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)(CHCMe₂R′)(Pyr)₂(bipy) (1a–1g; R = 2,6-Pr₃C₆H₃ (Ar), adamantyl (Ad), 2,6-Me₂C₆H₃ (Ar'), 2-PrC₆H₄ (ArPr), 2-ClC₆H₄ (ArCl), 2-t-BuC₆H₄ (ArBu), and 2-MesitylC₆H₄ (ArM'), 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)(CHCMe₂R')(Pyr)(OHMT) (3a–3g). DCMNBND (2,3-dicarbomethoxynorbornadiene) is polymerized employing 3a–3g as initiators to yield >98% cis,syndiotactic poly(DCMNBND). Attempts to prepare bipy adducts of bisdimethylpyrrolide complexes led to formation of imido.
alkylidyne complexes of the type Mo(NR)(CCMe₂R')(Me₂Pyr)(bipy) (Me₂Pyr = 2,5-dimethylpyrrolide; 4a – 4g) through a ligand-induced migration of an alkylidene α proton to a dimethylpyrrolide ligand. X-ray structures of Mo(NAr)(CHCMe₂Ph)(Pyr)(bipy) (1a), Mo(NArPr)(CHCMe₂Ph)(Pyr)(OHMT) (3d), Mo(NAr)(CCMe₂Ph)(Me₂Pyr)(bipy) (4a), and Mo(NArT})(CCMe₂)(Me₂Pyr)(bipy) (ArT = 2-(2,4,6-i-Pr₃C₆H₂)C₆H₄; 4g) showed structures with the normal bond lengths and angles.

INTRODUCTION

High oxidation state molybdenum and tungsten imido alkylidene complexes were discovered approximately 25 years ago. In the last several years new types of imido alkylidene complexes with the formula M(NR)(CHR')(OR'')(Pyr), where Pyr is a pyrrolide or substituted pyrrolide ligand and OR'' usually is an aryloxide, have been prepared and explored. We refer to these monoaryloxide monopyrrolide complexes as MAP species. MAP species were discovered in the process of adding alcohols or phenols to bispyrrolide complexes with the general formula M(NR)(CHR')(Pyr)² in order to prepare bisalkoxide or biphenolate catalysts in situ and screen them for olefin metathesis activity.

Bispyrrolide complexes have been prepared that contain pyrrolide, 2,3,4,5-Me₄pyrrolide, 2,5-i-Pr₂pyrrolide, 2,5-Ph₂pyrrolide, and 2-Mesitylpyrrolide. The majority of MAP species that have been prepared contain 2,5-dimethylpyrrolide. The relatively small number of MAP compounds that contain an unsubstituted pyrrolide is a consequence of the often poor crystallinity and instability of Mo(NR)(CHR')(pyrrolide)² species over a period of days, even in the solid state. Two exceptions are compounds in which the imido substituent (R) is 2,6-i-Pr₂C₆H₃ (Ar) or adamantyl (Ad), which are stable for many days at −35 °C under nitrogen. 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 phenoxide. Only one equivalent 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 in 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)₂[OC(CF₃₂)₂Me₂](bipy) in high yield. Eighteen electron Mo(NAr)(CH₂)₂[OC(CF₃₂)₂Me₂](bipy) is 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 air in solution through addition of ZnCl₂ to remove bipyridine; apparently little exchange of alkoxide 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. Other types of 18 electron alkylidene complexes that are activated upon addition of Lewis acids are known.

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 α abstraction of the alkylidene proton by one of the dimethylpyrrolide ligands.

RESULTS AND DISCUSSION

Addition of one equivalent 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 (equation 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 ¹³C 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 syn alkylidene isomers. Compound 1a dissolves more readily in CD₂Cl₂ than 1b so both ¹H and ¹³C 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 alkylidene and imido ligands. In contrast, Mo(NAr)(CHCMe₂Ph)[OC(CF₃)₂Me₂(bipy)] adopts a cis configuration in which bipy is bound trans to the alkylidene and one of the alkoxide ligands. The Mo-Nbipy bond lengths in 1a (2.330(3) and 2.354(3) Å) therefore are similar, whereas the two Mo-Nbipy bond lengths in Mo(NAr)(CHCMe₂Ph)[OC(CF₃)₂Me₂(bipy)] (2.3503(11) Å and 2.2462(10) Å) 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 equivalents of bipyridine to produce the insoluble compounds of type 1 shown in equation 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.

![Equation 1](image)

![Equation 2](image)
Only one alkylidene resonance is present in the alkylidene region in the $^1$H NMR spectrum (in CD$_2$Cl$_2$) of 1c and 1f, two are present for 1e and 1d, while 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 NAr$^M$ imido ligand could give rise to the third isomer. Unfortunately, due to the insolubility of samples 1b–1g no $J_{CH}$ coupling could be obtained from $^{13}$C NMR spectra in order to identify syn or anti isomers.

Mo(NR)(CHCMe$_2$Ph)(OTf)$_2$(bipy) complexes can be synthesized from Mo(NR)(CHCMe$_2$Ph)(OTf)$_2$(dme) complexes by suspending the latter in benzene that contains one equivalent of bipyridine at room temperature ($R =$ 2,6-i-Pr$_2$C$_6$H$_3$(Ar), 1-adamantyl (Ad), 2,6-Me$_2$C$_6$H$_3$(Ar'), and 2-MesC$_6$H$_4$(Ar$^M$), or in diethyl ether ($R =$ 2-ClC$_6$H$_4$(ArCl), 2-i-PrC$_6$H$_4$(Ar$i$Pr), 2-t-BuC$_6$H$_4$(Ar$t$Bu)) and stirring the mixtures for 12 h at 22 °C (equation 3). In all cases, the relatively insoluble Mo(NR)(CHCMe$_2$Ph)(OTf)$_2$(bipy) complexes can be collected by filtration in good yields. All Mo(NR)(CHCMe$_2$Ph)(OTf)$_2$(bipy) complexes are soluble in CD$_2$Cl$_2$ with the exception of 2a and 2b, which are only sparingly soluble and for which $^{13}$C NMR spectra could not be obtained. Proton NMR spectra of the complexes in CD$_2$Cl$_2$ show either one or two alkylidene resonances, which arise from cis and trans disposition of the triflates, a proposal that is corroborated by the $^{19}$F 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 equivalents of LiNC$_4$H$_4$ to generate the bispyrrolide species, 1a, 1c, and 1d (method C; equation 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, 2e, and 2f–2g are treated with two equivalents of LiNC$_4$H$_4$ 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 one equivalent of ZnCl₂(dioxane) and one equivalent 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) and recrystallizing the solid products from pentane at −35 °C (equation 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 equation 5. The in situ synthesis of 3b directly from Mo(NAd)(CHCMe₂Ph)(NC₄H₄)₂ has been reported elsewhere.v

The structure of 3d was obtained through an X-ray study. The complex crystallized in the space group P1̅ with both the R and S enantiomers present (Figures 2a and 2b). Details are available in the Supporting Information.

The efficacies of 3a–3g for polymerization of 50 equivalents 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 spectra to those for poly(DCMNBD) samples prepared with Mo(NAd)(CHCMe₂R)(Me₂Pyr)(OHMT) as an initiator and polymers prepared from menthoxy analogs of DCMNBD.iii Full details can be found in the Supporting Information. Similar behavior had been observed for the analogous Mo(NR)(CHCMe₂R')(Me₂Pyr)(OHMT) initiators in which the phenyl imido ligands were monosubstituted in the ortho positions with Cl, CF₃, or i-Pr groups, although t-Bu, mesityl, or 2,4,6-trisopropylphenyl groups in the ortho position of the phenylimido ligand led to formation of poly(DCMNBD) samples that contained some trans linkages.ix 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)₂ or Mo(NR)(CHCMe₂) (Me₂Pyr)₂ complexes led to the imido alkylidyne complexes 4a–4g shown in equation 6. Only the reaction between Mo(NArⅣ(Pr))(CHCMe₂Ph)(Me₂Pyr)₂ and one equivalent of bipy or Mo(NAd)(CHCMe₂Ph)(Me₂Pyr)₂ and five equivalents 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, one equivalent of Me$_2$PyrH 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 (equation 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.

\[ \text{4a} \quad \text{R} = \text{Ac}, \quad \text{R}^1 = \text{Ph}, \quad 60^\circ \text{C}, \quad \text{(60%)} \quad \text{4b} \quad \text{R} = \text{Ad}, \quad \text{R}^1 = \text{Ph}, \quad 22^\circ \text{C}, \quad \text{(44%)} \quad \text{4c} \quad \text{R} = \text{Ac}, \quad \text{R}^1 = \text{Ph}, \quad 60^\circ \text{C}, \quad \text{(60%)} \quad \text{4d} \quad \text{R} = \text{Ac}, \quad \text{R} = \text{Ph}, \quad 22^\circ \text{C}, \quad \text{(68%)} \quad \text{4e} \quad \text{R} = \text{Ad}, \quad \text{R} = \text{Me}, \quad 60^\circ \text{C}, \quad \text{(99%)} \quad \text{4f} \quad \text{R} = \text{Ac}, \quad \text{R} = \text{Ph}, \quad 60^\circ \text{C}, \quad \text{(53%)} \quad \text{4g} \quad \text{R} = \text{Ac}, \quad \text{R} = \text{Me}, \quad 06^\circ \text{C}, \quad \text{(69%)} \]

(6)

X-ray quality crystals of 4a and 4c were grown from a mixture of dichloromethane and pentane at −45 °C, while 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) while in the other it is not. 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 (159.05(14)°), 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 in 4a (159.6(2)°), the Mo(1)-N(1)-C(11) bond angle in 4c (162.64(12)°), and the Mo(1)-N(4)-C(31) bond angle in 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(CF$_3$)$_2$]$_2$]$^-$ 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(CF$_3$)$_2$]$_2$}$^-$.

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 alkylidene with a larger Mo-C-C angle, which activates that alkylidene’s α proton toward migration, ultimately to a pyrrolide, and generation of dimethylpyrrole (equation 7).
High oxidation state alkylidyne complexes of tantalum, tungsten, molybdenum, and rhenium have been synthesized through several routes in the last thirty years.\textsuperscript{xi} Formation of a neopentylidyne ligand through deprotonation of a neopentylidene ligand was first demonstrated in a reaction between Ta(CHCMe\textsubscript{3})\textsubscript{3}(CH\textsubscript{2}CMe\textsubscript{3})\textsubscript{3} and butyllithium to give a lithium salt of \{Ta(CHCMe\textsubscript{3})(CH\textsubscript{2}CMe\textsubscript{3})\textsubscript{3}\}\textsuperscript{−}.\textsuperscript{xii} Dehydrohalogenation of W(NPh)(CHCMe\textsubscript{3})(PEt\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} by Ph\textsubscript{3}P=CH\textsubscript{2} led to W(NPh)(CMe\textsubscript{3})(PEt\textsubscript{3})\textsubscript{2}Cl, a compound that is most similar to 4a±4g, although no X-ray structure of W(NPh)(CMe\textsubscript{3})(PEt\textsubscript{3})\textsubscript{2}Cl was determined. Deprotonation of Mo(NAr)(CHCMe\textsubscript{3})[OCMe(CF\textsubscript{3})\textsubscript{2}]\textsubscript{2} by Ph\textsubscript{3}P=CH\textsubscript{2} led to the alkylidyne complex, \{Ph\textsubscript{3}PMe\}Mo(NAr)(CMe\textsubscript{3})[OCMe(CF\textsubscript{3})\textsubscript{2}], \textsuperscript{x} as noted earlier. Attempts to prepare certain types of imido neopentylidyne complexes have resulted in formation of amido neopentylidyne complexes as a consequence of migration of a proton from an alkylidene to an imido ligand, or as a consequence of an actual deprotonation/readdition sequence.\textsuperscript{xiv} 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)(CH\textsubscript{2}-t-Bu)\textsubscript{3} to be synthesized;\textsuperscript{xv} α-deprotonation of a neopentyl ligand to give an intermediate neopentylidene ligand is probably the rate-limiting deprotonation step in these reactions. Rhenium neopentylidyne complexes have been prepared through deprotonation of neopentylidyne ligands, either by transfer of a proton to a neopentyl group or to an imido or amido group.\textsuperscript{xvi} A proton also has been added to an alkylidyne α carbon atom in several circumstances to give an alkylidene complex. For example, transfer of a proton from an amido ligand to a neopentylidyne α carbon atom was the first general method of preparing imido alkylidene complexes of tungsten.\textsuperscript{vi} Intramolecular α proton migration has been known to be promoted in more sterically crowded circumstances, the first being ligand induced formation of tantalum neopentylidyne complexes from tantalum dineopentyl complexes through addition of various phosphines or simply THF.\textsuperscript{xvii} On the basis of all of the above reports, it is fair to say that there is ample precedent for intramolecular migration of a proton from a neopentylidene 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 pyrrolide α or β carbon atom.\textsuperscript{ia}

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)(CMe\textsubscript{3}R')\textsuperscript{(−)}(Me\textsubscript{2}Pyr)(bipy) complexes probably would have to be accessible more directly in order for this approach to be competitive with existing approaches to MAP species.

CONCLUSION

Seven bipyridine adducts of molybdenum imido alkylidene bispyrrolide complexes of the type Mo(NR)(CMe\textsubscript{3}R')(Pyr)\textsubscript{2}(bipy) (1a–1g) have been prepared using three different methods. The adducts are isolated readily and appear to be stable under dinitrogen over a
long period, unlike Mo(NR)(CHCMe₂R')(Pyr)₂ complexes themselves. They can be employed as starting materials for formation of MAP species of the type Mo(NR)(CHCMe₂R')(Pyr)(OHMT) (3a–3g) through sonication of a mixture containing 1a–1g, HMTOH, and ZnCl₂(dioxane). Reactivity studies of 3a–3g with DCMNBD reveal that they are all efficient Z-selective initiators for formation of >98% cis,syndiotactic poly(DCMNBD), more so than analogous MAP complexes that contain dimethylpyrrolide. In contrast, attempts to prepare bipy adducts of bisdimethylpyrrolide complexes led to formation of imido alkylidyne complexes of the type Mo(NR)(CCMe₂R')(Me₂Pyr)(bipy) (4a – 4g) through a ligand-induced migration of an alkylidene α proton to a dimethylpyrrolide ligand.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References


Figure 1.
A drawing of the solid-state structure of Mo(NAr)(CHCMe$_2$Ph)(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 (°): 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).
Figure 2a.

Figure 2b.

Figure 2.
Figure 2a. A drawing of the solid-state structure of (R)-Mo(NAr$iPr$)(CHCMe$_2$Ph)(Pyr) (OHMT) (R-3d, 50% probability ellipsoids). Selected bond lengths (Å) and angles (°):
Mo(1)-C(1) = 1.8769(15), Mo(1)-N(1) = 1.7300(12), Mo(1)-N(2) = 2.0198(13), Mo(1)-O(1) = 1.9186(10), Mo(1)-C(1)-C(2) = 145.61(11), Mo(1)-N(1)-C(11) = 178.12(11), Mo(1)-O(1)-C(31) = 143.14(9).

Figure 2b. A drawing of the solid-state structure of (S)-Mo(NAr$iPr$)(CHCMe$_2$Ph)(Pyr) (OHMT) (S-3d, 50% probability ellipsoids). Selected bond lengths (Å) and angles (°):
Mo(2)-C(101) = 1.8759(15), Mo(2)-N(3) = 1.7263(12), Mo(2)-N(4) = 2.0294(13), Mo(2)-O(2) = 1.9168(10), Mo(2)-C(101)-C(102) = 143.31(11), Mo(2)-N(3)-C(111) = 177.45(11), Mo(2)-O(2)-C(131) = 150.15(9).
Figure 3.
A drawing of the solid-state structure of (NAr)(CCMe₂Ph)(Me₂Pyr)(bipy) (4a; 50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Mo(1)-C(29) = 1.764(3), Mo(1)-N(1) = 2.326(3), Mo(1)-N(2) = 2.209(3), Mo(1)-N(3) = 1.804(3), Mo(1)-N(4) = 2.098(3), Mo(1)-C(29)-C(30) = 161.5(2), Mo(1)-N(3)-C(11) = 159.6(2), N(1)-Mo(1)-N(3) = 144.12(10), N(2)-Mo(1)-N(4) = 144.12(10), N(3)-Mo(1)-N(3) = 153.05(10).
Figure 4.
A drawing of the solid-state structure of Mo(NAr')CCMe₂Ph(Me₂Pyr)(bipy) (4c; 50% probability ellipsoids). Selected bond lengths (Å) and angles (°): 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)-N(3) = 137.44(6), 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.
A drawing of the solid-state structure of Mo(NArT)(CCMe$_3$)(Me$_2$Pyr)(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 (°): 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(3), Mo(1)-N(4) = 1.823(3), Mo(1)-C(1)-C(2) = 167.1(4), Mo(1)-N(4)-C(31) = 152.6(3), N(1)-Mo(1)-N(3) = 153.28(14), N(2)-Mo(1)-N(4) = 140.98(15).