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Dipyrrolyl Precursors to Bisalkoxide Molybdenum Olefin Metathesis Catalysts

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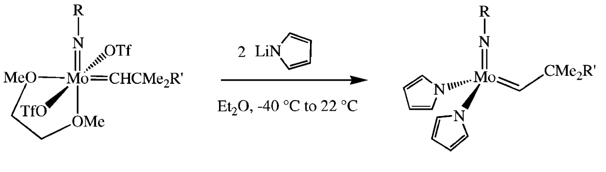
Abstract: Addition of 2 equiv of lithium pyrrolide to $Mo(NR)(CHCMe_2R')(OTf)_2(DME)$ ($OTf = OSO_2CF_3$; R = 2,6-i-$Pr_2C_6H_3$, 1-adamantyl, or 2,6-Br_2-4-MeC_6H_2; R′ = Me or Ph) produces $Mo(NR)(CHCMe_2R')(NC_4H_4)_2$ complexes in good yield. All compounds can be recrystallized readily from toluene or mixtures of pentane and ether and are sensitive to air and moisture. An X-ray structure of a 2,6-diisopropylphenylimido species shows it to be an unsymmetric dimer, $\{Mo(NAr)(\textit{syn}\text{-}CHCMe_2Ph)(\eta^5\text{-}NC_4H_4)(\eta^1\text{-}NC_4H_4)\}\{Mo(NAr)(\textit{syn}\text{-}CHCMe_2Ph)(\eta^1\text{-}NC_4H_4)_2\}$, in which the nitrogen in the η^5-pyrrolyl bound to one Mo behaves as a donor to the other Mo. All complexes are fluxional on the NMR time scale at room temperature, with one symmetric species being observed on the NMR time scale at 50 °C in toluene-d_8. The dimers react with PMe_3 (at Mo) or $B(C_6F_5)_3$ (at a η^5-NC_4H_4 nitrogen) to give monomeric products in high yield. They also react rapidly with 2 equiv of monoalcohols (e.g., Me_3COH or $(CF_3)_2MeCOH$) or 1 equiv of a biphenol or binaphthol to give 2 equiv of pyrrole and bisalkoxide or diolate complexes in ~100% yield.

We have been searching for methods of synthesizing $Mo(NR)(CHCMe_2R')(OR'')_2$ (R′ = Me or Ph) species (or species that contain enantiomerically pure biphenolate or binaphtholate ligands[1]) in situ by treating an appropriate $Mo(NR)(CHCMe_2R')X_2$ species with a monoalcohol or diol. The main reason is that an increasing number of applications (e.g., asymmetric olefin metathesis[1]) require that many catalysts having different combinations of imido and alkoxide ligands be evaluated for a given metathesis transformation and, therefore, that many catalysts be synthesized, isolated, stored, and manipulated. In the long run the synthesis and isolation of many catalysts will be impractical. Of course the synthesis of $Mo(NR)(CHCMe_2R')(OR'')_2$ species from $Mo(NR)(CHCMe_2R')X_2$ species requires that both X groups be replaced readily with OR, that the HX product of this reaction not interfere to any significant degree with subsequent reactions that involve $Mo(NR)(CHCMe_2R')(OR'')_2$, and that the HX product not react with any organic species in the reaction. We found that when X = CH_2CMe_3 only *1* equiv of alcohol reacts readily to yield Mo(NAr)(CH-*t*-Bu)(CH_2-*t*-Bu)(OR) or Mo(NAr)(CH_2-*t*-Bu)$_3$(OR) species.[2,3] A second approach in which X = NPh_2 allows both X groups to be replaced, but often slowly and incompletely and not at all when NR = NAr (Ar = 2,6-diisopropylphenyl) and the diol is the bulky H_2[Biphen] (H_2[Biphen] = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol).[4] Syntheses of $Mo(NR)(CHCMe_2R')(NPh_2)_2$ species from $Mo(NR)(CHCMe_2R')(OTf)_2$(dimethoxyethane) species[5] are also plagued by poor yields as a consequence of competitive deprotonation of the alkylidene. We have now found that a variety of dipyrrolyl complexes, $Mo(NR)(CHCMe_2R')(NC_4H_4)_2$, can be prepared in good yield from bistriflate precursors and that they react rapidly, even with H_2[Biphen] when NR = NAr, to yield 2 equiv of pyrrole and bisalkoxide or biphenolate or binaphtholate species.

Addition of 2 equiv of lithium pyrrolide to a stirred diethyl ether suspension of $Mo(NR)(CHCMe_2R')(OTf)_2(DME)$ ($OTf = OSO_2CF_3$; R = 2,6-i-$Pr_2C_6H_3$ or 1-adamantyl) produces yellow to orange $Mo(NR)(CHCMe_2R')(NC_4H_4)_2$ complexes in ~75% yield (eq 1). An analogous reaction when R = 2,6-Br_2-4-MeC_6H_2 is successful when the solvent is a mixture of diethyl ether and dichloromethane. Little or no competitive deprotonation of the alkylidene to give an alkylidyne complex[6,7] has been observed in any case. All compounds are sensitive to air and moisture and can be recrystallized readily from toluene or mixtures of pentane and ether.



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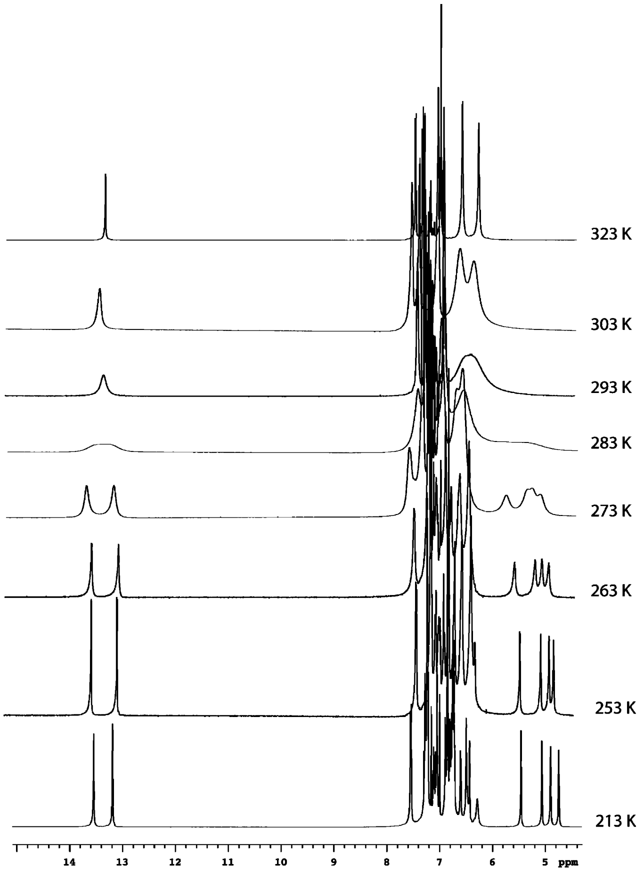

Figure 1. Variable temperature proton NMR spectrum of Mo(NAr)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$ in toluene-d_8.

All dipyrrolyl complexes are fluxional on the proton NMR time scale. At 22 °C the spectra contain broad resonances, as shown, for example, for Mo(NAr)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$ in toluene-d_8 (at 500 MHz) in Figure 1. At high temperature one alkylidene resonance at ~13.3 ppm and two pyrrolyl resonances at ~6.1 and ~6.3 ppm are observed. At low temperatures two alkylidene resonances at ~13.2 and ~13.6 ppm are observed in a 1:1 ratio, and the pyrrolyl proton resonances are resolved into an obscured set of resonances downfield of 6.3 ppm, along with a pattern of four sharp resonances near 5 ppm.[8] No fluoride resonance is observed in the ^{19}F NMR spectrum, and no solvent resonances are observed in the ^{1}H NMR spectrum upon addition of trimethylphosphine, which yields a base adduct (vide infra). A ^{13}C NMR spectrum of Mo(NAr)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$ at −50 °C in methylene chloride-d_2 reveals resonances at 313.9 ppm (J_{CH} = 122.8 Hz) and 293.9 ppm (J_{CH} = 121.3 Hz) characteristic of syn alkylidene species.[9]

An X-ray structural study of Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$ shows it to be an unsymmetric dimer, {Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$)}{Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$}, in which the nitrogen in the η^5-pyrrolyl behaves as a donor to the other Mo (Figure 2). The electron count in the Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$) half is 18, and in the Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$(donor) half it is 16. The Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$(donor) fragment is approximately a square pyramid with the alkylidene in the apical position. Bond distances and angles are unexceptional. (See figure caption for selected values.) This dimeric structure is consistent with the NMR spectra at low temperature; i.e., one half (containing Mo(2)) has no symmetry, while the second (containing Mo(1)) effectively is C_s symmetric. (The asymmetry that is present at Mo(2) apparently cannot be detected at Mo(1), at least under the NMR conditions employed so far.) The four sharp resonances near 5 ppm are assigned to the four protons in the η^5-NC$_4$H$_4$ that is bound to a chiral metal center. η^5-Pyrrolyl complexes (most of them di- or tetrasubstituted pyrroles[10]) have been prepared and studied for many years, the main driving force being the analogy between η^5-NC$_4$H$_4$ and η^5-C$_5$H$_5$.[11] To the best of our knowledge, only one other molybdenum pyrrolyl complex, Mo(Tp*)(NO)(η^1-NC$_4$H$_4$)$_2$ (Tp* = HB(3,5-Me$_2$C$_3$N$_2$H)$_3^-$), has been structurally characterized.[12]

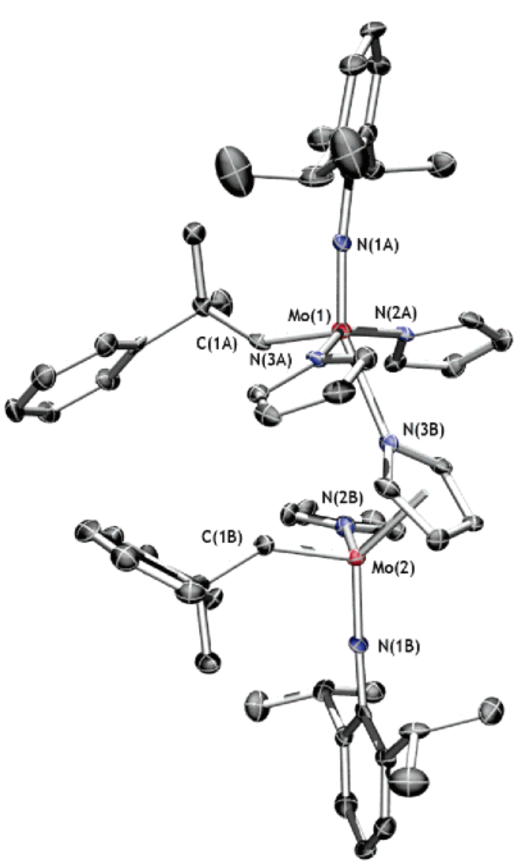

Figure 2. Structure of Mo(NAr)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$}$_2$. Hydrogen atoms and cocrystallized solvent have been removed for clarity. Thermal ellipsoids are at 50%. Selected bond distances (Å): Mo(1)−C(1A), 1.859(5); Mo(2)−C(1B), 1.912(5); Mo(1)−N(2A), 2.082(4); Mo−N(3A), 2.097(4); Mo(2)−N(2B),2.060(4); Mo(2)−N(3B), 2.479(4); Mo(1)···Mo(2), 4.53. Selected bond angles (deg): N(1A)−Mo(1)−C(1A), 99.5(2); N(1A)−Mo(1)−N(3B), 155.16(16); N(2A)−Mo(1)−N(3A), 150.98(16); pyrrolyl centroid−Mo(2)−N(1B), 157.3; N(1B)−Mo(2)−C(1B), 100.5(2); N(1B)−Mo(2)−N(2B), 101.80(17).

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[8] In structurally characterized η^5-pyrrolyl complexes in which the pyrrolyl is disubstituted an upfield shift is observed compared to η^1-pyrrolyl proton resonances. For example the pyrrole hydrogens in Ti(η^5-2,5-Me$_2$C$_4$H$_2$N)(NMe$_2$)$_2$-Cl are found at 5.93 ppm; Duarte, M. T.; Ferreira, A.; Dias, A. R.; Salema, M. M.; da Silva, J. F. *Acta Crystallogr., Sect. C* **2005**, C61, m104.

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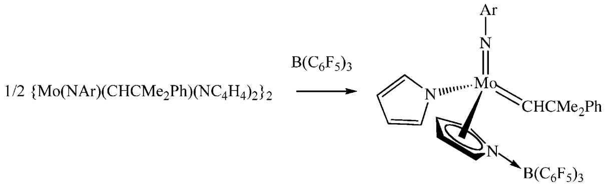
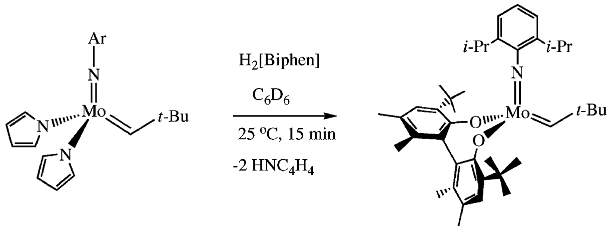
The NMR spectra at high temperatures are consistent with a C_s symmetric Mo(NR)(CHCMe$_2$R′)(η^1-NC$_4$H$_4$)$_2$ species on the NMR time scale in which the pyrrolyl ligands are η^1 (on average) and rotate rapidly about the Mo−N bonds. Variable temperature spectra are identical at different concentrations, a result that does not reveal whether a small fraction of the dimer breaks up into monomers in which interconversion of η^1-NC$_4$H$_4$ and η^5-NC$_4$H$_4$ ligands is facile, or whether the equilibration process takes place entirely within the dimer. We favor the former in view of the high reactivity of the {Mo(NR)(CHCMe$_2$R′)(NC$_4$H$_4$)$_2$}$_2$ species toward alcohols and a Lewis acid or base (vide infra).

Addition of 1 equiv of trimethylphosphine to Mo(NAd)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$ results in immediate formation of *syn*-Mo(NAd)(CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$(PMe$_3$), in which the alkylidene proton resonance is found at 12.49 ppm with J_{HP} = 5 Hz. An X-ray structural study[13] shows that trimethylphosphine binds to one of the CN$_{imido}$N$_{pyrrolyl}$ faces of the pseudotetrahedral species, which is the face analogous to the CNO face where trimethylphosphine is observed to bind in bisalkoxide species.[9] The Lewis acid B(C$_6$F$_5$)$_3$ also reacts immediately with {Mo(NAr)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$}$_2$ to yield a mixture of what we propose are syn and anti alkylidenes of the adduct shown in eq 2. The four η^5-pyrrolyl protons in the major (syn) isomer are found at 7.7, 7.2, 5.7, and 5.4 ppm in benzene-d_6.



(2)

Addition of 2 equiv of monoalcohols (e.g., Me$_3$COH or (CF$_3$)$_2$MeCOH) or 1 equiv of a biphenol or binaphthol to ∼10 mM solutions of the Mo(NR)(CHCMe$_2$R′)(NC$_4$H$_4$)$_2$ (NR = NAd or NAr) species described above results in rapid formation of 2 equiv of pyrrole and previously characterized bisalkoxide or diolate complexes. The reaction is rapid and gives an ∼100% yield in all combinations screened thus far, including the combination of what we consider to be sterically the most challenging, a 2,6-diisopropylphenylimido precursor reacting with H$_2$[Biphen] (H$_2$[Biphen] = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol (eq 3). In the case of 3,3′-bis(2,4,6-triisopropylphenyl)-2,2′-binaphthol[1] the resulting binaphtholate appears to bind 1 equiv of pyrrole weakly, but the known THF adduct is generated immediately upon addition of one or more equivalents of THF. Catalysts that have been isolated only as THF adducts, or that have proven to be too unstable to isolate, are likely to be preparable from dipyrrolyl complexes. One example is Mo(N-2,6-Br$_2$-4-MeC$_6$H$_2$)(CHCMe$_3$)[Biphen]. Previous attempts to prepare this species through addition of K$_2$[Biphen] to Mo(N-2,6-Br$_2$-4-MeC$_6$H$_2$)(CHCMe$_3$)(OTf)$_2$(DME) failed to produce the desired species in pure form and in a practical yield.[14] We find that Mo(N-2,6-Br$_2$-4-MeC$_6$H$_2$)(CHCMe$_3$)(NC$_4$H$_4$)$_2$ reacts with *rac*-H$_2$[Biphen] in benzene rapidly to yield the previously unknown Mo(N-2,6-Br$_2$-4-MeC$_6$H$_2$)(CHCMe$_3$)[*rac*-Biphen] species in high yield. The alkylidene proton in Mo(N-2,6-Br$_2$-4-MeC$_6$H$_2$)(CHCMe$_3$)[*rac*-Biphen] is found at 11.3 ppm with a J_{CH} coupling constant of 132.6 Hz, consistent with a syn alkylidene isomer. The catalytic activity of in situ prepared Mo(N-2,6-Br$_2$-4-MeC$_6$H$_2$)(CHCMe$_3$)[*rac*-Biphen] was confirmed through the ring-closing metathesis of ∼80 equiv of diallyl ether to dihydrofuran in 15 min at room temperature in C$_6$D$_6$.



(3)

In conclusion we have found that dimeric dipyrrolyl complexes, {Mo(NR)(CHCMe$_2$R′)(NC$_4$H$_4$)$_2$}$_2$, can be prepared readily and in good yield from Mo(NR)(CHCMe$_2$R′)(OTf)$_2$(DME) species. All {Mo(NR)(CHCMe$_2$R′)(NC$_4$H$_4$)$_2$}$_2$ species react rapidly and completely with monoalcohols and diols to yield known and, in one case, an unknown catalyst, even those that contain sterically the most challenging combination of imido, neopentylidene or neophylidene, and diolate ligands. On the basis of these results we expect to be able to prepare catalysts in situ and use them for a wide variety of reactions. We expect that in some cases we can generate relatively unstable catalysts that could not be isolated but that still may be useful for catalytic purposes. We believe the possibilities for rapid screening of known and new catalysts to be significant. We also are exploring the fundamental organometallic chemistry of dipyrrolyl alkylidene complexes and their derivatives.

Acknowledgment. This research was funded by the NIH (GM-59426 to A.H.H. and R.R.S.) and the National Science Foundation (CHE-0138495 and CHE-0554734 to R.R.S.). We thank Dr. Peter Müller for assistance with the X-ray structural solution.

Supporting Information Available: Experimental details for the synthesis of all compounds. Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters for {Mo(NAd)(CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$}$_2$. Data for the structure (06172) are available to the public at http://www.reciprocalnet.org/. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Details will be provided in a full paper in due course.

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