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Dipyrrolyl Precursors to Bisalkoxide Molybdenum Olefin Metathesis Catalysts

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Abstract

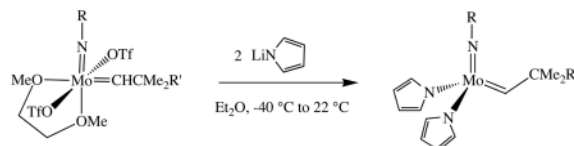
Addition of two equivalents of lithium pyrrolide to $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\text{OTf})_2(\text{DME})$ ($\text{OTf} = \text{OSO}_2\text{CF}_3$; $\text{R} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$, 1-adamantyl, or 2,6- $\text{Br}_2\text{-4-MeC}_6\text{H}_2$; $\text{R}' = \text{Me}$ or Ph) produces $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\text{NC}_4\text{H}_4)_2$ 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, $\{\text{Mo}(\text{NAr})(\text{syn-CHCMe}_2\text{Ph})(\eta^5\text{-NC}_4\text{H}_4)(\eta^1\text{-NC}_4\text{H}_4)\}\{\text{Mo}(\text{NAr})(\text{syn-CHCMe}_2\text{Ph})(\eta^1\text{-NC}_4\text{H}_4)(\eta^5\text{-NC}_4\text{H}_4)\}$, 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 $\text{B}(\text{C}_6\text{F}_5)_3$ (at a $\eta^5\text{-NC}_4\text{H}_4$ nitrogen) to give monomeric products in high yield. They also react rapidly with two equivalents of monoalcohols (e.g., Me_3COH or $(\text{CF}_3)_2\text{MeCOH}$) or one equivalent of a biphenol or binaphthol to give two equivalents of pyrrole and bisalkoxide or diolate complexes in ~100% yield.

We have been searching for methods of synthesizing $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\text{OR})_2$ ($\text{R}' = \text{Me}$ or Ph) species (or species that contain enantiomerically pure biphenolate or binaphtholate ligands¹) *in situ* by treating an appropriate $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')\text{X}_2$ species with a monoalcohol or diol. The main reason is that an increasing number of applications (e.g., asymmetric olefin metathesis¹) 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 $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\text{OR})_2$ species from $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')\text{X}_2$ 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 $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\text{OR})_2$, and that the HX product not react with any organic species in the reaction. We found that when $\text{X} = \text{CH}_2\text{CMe}_3$ only *one* equivalent of alcohol reacts readily to yield $\text{Mo}(\text{NAr})(\text{CH-t-Bu})(\text{CH}_2\text{-t-Bu})(\text{OR})$ or $\text{Mo}(\text{NAr})(\text{CH}_2\text{-t-Bu})_3(\text{OR})$ species.^{2,3} A second approach in which $\text{X} = \text{NPh}_2$ allows both X groups to be replaced, but often slowly and incompletely, and not at all when $\text{NR} = \text{NAr}$ ($\text{Ar} = 2,6\text{-diisopropylphenyl}$) and the diol is the bulky $\text{H}_2[\text{Biphen}]$ ($\text{H}_2[\text{Biphen}] = 3,3'\text{-Di-t-butyl-5,5',6,6'-tetramethyl-1,1'-Biphenyl-2,2'-diol}$).⁴ Syntheses of $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\text{NPh}_2)_2$ species from $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\text{OTf})_2(\text{dimethoxyethane})$ species⁵ 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, $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\text{NC}_4\text{H}_4)_2$, can be prepared in good yield from bistriflate precursors and that they react rapidly,

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even with $\text{H}_2[\text{Biphen}]$ when $\text{NR} = \text{NAr}$, to yield two equivalents of pyrrole and bisalkoxide or biphenolate or binaphtholate species.

Addition of two equivalents of lithium pyrrolide to a stirred diethyl ether suspension of $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\text{OTf})_2(\text{DME})$ ($\text{OTf} = \text{OSO}_2\text{CF}_3$; $\text{R} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$ or 1-adamantyl) produces yellow to orange $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\text{NC}_4\text{H}_4)_2$ complexes in ~75% yield (equation 1). An analogous reaction when $\text{R} = 2,6\text{-Br}_2\text{-4-MeC}_6\text{H}_2$ 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.



(1).

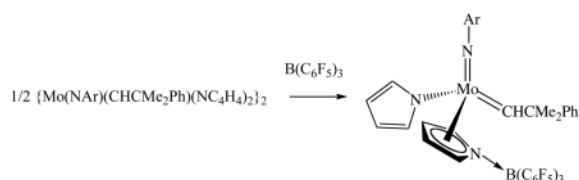
All dipyrrolyl complexes are fluxional on the proton NMR time scale. At 22 °C the spectra contain broad resonances, as shown, for example, for $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{NC}_4\text{H}_4)_2$ in toluene- d_8 (at 500 MHz) in Figure 1. At high temperature one alkylidene resonance 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 ^1H NMR spectrum upon addition of trimethylphosphine, which yields a base adduct (*vide infra*). A ^{13}C NMR spectrum of $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{NC}_4\text{H}_4)_2$ at -50 °C in methylene chloride- d_2 reveals resonances at 313.9 ppm ($J_{\text{CH}} = 122.8$ Hz) and 293.9 ppm ($J_{\text{CH}} = 121.3$ Hz) characteristic of *syn* alkylidene species.⁹

An X-ray structural study of $\text{Mo}(\text{N-}2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{NC}_4\text{H}_4)_2$ shows it to be an unsymmetric dimer, $\{\text{Mo}(\text{NAr})(\text{syn-CHCMe}_2\text{Ph})(\eta^5\text{-NC}_4\text{H}_4)(\eta^1\text{-NC}_4\text{H}_4)\}\{\text{Mo}(\text{NAr})(\text{syn-CHCMe}_2\text{Ph})(\eta^1\text{-NC}_4\text{H}_4)_2\}$, in which the nitrogen in the η^5 -pyrrolyl behaves as a donor to the other Mo (Figure 2). The electron count in the $\text{Mo}(\text{NAr})(\text{syn-CHCMe}_2\text{Ph})(\eta^5\text{-NC}_4\text{H}_4)(\eta^1\text{-NC}_4\text{H}_4)$ half is 18, and in the $\text{Mo}(\text{NAr})(\text{syn-CHCMe}_2\text{Ph})(\eta^1\text{-NC}_4\text{H}_4)_2(\text{donor})$ half is 16. The $\text{Mo}(\text{NAr})(\text{syn-CHCMe}_2\text{Ph})(\eta^1\text{-NC}_4\text{H}_4)_2(\text{donor})$ 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 has C_s symmetry. (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 $\eta^5\text{-NC}_4\text{H}_4$ that is bound to a chiral metal center. η^5 -Pyrrolyl complexes (most of them di- or tetrasubstituted pyrroles¹⁰) have been prepared and studied for many years, the main driving force being the analogy between $\eta^5\text{NC}_4\text{H}_4$ and $\eta^5\text{-C}_5\text{H}_5$.¹¹ To the best of our knowledge, only one other molybdenum pyrrolyl complex, $\text{Mo}(\text{Tp}^*)(\text{NO})(\eta^1\text{-NC}_4\text{H}_4)_2$ ($\text{Tp}^* = \text{HB}(3,5\text{-Me}_2\text{C}_3\text{N}_2\text{H})_3^-$), has been structurally characterized.¹²

The NMR spectra at high-temperatures are consistent with a C_s symmetric $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\eta^1\text{-NC}_4\text{H}_4)_2$ 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

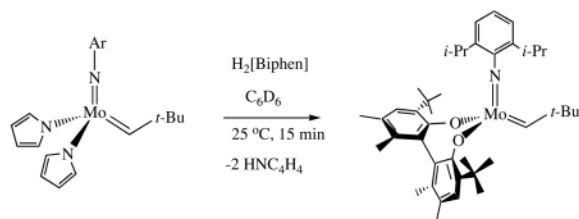
identical at different concentrations, a result that does not reveal whether a small fraction of the dimer breaks up into monomers in which interconversion of $\eta^1\text{-NC}_4\text{H}_4$ and $\eta^5\text{-NC}_4\text{H}_4$ ligands is facile, or whether the equilibration process takes place entirely within the dimer. We favor the former in view of the high reactivity of the $\{\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\text{NC}_4\text{H}_4)_2\}_2$ species toward alcohols and a Lewis acid or base (*vide infra*).

Addition of one equivalent of trimethylphosphine to $\text{Mo}(\text{NAd})(\text{CHCMe}_2\text{Ph})(\text{NC}_4\text{H}_4)_2$ results in immediate formation of *syn*- $\text{Mo}(\text{NAd})(\text{CHCMe}_2\text{Ph})(\eta^1\text{-NC}_4\text{H}_4)_2(\text{PMe}_3)$, in which the alkylidene proton resonance is found at 12.49 ppm with $J_{\text{HP}} = 5$ Hz. An X-ray structural study¹³ shows that trimethylphosphine binds to one of the $\text{CN}_{\text{imido}}\text{N}_{\text{pyrrolyl}}$ 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 $\text{B}(\text{C}_6\text{F}_5)_3$ also reacts immediately with $\{\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{NC}_4\text{H}_4)_2\}_2$ to yield a mixture of what we propose are *syn* and *anti* alkylidenes of the adduct shown in equation 2. The four $\eta^5\text{-pyrrolyl}$ 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 two equivalents of monoalcohols (e.g., Me_3COH or $(\text{CF}_3)_2\text{MeCOH}$) or one equivalent of a biphenol or binaphthol to ~ 10 mM solutions of the $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{R}')(\text{NC}_4\text{H}_4)_2$ ($\text{NR} = \text{NAd}$ or NAr) species described above results in rapid formation of two equivalents of pyrrole and previously characterized bisalkoxide or diolate complexes. The reaction is rapid and $\sim 100\%$ 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 $\text{H}_2[\text{Biphen}]$ ($\text{H}_2[\text{Biphen}] = 3,3'\text{-Di-}t\text{-butyl-5,5',6,6'-tetramethyl-1,1'-Biphenyl-2,2'-diol}$ (equation 3). In the case of 3,3'-bis(2,4,6-triisopropylphenyl)-2,2'-binaphthol¹ the resulting binaphtholate appears to bind one equivalent 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



(3).

example is $\text{Mo}(\text{N-2,6-Br}_2\text{-4-MeC}_6\text{H}_2)(\text{CHCMe}_3)[\text{Biphen}]$. Previous attempts to prepare this species through addition of $\text{K}_2[\text{Biphen}]$ to $\text{Mo}(\text{N-2,6-Br}_2\text{-4-MeC}_6\text{H}_2)(\text{CHCMe}_3)(\text{OTf})_2(\text{DME})$ failed to produce the desired species in pure form and in a practical yield.¹⁴ We find that $\text{Mo}(\text{N-2,6-Br}_2\text{-4-MeC}_6\text{H}_2)(\text{CHCMe}_3)(\text{NC}_4\text{H}_4)_2$ reacts with *rac*- $\text{H}_2[\text{Biphen}]$ in benzene rapidly to yield the previously unknown $\text{Mo}(\text{N-2,6-Br}_2\text{-4-MeC}_6\text{H}_2)(\text{CHCMe}_3)[\text{rac-Biphen}]$ species in high yield. The alkylidene proton in $\text{Mo}(\text{N-2,6-Br}_2\text{-4-MeC}_6\text{H}_2)$

(CHCMe₃)[*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-Br₂-4-MeC₆H₂)(CHCMe₃)[*rac*-Biphen] was confirmed through the ring-closing metathesis of ~80 equivalents of diallyl ether to dihydrofuran in 15 minutes at room temperature in C₆D₆.

In conclusion we have found that dimeric dipyrrolyl complexes, {Mo(NR)(CHCMe₂R')(NC₄H₄)₂}₂, can be prepared readily and in good yield from Mo(NR)(CHCMe₂R')(OTf)₂(DME) species. All {Mo(NR)(CHCMe₂R')(NC₄H₄)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. The possibilities for rapid screening of known and new catalysts we believe to be significant. We also are exploring the fundamental organometallic chemistry of dipyrrolyl alkylidene complexes and their derivatives.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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