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Dipyrrolyl Precursors to Bisalkoxide Molybdenum Olefin Metathesis Catalysts

Adam Hock, **Richard R. Schrock**[‡,*], and **Amir H. Hoveyda**[†]

‡ *Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

† *Department of Chemistry, Merkert Chemistry Center, Boston College Chestnut Hill, Massachusetts 02467*

Abstract

Addition of two equivalents 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-di*iso*propylphenylimido species shows it to be an unsymmetric dimer, {Mo(NAr)(*syn*-$CHCMe_2Ph)(\eta^5$-$NC_4H_4)(\eta_1$-$NC_4H_4)$}{Mo(NAr)(*syn*-$CHCMe_2Ph)(\eta^1$-$NC_4H_4)_2$}, 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 two equivalents of monoalcohols (e.g., Me_3COH or $(CF_3)_2MeCOH$) 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 $Mo(NR)(CHCMe_2R')(OR'')_2$ (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 *one* equivalent 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-t-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,

*email: rrs@mit.edu.

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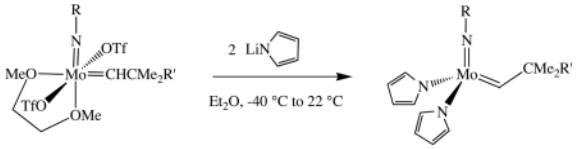
even with H_2[Biphen] when NR = NAr, to yield two equivalents of pyrrole and bisalkoxide or biphenolate or binaphtholate species.

Addition of two equivalents of lithium pyrrolide to a stirred diethyl ether suspension of Mo(NR)($CHCMe_2R'$)$(OTf)_2$(DME) (OTf = OSO_2CF_3; R = 2,6-*i*-P $r_2C_6H_3$ or 1-adamantyl) produces yellow to orange Mo(NR)($CHCMe_2R'$)$(NC_4H_4)_2$ complexes in ~75% yield (equation 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.



(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 Mo(NAr)($CHCMe_2Ph$)$(NC_4H_4)_2$ 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 Mo(NAr)($CHCMe_2Ph$)$(NC_4H_4)_2$ 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*-$Pr_2C_6H_3$)($CHCMe_2Ph$)$(NC_4H_4)_2$ shows it to be an unsymmetric dimer, {Mo(NAr)(*syn*-$CHCMe_2Ph$)(η^5-NC_4H_4)(η^1-NC_4H_4)}{Mo(NAr)(*syn*-$CHCMe_2Ph$)(η^1-$NC_4H_4)_2$}, 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*-$CHCMe_2Ph$)(η^5-NC_4H_4)(η^1-NC_4H_4) half is 18, and in the Mo(NAr)(*syn*-CHCMe2Ph)(η1-NC4H4)2(donor) half is 16. The Mo(NAr)(*syn*-$CHCMe_2Ph$)(η^1-$NC_4H_4)_2$(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 has 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_4H_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_4H_4 and η^5-C_5H_5.[11] To the best of our knowledge, only one other molybdenum pyrrolyl complex, Mo(Tp*)(NO)(η^1-$NC_4H_4)_2$ (Tp* = $HB(3,5\text{-}Me_2C_3N_2H)_3^-$), has been structurally characterized.[12]

The NMR spectra at high-temperatures are consistent with a C_s symmetric Mo(NR)($CHCMe_2R'$)(η^1-$NC_4H_4)_2$ 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

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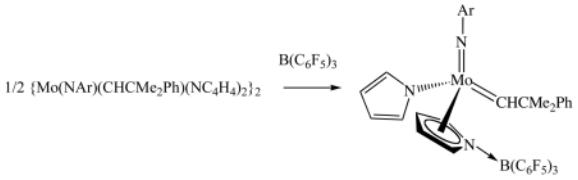
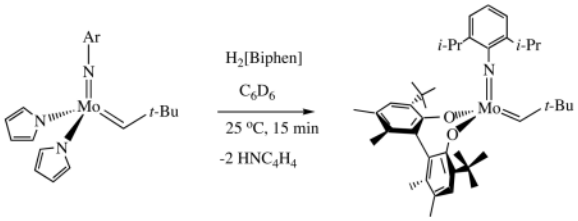
identical at different concentrations, a result that does not reveal whether a small fraction of the dimer breaks up into monomers in which interconversion of η^1-NC_4H_4 and η^5-NC_4H_4 ligands is facile, or whether the equilibration process takes place entirely within the dimer. We favor the former in view of the high reactivity of the $\{Mo(NR)(CHCMe_2R')(NC_4H_4)_2\}_2$ species toward alcohols and a Lewis acid or base (*vide infra*).

Addition of one equivalent of trimethylphosphine to $Mo(NAd)(CHCMe_2Ph)(NC_4H_4)_2$ results in immediate formation of *syn*-$Mo(NAd)(CHCMe_2Ph)(\eta^1\text{-}NC_4H_4)_2(PMe_3)$, 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 $B(C_6F_5)_3$ also reacts immediately with $\{Mo(NAr)(CHCMe_2Ph)(NC_4H_4)_2\}_2$ to yield a mixture of what we propose are *syn* and *anti* alkylidenes of the adduct shown in equation 2. The four 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 two equivalents of monoalcohols (e.g., Me_3COH or $(CF_3)_2MeCOH$) or one equivalent of a biphenol or binaphthol to ~10 mM solutions of the $Mo(NR)(CHCMe_2R')(NC_4H_4)_2$ (NR = 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 ~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-t-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′-binaphthol[1] 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 $Mo(N\text{-}2,6\text{-}Br_2\text{-}4\text{-}MeC_6H_2)(CHCMe_3)$[Biphen]. Previous attempts to prepare this species through addition of K_2[Biphen] to $Mo(N\text{-}2,6\text{-}Br_2\text{-}4\text{-}MeC_6H_2)(CHCMe_3)(OTf)_2(DME)$ failed to produce the desired species in pure form and in a practical yield.[14] We find that $Mo(N\text{-}2,6\text{-}Br_2\text{-}4\text{-}MeC_6H_2)(CHCMe_3)(NC_4H_4)_2$ reacts with *rac*-H2[Biphen] in benzene rapidly to yield the previously unknown $Mo(N\text{-}2,6\text{-}Br_2\text{-}4\text{-}MeC_6H_2)(CHCMe_3)$[*rac*-Biphen] species in high yield. The alkylidene proton in $Mo(N\text{-}2,6\text{-}Br_2\text{-}4\text{-}MeC_6H_2)$

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($CHCMe_3$)[*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_6H_2)($CHCMe_3$)[*rac*-Biphen] was confirmed through the ring-closing metathesis of ~80 equivalents of diallyl ether to dihydrofuran in 15 minutes at room temperature in C_6D_6.

In conclusion we have found that dimeric dipyrrolyl complexes, {Mo(NR)($CHCMe_2R'$)($NC_4H_4)_2$}$_2$, can be prepared readily and in good yield from Mo(NR)($CHCMe_2R'$)($OTf)_2$(DME) species. All {Mo(NR)($CHCMe_2R'$)($NC_4H_4)_2$}$_2$ 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. 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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