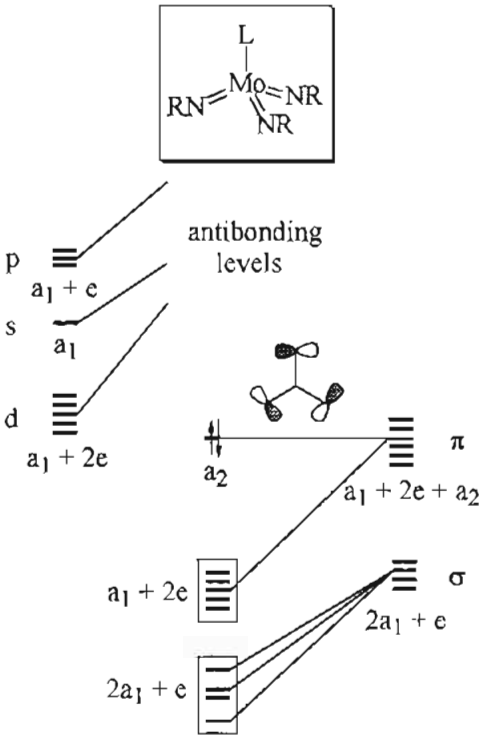

Figure 1. Orbital interaction diagram for C_{3v}, d^0 tris(imido) complexes of the form $Mo(NR)_3L$ and an illustration of the nonbonding a_2 MO composed of the $\pi_\perp$ set of N(2p) orbitals.

has a_2 symmetry, for which there is no corresponding metal orbital.[31] Therefore, as depicted in the orbital interaction diagram for $Mo(NR)_3L$ in Figure 1, two electrons are consigned to occupy a ligand-based, nonbonding a_2 molecular orbital comprised of N(2p) orbitals lying perpendicular to the C_3 axis, i.e. the $\pi_\perp$ set, Figure 1. Thus, π-loaded $Mo(NR)_3L$ complexes such as **3** are formally 18-electron species (not 20), which further restricts any axial ligand L to donating a maximum of 2 electrons to attain saturation. A similar electronic structure has been described for the D_{3h} complexes $Os(NR)_3$.[31] In these trigonal planar osmium species however, the metal-based d_{z^2} orbital constitutes the HOMO of the d^2 complex rather than the nonbonding, ligand-based a_2' orbital.

The chloride ion in $[Mo(NAr)_3Cl]^-$ (**3**) is subject to nucleophilic displacement; thus purple crystals of $Mo(NAr)_3(PMe_3)$ (**5**) can be obtained in high yield from the reaction of **3** with excess PMe_3, Scheme 1. Similarly, $[Li(THF)_4][Mo(NAr)_3Cl]$ reacts with MeLi (in THF/Et_2O) to provide orange crystals of $[Li(THF)_4][Mo(NAr)_3Me]$ (**6**), with Me_3CCH_2Li (in Et_2O) to form orange $[Li(THF)_4][Mo(NAr)_3(CH_2CMe_3)]$ (**7**), and with bromide ion from $[n\text{-}Bu_4N]Br$ (in benzene) to afford red, crystalline $[n\text{-}Bu_4N][Mo(NAr)_3Br]$ (**8**). Each of the compounds **5**−**8** is characterized by the bonding description developed above for C_{3v} symmetric $[Mo(NAr)_3Cl]^-$.

As suggested by the simple orbital picture of these complexes, the imido ligands of $[Mo(NAr)_3Cl]^-$ and $Mo(NAr)_3(PMe_3)$ are susceptible to electrophilic attack as indicated in Scheme 2. $Mo(NAr)_3(PMe_3)$ reacts with 2 equiv of Me_3COH to yield yellow-orange $Mo(NAr)_2(OCMe_3)_2$ (**9**) with the release of 1 equiv of H_2NAr. Since this reaction presumably proceeds *via* $[Mo(NAr)_2(NHAr)(OCMe_3)]$, the *amido* ligand is more susceptible to electrophilic attack than *imido* ligands in the same molecule.[32]

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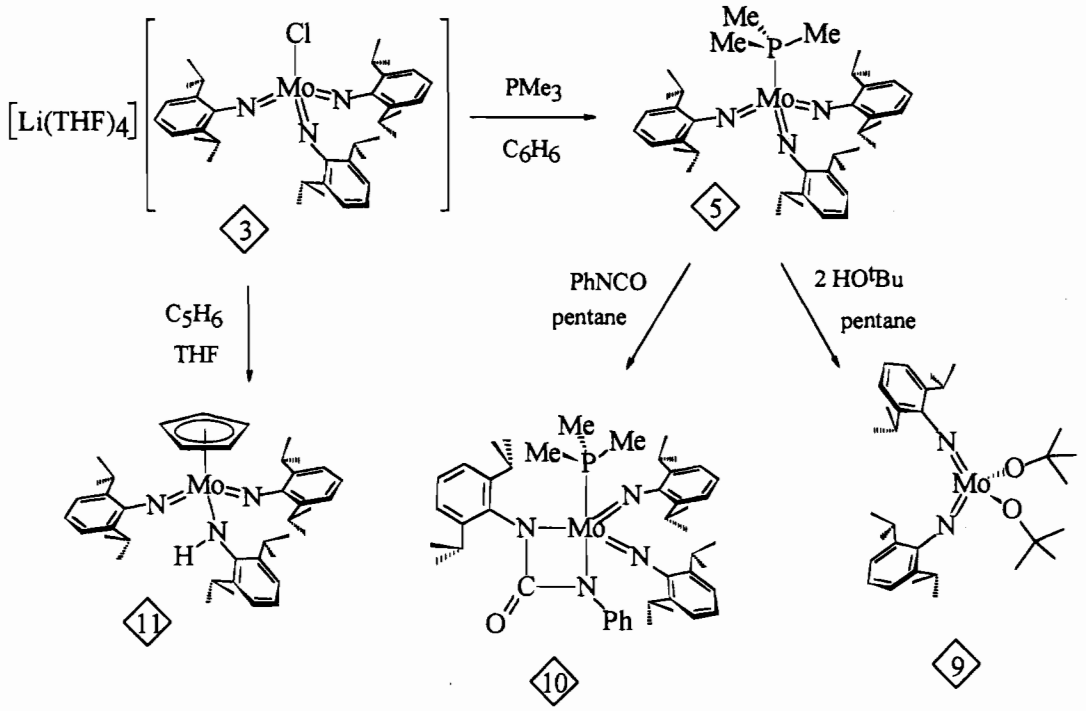
Scheme 2



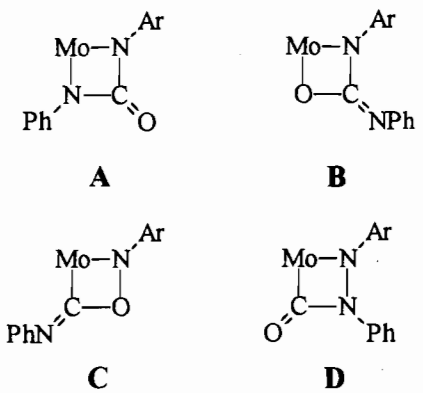
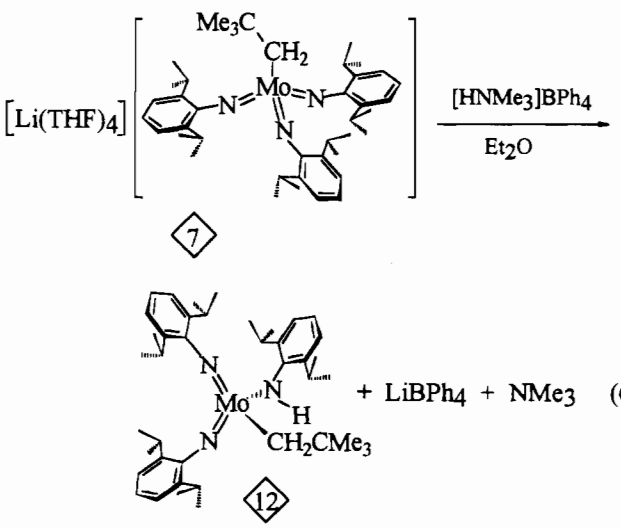


Figure 2. The four possible regioisomers arising from cycloaddition of a Mo=NAr ligand with PhNCO.

The cycloaddition reaction between PhNCO and a Mo=NAr bond in $Mo(NAr)_3(PMe_3)$ is observed to afford the metallacyclic complex $Mo[NArC(O)NPh](NAr)_2(PMe_3)$ (**10**). ^1H and ^{13}C NMR data for **10** indicate that only one imido ligand has reacted with isocyanate, even though excess PhNCO is present. Of the four *possible* regioisomers for **10** presented in Figure 2, only structures **A** [β-exo(O)] and **B** [β-exo(NPh)] are consistent with the cycloaddition regiochemistry expected from the polarity of the $Mo^{\delta+}-N^{\delta-}$ bond and the highly electropositive carbon in PhNCO. The proposed regiochemistry arising from cycloaddition of the C=N bond of PhNCO, structure **A**, is suggested by the strong mode at 1625 cm^{-1} (Nujol mull) in the IR spectrum of **10** that is assigned as ν(C=O), Scheme 2. These data can be compared to the ν(C=O) mode at 1626 cm^{-1} (KBr) in the IR spectrum of the β-exo(O) isomer of $Cp_2Mo[NPhC(O)O]$ ($Cp = [\eta^5\text{-}C_5H_5]^-$).[33] Metallacyclic structures have also been reported with this same regiochemistry.[34]

The active proton of cyclopentadiene monomer C_5H_6 is also observed to attack an imido ligand of **3** to provide $CpMo(NAr)_2(NHAr)$ (**11**) as dark red crystals, Scheme 2. Since the imido dianion $[NR]^{2-}$ and the cyclopentadienyl anion $[C_5H_5]^-$ may both be described as $\sigma+2\pi$ donors, the metal center in **11** appears to be π loaded in the same way that $[Mo(NAr)_3Cl]^-$ (**3**) is. Therefore electronic restrictions seem to prevent the *amido* ligand in $CpMo(NAr)_2(NHAr)$ from effectively π-donating to this metal center.[12] Consistent with this proposal is the δ 5.65 (C_6D_6) chemical shift of the rather shielded N*H*Ar proton that can be compared to the more typical value of δ 8.03 (C_6D_6) for the N*H*Ar protons of $Mo(NAr)_2(NHAr)_2$ (**4**).

Since metal–carbon bonds in early metal alkyl complexes are typically susceptible to electrophilic attack, the question arises as to whether $[Li(THF)_4][Mo(NAr)_3R]$ compounds **6** and **7** will be protonated at the alkyl or the imido ligand. Thus, $[Li(THF)_4][Mo(NAr)_3(CH_2CMe_3)]$ (**7**) is found to react with $[HNMe_3]BPh_4$ in Et_2O to form yellow crystals of $Mo(NAr)_2(NHAr)(CH_2CMe_3)$ (**12**), as indicated in eq 6.



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Discussion

When the reaction of $Mo(NAr)_2Cl_2(THF)_2$ with LiNHAr is allowed to proceed for more than several minutes (in THF), conversion of the kinetic products $[Li(THF)_4][Mo(NAr)_3Cl]$ (**3**) and H_2NAr to the thermodynamic products $Mo(NAr)_2(NHAr)_2$ (**4**) and LiCl is observed. The nucleophilic displacement reactions observed for **3** suggest that the **3** + $H_2NAr \rightarrow$ **4** reaction proceeds through the intermediacy of unstable $Mo(NAr)_3(NH_2Ar)$ and clearly demonstrates the thermodynamic preference of eq 7 (for $L = Cl^-$ or PR_3) since these equilibria

$$Mo(NAr)_2(NHAr)_2 \rightleftharpoons Mo(NAr)_3(NH_2Ar) \overset{\pm L}{\rightleftharpoons} Mo(NAr)_3L + NH_2Ar \quad (7)$$

are favored strongly to the left. Accordingly, prolonged heating of $Mo(NAr)_2(NHAr)_2$ in the presence of PMe_2Ph does not produce any detectable amounts of H_2NAr or the tris(imido) complex $Mo(NAr)_3(PMe_2Ph)$, eq 7.

Similar observations regarding the thermodynamic instability of the d^0 tris(imido) species $W(NAr)_3L$ as compared to their four- or five-coordinate bis(imido) relatives have been noted in complexes of tungsten as well. For example, $W(NAr)_2Cl_2(THF)_2$ reacts with 2 equiv of LiNHAr in THF to afford $[Li(THF)_4][W(NAr)_3Cl]$ and H_2NAr, and these products react further, forming $W(NAr)_2(NHAr)_2$.[29] However, the tungsten complexes are somewhat less labile than their molybdenum analogs, since the $[W(NAr)_3Cl]^- + H_2NAr \rightarrow W(NAr)_2(NHAr)_2$ reaction takes hours to approach completion. In related reactions, electrophilic attack on d^0 $Re(NAr)_3X$ species constitutes a viable synthetic approach to $Re(NAr)_2X_3L_n$ (n = 0 or 1) derivatives, since the $Re(NAr)_3X$ complexes are more readily available than their group 6 congeners.[35]

These experiments suggest one way to attain reactive imido complexes: π loading appears to enhance the polarity of the $Mo^{\delta+}-N^{\delta-}$ bonds in $[Mo(NAr)_3Cl]^-$ and renders the imido ligands more prone to electrophilic cycloadditions. The reactions with electrophiles also underscore the stability of four-coordinate bis(imido) complexes of Mo(VI) of the form $Mo(NAr)_2X_2$ and five-coordinate bis(imido) metallacyclic compounds relative to the higher energy $Mo(NAr)_3L$ derivatives.[1] Since the imido dianion $[NR]^{2-}$ and the cyclopentadienyl anion $[C_5H_5]^-$ may both be described as $\sigma+2\pi$ donors, $CpMo(NAr)_2(NHAr)$ constitutes one of a series of $M(\sigma+2\pi)_3$ compounds with 3-fold $\sigma+2\pi$ *orbital* symmetry. Evidence has been presented that supports this combination of three $\sigma+2\pi$ ligands contributing 2 electrons less than the maximum possible, despite the loss of overall 3-fold *molecular* symmetry.[11,12] Accordingly, the $[CpMo(NAr)_2]^+$ fragment is properly described as a 16-electron species which restricts the $[NHR]^-$ ligand to σ bonding with this fragment, a suggestion that is consistent with the NMR data for $CpMo(NAr)_2(NHAr)$ (**11**) described above. The preparation and reactivity of such species are areas of our continued interests.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques[36] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were distilled under N_2 from an appropriate drying agent[37] and were transferred to the drybox without exposure to air. The "cold" solvents used to wash isolated solid products were typically cooled to −35 °C before use. NMR solvents were passed down a short (5−6 cm) column of activated alumina prior to use. Throughout this paper Ar = 2,6-C_6H_3-*i*-Pr_2 and Cp = $[\eta^5$-$C_5H_5]^-$.

Starting Materials. $(NH_4)_2Mo_2O_7$ was obtained from Johnson-Matthey and was used as received. 2,6-Diisopropylaniline was obtained from Aldrich and vacuum-distilled before use. LiNHAr was prepared from 2,6-diisopropylaniline and *n*-BuLi in pentane according to a literature procedure.[38] Triethylamine was obtained from Aldrich and purified by refluxing over sodium, followed by distillation. Chlorotrimethylsilane was purchased from Petrarch and distilled prior to use. Alkyllithium solutions were obtained from Aldrich and used as received. Trimethylphosphine was prepared and purified by the literature procedure,[39] with the modification of using MeMgI rather than MeMgBr in the preparation. Cyclopentadiene dimer was purchased from Alfa and cracked by refluxing and distilled through a Vigreux column; the monomer was obtained by collecting the fraction boiling at 40 °C. (Cyclopentadiene monomer was stored at −78 °C if necessary.) [*n*-Bu_4N]Br was dried by heating to ca. 120 °C under high vacuum (> 10^{-6} Torr), followed by recrystallization from minimal THF at −35 °C. *tert*-Butyl alcohol was distilled prior to use. Phenyl isocyanate was obtained from Aldrich and distilled from P_2O_5 prior to use. $[HNMe_3]BPh_4$ was obtained from Aldrich and used as received.

Physical Measurements. ^1H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded at probe temperature (unless otherwise specified) on a Bruker AM-250 spectrometer in C_6D_6 or $CDCl_3$ solvent. Chemical shifts are referenced to protio impurities (δ 7.15, C_6D_6; δ 7.24, $CDCl_3$) or the solvent ^{13}C resonance (δ 128.0, C_6D_6; δ 77.0, $CDCl_3$) and are reported downfield of Me_4Si. Microanalytical samples were stored cold, handled under N_2, and combusted with WO_3 (Desert Analytics, Tucson, AZ).

Preparations. $Mo(NAr)_2Cl_2(THF)_2$ (1). A solution of triethylamine (23.8 g, 32.8 mL, 235 mmol) in 25 mL of THF was added over several minutes to a rapidly stirred suspension of $(NH_4)_2Mo_2O_7$ (10.0 g, 29.4 mmol) in 150 mL of THF in a very large Schlenk tube (Teflon stopcock). After this mixture was stirred for 20 min, Me_3SiCl (54.20 g, 63.3 mL, 498 mmol) was added over a period of several minutes. A solution of 2,6-diisopropylaniline (20.8 g, 22.1 mL, 117 mmol) in 25 mL of THF was then added over 10 min, whereupon the solution rapidly changed from milky white to bright yellow and then dark red over several minutes. The stopcock was sealed, and this mixture was heated in a 70 °C oil bath for 12 h, after which time the solution was allowed to cool and the salts that formed were filtered off. These salts were washed with THF until the washings were colorless, and the volatiles were removed from the dark red filtrate under reduced pressure, yielding a burgundy, microcrystalline solid. The solid was collected on a frit, washed with cold THF (−35 °C), and dried in vacuo, yielding 37.7 g (56.13 mmol, 96%) of product. $Mo(NAr)_2Cl_2(THF)_2$ obtained in this manner was found to be analytically pure. ^1H NMR (C_6D_6): δ 7.01−6.93 (A_2B mult, 6 H, H_{aryl}), 4.07 (spt, 4 H, $CHMe_2$), 3.91 (mult, 8 H, C_α, THF), 1.37 (mult, 8 H, C_β, THF), 1.22 (d, 12 H, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 154.3 (C_{ipso}), 145.2 (C_{ortho}), 128.6 (C_{para}), 123.1 (C_{meta}), 70.4 (C_α, THF), 28.6 ($CHMe_2$), 25.7 (C_β, THF), 24.3 ($CHMe_2$). Anal. Calcd for $C_{32}H_{50}Cl_2MoN_2O_2$: C, 57.99; H, 7.61; N, 4.23. Found: C, 57.79; H, 7.51; N, 4.28.

$Mo(NAr)_2Cl_2(THF)$ (2). Solid $Mo(NAr)_2Cl_2(THF)_2$ (**1**, 1.00 g, 1.51 mmol) was placed on a frit and was washed with room-temperature pentane (5 × 10 mL) by allowing the pentane to stand in the frit for several minutes prior to filtration. The resulting rust-colored solid was dried in vacuo to yield 0.80 g (1.35 mmol, 89%) of $Mo(NAr)_2Cl_2$-

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(THF). ^{1}H NMR (C_6D_6): δ 7.01−6.93 (A_2B mult, 6 H, H_{aryl}), overlapping 4.05 (spt, 4 H, C*H*Me$_2$), 4.08 (mult, 4 H, C_α, THF), 1.33 (mult, 4 H, C_β, THF), 1.21 (d, 24 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 154.4 (C_{ipso}, NAr), 145.4 (C_{ortho}, NAr), 128.9 (C_{para}, NAr), 123.0 (C_{meta}, NAr), 72.0 (C_α, THF), 28.7 (*C*HMe$_2$), 25.7 (C_β, THF), 24.1 (CH*Me*$_2$). Anal. Calcd for $C_{28}H_{42}Cl_2N_2OMo$: C, 56.93; H, 7.17; N, 4.75. Found: C, 57.08; H, 7.13; N, 4.82. Osborn and co-workers have previously prepared this complex by reacting MoO_2Cl_2 with ArNCO in THF.[20]

[Li(THF)$_4$][Mo(NAr)$_3$Cl] (3). To a THF solution of Mo(NAr)$_2$Cl$_2$(THF)$_2$ (2.00 g, 3.02 mmol, in 50 mL of THF) was added dropwise a solution of 1.11 g (6.05 mmol) of LiNHAr in 25 mL of THF. During addition, the reaction solution underwent a rapid but subtle color change from dark burgundy to very dark red-orange. After the addition was complete, the mixture was stirred for 15 min, at which point the reaction volatiles were removed under reduced pressure to yield a dark red, waxy solid. This solid was extracted with 50 mL of Et$_2$O, the extract was filtered through Celite, and the filtrate volume was reduced to ca. 5 mL in vacuo to afford a crop of bright, red-orange crystals. These crystals were collected and dried in vacuo to yield 1.75 g (1.84 mmol, 61%) of product. [Li(THF)$_4$][Mo(NAr)$_3$Cl] prepared and isolated in this fashion was found to be analytically pure; however it can be recrystallized from THF/pentane solutions at −35 °C. ^{1}H NMR (C_6D_6): δ 7.13−7.01 (A_2B mult, 9 H, H_{aryl}), 3.76 (spt, 6 H, C*H*Me$_2$), 3.46 (mult, 16 H, C_α, THF), 1.32 (mult, 16 H, C_β, THF), 1.24 (d, 36 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 155.9 (C_{ipso}), 139.2 (C_{ortho}), 124.0 (C_{para}), 122.8 (C_{meta}), 68.3 (C_α, THF), 28.6 (*C*HMe$_2$), 25.5 (C_β, THF), 24.2 (CH*Me*$_2$). Anal. Calcd for $C_{52}H_{83}ClLiMoN_3O_4$: C, 65.44; H, 8.77; N, 4.41. Found: C, 65.06; H, 8.73; N, 4.69.

Mo(NAr)$_2$(NHAr)$_2$ (4). Neat 2,6-diisopropylaniline (0.065 g, 0.367 mmol) was added to a stirred solution of 0.350 g (0.367 mmol) of [Li(THF)$_4$][Mo(NAr)$_3$Cl] in 25 mL of benzene. The red-orange solution was allowed to stir for 20 h, over which time a golden yellow color developed. The mixture was then filtered through Celite, and the reaction volatiles were removed from the filtrate under reduced pressure to afford the product as a golden yellow powder; yield 0.290 g (0.362 mmol, 98%). The compound was dissolved in minimal pentane and the solution cooled to −35 °C to afford golden yellow needles that were collected and dried in vacuo. Mo(NAr)$_2$(NHAr)$_2$ obtained in this fashion was analytically pure. ^{1}H NMR (C_6D_6): δ 8.03 (broad s, 2 H, N*H*Ar), 7.09−7.05 and 6.95−6.91 (A_2B mult, 6 H each, H_{aryl}, NAr and NHAr), 3.85 and 3.38 (spt, 4 H each, C*H*Me$_2$, NAr and NHAr), 1.24 and 1.01 (d, 24 H each, CH*Me*$_2$, NAr and NHAr). ^{13}C NMR (C_6D_6): δ 153.6 and 148.5 (C_{ipso}, NAr and NHAr), 142.3 and 140.4 (C_{ortho}, NAr and NHAr), 126.0 and 124.2 (C_{para}, NAr and NHAr), 123.7 and 122.6 (C_{meta}, NAr and NHAr), 29.0 and 28.7 (*C*HMe$_2$, NAr and NHAr), 24.3 and 23.6 (CH*Me*$_2$, NAr and NHAr). Anal. Calcd for $C_{48}H_{70}MoN_4$: C, 71.96; H, 8.81; N, 7.00. Found: C, 71.57; H, 8.68; N, 6.88. Osborn and co-workers have previously isolated and structurally characterized this complex.[20] Our spectroscopic data for this complex are identical with those reported by Osborn.

Mo(NAr)$_3$(PMe$_3$) (5). Neat PMe$_3$ (1.09 mL, 10.5 mmol) was added to a frozen solution of 1.00 g (1.05 mmol) of [Li(THF)$_4$][Mo(NAr)$_3$Cl] in 30 mL of benzene at −78 °C. The mixture was allowed to warm to room temperature, during which the solution changed from red-orange to dark purple. After this solution was stirred for an additional 30 min, the reaction volatiles were removed under reduced pressure to yield a dark purple solid. The solid was extracted with Et$_2$O, the extract was filtered through Celite, and solvent was removed from the filtrate in vacuo, yielding 0.782 g (0.996 mmol, 95%) of purple, crystalline Mo(NAr)$_3$(PMe$_3$). Analytically pure samples were obtained by recrystallization from pentane at −35 °C. ^{1}H NMR (C_6D_6): δ 7.14−6.99 (A_2B mult, 9 H, H_{aryl}), 3.99 (spt, 6 H, C*H*Me$_2$), 1.24 (d, 36 H, CH*Me*$_2$), 1.15 (d, 9 H, P*Me*$_3$). ^{13}C NMR (C_6D_6): δ 155.2 (C_{ipso}), 139.7 (C_{ortho}), 123.4 (C_{para}), 122.4 (C_{meta}), 28.4 (*C*HMe$_2$), 23.9 (CH*Me*$_2$), 16.3 (P*Me*$_3$). Anal. Calcd for $C_{39}H_{60}MoN_3P$: C, 66.93; H, 8.65; N, 6.01. Found: C, 67.18; H, 8.69; N, 5.87.

[Li(THF)$_4$][Mo(NAr)$_3$Me] (6). A solution of 0.250 g (0.262 mmol) of [Li(THF)$_4$][Mo(NAr)$_3$Cl] in 25 mL of THF was prepared and cooled to −35 °C. To this cold solution was added 1 equiv of MeLi (0.188 mL, 1.4 M in Et$_2$O, 0.262 mmol), and the reaction mixture was stirred at room temperature for 18 h. After this time, the reaction volatiles were removed in vacuo to afford a bright orange solid. The solid was extracted with Et$_2$O, the extract was filtered through Celite, and the solvent was removed from the filtrate in vacuo to afford the product as bright orange crystals. These crystals were collected, washed with cold (−35 °C) Et$_2$O, and dried in vacuo; yield 0.178 g (0.191 mmol, 73%). Analytically pure samples were obtained by recrystallization from THF at −35 °C. ^{1}H NMR (C_6D_6): δ 7.15−6.99 (A_2B mult, 9 H, H_{aryl}), 3.75 (spt, 6 H, C*H*Me$_2$), 3.43 (mult, 16 H, C_α, THF), 1.39 (s, 3 H, Me), 1.29 (mult, 16 H, C_β, THF), 1.27 (d, 36 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 155.5 (C_{ipso}), 138.3 (C_{ortho}), 122.6 (C_{meta}), 122.2 (C_{para}), 68.1 (C_α, THF), 28.5 (*C*HMe$_2$), 25.5 (C_β, THF), 24.2 (CH*Me*$_2$), 15.5 (Me). Anal. Calcd for $C_{53}H_{86}LiMoN_3O_4$: C, 68.12; H, 9.28; N, 4.50. Found: C, 67.87; H, 8.98; N, 4.53.

[Li(THF)$_4$][Mo(NAr)$_3$(CH$_2$CMe$_3$)] (7). An Et$_2$O solution of 1 equiv of Me$_3$CCH$_2$Li (0.015 g, 0.210 mmol, in 3 mL of Et$_2$O) was added to a −35 °C solution of [Li(THF)$_4$][Mo(NAr)$_3$Cl] (0.200 g, 0.210 mmol) in 10 mL of Et$_2$O. The reaction mixture was stirred at room temperature for 30 min, during which the color of the solution changed from red orange to bright orange. The solution was filtered through Celite and the solvent removed from the filtrate in vacuo, yielding a bright orange, microcrystalline solid. This solid was dissolved in a minimal volume of THF/Et$_2$O (4:1, v/v), and the solution was cooled to −35 °C to afford bright orange crystals of product (0.154 g, 0.155 mmol, 74%). Samples obtained in this manner were analytically pure. ^{1}H NMR (C_6D_6): δ 7.15−6.95 (A_2B mult, 9 H, H_{aryl}), 3.87 (spt, 6 H, C*H*Me$_2$), 3.36 (mult, 16 H, C_α, THF), 2.62 (s, 2 H, C*H*$_2$CMe$_3$), 1.35 (s, 9 H, CH$_2$C*Me*$_3$), 1.29 (mult, 16 H, C_β, THF), 1.26 (d, 36 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 155.6 (C_{ipso}), 133.7 (C_{ortho}), 122.8 (C_{meta}), 122.4 (C_{para}), 68.1 (C_α, THF), 52.5 (*C*H$_2$CMe$_3$), 35.3 (CH$_2$*C*Me$_3$), 34.8 (CH$_2$C*Me*$_3$), 28.3 (*C*HMe$_2$), 25.5 (C_β, THF), 24.3 (CH*Me*$_2$). Anal. Calcd for $C_{57}H_{94}LiMoN_3O_4$: C, 69.12; H, 9.57; N, 4.24. Found: C, 68.97; H, 9.23; N, 4.17.

[*n*-Bu$_4$N][Mo(NAr)$_3$Br] (8). A solution of 0.087 g (0.270 mmol) of tetra-*n*-butylammonium bromide in 5 mL of benzene was added to a stirred solution of 0.250 g (0.262 mmol) of [Li(THF)$_4$][Mo(NAr)$_3$Cl] in 20 mL of benzene. This reaction mixture was stirred for 20 h, over which time the solution color changed from red-orange to bright red. After this time, the mixture was filtered through Celite, and the reaction volatiles were removed from the filtrate in vacuo to afford the product as a bright red crystalline solid. This solid was collected on a frit, washed with cold (−35 °C) Et$_2$O, and dried in vacuo; yield 0.210 g (0.212 mmol, 81%). Product obtained in this manner was found to be analytically pure; however this compound can be recrystallized from THF/Et$_2$O solutions (5:1, v/v) at −35 °C. ^{1}H NMR (C_6D_6): δ 7.17−7.14 (A_2B mult, 9 H, H_{aryl}), 4.14 (spt, 6 H, C*H*Me$_2$), 2.53 (mult, 8 H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.40 (d, 36 H, CH*Me*$_2$), 1.02 (mult, 16 H, CH$_2$C*H*$_2$-CH$_2$CH$_3$ and CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.76 (t, 12 H, CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (C_6D_6): δ 157.0 (C_{ipso}), 138.5 (C_{ortho}), 122.0 (C_{meta}), 120.6 (C_{para}), 58.6 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 28.7 (*C*HMe$_2$), 24.2 (CH*Me*$_2$), 24.0 (CH$_2$*C*H$_2$-CH$_2$CH$_3$), 19.8 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.8 (CH$_2$CH$_2$CH$_2$*C*H$_3$). Anal. Calcd for $C_{52}H_{87}BrMoN_4$: C, 66.07; H, 9.28; N, 5.93. Found: C, 65.73; H, 9.22; N, 5.87.

Mo(NAr)$_2$(OCMe$_3$)$_2$ (9). A pentane solution of Mo(NAr)$_3$(PMe$_3$) (0.500 g, 0.637 mmol in 25 mL of pentane) was stirred at room temperature while 0.094 g (1.27 mmol) of *tert*-butyl alcohol in 5 mL of pentane was added dropwise. During the addition, the purple solution rapidly turned yellow-orange. The reaction mixture was stirred for 15 min, after which the reaction volatiles were removed under reduced pressure to yield an oily, yellow orange solid. This solid was dissolved in minimal Et$_2$O, and the solution was cooled to −35 °C to afford the product as yellow orange crystals. The crystals were collected and dried in vacuo; yield 0.268 g (0.452 mmol; 71%). Samples of Mo(NAr)$_2$(OCMe$_3$)$_2$ obtained in this fashion were analytically pure. ^{1}H NMR (C_6D_6): δ 7.02−6.95 (A_2B mult, 6 H, H_{aryl}), 3.84 (spt, 4 H, C*H*Me$_2$), 1.42 (s, 18 H, C*Me*$_3$), 1.18 (d, 24 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 153.9 (C_{ipso}), 142.8 (C_{ortho}), 125.8 (C_{para}), 122.9 (C_{meta}), 80.2 (*C*Me$_3$), 32.1 (C*Me*$_3$), 28.6 (*C*HMe$_2$), 23.8 (CH*Me*$_2$). Anal. Calcd for $C_{32}H_{52}MoN_2O_2$: C, 64.61; H, 8.82; N, 4.71. Found: C, 64.58; H, 9.16; N, 4.77.

Mo[NArC(O)NPh](NAr)$_2$(PMe$_3$) (10). A 10-fold excess of phenyl isocyanate (0.379 g, 0.346 mL, 3.18 mmol) was added neat to a

rapidly stirred solution of $Mo(NAr)_3(PMe_3)$ (0.250 g, 0.318 mmol) in 20 mL of pentane. The mixture was allowed to react for 30 min, during which time a red-brown precipitate formed, leaving behind a faint purple solution. The precipitate was collected, washed with cold (−35 °C) pentane until the washings were colorless, and dried in vacuo to afford the product as a brown powder (0.245 g, 0.299 mmol, 94%). This powder was dissolved in a minimal amount of CH_2Cl_2 and the product reprecipitated as a dark red powder upon cooling this solution to −35 °C. Product isolated in this manner was analytically pure. ^{1}H NMR ($CDCl_3$): δ 7.65 (d, 2 H, H_{ortho}, C_6H_5), 7.44−7.16 (overlapping mult, 11 H, H_{aryl} and H_{meta}), 6.89 (t, 1 H, H_{para}, C_6H_5), 3.75 and 3.72 (spt, 6 H total, C*H*Me$_2$, NAr and NArC(O)NPh), 1.48 and 1.44 (d, 6 H each, CH*Me*$_2$, NArC(O)NPh), 1.41 (d, 9 H, P*Me*$_3$), 1.23 and 1.09 (d, 12 H each, CH*Me*$_2$, NAr). ^{13}C NMR ($CDCl_3$): δ 165.5, 152.6, 146.9, 146.2, 144.0, 141.9, 128.1, 127.4, 125.7, 123.1, 122.5, 122.1, 119.7 (C_{aryl}; NAr, N*A*r*C*(O)NPh, NAr*C*(O)NPh, and *C*$_6$H$_5$), 29.0, 28.2, 26.1, 23.5, 23.3, 23.0 (*C*HMe$_2$ and CH*Me*$_2$; NAr and NArC(O)NPh), 14.4 (d, P*Me*$_3$). IR (Nujol mull): ν(C=O) = 1625 cm^{-1}. Anal. Calcd for $C_{46}H_{65}MoN_4OP$: C, 67.45; H, 8.00; N, 6.84. Found: C, 67.70; H, 7.64; N, 6.92.

CpMo(NAr)$_2$(NHAr) (11). An ampule (Teflon stopcock) was charged with 0.250 g (0.262 mmol) of $[Li(THF)_4][Mo(NAr)_3Cl]$ and 25 mL of THF. An excess of freshly-cracked cyclopentadiene (ca. 0.50 mL, 0.623 g, 9.43 mmol) was added via syringe to the solution, the ampule was sealed, and the mixture was heated to reflux for 10 min during which time the solution color changed from red-orange to burgundy red. The reaction volatiles were then removed under reduced pressure to provide a dark red, almost black, residue. This residue was extracted with pentane, the extract was filtered through Celite, and the filtrate was concentrated to ca. 1 mL in vacuo. Cooling this solution to −35 °C afforded 0.110 g (0.160 mmol, 61%) of dark red, crystalline CpMo(NAr)$_2$(NHAr). Product obtained in this fashion was analytically pure. ^{1}H NMR (C_6D_6): δ 7.24−6.75 (overlapping A_2B mult, 9 H, H_{aryl}), 5.98 (s, 5 H, η^5-C_5H_5), 5.65 (broad s, 1 H, N*H*Ar), 3.80 (overlapping spt, 6 H total, C*H*Me$_2$, NAr and NHAr), 1.27, 1.22, and 1.18 (d, 12 H each, CH*Me*$_2$, NAr and NHAr). ^{13}C NMR (C_6D_6): δ 154.8 and 154.7 (C_{ipso}, NAr and NHAr), 141.0 and 139.5 (C_{ortho}, NAr and NHAr), 125.0 and 122.1 (C_{para}, NAr and NHAr), 123.6 and 122.9 (C_{meta}, NAr and NHAr), 109.3 (η^5-C_5H_5), 28.3 and 27.8 (*C*HMe$_2$, NAr and NHAr), 24.6, 24.5 and 23.8 (CH*Me*$_2$, NAr and NHAr). Anal. Calcd for $C_{41}H_{57}MoN_3$: C, 71.37; H, 8.33; N, 6.09. Found: C, 71.73; H, 8.21; N, 5.97.

Mo(NAr)$_2$(NHAr)(CH$_2$CMe$_3$) (12). To a solution of 0.375 g (0.379 mmol) of $[Li(THF)_4][Mo(NAr)_3(CH_2CMe_3)]$ (**7**) in 40 mL of THF was added 0.144 g (0.379 mmol) of solid $[HNMe_3]BPh_4$. This mixture was stirred at room temperature for 45 min, over which time the insoluble $[HNMe_3]BPh_4$ was observed to disappear upon reaction. The reaction volatiles were then removed in vacuo, the resulting dark orange oil was extracted with pentane (2 × 10 mL), and the extract was filtered through Celite. The solvent was removed in vacuo from the filtrate to afford an orange oil. The oil was reconstituted in minimal pentane, and the solution was cooled to −35 °C to yield yellow crystals of Mo(NAr)$_2$(NHAr)(CH$_2$CMe$_3$); yield (two crops) 0.162 g (0.233 mmol, 62%). Samples obtained in this fashion were analytically pure. ^{1}H NMR (C_6D_6): δ 8.96 (s, 1 H, N*H*Ar), 7.07−6.91 (overlapping A_2B mult, 9 H, H_{aryl}, NAr and NHAr), 3.75 (spt, 2 H, C*H*Me$_2$, NHAr), 3.65 (spt, 4 H, C*H*Me$_2$, NAr), 2.78 (s, 2 H, C*H*$_2$CMe$_3$), 1.35 (s, 9 H, CH$_2$-C*Me*$_3$), 1.29, 1.20, and 1.06 (d, 12 H each, CH*Me*$_2$, NAr and NHAr). ^{13}C NMR (C_6D_6): δ 153.1 (C_{ipso}, NHAr), 148.9 (C_{ipso}, NAr), 142.6 (C_{ortho}, NAr), 138.8 (C_{ortho}, NHAr), 125.9 (C_{para}, NAr), 124.0 (C_{para}, NHAr), 123.6 (C_{meta}, NHAr), 122.8 (C_{meta}, NAr), 67.0 (*C*H$_2$CMe$_3$), 34.0 (CH$_2$C*Me*$_3$), 33.5 (CH$_2$*C*Me$_3$), 29.8 (*C*HMe$_2$, NHAr), 28.8 (*C*HMe$_2$, NAr), 24.0, 23.8, and 23.3 (CH*Me*$_2$, NAr and NHAr). Anal. Calcd for $C_{41}H_{63}N_3Mo$: C, 70.75; H, 9.13; N, 6.04. Found: C, 70.90; H, 9.14; N, 6.18.

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