Bipyridine Adducts of Molybdenum Imido Alkylidene and Imido Alkylidyne Complexes

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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)(CHCMe$_2$R′)(Pyr)$_2$(bipy) (**1a–1g**; R = 2,6-*i*-Pr$_2$C$_6$H$_3$ (Ar), adamantyl (Ad), 2,6-Me$_2$C$_6$H$_3$ (Ar′), 2-*i*-PrC$_6$H$_4$ (Ar^{iPr}), 2-ClC$_6$H$_4$ (Ar^{Cl}), 2-*t*-BuC$_6$H$_4$ (Ar^{tBu}), and 2-MesitylC$_6$H$_4$ (Ar^{M}), 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 ZnCl$_2$(dioxane) led to the formation of MAP species of the type Mo(NR)(CHCMe$_2$R′)(Pyr)(OHMT) (**3a–3g**). DCMNBD (2,3-dicarbomethoxynorbornadiene) is polymerized employing **3a–3g** as initiators to yield >98% *cis,syndiotactic* poly(DCMNBD). Attempts to prepare bipy adducts of bisdimethylpyrrolide complexes led to formation of imido

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Supporting Information Available. Details of the synthesis and characterization of all complexes. Crystallographic details, fully labeled thermal ellipsoid diagrams for all crystallographically characterized species and crystallographic information files in CIF format. Supporting Information is available free of charge via the Internet at http://pubs.acs.org. Data for the X-ray structures are also available to the public at http://www.reciprocalnet.org.

alkylidyne complexes of the type Mo(NR)($CCMe_2R'$)(Me_2Pyr)(bipy) (Me_2Pyr = 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)($CHCMe_2Ph$)($Pyr)_2$(bipy) (**1a**), Mo(NAr^{iPr})($CHCMe_2Ph$)(Pyr)(OHMT) (**3d**), Mo(NAr)($CCMe_2Ph$)(Me_2Pyr)(bipy) (**4a**), and Mo(NAr^T)($CCMe_3$)(Me_2Pyr)(bipy) (Ar^T = 2-(2,4,6-i-$Pr_3C_6H_2$)C_6H_4; **4g**) showed structures with the normal bond lengths and angles.

INTRODUCTION

High oxidation state molybdenum and tungsten imido alkylidene complexes[i] were discovered approximately 25 years ago.[ii] 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;[ia,iii] 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')$(Pyr)_2$[iv] 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,[iva] 2,5-Me_2pyrrolide,[ivb] 2,3,4,5-Me_4pyrrolide,[ivc] 2,5-*i*-Pr_2pyrrolide,[ivc] 2,5-Ph_2pyrrolide,[ivc] and 2-Mesitylpyrrolide.[ivd] 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*-$Pr_2C_6H_3$ (Ar) or adamantyl (Ad), which are stable for many days at −35 °C under nitrogen. Mo(NAd)($CHCMe_2Ph$)$(NC_4H_4)_2$ has been employed as a precursor to Mo(NAd)($CHCMe_2Ph$)(NC_4H_4)(OAr) complexes that are especially useful as *Z*-selective olefin metathesis catalysts,[iiib,c,e,g–j,v] 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.

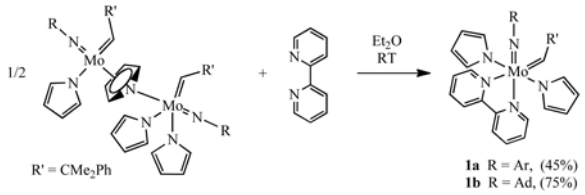
It has long been known that 14 electron bisalkoxide catalysts will form 16 or 18 electron adducts with donor ligands.[ia] Bipyridine was first employed as a ligand in imido alkylidene chemistry in order to isolate the methylidene complex, yellow crystalline Mo(NAr)(CH_2)$[OC(CF_3)_2Me]_2$(bipy) in high yield.[vi] Eighteen electron Mo(NAr)(CH_2)$[OC(CF_3)_2Me]_2$(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 $ZnCl_2$ to remove bipyridine;[viia] 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.[viib] Other types of 18 electron alkylidene complexes that are activated upon addition of Lewis acids are known.[viii]

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)($CHCMe_2Ph$)(NC_4H_4)(OAr) species; we have been able to prepare several of these MAP species only in this manner. We also report that attempts to prepare bispyridine adducts of bis-2,5-dimethylpyrrolide complexes lead to formation of imido alkylidyne complexes of the type Mo(NR)($CCMe_2R'$)(Me_2Pyr)(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)(CHCMe$_2$Ph)(Pyr)$_2$ in diethyl ether led to precipitation of complexes with the general formula Mo(NR)(CHCMe$_2$Ph)(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)(CHCMe$_2$Ph)(Pyr)$_2$(bipy) species are relatively insoluble, a property that

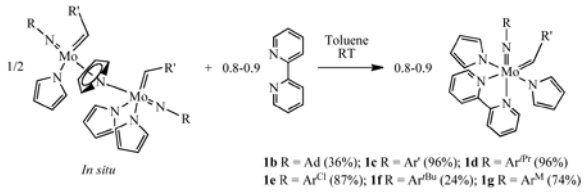


(1)

allows them to be isolated readily. A proton NMR spectrum of **1b** could be obtained in CD_2Cl_2, 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 *syn* alkylidene isomers. Compound **1a** dissolves more readily in CD_2Cl_2 than **1b** so both ^1H 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 alkylidene and imido ligands. In contrast, Mo(NAr)(CHCMe$_2$Ph)[OC(CF$_3$)$_2$Me]$_2$(bipy)[vii] adopts a *cis* configuration in which bipy is bound *trans* to the alkylidene and one of the alkoxide ligands. The Mo-N$_{bipy}$ bond lengths in **1a** (2.330(3) and 2.354(3) Å) therefore are similar, whereas the two Mo-N$_{bipy}$ bond lengths in Mo(NAr)(CHCMe$_2$Ph)[OC(CF$_3$)$_2$Me]$_2$(bipy) (2.3503(11) Å and 2.2462(10) Å)[vii] differ significantly, with the latter bond length (*trans* to the alkoxide) being the shorter of the two.

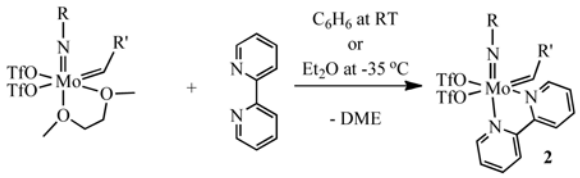
Bispyrrolide species also can be prepared *in situ* from Mo(NR)(CHCMe$_2$Ph)(OTf)$_2$(DME) complexes and treated with 0.8–0.9 equivalents of bipyridine to produce the insoluble compounds of type **1** shown in equation 2 (R′ = t-Bu or CMe$_2$Ph). This method will be referred to as method B. It is an 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.



(2)

Only one alkylidene resonance is present in the alkylidene region in the ^{1}H NMR spectrum (in CD_2Cl_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.

$Mo(NR)(CHCMe_2Ph)(OTf)_2(bipy)$ complexes can be synthesized from $Mo(NR)(CHCMe_2Ph)(OTf)_2(dme)$ complexes by suspending the latter in benzene that contains one equivalent of bipyridine at room temperature (R = 2,6-*i*-$Pr_2C_6H_3$ (Ar), 1-adamantyl (Ad), 2,6-$Me_2C_6H_3$ (Ar′), and 2-$MesC_6H_4$ (Ar^{M}), or in diethyl ether (R = 2-ClC_6H_4 (Ar^{Cl}), 2-*i*-PrC_6H_4 (Ar^{iPr}), 2-*t*-BuC_6H_4 (Ar^{tBu})) and stirring the mixtures for 12 h at 22 °C (equation 3). In all cases, the relatively insoluble $Mo(NR)(CHCMe_2Ph)(OTf)_2(bipy)$ complexes can be collected by

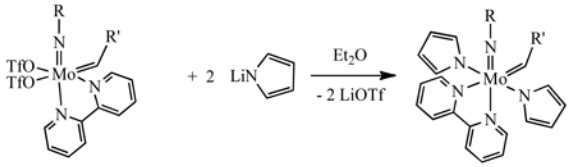


2a R = Ar (84 %); **2b** R = Ad (91 %); **2c** R = Ar′ (67 %);
2d R = Ar^{iPr} (76 %); **2e** R = Ar^{Cl} (66 %); **2f** R = Ar^{tBu} (76 %);
2g R = Ar^{M} (73 %)

(3)

filtration in good yields. All $Mo(NR)(CHCMe_2Ph)(OTf)_2(bipy)$ complexes are soluble in CD_2Cl_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_2Cl_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 $LiNC_4H_4$ 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.



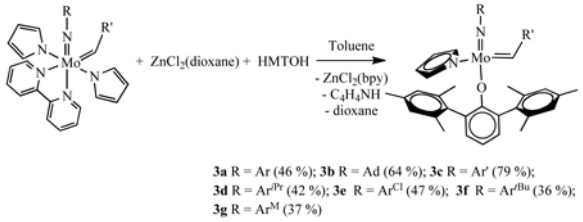
1a R = Ar (61 %); **1c** R = Ar′ (77 %); **1d** R = Ar^{iPr} (85 %)

(4)

When complexes **2b**, **2e**, and **2f–2g** are treated with two equivalents of $LiNC_4H_4$ 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 $ZnCl_2$(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 $ZnCl_2$(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)($CHCMe_2Ph$)(NC_4H_4)$_2$ has been reported elsewhere.[v]



3a R = Ar (46 %); **3b** R = Ad (64 %); **3c** R = Ar′ (79 %);
3d R = Ar^{iPr} (42 %); **3e** R = Ar^{Cl} (47 %); **3f** R = Ar^{tBu} (36 %);
3g R = Ar^{M} (37 %)

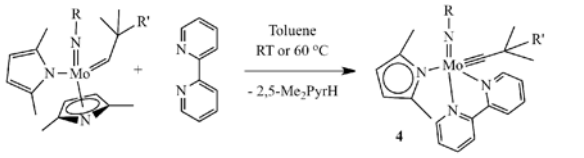
(5)

The structure of **3d** was obtained through an X-ray study. The complex crystallized in the space group $P\bar{1}$ 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 ^{1}H and ^{13}C 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)($CHCMe_2R'$)(Pyr)(OHIPT) as an initiator and polymers prepared from menthoxy analogs of DCMNBD.[iiii] Full details can be found in the Supporting Information. Similar behavior had been observed for the analogous Mo(NR)($CHCMe_2R'$)(Me_2Pyr)(OHMT) initiators in which the phenyl imido ligands were monosubstituted in the *ortho* positions with Cl, CF_3, or *i*-Pr groups, although *t*-Bu, mesityl, or 2,4,6-triisopropylphenyl 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)($CHCMe_2Ph$)(Me_2Pyr)$_2$ or Mo(NR)($CHCMe_3$)(Me_2Pyr)$_2$ complexes led to the imido alkylidyne complexes **4a–4g** shown in equation 6. Only the reaction between Mo(NAr^{iPr})($CHCMe_2Ph$)(Me_2Pyr)$_2$ and one equivalent of bipy or Mo(NAd($CHCMe_2Ph$)(Me_2Pyr)$_2$ 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.

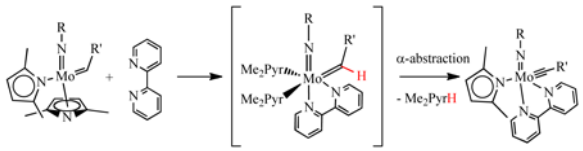
Other reactions require heating in toluene at 60 °C. In all cases the color of the reaction mixture changes from orange-brown to red-purple. Upon completion of the reaction, one equivalent of Me_2PyrH can be observed in solution in proton NMR spectra. Upon removing the solvent from the reaction mixture 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.



4a R = Ar, R' = Ph, 60 °C, (46%); **4b** R = Ad, R' = Ph, 22 °C, (44%)
4c R = Ar', R' = Ph, 60 °C, (60%); **4d** R = Ar^{iPr}, R' = Ph, 22 °C, (86%)
4e R = Ar^{CF3}, R' = Me, 60 °C, (69%); **4f** R = Ar^{M}, R' = Ph, 60 °C, (53%)
4g R = Ar^{T}, R' = Me, 60 °C, (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 $\{Mo(NAr)(C\text{-}t\text{-}Bu)[OCMe(CF_3)_2]_2\}^-$ is more bent[x] (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 $\{Mo(NAr)(C\text{-}t\text{-}Bu)[OCMe(CF_3)_2]_2\}^-$. 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).



(7)

High oxidation state alkylidyne complexes of tantalum, tungsten, molybdenum, and rhenium have been synthesized through several routes in the last thirty years.[xi] Formation of a neopentylidyne ligand through deprotonation of a neopentylidene ligand was first demonstrated in a reaction between $Ta(CHCMe_3)(CH_2CMe_3)_3$ and butyllithium to give a lithium salt of $\{Ta(CHCMe_3)(CH_2CMe_3)_3\}^-$.[xii] Dehydrohalogenation of $W(NPh)(CHCMe_3)(PEt_3)_2Cl_2$ by $Ph_3P{=}CH_2$ led to $W(NPh)(CCMe_3)(PEt_3)_2Cl$,[xiii] a compound that is most similar to **4a–4g**, although no X-ray structure of $W(NPh)(CCMe_3)(PEt_3)_2Cl$ was determined. Deprotonation of $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ by $Ph_3P{=}CH_2$ led to the alkylidyne complex, $\{Ph_3PMe\}\{Mo(NAr)(CCMe_3)[OCMe(CF_3)_2]_2\}$,[x] as noted earlier. Attempts to prepare certain types of imido neopentylidene 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.[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 $M(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ to be synthesized;[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 neopentylidene ligands, either by transfer of a proton to a neopentyl group or to an imido or amido group.[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.[ii] Intramolecular α proton migration has been known to be promoted in more sterically crowded circumstances, the first being ligand induced formation of tantalum neopentylidene complexes from tantalum dineopentyl complexes through addition of various phosphines or simply THF.[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.[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, $Mo(NR)(CCMe_2R')(Me_2Pyr)(bipy)$ 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 $Mo(NR)(CHCMe_2R')(Pyr)_2(bipy)$ (**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)($CHCMe_2R'$)$(Pyr)_2$ complexes themselves. They can be employed as starting materials for formation of MAP species of the type Mo(NR)($CHCMe_2R'$)(Pyr)(OHMT) (**3a–3g**) through sonication of a mixture containing **1a–1g**, HMTOH, and $ZnCl_2$(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)($CCMe_2R'$)(Me_2Pyr)(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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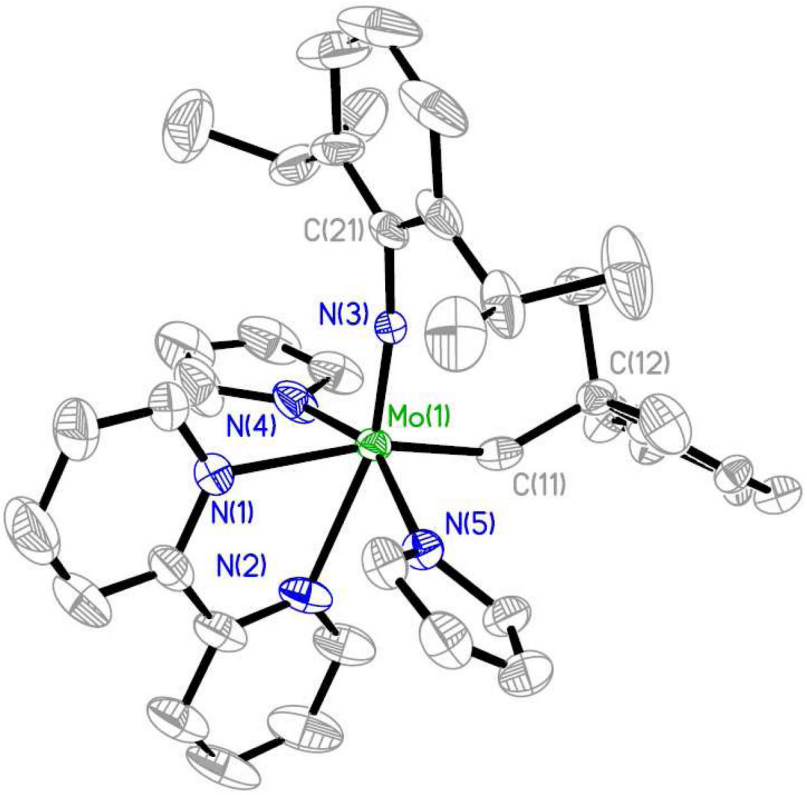

Figure 1.

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).

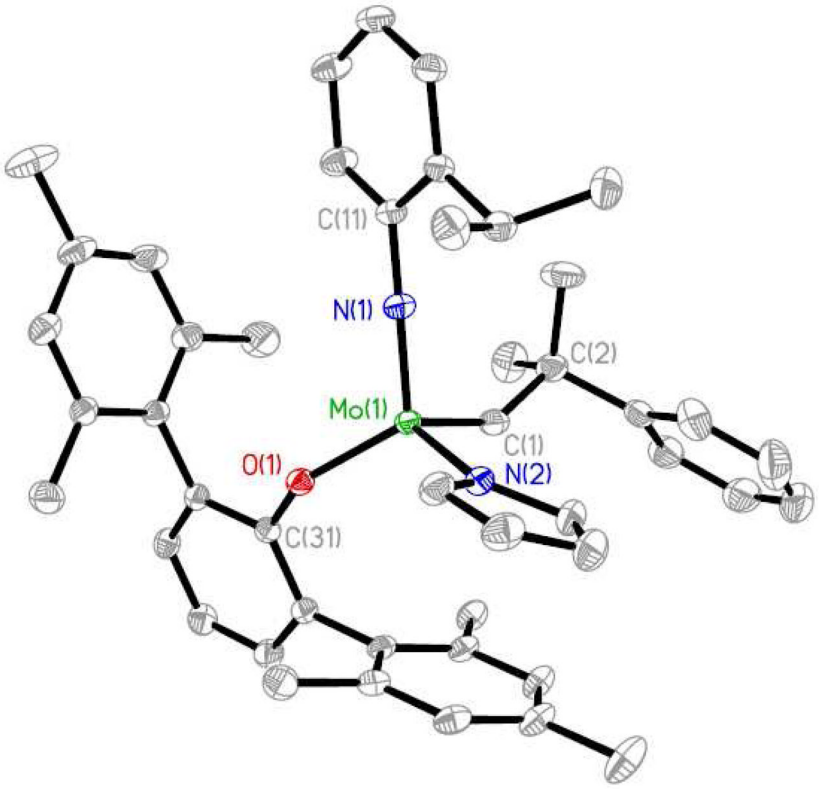

Figure 2a.

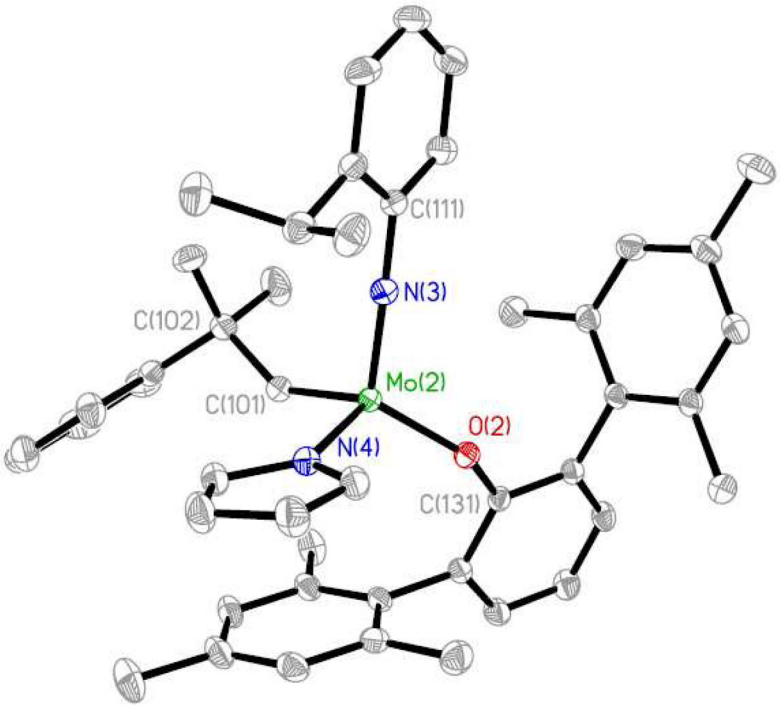

Figure 2b.

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).

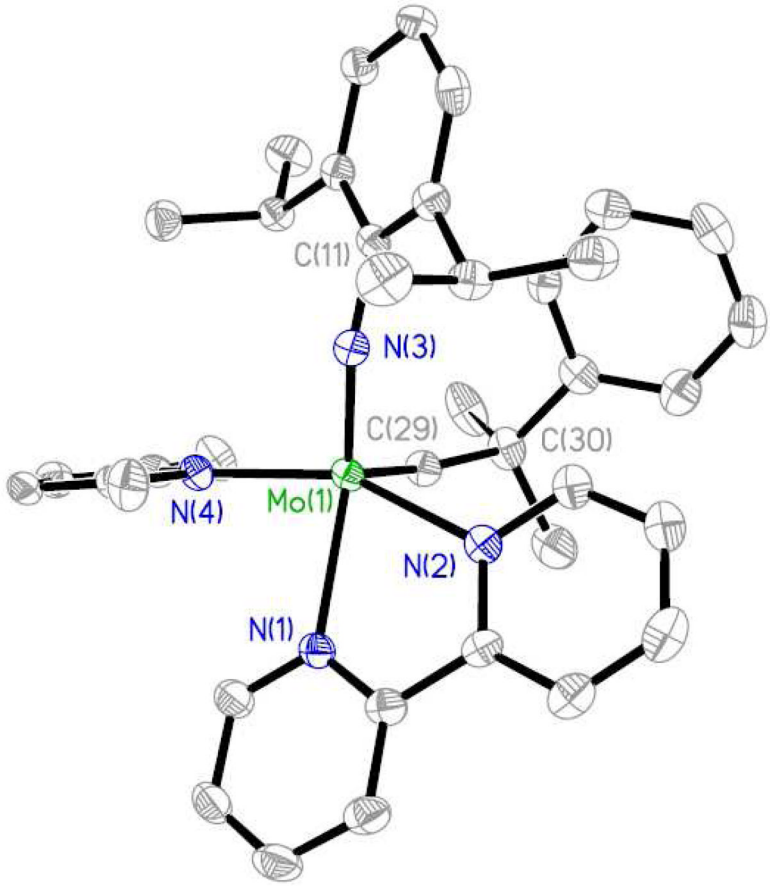

Figure 3.

A drawing of the solid-state structure of (NAr)($CCMe_2Ph$)(Me_2Pyr)(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) = 153.05(10).

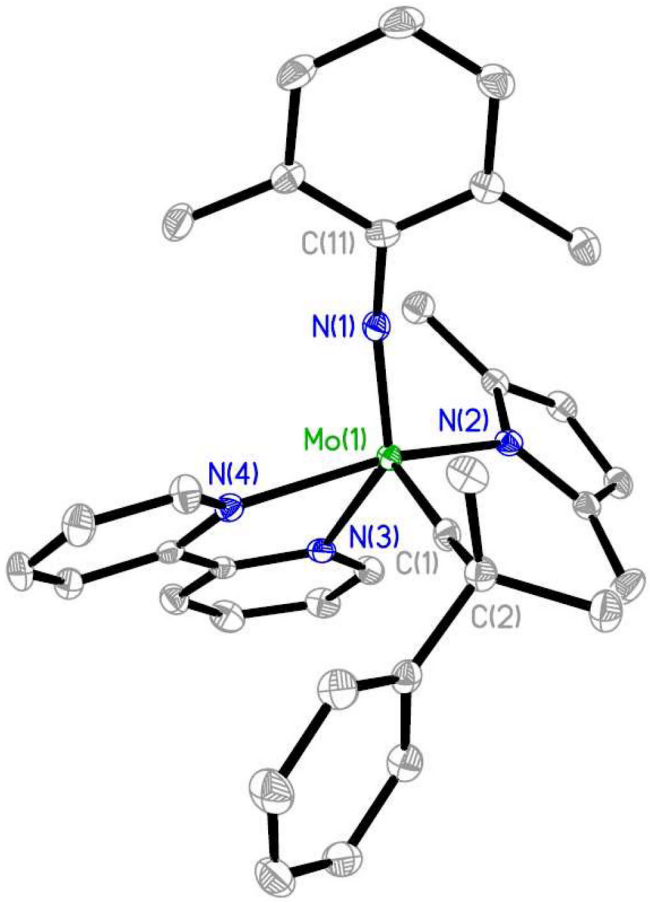

Figure 4.

A drawing of the solid-state structure of Mo(NAr′)(CCMe$_2$Ph)(Me$_2$Pyr)(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)-C(11) = 162.64(12), N(1)-Mo(1)-N(3) = 137.44(6), N(2)-Mo(1)-N(4) = 153.09(15).

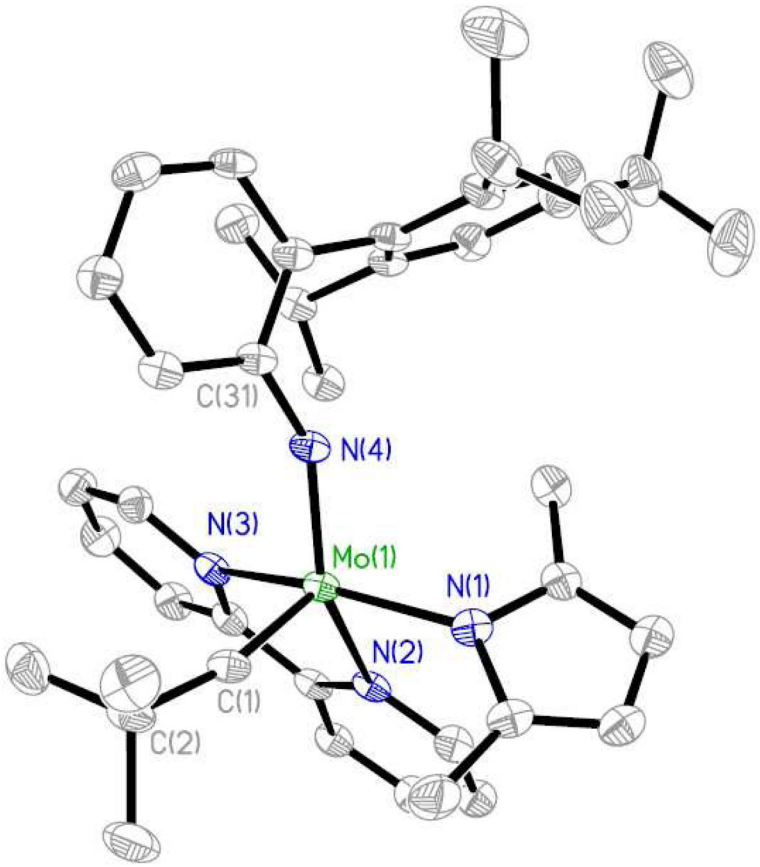

Figure 5.

A drawing of the solid-state structure of Mo(NAr^{T})(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(4), Mo(1)-N(4) = 1.823(4), 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).