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Synthesis of Molybdenum Alkylidene Complexes That Contain the 2,6-Dimesitylphenylimido Ligand

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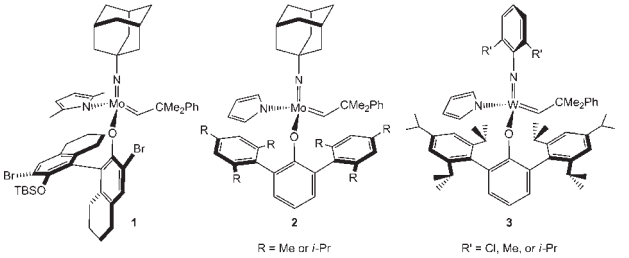
Supporting Information

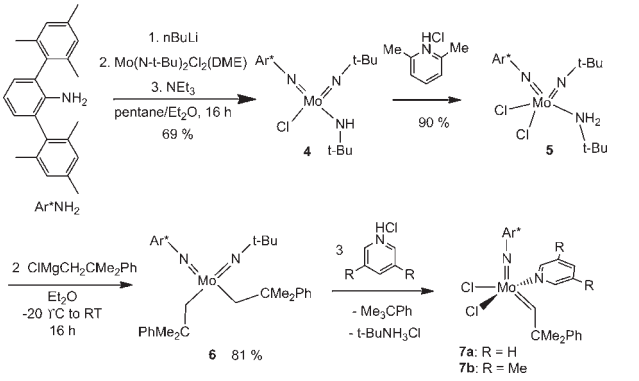
ABSTRACT: Compounds that have the formula M(NR)(CHR′)(OR″)(Pyrrolide), where OR″ is "large" relative to NR and M = Mo or W, have been shown to be *Z*-selective olefin metathesis catalysts. In this communication we report a new route to Mo complexes in which the relationship between NR and OR″ has been reversed; i.e., the imido ligand is the sterically demanding 2,6-dimesitylphenylimido ligand (NAr*).

In the past several years Mo and W imido alkylidene complexes that have the formula M(NR)(CHR′)(OR″)(Pyr), where Pyr is a pyrrolide or a substituted pyrrolide and OR″ is an aryloxide, have been prepared and explored as olefin metathesis initiators; examples are **1**, **2**, and **3**.[1,2] These MonoAlkoxidePyrrolide (MAP) species have been found to be efficient for many *Z*-selective reactions. It has been proposed that *Z* selectivity arises as a consequence of a "large" phenoxide, especially in combination with a "small" imido group, which in TBP (TBP = trigonal bipyramidal) intermediates restricts substituents on the equatorial metallacyclobutane ring from pointing toward the axial large phenoxide. Therefore, it seemed desirable to explore the syntheses and reactivities of MAP catalysts that contain an *imido* ligand analogous to the aryloxide ligands in **2** paired with a relatively small aryloxide or alkoxide. 2,6-Dimesitylphenyl (Ar*) was chosen as the target substituent for the imido ligand, since both main group metal compounds that contain NAr* imido ligands[3] as well as transition metal compounds (Ni[4] and Ta[5]) have been reported.



The traditional approach to Mo and W imido alkylidene complexes involves the synthesis of $M(NR)_2Cl_2$ derivatives (M = Mo or W), followed by alkylation (with neopentyl or neophyl Grignard reagents) to give $M(NR)_2(CH_2CMe_2R')_2$ derivatives, which upon treatment with 3 equiv of triflic acid yield RNH_3OTf and $M(NR)(CHCMe_2R')(OTf)_2(dme)$ derivatives (dme = dimethoxyethane, R′ = Me or Ph). All initial attempts to prepare Mo or W species that contain two Ar* imido ligands (e.g., $Mo(NAr^*)_2Cl_2$) failed.[6] Therefore, a new synthetic route had to be developed. The new route was inspired by the work of Gibson et al., who showed that reaction of $Mo(N\text{-}t\text{-}Bu)_2Cl_2(DME)$ with H_2NAr (Ar = 2,6-diisopropylphenyl) leads to formation of the mixed imido species, $Mo(NAr)(N\text{-}t\text{-}Bu)Cl_2(DME)$, and that $Mo(NAr)(N\text{-}t\text{-}Bu)(CH_2CMe_2R)_2$ (R = Me or Ph) reacts with pentafluorophenol to give exclusively $Mo(NAr)(CHCMe_2R)(OC_6F_5)_2$.[7]

Scheme 1. Synthesis of 7a and 7b



Ar*NH_2 was prepared by the reported method.[5b] As shown in Scheme 1, addition of LiNHAr* to $Mo(N\text{-}t\text{-}Bu)_2Cl_2(dme)$ yielded intermediate $Mo(N\text{-}t\text{-}Bu)_2Cl(NHAr^*)$, which upon addition of triethylamine rearranged to **4**. Addition of 2,6-dimethylpyridinium chloride to **4** led to protonation of the amido group to yield **5**; alkylation of **5** then yielded **6**. Attempts to convert **6** into the desired $Mo(NAr^*)(CHCMe_2Ph)(OTf)_2(dme)$ species under standard conditions employed for related syntheses of bistriflate derivatives failed. Among the alternatives that were attempted was treatment of **6** with 3 equiv of pyridinium chloride or 3,5-lutidinium chloride to give $Mo(NAr^*)(CHCMe_2Ph)Cl_2(L)$ (**7a**, L = pyridine; **7b**, L = 3,5-lutidine). To our knowledge, conversion of **6** to **7** is the first example of formation of an imido alkylidene employing HCl or an HCl derivative instead of triflic acid as the acid source. The key intermediate before α proton abstraction is likely to be $Mo(NAr^*)(CH_2CMe_2Ph)_2Cl_2(L)$ formed through selective protonation of the *tert*-butylimido ligand to give $t\text{-}BuNH_3Cl$.

An X-ray diffraction study of **4** (Figure 1) shows the Ar*N imido moiety and both *t*-BuNH and *t*-BuN ligands. The Mo1—N1 bond length (1.7545(8) Å) and the Mo1—N3 distance (1.7425(9) Å) are typical for a Mo═N distance in bisimido

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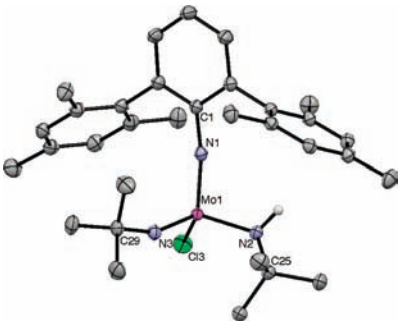


Figure 1. Thermal ellipsoid (50%) drawing of **4**. Hydrogen atom are omitted for clarity, except the hydrogen atoms attached to N2. Selected bond lengths (Å) and angles (deg): Mo1−N3 = 1.7425(9), Mo1−N1 = 1.7545(8), Mo1−N2 = 1.9403(9), Mo1−Cl1 = 2.3308(3), N1−C1 = 1.3874(13), N2−C25 = 1.4763(13), N3−C29 = 1.4602(13); N3−Mo1−N1 = 111.90(4), N3−Mo1−N2 = 107.89(4), N1−Mo1−N2 = 103.69(4), N3−Mo1−Cl1 = 108.87(3).

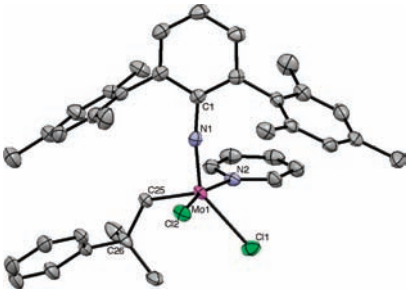
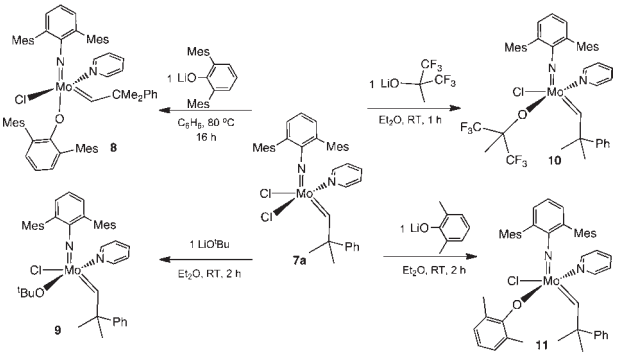


Figure 2. Thermal ellipsoid (50%) drawings of the predominant (87%) *anti* isomer of **7a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for the *anti* isomer: Mo1−C25 = 1.932(2), N1−Mo1−C25 = 95.48(8), C25−Mo1−N2 = 95.16(7), C25−Mo1−Cl1 = 122.32(6), C25−Mo1−Cl2 = 97.16(6), C26−C25−Mo1 = 128.92(18). Selected bond lengths (Å) and angles (deg) for the *syn* isomer: Mo1−C25A = 1.841(12), N1−Mo1−C25A = 128.0(4), C25A−Mo1−N2 = 96.0(4), C25A−Mo1−Cl1 = 90.0(4), C25A−Mo1−Cl2 = 90.9(4), C26A−C25A−Mo1 = 150.0(10).

complexes. The Mo1−N1−C1 and the Mo1−N3−C29 angles (165.16(7)° and 157.38(8)°, respectively) are also typical of Mo bisimido complexes. Upon comparison with N3, N2 is identified as an amide as a consequence of the longer Mo1−N2 bond length (1.9403(9) Å) and the smaller Mo1−N2−C25 angle (130.53(7)°). The hydrogen atom bonded to N2 was located in the difference map.

An X-ray diffraction study of **7a** (Figure 2) showed it has a structure that is approximately halfway (τ = 0.41)[8] between a square pyramid (τ = 0) and a trigonal bipyramid (τ = 1). Bond lengths and angles are similar to those found in other Mo imido alkylidene complexes. The alkylidene ligand was disordered over *anti* (where substituents on the alkylidene ligand point away from the imido group) and *syn* orientations, with 87% being in the *anti* orientation in this particular crystal. Interestingly, the only atoms that are in significantly different positions in the two isomers are C25 and the methyl groups; the phenyl group and C26 are in essentially the same position in both the *syn* and *anti* isomers. The Mo═C25 bond length in the *anti* alkylidene is 1.932(2) Å, while the Mo═C25A bond length in the *syn* alkylidene is 1.841(12) Å; these bond lengths are typical of *syn* and *anti* imido alkylidene complexes of this general type. Only

Scheme 2. Synthesis of 8, 9, 10, and 11



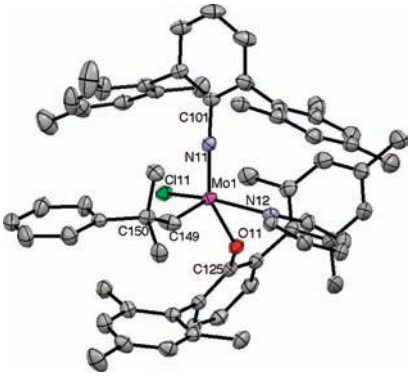


Figure 3. Thermal ellipsoid (50%) drawing of **8**. One independent molecule is shown with one component of each disorder. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1−N11 = 1.7442(19), Mo1−C149 = 1.874(3), Mo1−O11 = 1.992(15), Mo1−N12 = 2.267(7), Mo1−Cl11 = 2.3731(6), N11−Mo1−C149 = 102.45(10), N11−Mo1−O11 = 148.55(8), C149−Mo1−O11 = 108.32(9), N11−Mo1−N12 = 94.9(3), C149−Mo1−N12 = 98.5(2), O11−Mo1−N12 = 74.6(3), N11−Mo1−N32 = 96.6(4), N11−Mo1−Cl11 = 98.10(6), C149−Mo1−Cl11 = 99.45(8), O11−Mo1−Cl11 = 83.31(5), N12−Mo1−Cl11 = 155.0(3), C125−O11−Mo1 = 139.43(13), C150−C149−Mo1 = 146.4(3), C101−N11−Mo1 = 173.93(17).

the *anti* alkylidene is observed in the ^{1}H NMR spectrum of **7a** in C_6D_6 or CD_2Cl_2 (12.61 ppm in CD_2Cl_2, $^1J_{CH}$ = 151 Hz).

Reaction of **7a** with LiOAr* gives Mo(NAr*)($CHCMe_2Ph$)Cl(OAr*)(py), **8** (Scheme 2). An X-ray structure (Figure 3) revealed that pyridine remains bound to the metal to give a distorted square pyramid (τ = 0.10) with the alkylidene ligand at the apical site. Two independent molecules were found per unit cell, and there was much disorder in the mesityl groups, the pyridine ligands, and parts of the alkylidene ligands (although neither the α nor β alkylidene carbon atoms were disordered). The alkylidene ligand in **8** is in the *syn* orientation. It should be noted that the NAr* group is significantly more sterically demanding than the OAr* ligand since the Mo═N bond length (1.7442(19) Å) is ~0.25 Å shorter than the Mo1—O11 bond length (1.992(15) Å). In solution only the *syn* isomer is observed ($^1J_{CH}$ =127 Hz).

Similarly, Mo(NAr*)($CHCMe_2Ph$)Cl(O-*t*-Bu)(py) (**9**), Mo(NAr*)($CHCMe_2Ph$)Cl[$OCMe(CF_3)_2$](py) (**10**), and Mo(NAr*)($CHCMe_2Ph$)Cl(OAr′)(py) (**11**, Ar′ = 2,6-dimethylphenyl) can be

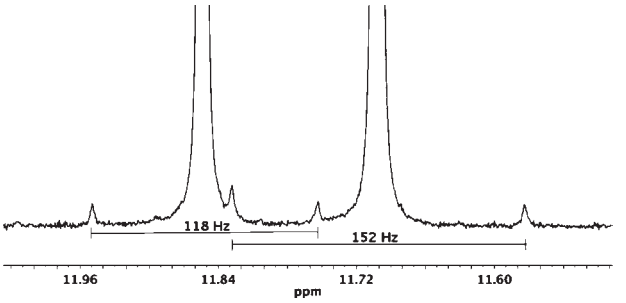


Figure 4. Vertically expanded alkylidene region of the ^{1}H NMR spectrum of **13**. *Syn* and *anti* isomer resonances are observed in a ratio of 1:1.1.

isolated by reaction of **7a** with 1 equiv of lithium alkoxide in diethyl ether (Scheme 2). The pyridine ligand remains bound in all cases. In solution, **9**, **10**, and **11** are observed as *anti* alkylidenes. The $^1J_{CH}$ values are 148 Hz for **9**, 150 Hz for **10**, and 151 Hz for **11**, all typical $^1J_{CH}$ values for *anti* alkylidenes.

Compound **7a** reacts with 2 equiv of Li(Me$_2$pyr) to yield Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)$_2$ (**12**) and free pyridine (visible in the ^{1}H NMR spectrum). No pyridine remains after removal of the volatiles *in vacuo*. Several broad resonances are observed in the ^{1}H NMR spectrum of **12**, but a spectrum obtained at −40 °C contains only sharp resonances; such fluxional behavior is typical of bispyrrolide complexes of this general type.[1]

Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O-*t*-Bu) (**13**) can be synthesized by two routes. Either reaction of **12** with HO-*t*-Bu or reaction of **9** with LiMe$_2$pyr gives clean conversion to **13** that has two alkylidene resonances (at 11.861 and 11.695 ppm in C_6D_6) in the proton NMR spectrum in a 1:1.1 ratio. The NMR spectrum is consistent with both species having the formula Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O-*t*-Bu). The $^1J_{CH}$ value for the downfield alkylidene proton resonance is 118 Hz, consistent with a *syn* alkylidene, while $^1J_{CH}$ of the upfield alkylidene proton resonance is 152 Hz, consistent with an *anti* alkylidene (Figure 4). Preliminary 2D ^{1}H−^{1}H EXSY experiments (mixing time 1−2 s; Figure S1) confirm that the two alkylidene protons interconvert at a rate of 0.05 s^{-1}. Little is known about rates of interconversion of *syn* and *anti* protons for MAP species,[2c] although rates of *syn*/*anti* interconversions in bisalkoxide Mo imido alkylidene complexes are known to vary over ~6 orders of magnitude.[9] It is unusual to find the *anti* alkylidene resonance close to and especially upfield of the *syn* alkylidene resonance in a Mo or W imido alkylidene complex. Slow interconversion of *syn* and *anti* isomers has been proposed to be an important characteristic of *Z*-selective MAP species.

In summary, we have shown how to prepare NAr* alkylidene complexes of molybdenum through a nontraditional route that does not employ triflic acid. *Anti* alkylidene isomers are readily observed in several cases, perhaps in part due to the sterically demanding nature of the NAr* ligand. Future studies will be aimed at assessing MAP complexes that contain the NAr* ligand for selective metathesis reactions analogous to those that have been reported in the past several years for MAP species that contain sterically demanding aryloxide ligands.[2]

■ ASSOCIATED CONTENT

Supporting Information. Experimental details for the synthesis of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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