ORGANOMETALLICS

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pubs.acs.org/Organometallics

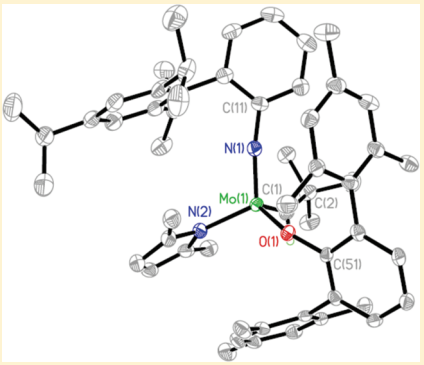
Molybdenum Monoaryloxide Pyrrolide Alkylidene Complexes That Contain Mono-*ortho*-substituted Phenyl Imido Ligands

Alejandro G. Lichtscheidl, Victor W. L. Ng, Peter Müller, Michael K. Takase, and Richard R. Schrock*

Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Supporting Information

ABSTRACT: Monaryloxide pyrrolide (MAP) molybdenum imido alkylidene complexes of the type $Mo(NAr^X)(CHCMe_2R)(Me_2Pyr)(OR')$ (Me_2Pyr = 2,5-dimethylpyrrolide) have been prepared in which NAr^X is an *ortho*-substituted phenylimido group (X = Cl (NAr^{Cl}), CF_3 (NAr^{CF3}), *i*-Pr (NAr^{iPr}), *t*-Bu (NAr^{tBu}), mesityl (NAr^M), or TRIP (TRIP = triisopropylphenyl; NAr^T)) and OR′ = O-2,3,5,6-$(C_6H_5)_4C_6H$ (OTPP), O-2,6-$(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3$ (OHMT), or O-2,6-$(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3$ (OHIPT). The object was to explore to what extent relatively "large" NAr^M or NAr^T ligands would alter the performance of MAP catalysts in reactions that have been proposed to depend upon the relative size of the imido and OR′ groups. Preliminary studies employing the ring-opening metathesis polymerization of 5,6-dicarbomethoxynorbornadiene as a measure of selectivity suggest that a single phenylimido *ortho* substituent, even in an NAr^M or NAr^T group, does not produce any unique behavior and that the outcome of the ROMP reaction correlates with the overall relative size of the imido and OR′ group. Single-crystal X-ray structures of six species that contain the new NAr^M or NAr^T groups are reported.



INTRODUCTION

High oxidation state molybdenum and tungsten imido alkylidene complexes[1] with the generic formula M(NR)(CHR′)(X)(Y) (where X and Y are monoanionic ligands, initially both alkoxides) were first prepared approximately 25 years ago.[2] Unlike an oxo ligand, which was present in the first high oxidation state group 6 complexes to be discovered,[3] the isoelectronic imido ligand can retard bimolecular decomposition of alkylidenes for steric reasons. Imido ligands also are available in many steric and electronic variations. Phenylimido ligands have been popular, especially 2,6-disubstituted versions ($2,6\text{-}i\text{-}Pr_2C_6H_3$, $2,6\text{-}Me_2C_6H_3$, $2,6\text{-}Cl_2C_6H_3$, etc). 2-Substituted imido ligands are less common,[4] while those with no *ortho* substituents are rare; one example is $N\text{-}3,5\text{-}Me_2C_6H_3$.[5] Complexes that contain phenylimido ligands with progressively less steric protection in *ortho* positions are more difficult to prepare, and the resulting imido alkylidene complexes appear to be less stable toward what is presumed to be bimolecular decomposition.

In the last several years new types of Mo and W imido alkylidene complexes that have 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.[1a,6] These monoaryloxide pyrrolide (MAP) species can be viewed as third-generation high oxidation state imido alkylidene catalysts (after "first-generation" bisalkoxides and "second-generation" biphenolates and binaphtholates[1]). MAP species have many features of fundamental interest. MAP species contain a stereogenic metal center, MAP species have proven to be much more efficient (higher turnover) than bisalkoxide catalysts in many cases, and MAP species can be engineered to be highly *Z*-selective for the coupling of terminal olefins.[7] MAP species also have been the subject of detailed calculations.[8]

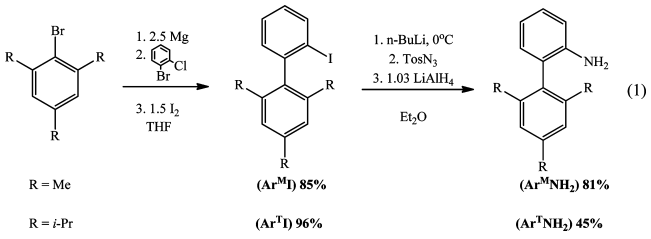
We have begun to explore the consequences of increasing the size of imido groups in MAP complexes to the point that their size approaches or exceeds that of sterically demanding O-2,6-$(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3$ (OHMT) or O-2,6-$(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3$ (OHIPT) ligands that have been employed in order to enforce *Z*-selective reactions.[9,10] Phenylimido ligands that are monosubstituted in the *ortho* position, $N\text{-}2\text{-}XC_6H_4$ species, especially those in which X is mesityl (NAr^M) or triisopropylphenyl (NAr^T), could prove to be interesting variations of MAP catalysts. The syntheses of NAr^M and NAr^T species and a comparison of them with NAr^{Cl}, NAr^{CF3}, NAr^{iPr}, and NAr^{tBu} species are the subject of this paper. The main question we wanted to answer is in what way, if any, do compounds that contain NAr^M or NAr^T ligands differ from those that contain NAr^{Cl}, NAr^{CF3}, NAr^{iPr}, or NAr^{tBu} ligands in some test reactions that may be sensitive to the size of X in $N\text{-}2\text{-}XC_6H_4$ MAP species.

RESULTS AND DISCUSSION

Anilines that contain either a Mes (2,4,6-trimethylphenyl) or a TRIP (2,4,6-triisopropylphenyl) substituent were prepared as shown in eq 1. Methods of preparing these crystalline anilines

Received: January 13, 2012
Published: March 5, 2012

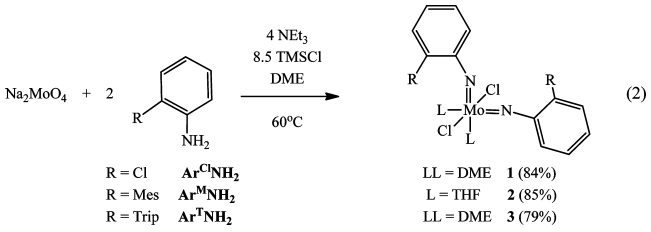
   dx.doi.org/10.1021/om3000289 | *Organometallics* 2012, 31, 2388−2394



(1)

are adapted from literature reports;[11,12] no palladium-catalyzed step is required.

Bisimido dichloride complexes in which the imido ligand is NAr^{Cl}, NAr^{M}, or NAr^{T} could be prepared by the standard method shown in eq 2. When a mixture of two equivalents of



(2)

$Ar^{M}NH_2$, Na_2MoO_4, NEt_3, and TMSCl in DME is heated at 60 °C overnight, an orange product is formed, but the DME adduct could not be isolated in crystalline form. However, recrystallization of the crude DME adduct from a mixture of pentane and THF led to red, crystalline **2** in 85% isolated yield. A proton NMR spectrum of **2** shows that four equivalents of THF are present, as confirmed through elemental analysis. We propose that two equivalents of THF are present as solvent of crystallization (*vide infra*) and that THF exchange is fast on the NMR time scale at room temperature.

The results of X-ray structural studies of **2** and **3** are shown in Figures 1 and 2, respectively. As proposed, crystals of **2** contain two THF molecules of crystallization (shown in Figure

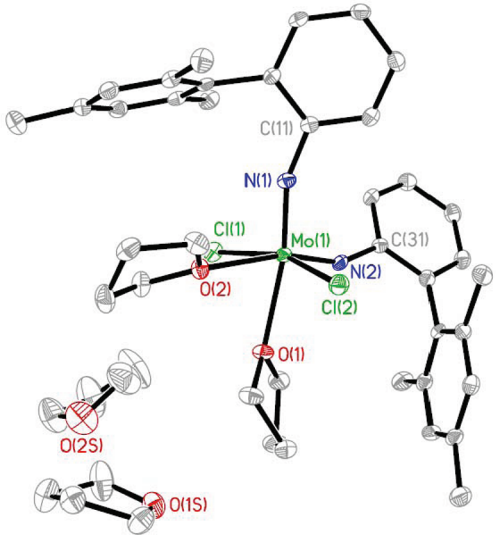


Figure 1. Solid-state structure of **2** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Mo(1)−N(1) = 1.750(2), Mo(1)−N(2) = 1.7535(19), Mo(1)−O(1) = 2.3138(18), Mo(1)−O(2) = 2.3394(6), Mo(1)−Cl(1) = 2.3863(9), Mo(1)−Cl(2) = 2.4119(9), N(1)−Mo(1)−N(2) = 102.95(10), C(11)−N(1)−Mo(1) = 160.05(19), C(31)−N(2)−Mo(1) = 156.4(2), Cl(1)−Mo(1)−Cl(2) = 160.63(3).

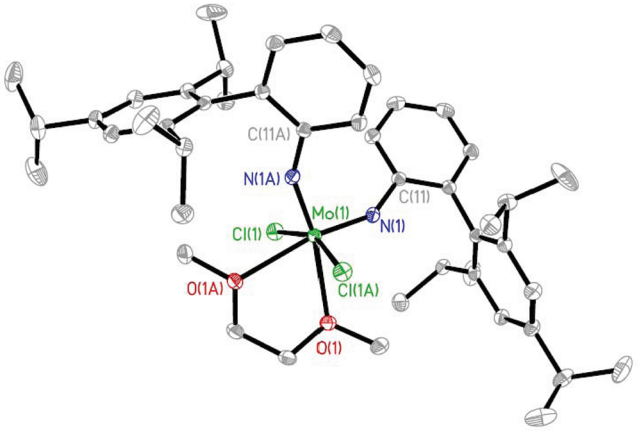
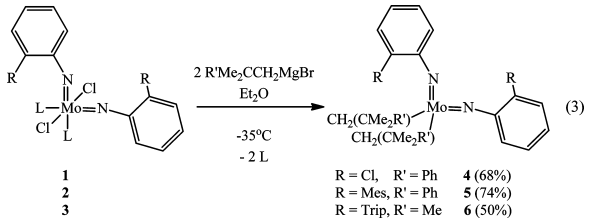


Figure 2. Solid-state structure of **3** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Mo(1)−N(1) = 1.7522(12), Mo(1)−O(1) = 2.3381(11), Mo(1)−Cl(1) = 2.4023(4), N(1)−Mo(1)−N(2) = 101.44(8), C(11)−N(1)−Mo(1) = 149.39(10), Cl(1)−Mo(1)−Cl(2) = 159.37(2).

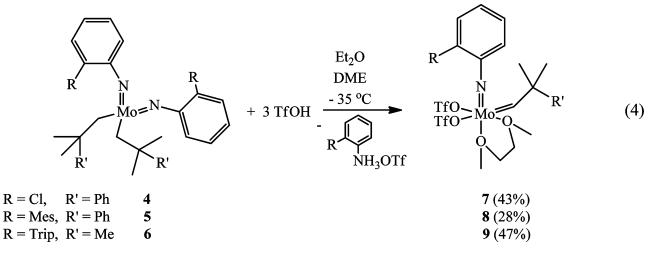
1). The imido ligands in both **2** and **3** are bent at the imido nitrogen; the smaller Mo−N−C angle in **3** (149.39(10)°) versus **2** (160.05(19)° and 156.4(2)°) can be attributed to the greater steric demand of the TRIP group in **3** compared to the Mes group in **2**. Other bond distances and angles are similar to other complexes of this general type that have been crystallographically characterized.[1] A complete list of bond distances and angles can be found in the Supporting Information.

Dichloride complexes **1**, **2**, and **3** were converted into dineopentyl or dineophyl complexes **4**, **5**, and **6** in good yield through standard procedures (eq 3). The alkyl ligand is chosen



(3)

on the basis of the ease of isolating the dialkyl product. Compounds **4**, **5**, and **6** were then treated with three equivalents of triflic acid to yield **7**, **8**, and **9** (eq 4). We



(4)

found it difficult to separate **8** from the anilinium triflate byproduct. So far, trituration with diethyl ether is the only way to remove all anilinium triflate; the isolated yield of **8** (28%) therefore suffers as a consequence of it being partially soluble in ether. Although the reaction between **6** and triflic acid yields **9** smoothly, separation of **9** from the anilinium triflate is again problematic; the isolated yield of **9** is only 47%. Bistriflate complexes that contain NAr^{CF3}, NAr^{iPr}, and NAr^{tBu} imido

dx.doi.org/10.1021/om3000289 | *Organometallics* 2012, 31, 2388−2394

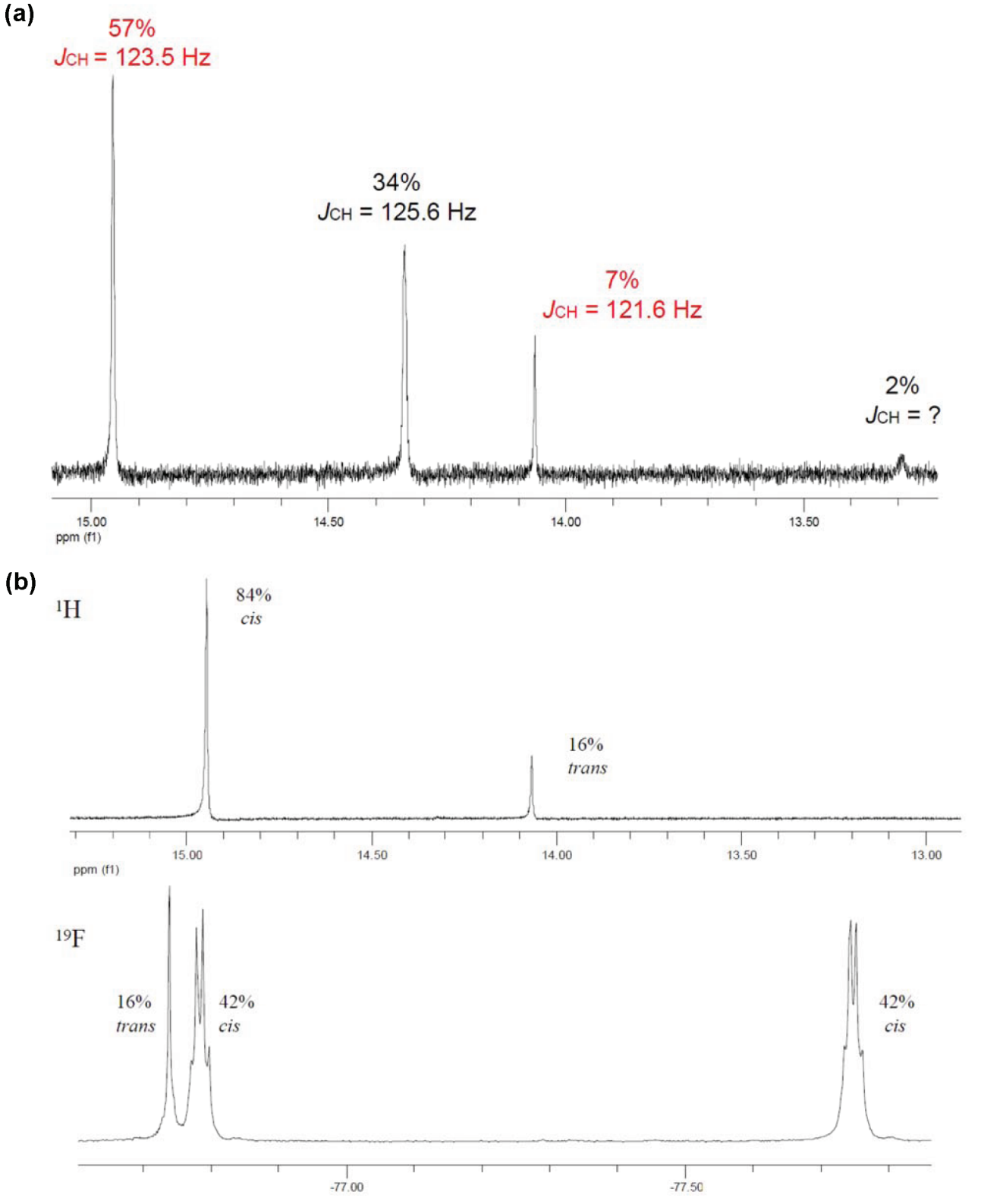


Figure 3. (a) The four alkylidene proton resonances in the ^{1}H NMR spectrum of **9**. (b) ^{1}H (top) and ^{19}F (bottom) NMR spectra of two of the isomers of **9**.

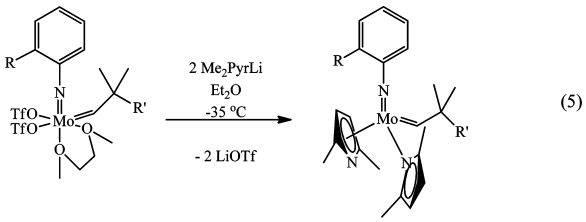
groups have been reported previously.[4a] Details can be found in the Supporting Information.

Bistriflate complexes that contain NAr^{CF3}, NAr^{iPr}, NAr^{tBu}, and NAr^{Cl} groups all show resonances for two isomers in solution. Fluorine NMR spectra suggest that these isomers contain triflate ligands that are either *cis*, as shown in eq 4, or *trans* with respect to one another. Proton NMR data suggest that they are *syn* isomers (J_{CH} = 125 ± 3 Hz), in which the alkylidene group points toward the imido group, as shown in eq 4. In contrast, ^{1}H NMR spectra (in C_6D_6) of both **8** and **9** each show more than the expected two alkylidene resonances for *cis* and *trans*

dx.doi.org/10.1021/om3000289 | *Organometallics* 2012, 31, 2388−2394

isomers, and ratios of the alkylidene resonances vary from run to run. The three most prominent resonances for **8** have J_{CH} values that range from 122 to 129 Hz; for **9** (Figure 3) they range from 122 to 126 Hz. All J_{CH} values that can be measured are characteristic of *syn* species. Two isomers of compounds in the mixture whose NMR spectrum is shown in Figure 3 are isolated upon recrystallizing the compound from diethyl ether at −35 °C. Proton and fluorine NMR spectra (Figure 3) are consistent with these isomers of **9** being *cis* (84%) and *trans* (16%) species. *Cis* and *trans* mixtures of bistriflate dimethoxyethane complexes of this general type have been observed in other circumstances;[13] only two isomers are possible if the alkylidene and imido ligands are required to be *cis* to one another, which is what has been observed in all imido alkylidene complexes to date. The observation of more than two isomers suggests several possibilities. One or more of the adducts loses DME in the solid state, one or more of the isomers is actually not a solvent adduct, or the large mesityl and TRIP substituents give rise to isomers in which the mesityl or TRIP substituents limit free rotation of the imido phenyl group about the Mo═N axis on the NMR time scale. Spectra in the alkylidene region did not change significantly when several equivalents of DME were added, and the amount of DME in a complex mixture could not be measured accurately through integration. Therefore, we cannot determine the exact reason for isomer formation. Unfortunately, multiple elemental analyses of **8** and **9** as mixtures of four isomers were variable, as were elemental analyses of the mixture of *cis* and *trans* isomers shown in Figure 3; the reasons are not known.

Treatment of the bistriflate complexes with two equivalents of Li-2,5-$Me_2C_4H_2N$ led to bispyrrolide compounds in yields ranging from 36% to 85% (eq 5). The neophylidene analogue



(5)

10 R = Cl, R' = Ph; (57%) **13** R = *t*-Bu, R' = Me; (82%)
11 R = CF_3, R' = Me; (53%) **14** R = Mes, R' = Ph; (85%)
12 R = *i*-Pr, R' = Ph; (59%) **15** R = Trip, R' = Me; (36%)

of **11** has been reported previously.[4d] The low isolated yield of **15** we propose is the result of its poor crystallinity. Proton NMR spectra of complexes **10**−**13** exhibit a single alkylidene peak and broad peaks corresponding to fluxional pyrrolide ligands, behavior which is analogous to other bispyrrolide compounds of this general type.[14] An X-ray structural study of **14** shows it to contain both η^1 and η^5 pyrrolide ligands and a *syn* alkylidene, as expected (Figure 4).

Addition of *t*-BuOH, $(CF_3)_2MeCOH$, or Ph_3SiOH to complexes **10**−**15** led to formation of bisalkoxide complexes as the only observable product, instead of the desired MAP species. Since N-2,6-*i*-$Pr_2C_6H_3$ (NAr) MAP species that contain *tert*-butoxide, hexafluoro-*tert*-butoxide, or triphenylsiloxide can be obtained in good yields in similar reactions,[6a] these findings suggest that NAr^M and NAr^T ligands offer less steric protection toward rapid protonation of the second pyrrolide than bispyrrolides that contain the NAr ligand.

Addition of one equivalent of 2,3,5,6-tetraphenylphenol (TPPOH) to **14** led to a mixture that contains 25% **14**, 50% of a MAP product, and 25% of the bisphenoxide. The

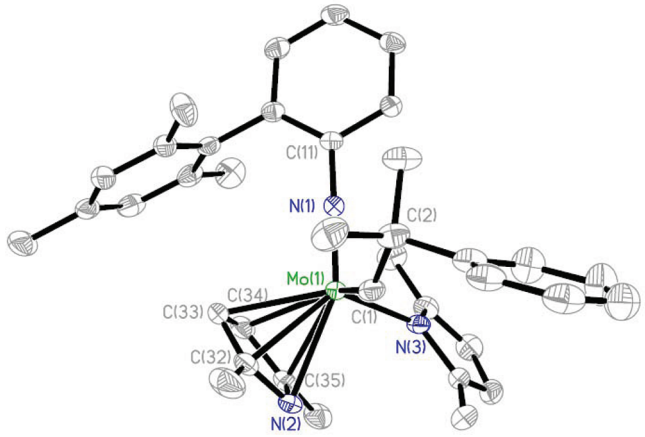
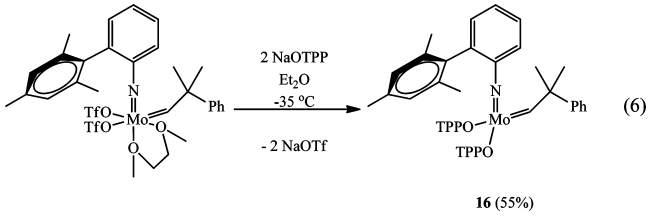


Figure 4. Solid-state structure of **14** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Mo(1)−N(1) = 1.7340(16), Mo(1)−C(1) = 1.940(2), Mo(1)−N(2) = 2.4117(17), Mo(1)−N(3) = 2.1134(17), Mo(1)−C(32) = 2.391(2), Mo(1)−C(33) = 2.376(2), Mo(1)−C(34) = 2.458(2), Mo(1)−C(35) = 2.458(2), C(11)−N(1)−Mo(1) = 175.40(15), C(2)−C(1)−Mo(1) = 139.84(15).

bisphenoxide species (**16**) could be prepared (in 55% yield) from the bistriflate as shown in eq 6. Since **16** would appear to



(6)

16 (55%)

be a relatively crowded species, an X-ray structural determination (Figure 5) was carried out. Compound **16** is a distorted tetrahedron with the smallest and largest angles being 99.29(12)° (N(1)−Mo(1)−C(1)) and 120.85(9)° (N(1)−Mo(1)−O(2)). The Mo(1)−O(1)−C(31)and Mo(1)−O(2)−

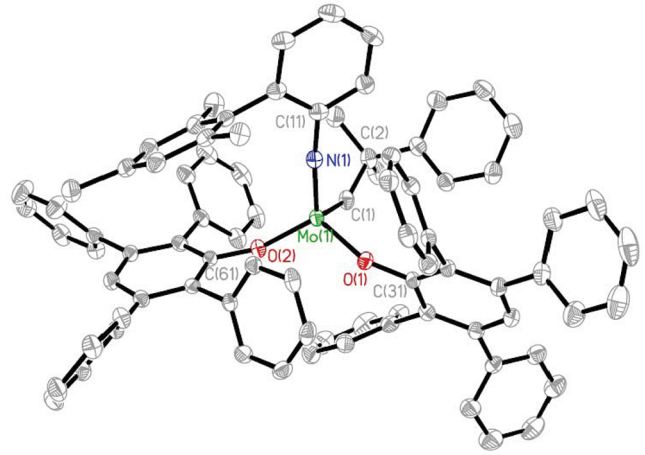
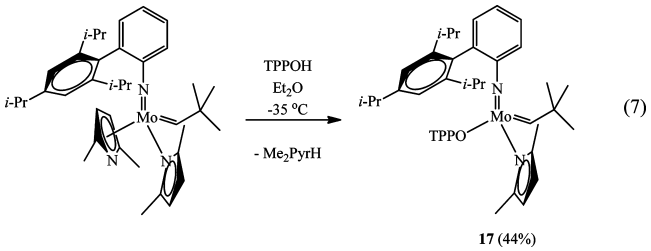


Figure 5. Solid-state structure of **16** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Mo(1)−N(1) = 1.732(2), Mo(1)−C(1) = 1.880(3), Mo(1)−O(1) = 1.9402(18), Mo(1)−O(2) = 1.9303(17), Mes-TPP = 4.343, C(11)−N(1)−Mo(1) = 173.13(19), C(2)−C(1)−Mo(1) = 141.8(2), C(31)−O(1)−Mo(1) = 147.00(17), C(61)−O(2)−Mo(1) = 148.18(16).

dx.doi.org/10.1021/om3000289 | *Organometallics* 2012, 31, 2388−2394

C(61) bond angles (147.00(17)° and 148.18(16)°, respectively) are relatively large, as might be expected as a consequence of steric crowding. The Mo(1)−N(1)−C(11) bond angle is close to 180° (173.13(19)°). The ready formation of **16** confirms that 2,3,5,6-tetraphenoxide ligands are operationally not as large as one might think, as has been found in other circumstances.[5] In contrast, the reaction between **15** and one equivalent of TPPOH yields only Mo(NAr^T)(CH-*t*-Bu)(Me$_2$Pyr)(OTPP) (**17**; eq 7); that is, increasing the bulk

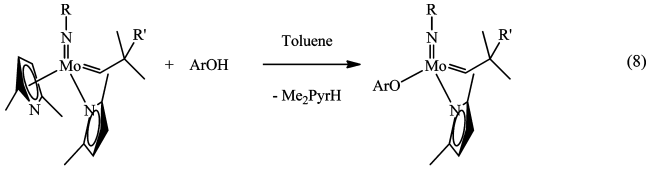


(7)

17 (44%)

of the imido group (from Ar^M to Ar^T) decreases the rate of formation of the bisphenoxide and, therefore, allows the synthesis of the MAP species.

2,6-Dimesitylphenol (HMTOH) reacts readily at 22 °C with **10**−**13** to generate MAP products in modest to good yields (eq 8). However, reactions of HMTOH or hexaisopropylterphenol



(8)

18 R = Ar^{Cl}, R' = Ph, Ar = HMT (40%)
19 R = Ar^{CF3}, R' = Me, Ar = HMT (76%)
20 R = Ar^{iPr}, R' = Ph, Ar = HMT (48%)
21 R = Ar^{tBu}, R' = Me, Ar = HMT (68%)
22 R = Ar^M, R' = Ph, Ar = HMT (51%)
23 R = Ar^M, R' = Ph, Ar = HIPT (35%)
24 R = Ar^T, R' = Me, Ar = HMT (57%)
25 R = Ar^T, R' = Me, Ar = HIPT (*in-situ*)

(HIPTOH) with **14** and **15** are slow. Therefore, their preparation must be carried out at high temperatures in toluene for hours to days, depending on the phenol. The reactions at 110 °C between **14** or **15** and one equivalent of HMTOH to give **22** and **24**, respectively, required 18 h, while that between **14** and one equivalent of HIPTOH to give **23** required 5 days. Reaction between **15** and HIPTOH required 14 days at 80 °C to give 97% of the desired product. These data show that reactions between HMTOH and **14** or **15** clearly take place more readily. It is noteworthy that the MAP products do not decompose under the relatively harsh conditions required to prepare **22**−**25**. The isolated yields of **22**−**24** are modest (35−57%), the lowest being that for **23** as a consequence of its high solubility in solvents such as pentane or tetramethylsilane. Complexes **22** and **24** are more crystalline than **23** and, therefore, can be isolated in higher yields. Due to the long times required for reactions between **25** and HIPTOH and possible complications during purification, **25** could be prepared only *in situ*. All reactions benefit from being run under more concentrated conditions, but a large excess of HMTOH or HIPTOH cannot be employed without creating problems with isolation of the desired pure product in the presence of the phenol.

The structures of **22** and **24** are shown in Figures 6 and 7, respectively. Both are distorted tetrahedra, with angles at the

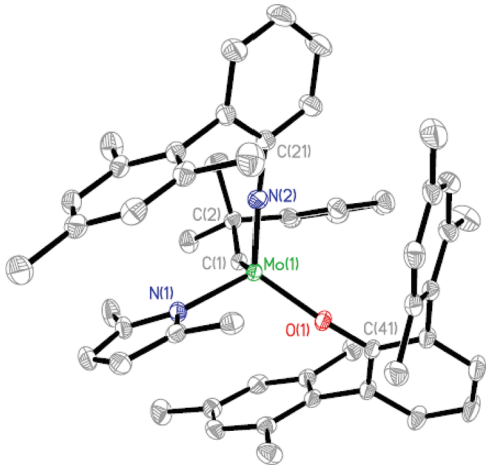


Figure 6. Solid-state structure of **22** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Mo(1)−C(1) = 1.8752(13), Mo(1)−N(1) = 2.0230(11), Mo(1)−N(2) = 1.7302(11), Mo(1)−O(1) = 1.8997(9), Mes−Pyr = 3.837, C(21)−N(2)−Mo(1) = 175.50(10), C(2)−C(1)−Mo(1) = 146.02(10), C(41)−O(1)−Mo(1) = 158.89(9).

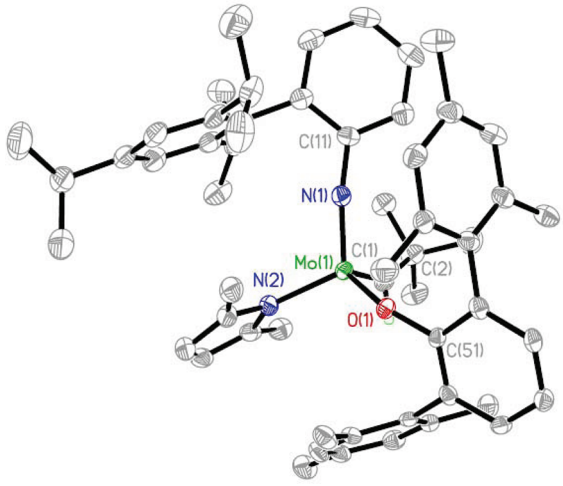


Figure 7. Solid-state structure of **24** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Mo(1)−C(1) = 1.862(3), Mo(1)−N(1) = 1.736(2), Mo(1)−N(2) = 2.037(2), Mo(1)−O(1) = 1.9103(19), C(11)−N(1)−Mo(1) = 170.9(2), C(2)−C(1)−Mo(1) = 147.5(2), C(51)−O(1)−Mo(1) = 147.32(19).

metal ranging from 102.97(5)° to 117.48(5)° and 101.41(12)° to 116.40(10)°, respectively. The Mo−N−C(imido) and the Mo(1)−C(1)−C(2) angles are similar in the two complexes and to analogous angles in other complexes of this general type. On the other hand, the Mo(1)−O(1)−C(41) angle of **22** is 158.89(9)°, which is 10° larger than the Mo−O−C angle in either **24** or **16**; large M−O−C angles are not uncommon among MAP complexes containing HMTO or HIPTO. In both **22** and **24** the Mes and Trip groups point away from the alkylidene and therefore would not seem to block an olefin from binding to the metal *trans* to the pyrrolide. In **22** an additional feature worth mentioning is a possible π-stacking interaction between the mesityl ring of the NAr^M ligand and the pyrrolide ring beneath it. However, this interaction is weak due

dx.doi.org/10.1021/om3000289 | *Organometallics* 2012, 31, 2388−2394

to the distance between the rings (3.837 Å from the centroid of the mesityl ring to the centroid of the pyrrolide ring).[15]

Compounds **22**–**25** show different numbers of isomers in solution, as evidenced by their respective ^{1}H NMR spectrum. A trend is clearly observed between the overall steric hindrance at the metal center and the number of isomers observed in solution; the greater the steric hindrance, the higher the number of isomers present. Thus, **22**, which has the smallest combination of imido and aryloxide ligands (among these four catalysts), has only one isomer, while **24**, which contains the slightly larger NAr^T imido group, has two isomers. In the case where the aryloxide is HIPTO there are four isomers present in both NAr^M and NAr^T imido complexes. These findings can be rationalized in terms of steric crowding overall. As steric crowding around the metal increases, restricted rotation results in locking of the ligands on the NMR time scale in various positions that give rise to more than the expected number of isomers. On this basis we can propose that complex **16** (two observable isomers) is less crowded than **24** or **25** but more crowded than **22**.

The ROMP of 2,3-dicarbomethoxynorbornadiene (DCMNBD) has been employed as a means of judging the stereospecificity (*cis*/*trans* selectivity and *tacticity*) of a MAP metathesis catalyst.[16] Therefore, all MAP catalysts (**17**–**24** plus **25** prepared *in situ*) were treated with 25–100 equivalents of monomer in toluene at 22 °C. The polymerization was complete after one hour, and the resulting polymers were isolated and analyzed by NMR methods. The results are summarized in Table 1. All ROMP reactions are relatively fast.

Table 1. ROMP of DCMNBD with MAP Initiators 17–25 in Toluene at 22 °C

catalyst	[catalyst] (mM)	DCMNBD equivalents	polymer structure
17	12	50	50% *cis*
18	1.9	100	>98% *cis, syndio*
19	5.5	50	>98% *cis, syndio*
20	1.9	100	>98% *cis, syndio*
21	5.8	50	76% *cis*
22	13	25	69% *cis*
23	48	25	∼93% *cis, syndio*
24	13	25	77% *cis*
25	62	25	83% *cis*

Compound **17** fails to initiate formation of a highly structured polymer, presumably as a consequence of the imido group being too large relative to the aryloxide (OTPP). There is a drop in *cis*-selectivity from >98% to ∼70% in MAP species **21** and **22** when the imido ligand is larger than NAr^{iPr}. However, increasing the size of the phenoxide from HMTO to HIPTO (with initiator **23**) again leads to a polymer that is >93% *cis,syndiotactic*. Initiators **24** and **25** are unsuccessful, presumably because NAr^T is too large in combination with OHMT or OHIPT aryloxides. A lower *cis*-selectivity also has been observed when Mo(NAr)(CHCMe$_2$Ph)(Pyr)(OHIPT) is employed as an initiator in place of Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OHIPT) (Ad = adamantyl and Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$).[6h] The fact that **23** is almost as *Z*-selective as Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OHIPT) and **22**–**25** is surprising since it suggests that NAr^M is in the same category as NAr^{Cl}, NAr^{CF3}, and NAr^{iPr} imido ligands as far as producing polymers that have a high *cis,syndiotactic* content; that is, NAr^M is operationally relatively "small".

CONCLUSION

We have found that MAP catalysts that contain NAr^M and NAr^T ligands can be prepared through traditional synthetic routes analogous to those employed to prepare catalysts that contain NAr^{Cl}, NAr^{CF3}, NAr^{iPr}, and NAr^{tBu} imido groups. However, no imido ligands investigated in this report have properties that lead to unusual results for ROMP polymerization of DCMNBD. We conclude that a single *ortho* substituent in the 2-substituted imido groups explored here can point away from the C–M–N$_{imido}$ face where the olefin is proposed to bind, thereby minimizing interaction with the approaching olefin. Complexes that contain a 2-substituted imido ligand behave like much smaller imido groups in reactions that have been explored so far. The results reported here seem to imply that any attempt to employ a highly sterically demanding phenyl imido group will lead to unique metathesis behavior only if that catalyst contains a 2,6-disubstituted phenylimido ligand such as 2,6-dimesitylphenyl imido.[10] Therefore we are now exploring the synthesis and reactions of catalysts that contain a 2,6-dimesitylphenylimido ligand.[9]

ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization details for all complexes. Crystallographic details, fully labeled thermal ellipsoid diagrams for all crystallographically characterized species, and crystallographic information files in CIF format. This 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.

AUTHOR INFORMATION

Corresponding Author

*E-mail: rrs@mit.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

R.R.S. thanks the National Science Foundation (CHE-0841187 and CHE-1111133) for research support and for support for departmental X-ray diffraction instrumentation (CHE-0946721). V.W.L.N. thanks the Agency for Science, Technology and Research (Singapore) for an A*STAR International Fellowship.

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