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

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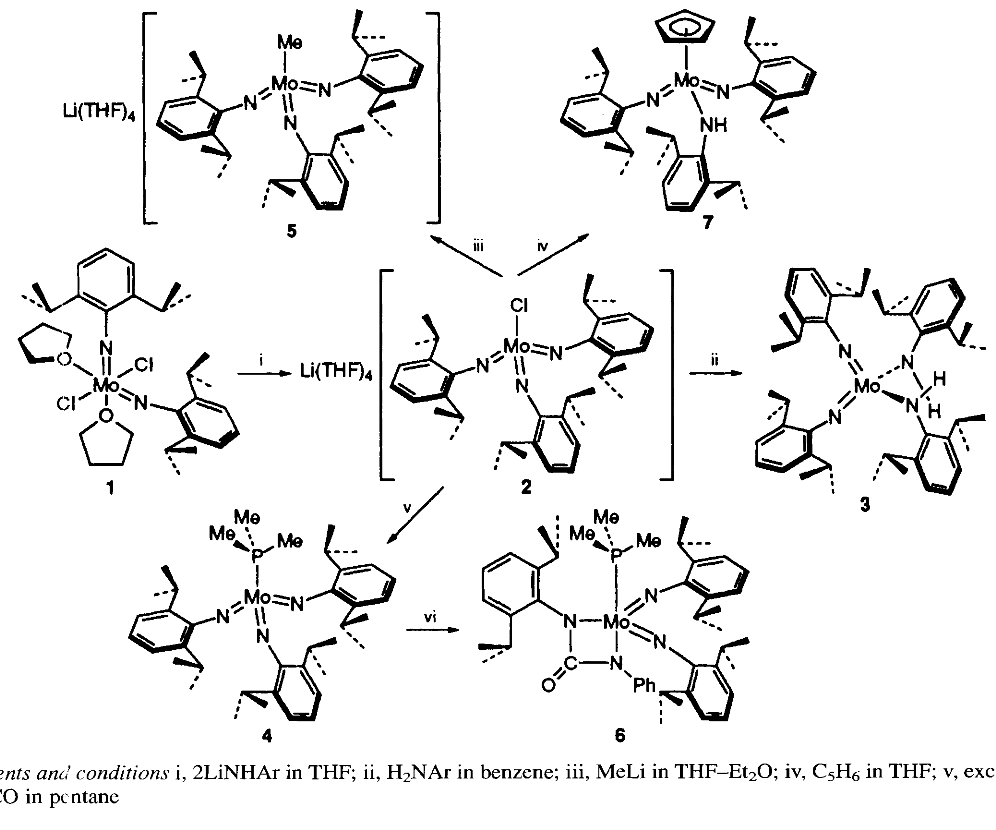
The unprecedented tris(imido) complex of molybdenum, $[Li(THF)_4][Mo(NAr)_3Cl]$ ($Ar = C_6H_3Pr^i_2$-2,6), is the kinetic product of the reaction between $[Mo(NAr)_2Cl_2(THF)_2]$ and 2 equiv. of LiNHAr in THF; $[Li(THF)_4][Mo(NAr)_3Cl]$ and byproduct H_2NAr react further to form the thermodynamic product $[Mo(NAr)_2(NHAr)_2]$.

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* $[Mo(NAr)_2Cl_2(THF)_2]$† (**1**, $Ar = C_6H_3Pr^i_2$-2,6) with 2 equiv. of LiNHAr in THF (15 min), bright red–orange crystals of $[Li(THF)_4][Mo(NAr)_3Cl]$ **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 $[Mo(NAr)_3Cl]^-$ 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 $[Li(THF)_4][Mo(NAr)_3Cl]$ **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 $[Mo(NAr)_3(NH_2Ar)]$, 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 $[Mo(NAr)_3Cl]^- + H_2NAr \rightleftharpoons [Mo(NAr)_2(NHAr)_2] + Cl^-$ 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_2Ph does *not* produce any detectable amounts of either H_2NAr or a tris(imido) complex $[Mo(NAr)_3(PMe_2Ph)]$ (*vide infra*) is consistent with this view. 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*) and provide precedent for the steps illustrated in eqns (1)–(4) for the formation of $[Mo(NAr)_3Cl]^-$ **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_2O; iv, C_5H_6 in THF; v, excess PMe_3, benzene; vi, excess PhNCO in pentane

prepare $[Mo(NR)_3L]$ complexes with less-hindered substituents have met with limited success.

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

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

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

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

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 $[W(NAr)_3Cl]^-$[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] $[Mo(NAr)_3L]$ 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 $[Mo(NAr)_3Cl]^-$ **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 $[Li(THF)_4][Mo(NAr)_3Cl]$ (in THF–Et_2O) to provide orange crystals of $[Li(THF)_4][Mo(NAr)_3Me]$ **5**. The imido ligands of $[Mo(NAr)_3Cl]^-$ 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 $[\overline{Mo\{NArC(O)NPh\}}(NAr)_2(PMe_3)]$ **6**. The active proton of cyclopentadiene monomer is also observed to attack an imido ligand of **2** to provide $[Mo(\eta^5\text{-}C_5H_5)(NAr)_2(NHAr)]$ **7** as dark red crystals. Since the imido dianion $[NR]^{2-}$ and the cyclopentadienyl anion $[C_5H_5]^-$ may both be described as $1\sigma,2\pi$ donors, $[Mo(\eta^5\text{-}C_5H_5)(NAr)_2(NHAr)]$ constitutes one of a series of $M(1\sigma,2\pi)_3$ compounds with threefold $1\sigma,2\pi$ orbital symmetry. Evidence has been presented that supports this combination of three $1\sigma,2\pi$ ligands contributing two electrons less than the maximum possible.[1,5c] Therefore electronic restrictions appear to prevent the amido ligand in $[Mo(\eta^5\text{-}C_5H_5)(NAr)_2(NHAr)]$ from π donating to this metal centre. Consistent with this notion is the chemical shift (δ 5.65 in C_6D_6) 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 $[Mo(NAr)_2(NHAr)_2]$ **3**.

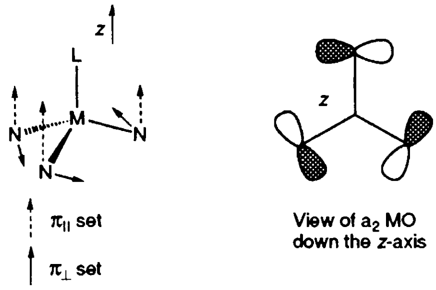


Fig. 1 Illustration of the non-bonding a_2 MO composed of the $\pi_\perp$ set of N(2p) orbitals

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.

Acknowledgement is made to the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (DE-FG03-93ER14349) for support of this research. We also thank Dr Michael A. Bruck for the structural study of $[Li(THF)_4][Mo(NAr)_3Cl]$. D. L. M. is the Carl S. Marvel Fellow, 1994–1995.

Received, 20th September 1994; Com. 4/05734A

Footnotes

† $[Mo(NAr)_2Cl_2(THF)_2]$ 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 $[Mo(NAr)_2Cl_2(THF)_2]$ can be converted to $[Mo(NAr)_2Cl_2(THF)]$ upon extensive washing with pentane and reformed from $[Mo(NAr)_2Cl_2(THF)]$ in the presence of THF.

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

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