Bipyridine Adducts of Molybdenum Imido Alkylidene and Imido Alkylidyne Complexes

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ABSTRACT: Seven bipyridine adducts of molybdenum imido alkylidene bispyrrolide complexes of the type Mo(NR)(CHMe2R)(Pyr)(2)bipy (1a–1g; R = 2,6-i-Pr2C6H3 (Ar), adamantyl (Ad), 2,6-Me2C6H3 (Ar’), 2-i-Pr2C6H3 (Ar″), 2-i-BuC6H4 (Ar‴), and 2-MesitylC6H4 (Ar‴′)), respectively; R = Me, Ph) have been prepared using three different methods. Up to three isomers of the adducts are observed that are proposed to be the trans- and two possible cis-pyrrolide isomers of syn-alkylidenes. Sonication of a mixture containing 1a–1g, HMTOH (2,6-dimesitylphenol), and ZnCl2(dioxane) led to the formation of MAP species of the type Mo(NR)(CHMe2R)(Pyr)(OHMT) (3a–3g). DCMNBD (2,3-dicarbomethoxynorbornadiene) is polymerized employing 3a–3g as initiators to yield >98% cis,syn,trans-polyyne. Attempts to prepare bipy adducts of bisdimethylpyrrolide complexes led to the formation of imido alkylidene complexes of the type Mo(NR)(CHCMe2R)(Pyr)2(bipy) (4a–4g) through a ligand-induced migration of an alkylidene α proton to a dimethylpyrrolide ligand. X-ray structures of Mo(NAr)(CHMe2Ph)(Pyr)(bipy) (1a), Mo(NAr′)(CHMe2Ph)(Pyr)(OHMT) (3d), Mo(NAr′′)(CCMe2Ph)(Me2Pyr)(bipy) (4a), and Mo(NAr‴′)(CCMe3)(Me2Pyr)(bipy) (Ar‴′′ = 2-(2,4,6-i-Pr3C6H2)C6H4; 4g) showed normal bond lengths and angles. Mo(NAd)(CHCMe2Ph)(NC4H4)2 has been employed as a precursor to Mo(NAd)(CHCMe2Ph)(NC4H4)(OAr) complexes that are especially useful as Z-selective olefin metathesis catalysts, where OAr is a large 2,6-disubstituted phenoxy. Only 1 equiv of a large 2,6-terphenol adds to the metal in bispyrrolide complexes for steric reasons, a circumstance that allows the MAP species to be generated and/or isolated at relatively high yields. It has long been known that 14-electron bisalkoxide catalysts will form 16- or 18-electron adducts with donor ligands. Bipyridine was first employed as a ligand in imido alkylidene chemistry in order to isolate the methylidene complex, yellow crystalline Mo(NAr)(CH2)[OC(CF3)2Me]2(bipy) in high yield. Eighteen-electron Mo(NAr)(CH2)[OC(CF3)2Me]2(bipy) is essentially inactive as a metathesis catalyst and stable toward bimolecular decomposition reactions. Fürstner has reported that bipyridine adducts of several related molybdenum species are relatively stable to air and can be activated toward metathesis in the absence of alkoxy in solution through addition of ZnCl2 to remove bipyridine; apparently, little exchange of alkoxy for chloride on the molybdenum is...
observed during the activation process. He also has reported examples of 18-electron alkylidyne complexes that are relatively stable in air and can be activated through addition of Lewis acids.\(^7\) Other types of 18-electron alkylide complexes that are activated upon addition of Lewis acids are known.\(^8\)

In this paper, we report the synthesis of relatively air-stable bipyridine adducts of bispyrrolide complexes that contain a variety of different imido groups and their use as catalyst precursors for the preparation of Mo(NR)(CHCMe₂Ph)-(NC₄H₄)(OAr) species; we have been able to prepare several of these MAP species only in this manner. We also report that attempts to prepare bipyridine adducts of bis-2,5-dimethylpyrrolide complexes lead to formation of imido alkylidyne complexes of the type Mo(NR)(CCMe₂R')(Me₂Pyr)(bipy) through sterically induced \(\alpha\) abstraction of the alkylidyne proton by one of the dimethylpyrrolide ligands.

**RESULTS AND DISCUSSION**

Addition of 1 equiv of bipyridine to Mo(NR)(CHCMe₂Ph)-(Pyr)₂ in diethyl ether led to precipitation of complexes with the general formula Mo(NR)(CHCMe₂Ph)(Pyr)₂(bipy) (R = Ar, 1a; R = Ad, 1b) in good yields (eq 1). This procedure will be referred to as method A. Mo(NR)(CHCMe₂Ph)(Pyr)₂(bipy) species are relatively insoluble, a property that allows them to be isolated readily. A proton NMR spectrum of 1b could be obtained in CD₂Cl₂, but no high-quality \(^{13}\)C NMR spectrum could be obtained readily as a consequence of insolubility of 1b. The three alkylidene isomers of 1b are proposed to arise from one adduct with trans-pyrrolide ligands and two adducts that contain cis-pyrrolide ligands; all are proposed to be \(\text{syn-alkylidene isomers. Compound 1a}\) dissolves more readily in CD₂Cl₂ than 1b, so both \(^1\)H and \(^{13}\)C NMR spectra could be obtained. Only one isomer of 1a is observed.

An X-ray study of 1a shows it to have a structure (Figure 1) in which the pyrrolide ligands are trans to one another and bipy is bound trans to the alkylidyne and imido ligands. In contrast, Mo(NAr)(CHCMe₂Ph)[OC(CF₃)₂Me]₂(bipy)\(^7\) adopts a cis configuration in which bipy is bound trans to the alkylidyne and one of the alkoxide ligands. The Mo–N\(_{\text{bipy}}\) bond lengths in 1a (2.330(3) and 2.354(3) Å) are, therefore, similar, whereas the two Mo–N\(_{\text{bipy}}\) bond lengths in Mo(NAr)(CHCMe₂Ph)[OC-(CF₃)₂Me]₂(bipy) (2.3503(11) and 2.2462(10) Å)\(^7\) differ significantly, with the latter bond length (trans to the alkoxide) being the shorter of the two.

**Bispyrrolide species also can be prepared in situ from Mo(NR)(CHCMe₂Ph)(OTf)₂(DME) complexes and treated with 0.8–0.9 equiv of bipyridine to produce the insoluble compounds of type 1 shown in eq 2 (R' = t-Bu or CMe₂Ph).**

This method will be referred to as method B. It is an effective way to make six of the seven bipyridyl adducts of type 1. Compounds 1b–1g were obtained in analytically pure form simply through filtration. The yield of 1f suffers from some solubility in toluene.

Only one alkylidyne resonance is present in the alkylidene region in the \(^1\)H NMR spectrum (in CD₂Cl₂) of 1c and 1f, two are present for 1e and 1d, whereas three are present for 1g. All isomers are presumed to arise from cis/trans isomerism of the pyrrolide ligands, as noted earlier, although, in the case of 1g, restricted rotation of the NArM imido ligand could give rise to the third isomer. Unfortunately, because of the insolubility of

![Figure 1. Drawing of the solid-state structure of Mo(NAr)-(CHCMe₂Ph)(Pyr)₂(bipy) (1a; 50% probability ellipsoids). The solvent molecule, hydrogen atoms, and the disorder are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)–C(11) = 1.932(3), Mo(1)–N(1) = 2.330(3), Mo(1)–N(2) = 2.354(3), Mo(1)–N(3) = 1.730(2), Mo(1)–N(4) = 2.135(3), Mo(1)–N(5) = 2.143(2); Mo(1)–C(11)–C(12) = 138.3(2), Mo(1)–N(3)–C(21) = 171.0(2), N(5)–Mo(1)–N(4) = 155.75(10).](image)
samples 1b–1g, no JCH coupling could be obtained from 13C NMR spectra in order to identify syn or anti isomers.

Mo(NR)(CHCMe2Ph)(OTf)2(bipy) complexes can be synthesized from Mo(NR)(CHCMe2Ph)(OTf)2(dme) complexes by suspending the latter in benzene that contains 1 equiv of bipyridine at room temperature (R = 2,6-i-Pr2C6H4 (Ar1), 1-adamantyl (Ad), 2,6-Me2C6H3 (Ar2), and 2-MesC6H4 (Ar3)) or in diethyl ether (R = 2-ClC6H4 (ArCl), 2-i-PrC6H4 (ArPr), 2-t-BuC6H4 (ArBu) and stirring the mixtures for 12 h at 22 °C (eq 3). In all cases, the relatively insoluble Mo(NR)(CHCMe2Ph)-

\[
\text{R} \begin{array}{c}
\text{TIO} \\
\text{TIO}
\end{array} \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \begin{array}{c}
\text{R'} \\
\text{R'}
\end{array} + \begin{array}{c}
\text{C}6\text{H}4 \text{Bipy} \text{at RT} \\
\text{or DME}
\end{array} = \begin{array}{c}
\text{TIO} \\
\text{TIO}
\end{array} \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \begin{array}{c}
\text{R} \\
\text{R}
\end{array} \begin{array}{c}
\text{R'} \\
\text{R'}
\end{array} \begin{array}{c}
\text{C}6\text{H}4 \text{Bipy} \text{at } -35 \degree \text{C}
\end{array}
\] (3)

\[
\begin{align*}
2a & \text{ R} = \text{Ar} (84 \%); \\
2b & \text{ R} = \text{Ad} (91 \%); \\
2c & \text{ R} = \text{Ar}’ (67 \%); \\
2d & \text{ R} = \text{Ar}^{\text{Pr}} (76 \%); \\
2e & \text{ R} = \text{Ar}^{\text{Cl}} (66 \%); \\
2f & \text{ R} = \text{Ar}^{\text{Bu}} (76 \%); \\
2g & \text{ R} = \text{Ar}^\text{M} (73 \%)
\end{align*}
\]

(OTf)2(bipy) complexes can be collected by filtration in good yields. All Mo(NR)(CHCMe2Ph)(OTf)2(bipy) complexes are soluble in CD2Cl2 with the exception of 2a and 2b, which are only sparingly soluble and for which, 13C NMR spectra could not be obtained. Proton NMR spectra of the complexes in CD2Cl2 show either one or two alkylidene resonances, which arise from cis and trans disposition of the triflates, a proposal that is corroborated by the 19F NMR spectra of each compound. Two isomers are observed when the imido group has only one ortho substituent.

Complexes 2a, 2c, and 2d react with 2 equiv of LiNC4H4 to generate the bipyrrrolide species, 1a, 1c, and 1d (method C; eq 4). These compounds can be isolated in moderate to good yields by running the reaction in diethyl ether for 12 h, filtering off the precipitated product, and washing the precipitate with diethyl ether.

When complexes 2b and 2e–2g are treated with 2 equiv of LiNC4H4 under the same conditions, impure products are obtained as a consequence of what is proposed to be incomplete substitution. The reaction is not driven to completion when longer times (1–2 days) are employed, and complications arise in subsequent reactions if these impure compounds are employed.

In general, bipyridine adducts of type 1 are easy to isolate, handle, and store for long periods of time, but they would be useful only if bipy could be removed and MAP species prepared. Complexes 1a–1g were mixed with 1 equiv of ZnCl2(dioxane) and 1 equiv of 2,6-dimesitylphenol (HMTOH) in 10–15 mL of toluene in a Teflon-sealed Schlenk flask. The flask was placed in a conventional ultrasonic cleaner for 3–5 h at 22 °C. The choice of solvent is key because the reagents, except for HMTOH and the ZnCl2(bipy) byproduct, are only slightly soluble in toluene, whereas the MAP complexes are highly soluble. The MAP complexes 3a–3g are obtained in crystalline form by filtering off any remaining insoluble material(s), removing the solvent from the filtrate, and recrystallizing the solid products from pentane at −35 °C (eq 5). Proton NMR and carbon NMR spectra of 3a–3g are consistent with the presence of only one isomer (syn) in solution. Apparently, exchange of pyrrolide (on Mo) for chloride (on Zn) is not a significant problem in the reaction shown in eq 5. The in situ synthesis of 3b directly from Mo(NAD)(CHCMe2Ph)(NC4H4)2 has been reported elsewhere.

The structure of 3d was obtained through an X-ray study. The complex crystallized in the space group P1 with both the R and S enantiomers present (Figure 2a,b). Details are available in the Supporting Information.

The efficacies of 3a–3g for polymerization of 50 equiv of 2,3-dicarbomethoxynorbornadiene (DCMNBD) over a period of 1–2 h to give cis-poly(DCMNBD) were explored with each as an initiator at 22 °C. The cis content of poly(DCMNBD) was determined through 1H and 13C NMR spectroscopy. All reactions are relatively fast and all give >98% cis polymer that we presume is syndiotactic on the basis of the similarity of NMR spectra to those for poly(DCMNBD) samples prepared with Mo(NAD)(CHCMe2R)(Pyr)(OHMT) as an initiator and polymers prepared from menthoxy analogues of DCMNBD. Full details can be found in the Supporting Information. Similar behavior had been observed for the analogous Mo(NR)-(CHCMe2R’)(MePy)(OHMT) initiators in which the phenyl imido ligands were monosubstituted in the ortho positions with Cl, CF3, or i-Pr groups, although i-Bu, mesityl, or 2,4,6-trisopropylphenyl groups in the ortho position of the phenylimido ligand led to the formation of poly(DCMNBD) samples that contained some trans linkages. Therefore, at least for polymerization of DCMNBD and similar diesters, the MAP species that contains the parent pyrrolide is preferred.

In contrast to the results presented so far concerning bipyridine adduct formation, attempted syntheses of bipyridine adducts of Mo(NR)(CHCMe2Ph)(Me2Pyr) or Mo(NR)-(CHCMe2)(Me2Pyr) complexes led to the imido alkylidyne complexes 4a–4g shown in eq 6. Only the reaction between Mo(NAr3′)(CHCMe2Ph)(Me2Pyr)2 and 1 equiv of bipy or Mo(NAD)(CHCMe2Ph)(Me2Pyr)2 and 5 equiv of bipy can be carried out to completion at 22 °C in a 1:1 mixture of toluene and pentane or diethyl ether, respectively. Other reactions
require heating in toluene at 60 °C. In all cases, the color of the reaction mixture changes from orange-brown to red-purple. Upon completion of the reaction, 1 equiv of Me₂PyrH can be observed in solution in proton NMR spectra. Upon removing the solvent from the reaction mixture and washing the resulting solids with pentane, compounds 4a−4g can be obtained as purple or red-purple solids in good to very good yields (eq 6). The relatively low solubility of 4a−4g along with the low sensitivity of alkylidyne carbon atoms in general in natural abundant carbon NMR spectra prevented confirmation that compounds 4 were in fact alkylidyne complexes.

X-ray quality crystals of 4a and 4c were grown from a mixture of dichloromethane and pentane at −45 °C, whereas crystals of 4g were grown from benzene at 22 °C. Complex 4a crystallized in the monoclinic space group P2(1)/n, whereas 4c and 4g crystallized in the monoclinic space group P2(1)/c. The structures are shown in Figures 3−5. In the case of 4g, two independent molecules were present in the asymmetric unit along with six benzene molecules. The phenyl imido ligand in one of the complexes is disordered (disorder not shown), whereas in the other, it is not disordered. Compounds 4a, 4c, and 4g can best be regarded as distorted square pyramids with the alkylidyne ligand located in the apical position. The most striking features are the bond lengths Mo(1)−C(29) in 4a (1.764(3) Å), Mo(1)−C(1) in 4c (1.7643(17) Å), and Mo(1)−C(1) in 4g (1.780(5) Å), and the relatively large Mo(1)−C(29)−C(30) bond angle in 4a (161.5(2)°), the Mo(1)−C(1)−C(2) bond angle in 4c (159.6(2)°), and the Mo(1)−C(1)−C(2) bond angle in 4g (167.1(4)°); all are consistent with formation of alkylidyne complexes. The Mo═NR bond lengths of 4a (1.804(3) Å), 4c (1.7958(14) Å), and 4g (1.823(4) Å) are longer than in analogous alkylidene complexes, as expected in view of competition between the imido and...
alkylidyne ligands for π-type d orbitals. The Mo(1)−N(3)−C(11) bond angle of 4a (159.6(2)°), the Mo(1)−N(1)−C(11) bond angle of 4c (162.64(12)°), and the Mo(1)−N(4)−C(31) bond angle of 4g (152.6(3)°) are relatively small, consistent with a Mo−N double bond more than a triple bond in the bent imido ligands. However, the imido ligand in {Mo(NAr)(C-t-Bu)OCMe(CF3)2}2+ is more bent (Mo−N−C = 141.16(17)°) than any in 4a, 4c, or 4g. We propose that steric interactions between ligands in five-coordinate 4a, 4c, and 4g prevent the imido ligands being bent as much as the imido ligand in four-coordinate {Mo(NAr)(C-t-Bu)OCMe-

High oxidation state alkylidyne complexes of tantalum, tungsten, molybdenum, and rhenium have been synthesized through several routes in the last 30 years. Formation of a neopentylidyne ligand through deprotonation of a neopentylidyne ligand was first demonstrated in a reaction between Ta(CHCMe3)(CH2CMe3)3 and butyllithium to give a lithium salt of {Ta(CHCMe3)(CH2CMe3)3}+.12 Dehydrohalogenation of W(NPh)(CHCMe3)(PEt3)2Cl by Ph3P==CH2 led to W(NPh)(CCMe3)(PEt3)2Cl3, a compound that is most similar to 4a−4g, although no X-ray structure of W(NPh)(CCMe3)(PEt3)2Cl was determined. Deprotonation of Mo(NAr)(CHCMe3)OCMe(CF3)2 by Ph3P==CH2 led to the alkylidyne complex, {Ph2PMe}{Mo(NAr)(CCMe3)OCMe(CF3)2}3, as noted earlier. Attempts to prepare certain types of imido neopentylidyne complexes have resulted in formation of imido neopentylidyne complexes as a consequence of migration of a proton from an alkylidyne to an imido ligand, or as a consequence of an actual deprotonation/readdition sequence.14 Neopentylidyne ligands have been generated from neopentyl ligands early in the development of high oxidation state organometallic chemistry of tungsten and molybdenum, a circumstance that has allowed tungsten and molybdenum alkylidyne complexes of the type M(C-t-Bu)-

(CF3)2]2−. Although adducts analogous to 1a−1g are not formed readily upon addition of bipyridine to bisdimethylpyrrolide complexes, we propose that adducts are likely intermediates in the process of forming 4a, 4c, and 4g and that steric crowding leads to an alkylidyne with a larger Mo−C−C angle, which activates that alkylidyne’s α proton toward migration, ultimately to a pyrrolide, and generation of dimethylpyrrole (eq 7).

Figure 4. Drawing of the solid-state structure of Mo(NAr2)(CCMePh)(Me2Pyr)(bipy) (4c; 50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Mo(1)−C(1) = 1.7643(17), Mo(1)−N(1) = 1.7958(14), Mo(1)−N(2) = 2.1228(14), Mo(1)−N(3) = 2.3165(13), Mo(1)−N(4) = 2.2100(13); Mo(1)−C(1)−C(2) = 159.05(14), Mo(1)−N(1)−C(11) = 162.64(12), N(1)−Mo(1)−N(3) = 137.44(6), N(2)−Mo(1)−N(4) = 153.09(15).

Figure 5. Drawing of the solid-state structure of Mo(NAr7)(CCMePh)(Me2Pyr)(bipy) (4g; 50% probability ellipsoids). Solvent molecules and the second independent molecule, which shows some disorder, as well as the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)−C(1) = 1.780(5), Mo(1)−N(1) = 2.105(4), Mo(1)−N(2) = 2.306(3), Mo(1)−N(3) = 2.225(4), Mo(1)−N(4) = 1.823(4); Mo(1)−C(1)−C(2) = 167.1(4), Mo(1)−N(1)−C(31) = 152.6(3), N(1)−Mo(1)−N(3) = 153.28(14), N(2)−Mo(1)−N(4) = 140.98(15).
of all of the above reports, it is fair to say that there is ample precedent for intramolecular migration of a proton from a neopentyldiene ligand to a dimethylpyrrolide ligand, even though there is no example of this particular reaction in the literature to our knowledge. It is not possible to determine on the basis of data in hand whether the proton migrates to the pyrrolide nitrogen directly or first to a pyrrolyl α or β carbon atom.

We felt that phenols might add across the metal–carbon triple bond in complexes 4a−4g to regenerate MAP species. Although preliminary studies show promise for reactions of this type, Mo(NR)(CHCMe2R)4a ligand.

DCMNBD reveal that they are all e

-selective initiators. The adducts are isolated readily and appear to be stable under dinitrogen over a long period, unlike species of the type Mo(NR)(CHCMe2R)4b approach to be competitive with existing approaches to MAP would have to be accessible more directly in order for this type, Mo(NR)(CCMe2R)4c

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■ REFERENCES


