Tris(2,6-diisopropylphenylimido) Complexes of Molybdenum: Kinetic Accessibility of the d^0 Mo(=NR)$_3$ Functional Group

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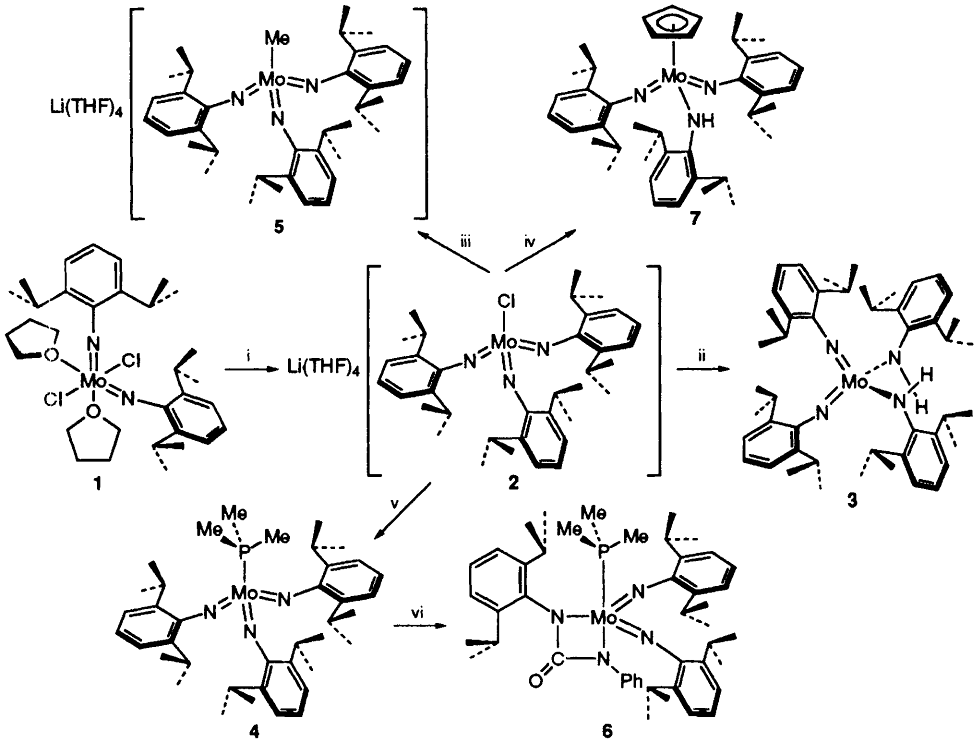
The unprecedented tris(imido) complex of molybdenum, [Li(THF)$_4$][Mo(NAr)$_3$Cl] (Ar = $C_6H_3Pr^i{}_2$-2,6), is the kinetic product of the reaction between [Mo(NAr)$_2$Cl$_2$(THF)$_2$] and 2 equiv. of LiNHAr in THF; [Li(THF)$_4$][Mo(NAr)$_3$Cl] and byproduct H_2NAr react further to form the thermodynamic product [Mo(NAr)$_2$(NHAr)$_2$].

Recent advances in transition-metal imido chemistry[1] include the generation of reactive M=NR ligands that can activate the C–H bonds of methane,[2] engage in cycloaddition chemistry,[3] or function as [NR] transfer reagents.[4] One common feature of these reactive compounds is a coordination sphere containing *multiple* π-donor ligands,[5,6] a property that has aroused interest in 'π loaded' multiple imido complexes.[5c] Despite the well established bis [Mo(=NR)$_2$][1,7,8] and tetrakis {[Mo(=NR)$_4$]$^{2-}$}[9] imido complexes of d^0 molybdenum, the tris(imido) functional group Mo(=NR)$_3$ has not been reported. Herein we describe the kinetic accessibility of this group and demonstrate its reactivity towards both nucleophiles and electrophiles.

Upon reacting *extremely pure* [Mo(NAr)$_2$Cl$_2$(THF)$_2$]† (**1**, Ar = $C_6H_3Pr^i{}_2$-2,6) with 2 equiv. of LiNHAr in THF (15 min), bright red–orange crystals of [Li(THF)$_4$][Mo(NAr)$_3$Cl] **2** are isolated after appropriate work-up, Scheme 1.‡ This tris(imido) anion constitutes the kinetic product of the reaction, since byproduct H_2NAr reacts with [Mo(NAr)$_3$Cl]$^-$ over a period of hours (in THF) to minutes (in pentane) to afford stable [Mo(NAr)$_2$(NHAr)$_2$] **3** and LiCl. This feature is established by reacting isolated **2** with 1 equiv. of H_2NAr which affords golden-yellow [Mo(NAr)$_2$(NHAr)$_2$] **3** in near quantitative yield, therefore reaction time is crucial for the successful isolation of **2**.

The reaction [Li(THF)$_4$][Mo(NAr)$_3$Cl] **2** + H_2NAr $\rightarrow$ [Mo(NAr)$_2$(NHAr)$_2$] **3** addresses the question of how the tris(imido) complex **2** arises. One can envision the **1** + 2 LiNHAr $\rightarrow$ **2** reaction proceeding by either: (*i*) the formation of intermediate [Mo(NAr)$_2$(NHAr)$_2$] which transfers an amido α-H *intra*molecularly to afford [Mo(NAr)$_3$(NH$_2$Ar)], followed by displacement of H_2NAr by Cl$^-$; or (*ii*) by the intermediacy of nascent [Mo(NAr)$_2$(NHAr)Cl] {*cf.* [W(NAr)$_2$ (NEt$_2$)Cl][6]} that undergoes an *inter*molecular deprotonation by the second equiv. of [NHAr]$^-$. Clearly, thermodynamics dictate that the reaction [Mo(NAr)$_3$Cl]$^-$ + H_2NAr $\rightleftharpoons$ [Mo(NAr)$_2$(NHAr)$_2$] + Cl$^-$ is strongly favoured to the right. The fact that prolonged heating of solutions of [Mo(NAr)$_2$(NHAr)$_2$] in the presence of excess PMe$_2$Ph does *not* produce any detectable amounts of either H_2NAr or a tris(imido) complex [Mo(NAr)$_3$(PMe$_2$Ph)] (*vide infra*) is consistent with this view. These experiments support the notion that [Mo(NAr)$_3$Cl]$^-$ arises *via* an intermolecular deprotonation of 'Mo(NAr)$_2$(NHAr)Cl' as suggested above in pathway (*ii*) and provide precedent for the steps illustrated in eqns (1)–(4) for the formation of [Mo(NAr)$_3$Cl]$^-$ **2** and its conversion to the thermodynamic product [Mo(NAr)$_2$(NHAr)$_2$] **3**. We note the influence of a bulky aryl substituent such as $C_6H_3Pr^i{}_2$-2,6 in determining both the course of these reactions and the kinetic stability of **2**, since attempts to



Scheme 1 *Reagents and conditions* i, 2LiNHAr in THF; ii, H_2NAr in benzene; iii, MeLi in THF–Et$_2$O; iv, C_5H_6 in THF; v, excess PMe$_3$, benzene; vi, excess PhNCO in pentane

prepare [Mo(NR)$_3$L] complexes with less-hindered substituents have *met with limited* success.

$$[\mathrm{Mo(NAr)_2Cl_2(THF)_2}] + [\mathrm{NHAr}]^- \rightarrow [\mathrm{Mo(NAr)_2(NHAr)Cl}] + \mathrm{Cl}^- \quad (1)$$

$$[\mathrm{Mo(NAr)_2(NHAr)Cl}] + [\mathrm{NHAr}]^- \rightarrow [\mathrm{Mo(NAr)_3Cl}]^- + \mathrm{H_2NAr} \quad (2)$$

$$[\mathrm{Mo(NAr)_3Cl}]^- + \mathrm{H_2NAr} \rightarrow [\mathrm{Mo(NAr)_3(NH_2Ar)}] + \mathrm{Cl}^- \quad (3)$$

$$[\mathrm{Mo(NAr)_3(NH_2Ar)}] \rightarrow [\mathrm{Mo(NAr)_2(NHAr)_2}] \quad (4)$$

Although an X-ray structure determination of **2** has been carried out, poor crystal quality limited the precision of the analysis. However, overall C_{3v} symmetry analogous to the structure of [W(NAr)$_3$Cl]$^-$[6] is apparent. Under threefold symmetry, one combination of the imido nitrogen pπ orbitals has a$_2$ symmetry, for which there is no corresponding metal orbital.[1] Therefore two of the total number of electrons available from three [NR]$^{2-}$ ligands are consigned to occupy a ligand-based, non-bonding a$_2$ molecular orbital comprised of N(2p) orbitals lying perpendicular to the C_3 axis, *i.e.* the $\pi_\perp$ set, Fig. 1. Thus, π-loaded[5c,6] [Mo(NAr)$_3$L] complexes are formally 18-electron species (not 20), which further restricts any axial ligand L to donating a maximum of two electrons to the metal to attain saturation.

The chloride ion in d^0 [Mo(NAr)$_3$Cl]$^-$ **2** is subject to nucleophilic displacement, thus purple crystals of [Mo(NAr)$_3$(PMe$_3$)] **4** can be obtained in high yield from the reaction of **2** with excess PMe$_3$. Similarly, MeLi reacts with [Li(THF)$_4$][Mo(NAr)$_3$Cl] (in THF–Et$_2$O) to provide orange crystals of [Li(THF)$_4$][Mo(NAr)$_3$Me] **5**. The imido ligands of [Mo(NAr)$_3$Cl]$^-$ and [Mo(NAr)$_3$(PMe$_3$)] are also susceptible to electrophilic attack as indicated in Scheme 1. Thus, cycloaddition of a Mo=NAr moiety of **4** occurs upon its reaction with PhNCO to afford metallacyclic [Mo{NArC(O)NPh}(NAr)$_2$(PMe$_3$)] **6**. The active proton of cyclopentadiene monomer is also observed to attack an imido ligand of **2** to provide [Mo(η^5-C$_5$H$_5$)(NAr)$_2$(NHAr)] **7** as dark red crystals. Since the imido dianion [NR]$^{2-}$ and the cyclopentadienyl anion [C$_5$H$_5$]$^-$ may both be described as 1σ,2π donors, [Mo(η^5-C$_5$H$_5$)(NAr)$_2$(NHAr)] constitutes one of a series of M(1σ,2π)$_3$ compounds with threefold 1σ,2π orbital symmetry. Evidence has been presented that supports this combination of three 1σ,2π ligands contributing two electrons less than the maximum possible.[1,5c] Therefore electronic restrictions appear to prevent the amido ligand in [Mo(η^5-C$_5$H$_5$)(NAr)$_2$(NHAr)] from π donating to this metal centre. Consistent with this notion is the chemical shift (δ 5.65 in C$_6$D$_6$) of the rather shielded N*H*Ar proton that can be compared to the more typical value of δ 8.03 (C$_6$D$_6$) for the N*H*Ar protons of [Mo(NAr)$_2$(NHAr)$_2$] **3**.

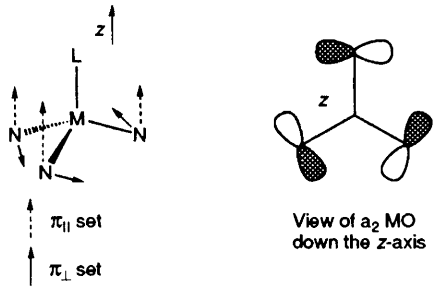


Fig. 1 Illustration of the non-bonding a$_2$ MO composed of the $\pi_\perp$ set of N(2p) orbitals

These experiments suggest one way to activate imido ligands towards cycloaddition reactions: π loading restricts the metal–nitrogen bond order to less than three, induces highly polar M$^{\delta+}$=N$^{\delta-}$ linkages, and renders the imido ligand particularly susceptible to electrophilic cycloadditions.

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Footnotes

† [Mo(NAr)$_2$Cl$_2$(THF)$_2$] has been prepared in 95% yield by a modification of the method developed by Schrock and coworkers.[7] Osborn and coworkers report[8] the preparation of the monokis THF adduct and we note that [Mo(NAr)$_2$Cl$_2$(THF)$_2$] can be converted to [Mo(NAr)$_2$Cl$_2$(THF)] upon extensive washing with pentane and reformed from [Mo(NAr)$_2$Cl$_2$(THF)] in the presence of THF.

‡ All new compounds gave analytical and ^{1}H and ^{13}C NMR spectroscopic data in accord with their assigned structures.

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