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Catalytic C═N Bond Formation by Metal-Imide-Mediated Imine Metathesis

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Abstract: Molybdenum bis(imide) complexes of the general formula (DME)$Cl_2Mo({=}NR)_2$ catalytically metathesize acyclic imine substrates. This C═N bond-forming reaction has significant implications for the synthesis of small molecules by ring-closing metathesis and polymers by ring-opening metathesis. A series of closely related ═NR transfer reactions were examined in an effort to fully understand the process. $(RO)_2Mo({=}CHR')({=}NAr)$ (**1a**, Ar = 2,6-diisopropylphenyl in all cases; R = $C(CF_3)_2CH_3$) underwent alkylidene/imine exchange with a variety of imines in situ to give a mixed bis(imide) product and an olefin. The reactivity decreased if the alkoxide substituents were changed for more electron donating ones. (DME)$Cl_2Mo({=}NR)_2$ (**3a**, R = 2,6-diisopropylphenyl; **4**, R = *t*-Bu) reacted with imines in an imide/imine metathesis to give mixed bis(imide) complexes and new imines. The reaction rates depended strongly on the steric demands of the imide NR substituent. Replacement of the chlorides with more electron donating alkoxide ligands inhibited the reactions. Compounds **3a** and **4** also exchanged imide ligands with each other (imide/imide metathesis). Finally, compounds **3a** and **4** were found to catalytically metathesize mixtures of two imines at 80 °C in 105 and 22 h, respectively. It was established that the reaction is mediated by the presence of unique initiation products in catalytic mixtures. A catalytic cycle is proposed and the nature of the mechanism is discussed in terms of the data gathered on all of the metatheses.

Catalytic double bond metathesis, a reaction that has been used extensively in the synthesis of polymers and small molecules, is no longer limited to the formation of C═C bonds. With our recent discovery that known molybdenum bis(imide) complexes of the type (DME)$Cl_2Mo({=}NR)_2$[1] metathesize imines catalytically we have established that this approach can be used to make C═N bonds.[2] In this paper we present evidence that the imine metathesis is mediated by metal imides and we discuss the mechanistic implications of a series of stoichiometric ═NR transfer reactions. Ultimately these studies will enable the exploitation of imine substrates for living polymer synthesis by ring-opening metathesis polymerization (ROMP),[3] condensation polymer synthesis by acyclic diene metathesis (ADMET),[4,5] and small molecule synthesis by ring-closing metathesis (RCM).[6,7]

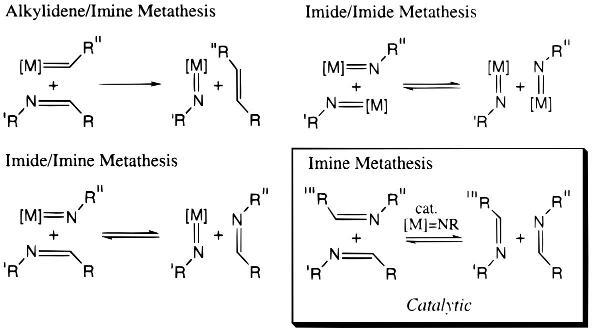

Figure 1. Four classes of ═NR transfer by metathesis

To understand the catalytic metathesis of imines, we have found it essential to concurrently examine several classes of ═NR transfer reactions within the same metal/ligand framework. The selected class of compounds, which can be generalized as a molybdenum(VI) system with two multiply bonded ligands and two singly bonded ancillary ligands, includes not only bis(imide) complexes, but also the well-known Schrock-type olefin metathesis catalysts of the general formula $(RO)_2Mo({=}NAr)({=}CHR')$.[1] Within this framework, we consider four reactions: three stoichiometric and one catalytic (Figure 1). The stoichiometric reactions are alkylidene/imine, imide/imine, and imide/imide metathesis, and the catalytic reaction is imine/imine metathesis (henceforth referred to simply as imine metathesis). Alkylidene/imine metathesis is a Wittig-like reaction of an imine with an alkylidene to give a metal imide and an olefin as products. Imide/imine metathesis is the stoichiometric metathesis of a metal imide with a single imine. A regiospecific reaction of this type that favors M═N bond formation will produce a new metal imide and a new imine. Imide/imide metathesis is a reaction in which the ═NR groups between metal centers are exchanged. Finally, catalytic imine metathesis, which is analogous to olefin metathesis, is the catalytic reaction of two different imines to give a statistical mixture of all possible ═NR exchange products. Although this final reaction differs from the stoichiometric ones, in that the imine substrates do not react directly with each other, it is useful to consider them

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(1) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875−3886.

(2) Portions of this work have appeared in a preliminary form. (a) Cantrell, G. K.; Meyer, T. Y. *J. Chem. Soc., Chem. Commun.* **1997**, 1551−1552. (b) Cantrell, G. K.; Meyer, T. Y. *Organometallics* **1997**, *16*, 5381−5383.

(3) For reviews of olefin metathesis see: (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (c) Amass, A. J. In *New Methods of Polymer Synthesis*; Ebdon, J. R., Ed.; Chapman and Hall: New York, 1991; p 76.

(4) Lindmark-Hamberg, M.; Wagener, K. B. *Macromolecules* **1987**, *20*, 2949−2951.

(5) For a leading reference see: Wolfe, P. S.; Gómez, F. J.; Wagener, K. B. *Macromolecules* **1997**, *30*, 714−717.

(6) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5426−5427.

(7) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324−7325.

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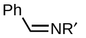
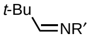
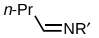
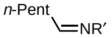
Table 1. Imine Designations for R(H)C═NR′ Comprise a Roman Numeral Portion That Specifies the C-Substituent and a Standard Group Abbreviation That Identifies the N-Substituent

	R′ =				
	n-Pr	Bn	*t*-Bu	Ph	Ar[a]
 **I**	**I-Pr**		**I-Bu**	**I-Ph**	**I-Ar**
 **II**	**II-Pr**		**II-Bu**	**II-Ph**	**II-Ar**
 **III**	**III-Pr**	**III-Bn**			
 **IV**	**IV-Pr**		**IV-Bu**		

[a] Ar = 2,6-diisopropylphenyl.

together since the overall metathetical transformation of reagents to products parallels that of the stoichiometric reactions.

Prior to our work only a few, isolated examples of these four classes of metatheses were known. Alkylidene/imine metathesis was first reported by Schrock et al. for a series of tantalum alkylidene complexes.[8] Both imide/imine and imine metatheses have been described by Bergman and co-workers for $Cp^*_2Zr({=}N\text{-}t\text{-}Bu)(THF)$. This zirconium imide complex reacts with imines to form diazametallacycles that undergo further metathetical exchange with external imines.[9,10] Although catalytic and relevant to our studies, the tendency of the zirconium imide products to dimerize decreases the practical utility of the system. All other examples of metathetical reactions involving a C═N bond involve the more activated substrates, isocyanates[11] and carbodiimides.[12,13] Imide/imide metathesis was originally documented for molybdenum bis(imide) complexes by Gibson *et al.*[14,15]

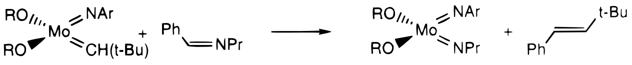
In this report we endeavor to combine these important precedents with our studies on reactions of complexes of the general formula $X_2Mo({=}Y)_2$ with imines to form a comprehensive picture of the molybdenum-imide-mediated metathesis of imines.

Results

Throughout the course of our studies, several imines were used and produced. To avoid the ambiguity that might arise by assigning arbitrary compound numbers to each imine, we have adopted a labeling system that emphasizes the ═NR′ group that is transferred. Each R(H)C═ group is given a Roman numeral designation, while each ═NR′ group is labeled as its R′ substituent. Thus, imines **II-Pr** and **II-Bu** have different ═NR′ groups (*n*-Pr vs *t*-Bu) but share a common carbon substituent. The designations are summarized in Table 1.

Alkylidene/Imine Metathesis. Since the imide metathesis catalysts that we are using are closely related to the Schrock-type olefin metathesis catalysts[1] of the general formula $(RO)_2Mo({=}CHR')({=}NAr)$ (Ar = 2,6-diisopropylphenyl in all cases; **1a**, R = $C(CF_3)_2CH_3$, R′ = *t*-Bu; **1b**, R = $C(CF_3)(CH_3)_2$, R′ = *t*-Bu; **1c**, R = *t*-Bu, R′ = $C(Ph)(CH_3)_2$)), the study of their reactions with imines provides a natural bridge between ═CR and ═NR transfer. Alkylidene/imine exchange would be expected to be facile since an analogous exchange has been reported with aldehydes.[16] We have studied this class of reactions and examined the role of ancillary ligands and imine substrates.

Scheme 1



1a R = $C(CF_3)_2CH_3$
1b R = $C(CF_3)(CH_3)_2$
Ar-2,6-diisopropylphenyl

I-Pr

2a R = $C(CF_3)_2CH_3$
2b R = $C(CF_3)(CH_3)_2$

The reaction of alkylidene complex **1a** with imine **I-Pr** (see Table 1 for imine designations) to give the alkylidene/imine exchange product *trans*-Ph(H)C═C(H)(*t*-Bu) is representative of this class and will be described in detail (Scheme 1). Two doublets associated with the olefin product at δ 6.34 and 6.20 were observed by ^1H NMR spectroscopy after 4 h when complex **1a** was heated at 60 °C in C_6D_6 with 11 equiv of imine **I-Pr**. An excess of imine was necessary to inhibit bimolecular decomposition of **1a**, a reaction that has previously been observed by Schrock and co-workers.[1] As the reaction proceeded, growth of product olefin resonances was accompanied by a reduction in intensity of the alkylidene resonance of **1a** at δ 12.05. After 20 h all of the alkylidene had been consumed. The identity of the olefin was confirmed by GC/MS analysis of the reaction mixture. By comparing the intensities of both reactant and product resonances to an internal standard, we verified that >90% of the alkylidene was converted to the product olefin.

Reaction of complex **1b** with **I-Pr** also gave the expected exchange products, although the rate was significantly slower (Scheme 1). After 20 h at 60 °C, the reaction of alkylidene **1b** with 7−10 equivalents of imine **I-Pr** was less than 10% complete. An additional 7 d at 60−80 °C was necessary to consume all of alkylidene **1b.** A significant amount of the bimolecular decomposition product, (*t*-Bu)HC═CH(*t*-Bu), was also produced. The nonfluorinated derivative **1c** did not react with **I-Pr**.

Of the imines surveyed, **I-Pr, III-Pr**, **III-Bn**, and **IV-Pr** were found to react at room temperature with **1a** over 4−5 d to give the expected products (summarized in Table 2). The olefins produced in the C-alkyl imine reactions (imine classes **III** and **IV**) were identified by their distinctive ^1H NMR signatures, a doublet and doublet of triplets in the δ 5−6 region due to the olefinic protons, and GC/MS analysis of the reaction mixtures. Imine **IV-Bu** also underwent alkylidene/imine metathesis with **1a** to give the expected olefin product. In this case, however, the rate was significantly slower (9 d at 80 °C) and the products were found to decompose under the reaction conditions. All olefin product resonances exhibited trans couplings. Imines **I-Bu**, **I-Ph**, and **II-Ph** did not react with **1a** even after 1 week at 60−80 °C. No indication of a competing reaction of the imine substrate with the ancillary aryl imide ligand was observed in any of the reactions described above.

Evidence for pre-coordination of the imine substrate to **1a** prior to metathesis was observed only for imines **III-Bn**, **III-Pr**, and **IV-Pr**. For example, when **1a** was treated with **III-Bn** the original alkylidene resonance at δ 12.1 decreased as new resonances at δ 13.2 and 13.6 appeared. An accompanying downfield shift in the sp^2 C−H imine resonance, from δ 7.28

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[8] (a) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7808−7809. (b) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077−81. (c) Turner, H. W.; Fellmann, J. D.; Rocklage, S.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7809−7811.

[9] Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 2669−2670.

[10] Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 974−85.

[11] Green, M. L. H.; Hogarth, G.; Konidaris, P. C.; Mountford, P. *J. Organomet. Chem.* **1990**, *394*, C9−C15.

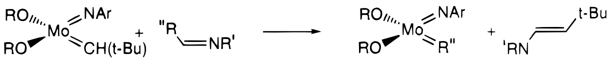
[12] Meisel, I.; Hertel, G.; Weiss, K. *J. Mol. Catal.* **1986**, *36*, 159−162.

[13] Birdwhistell, K. R.; Gross, R.; Harris, S.; Toporek, S. presented at the *203rd National Meeting of the American Chemical Society*; 1993; INOR O152.

[14] Jolly, M.; Mitchell, J. P.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 1331−1332.

[15] Bell, A.; Clegg, W.; Dyer, P. W.; Elsegood, M. R. J.; Gibson, V. C.; Marshall, E. L. *J. Chem. Soc., Chem. Commun.* **1994**, 2247−2248.

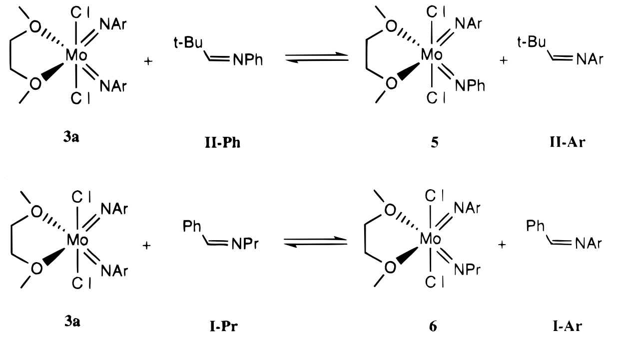
Table 2. Alkylidene/Imine Metathesis



alkylidene complex	imine							
	I-Pr	**I-Bu**	**I-Ph**	**II-Ph**	**III-Pr**	**III-Bn**	**IV-Pr**	**IV-Bu**
1a	R[a]	NR[b]	NR[b]	NR[b]	R/coord[c]	R/coord[c]	R/coord[c]	R/dec[d]
1b	R/slow[e]							
1c	NR							

[a] R = reaction. [b] NR = no reaction. [c] Precoordinates prior to reaction. [d] Products decompose. [e] Reacts significantly slower than **1a**.

Scheme 2



Ar-2,6-diisopropylphenyl

to 7.45, was also observed. Similar alkylidene shifts were observed in the presence of imines **III-Pr** and **IV-Pr**. The resonances associated with these putative intermediates decreased at the same rate as product olefin was produced.

Imide/Imine Metathesis. Bis(imides) of the type (DME)-$Cl_2Mo({=}NR)_2$ (**3a**, R = 2,6-diisopropylphenyl; **4**, R = *t*-Bu) react metathetically with imines to give a mixed bis(imide) and a new imine. This exchange is more relevant to catalytic imine metathesis than alkylidene/imine exchange because the nature of the active site is not changed; it remains an imide and could, therefore, be part of the cycle. A representative reaction of this type will be described in detail. Treatment of bis(imide) **3a** with 0.8 equiv of imine **II-Ph** in C_6D_6 at 100 °C yielded metathesis products **II-Ar** and **5** as observed by ^1H NMR spectroscopy (Scheme 2). After 18 d the ratio of **II-Ph** and **II-Ar** was ca. 1:1. ^1H NMR data for a reaction of this type are shown in Figure 2. The identity of **II-Ar** was confirmed by GC/MS analysis of the reaction mixture and by comparison of the ^1H NMR spectrum with that of an authentic sample. The identity of the mixed bis(imide) product **5** was confirmed by comparison of the ^1H NMR spectrum with that of an independently prepared sample (prepared by reaction of **3a** with phenyl isocyanate).[2a]

Complex **3a** was then treated with an excess of imine since the slow rate of this nearly stoichiometric experiment made the determination of an equilibrium point difficult. The reaction of **3a** with 12 equiv of **II-Ph** at 85 °C reached equilibrium, producing 1.4 equivalents of product imine **II-Ar**, after 8 days. If each imide ligand is assumed to react independently, a K_{eq} of 1.1 ± 0.2 can be calculated for this process. Inversion of the stoichiometry, 9 equiv of **3a** to 1 equiv of imine **II-Ph**, slowed the reaction to the extent that only a trace of product imine **II-Ar** was observed after 8 days at 85 °C. Bis(arylimide) **3a** also reacted metathetically with imine **I-Pr** (Scheme 2).

Bis(*tert*-butylimide) **4** reacted with imines **II-Ph** and **I-Pr** at a faster rate than bis(arylimide) **3a** (Scheme 3). To qualitatively determine relative reaction rates of complexes **3a** and **4** each catalyst was treated in parallel experiments with 14 equiv of imine **I-Pr**. The reactions were monitored by ^1H NMR

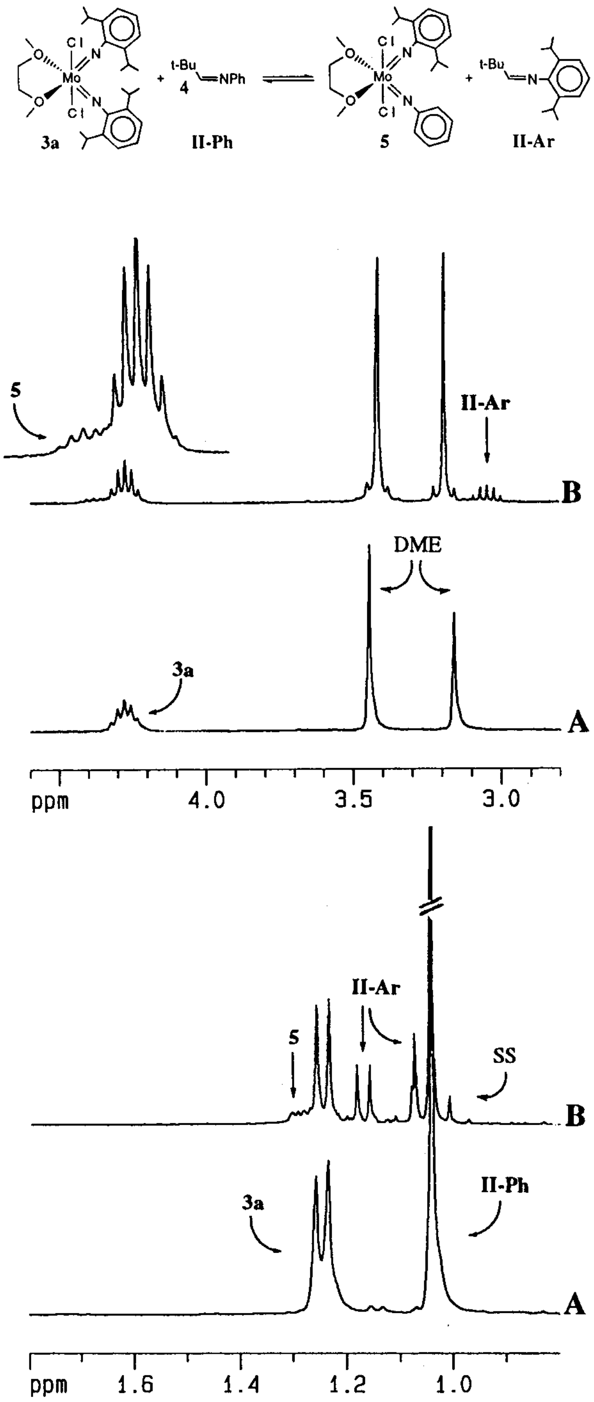


Figure 2. Isopropyl and *tert*-butyl region of the ^1H NMR spectra in C_6D_6 of an in situ reaction of bis(imide) **3a** with 4 equiv of **II-Ph.** (A) immediately after mixing and (B) after 3 d at 85 °C. Approximately 10% of the imine has been consumed. Spinning sidebands (ss) are visible in spectrum B.

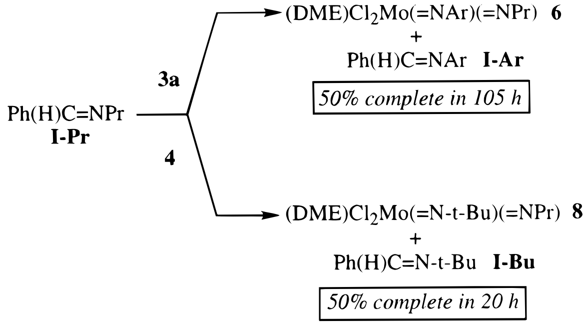
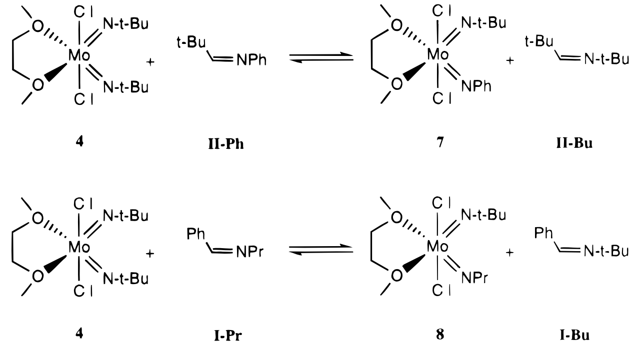


Figure 3. Relative rates of reaction for bis(imides) **3** and **4.**

Scheme 3



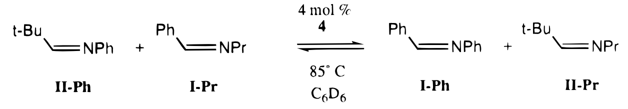
spectroscopy until 0.5 equiv of product imine, **I-Ar** or **I-Bu**, respectively, was produced. Bis(imide) **4** required only 20 h at 85 °C while **3a** required ∼4 days to reach the same point (Figure 3).

It is important to note that, in general, the reaction mixtures containing **3a** and **4** were stable under the reaction conditions employed and no significant concentration of any species other than the reagents and products was present. In particular, no resonances were observed that would be consistent with the presence of olefins, diazametallacycles, or imines coordinated to the metal center. Also significant is the fact that, without reagents present, the bis(imide) catalysts **3a** and **4** were stable at 100 °C in C_6D_6 for >2 weeks. In the presence of imines, decomposition to form insoluble materials was observed in the reaction mixtures only after prolonged periods of heating (>10 days at 85 °C).

The DME ligand is somewhat labile; addition of DME to either **3a** or **4** resulted in broadening and coalescing of the free and bound DME resonances in the ^1H NMR spectrum. In reaction mixtures of bis(imide) **3a** with imines, however, no broadening and only minor changes in chemical shift were observed. In the case of bis(imide) **4**, some differences in line width and chemical shift were noted although free DME was not observed.

To investigate electronic effects of the ancillary ligands, several bis(imide) bis(alkoxide) complexes, $(RO)_2Mo(=NAr)_2$ (**3b**, R = $C(CF_3)_2CH_3$; **3c**, R = *t*-Bu; **3d**, R = 2,6-diisopropylphenyl), were prepared. Complexes **3b** and **3d** exhibited no reaction with imine **I-Pr**, while complex **3c**, as reported previously, does react to give imine **I-Ar**.[2a] This latter reaction proceeds through an initial decomposition of **3c** that involves the *tert*-butoxide ligands and is not, therefore, relevant to the current discussion. The details of this reaction pathway will be described elsewhere.[17] The fact that the fluoroalkoxide bis(imide) **3b** showed no reactivity toward imines (nor decomposition), even though precedent would predict that it should be the most activated in the series, confirms the anomalous nature of the behavior of **3c**.

Scheme 4



Catalytic Imine Metathesis. Both of the bis(imide) complexes that underwent imide/imine metathesis were also found to be imine metathesis catalysts. For example, when imines **I-Pr** and **II-Ph** were combined with 4 mol % of bis(*tert*-butylimide) **4**, at 85 °C in C_6D_6, the metathesis products, imines **I-Ph** and **II-Pr**, were produced (Scheme 4). After 22 h, equilibrium was achieved and the imines were present in a 1:1:1:1 ratio. The imide/imine metathesis products, **I-Bu** and **II-Bu**, were also identified in the reaction mixture. Bis(arylimide) **3a** also catalyzed the metathesis of **I-Pr** and **II-Ph**. However, the reaction rate was much slower, requiring 4 days at 85 °C to reach equilibrium. The alkoxy-substituted bis(imide) complexes, **3b**−**d**, did not catalyze the metathesis of imines, nor did the alkylidene complexes **1a** or **1b**. The relative catalytic activity of the mixed bis(imide) products **6** and **8** was also investigated by generating them in situ from **3a** and **4**. Since the reactions to generate these species require a significant amount of time to reach equilibrium, we employed 50/50 mixtures of the homo- and mixed-bis(imide) complexes. Imines **I-Pr** and **II-Ph** were added to these mixtures (**3a** + **6** or **4** + **8**, prepared as in relative rate studies; see Figure 3). In each case imine metathesis with the catalyst mixtures was much faster than with the simple homo bis(imides). Catalysts **3a** + **6** equilibrated imines **I-Pr** and **II-Ph** in 10 h, and catalysts **4** + **8** required only 5 h.

In control experiments the uncatalyzed and acid-catalyzed reactions of imines **I-Pr** and **II-Ph** were studied for comparison to the metal-mediated reactions. We found that in C_6D_6, under reaction conditions designed to mimic those used for the metal-mediated reaction, these imines undergo Brønsted[18] and Lewis acid (ZnI_2 and $TiCl_4$) catalyzed exchange. HCl-catalyzed exchange reached equilibrium in days at room temperature; ZnI_2 required days at 60 °C; and $TiCl_4$ required hours at 80 °C. Without either molybdenum or acid catalyst only a small amount of exchange (<5%) was observed when the imines were heated at 80 °C for 2 weeks.

Imide/Imide Metathesis. Not surprisingly, we observed concurrent imide/imide exchange in the reaction mixtures for both imide/imine and alkylidene/imine metatheses. This type of reaction was originally reported for alkoxide derivatives of **3** and **4** by Gibson *et al.*[14] To verify that this comproportionation was also possible for the DME-ligated dichloride complexes **3a** and **4**, equimolar amounts of these two were mixed. Exchange of the =NR groups was observed within 3 h at 70 °C (Scheme 5). Equilibrium was attained within 24 h. The equilibrium constant was ca. 12 at 25 °C, which is similar in magnitude to the $K_{60\,°C} = 25$ reported by Gibson and co-workers for alkoxide analogues. To complete the series, the metathesis of the alkoxide complex $((CF_3)_2CH_3CO)_2Mo(=NAr)_2$ (**3b**) with $(DME)Cl_2Mo(=N\text{-}t\text{-}Bu)_2$ (**4**) was also examined**.** As expected, the reaction proceeded to an equilibrium mixture of the imide exchange products.[19]

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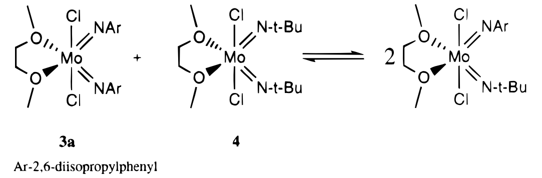
(16) Bazan, G.; Schrock, R. R.; O'Regan, M. *Organometallics* **1991**, *10*, 1062−1067.

(17) Yahner, A. C.; Cantrell, G. K.; Meyer, T. Y. Manuscript in preparation.

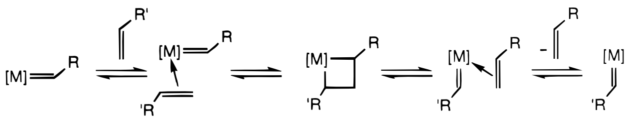
(18) Toth, G.; Pinter, I.; Messmer, A. *Tetrahedron Lett.* **1974**, *9*, 735−38.

(19) Cl-alkoxide exchange is also possible. We cannot rule out this pathway based on the data from this single experiment.

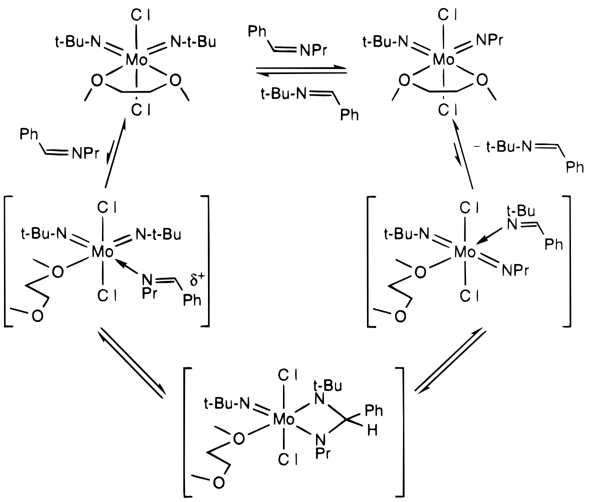
Scheme 5



Scheme 6



Scheme 7



Discussion

Mechanism. The olefin metathesis reaction provides a reasonable starting point for thinking about imine metathesis. Based on the substantial body of research in this area,[3,20] it is generally accepted that the olefin metathesis reaction proceeds via initial coordination of olefin, followed by a [2+2] addition. The resulting metallacycle may then cleave either degeneratively or productively to give the new alkylidene and olefin products (Scheme 6).

An analogous mechanism can be proposed for heteroolefin metathesis. The imide/imine exchange of bis(imide) **4** will be used for illustration. Imine coordination, accompanied by partial DME dissociation, is followed by formation of a metallacycle. Productive cleavage of the metallacycle then gives the imide and imine products. DME can then recoordinate to give the resting state of the imide complexes (Scheme 7). The mechanism for alkylidene/imine metathesis would be essentially the same, except for the steps involving DME.

By examining the results obtained from the entire set of ═NR transfer reactions, we can evaluate the applicability of this mechanism to our reaction. In the first step, DME dissociation is postulated. Although no direct ^{1}H NMR evidence supports this supposition, the examination of a space-filling model of the closely related mixed bis(imide) (DME)Cl_2Mo(═N-*t*-Bu)(═NAr), which was prepared and structurally characterized by Gibson and co-workers,[21] shows little space for an incoming ligand. We cannot rule out a purely associative pathway, though the lack of space and the competition of imide lone pairs for the empty orbital reduce its probability.[22]

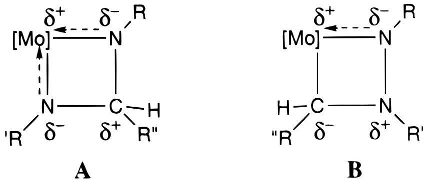


Figure 4. Possible intermediate metallacycles for imide/imine metathesis.

In the first step imine coordination is also postulated. Although we do not observe this in the imide/imine metathesis reaction, there is clear evidence for precoordination prior to alkylidene/imine metathesis by complex **1a**. The NMR spectra of the observed imine adducts are qualitatively similar to those reported for coordination of PMe_3 to this type of complex.[23] The fact that precoordination was not observed in the bis(imide) systems can be explained in terms of effective competition by chelating DME. If DME is slow to disassociate and the imine does not act as a good trap for the unsaturated metal center, then the imine-coordinated intermediate would not be observable. We do not have sufficient data to comment on the exact order of imine coordination and DME dissociation.

After coordination, the olefin analogy would predict a [2+2] addition to give a diazametallacycle. Although we do not directly observe such a product, the regiospecificity of the reaction can be explained in terms of this type of intermediate. Alkylidene/imine and imide/imine metatheses proceed to give exclusively the imide product. This regiospecificity is consistent with prior observations in related systems[9] and is not surprising given the electrophilic nature of these early transition metal complexes. If we assume that some sort of metallacyclic species lies on the reaction coordinate for this reaction we can explain this preference in terms of intermediate/transition state stabilization. A 2,4-diazametallacycle (**A**) would be able to stabilize the expected distribution of partial charges more effectively than would a 2,3-diazametallacycle (**B**) (Figure 4). Similar arguments have been offered by Crowe and co-workers to explain the selectivity observed in the cross metathesis of polar acyclic olefins.[24] The fact that no metallacycle is observed in the reaction mixture does not contradict this mechanism since in olefin metathesis by complexes **1a**−**c** metallacyclobutanes are rarely observed.[1] It is reasonable to postulate that bis(imide) complexes would exhibit a similar preference for an unsaturated resting state. Since the final steps of the reaction are simply the reverse of the first two steps, they will not be discussed separately.

We also note that the steric requirements of the imide/imine reaction are consistent with the direct reaction of the imide and imine groups to form a metallacycle. The 5-fold difference in the time required for bis(imide) complexes **3a** and **4** to reach equilibrium in an imide/imine exchange is most probably due to the variation in size of the two imide nitrogen substituents. This type of steric dependence would not be expected if the mechanism involved disassociation of a ═NR unit from the metal center as the first, rate-determining step.

To definitively determine the mechanism it would be desirable to undertake detailed kinetic studies. Unfortunately, kinetics

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[20] Hérisson, J.-L.; Chauvin, Y. *Macromol. Chem.* **1970**, *141*, 161.

[21] Copley, R. C. B.; Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Marshall, E. L.; Wang, W.; Whittle, B. *Polyhedron* **1996**, *15*, 3001−3008.

[22] A coordination site could also be generated by Cl^- dissociation. Experiments to date do not distinguish between Cl and DME dissociation.

[23] Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832−1843.

[24] Crowe, W. E.; Goldberg, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 5162−5163.

are challenging with this bis(imide) system due to the presence of a second reactive imide functionality. Upon activation of both sites the metal is partitioned among three very similar species in solution; it is very difficult to quantify them due to the overlap of ^{1}H NMR resonances. More problematic for the interpretation of kinetic results is the fact that bimolecular imide/imide exchange, which equilibrates the mixed and homo bis(imides), is on a time scale similar to that of the imide/imine metathesis reaction. This disproportionation/comproportionation reaction also precludes the isolation of any of the mixed bis(imide) products from the reaction mixtures and dictates that these reactions be monitored *in situ.*

Despite the difficulties in acquiring accurate kinetic data, we have qualitatively determined that the rate of alkylidene/imine and imide/imine metathesis decreases with increasing electron-donating character of the ancillary alkoxide ligands. The fact that the same activity order (**1a** > **1b** > **1c**) was reported by Schrock and co-workers for olefin metathesis with these complexes is further evidence for some correlation of the olefin and imine mechanisms.[1] There is a significant difference in the ancillary ligand dependence, however. The alkylidene/imine exchange does not occur for **1c** and imide/imine exchange will not proceed for any of the three; only complexes with the least electron-donating ligands, chlorines, underwent metathesis. The deactivating effect of the alkoxide ligands explains the inertness of the "ancillary" imide group of the alkylidene complexes **1a**−**c** toward imide/imine exchange.

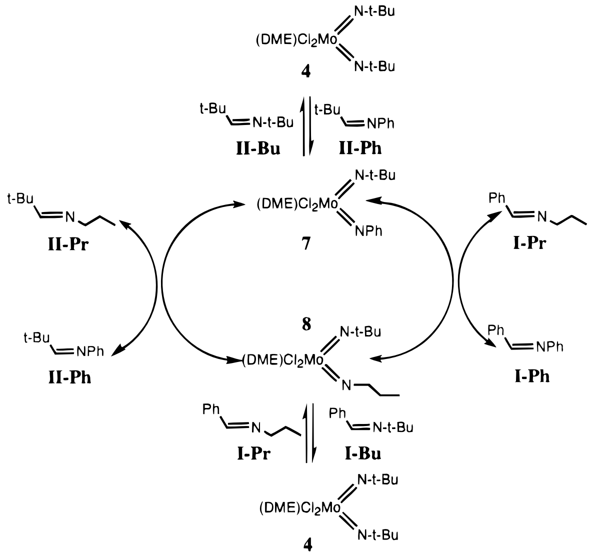
The preference for a more electrophilic center raises serious questions about the validity of adopting the olefin metathesis mechanism to explain imide/imine exchange. Although precoordination and metallacycle intermediates appear viable, there may very well be significant differences in their nature and formation. An imine, by virtue of its lone pair and its inherent polarity, is quite different from an olefin and would be expected to exhibit differences in coordination mode and in reaction pathway. There may, for example, be significantly less synchronicity in the formation of the metallacycle than is apparently the case for alkylidene/olefin metathesis. The data collected to date on these systems do not yet allow us to make these distinctions nor do they rule out alternate mechanisms involving other low-concentration intermediates or catalysts.

Catalysis. Based on our understanding of the imide/imine metathesis, we have proposed a catalytic cycle for imine metathesis (Scheme 8). In an initiation step, the initial bis(imide) complex **4** undergoes imide/imine metathesis with **II-Ph** and **I-Pr** to generate one of the catalytically active species, **7** or **8**. The mixed bis(imide) complexes **7** and **8** then react with the complementary imine in the propagation step to give the observed products. All reactions are reversible such that an equilibrium mixture of all possible imine combinations is expected. Also, the second site must be assumed to participate in the cycle to some degree although for the sake of clarity both the second site reaction and imide/imide metathesis have been omitted from the cycle.

The accuracy of our proposed catalytic cycle is supported by experimental observations. The most important of these is the presence of initiation products, **I-Bu** and **II-Bu** in Scheme 8, in the reaction mixtures. Since these imines can only arise through imide/imine metathesis, and since the initiation studies show that they are the *slowest* of the imide/imine combinations, we can be confident that the proposed catalytic pathway is operating in the reaction mixture.

The proposed initiation step in this pathway is also consistent with our data. The times required to equilibrate identical solutions of two imines with catalysts **3a** and **4** were reduced by factors of 1/10 and 1/4, respectively, when the catalysts were preinitiated by reaction with an imine with a smaller N substituent. In the reaction depicted in Scheme 8, for example, the reaction time decreased when **4** was partly converted to **7** prior to the addition of the other imine. Moreover, the decrease in reaction times concurs qualitatively with the relative decreases in N-substituent size; the change from 2,6-diisopropylphenyl to *n*-propyl (105 h to 10 h) is more dramatic than the change from *tert*-butyl to *n*-propyl (22 h to 5 h).

Scheme 8



One reaction that does not appear to affect the chemistry significantly is dimerization of the catalyst. Although it is likely that such dimers are present, both Gibson and Chisholm have concluded that, despite the imide/imide exchange, this class of complexes are primarily monomeric in solution.[14,25,26] Our observations concur with theirs. The lack of an irreversible dimerization is significant since, as was observed in the zirconacene imide system reported by Bergman and co-workers,[9,10] it is one of the most likely termination steps for an unsaturated imide catalyst. The bis(imide) catalysts described in this paper have two forms of steric protection, chelating DME and the other imide substituent. We have already discussed the role of DME, but the steric protection offered by the second imide is more subtle since this group is also an active catalytic site. We speculate that after initial activation of imide 1 on a metal center, it becomes the active site while imide 2, which is sterically less accessible, becomes ancillary. Only at long reaction times will significant conversion of imide 2 to an active site occur. Until this second exchange happens, the catalyst enjoys a exceptionally sterically protected environment. Unfortunately, the same steric protection may also contribute to the low overall rate of metathesis.

A key question arises when thinking about catalytic imine metathesis: How do we know that it is metal mediated? Since we know that metathesis is catalyzed by conventional acids, it could be hypothesized that adventitious acid is responsible for the observed reactions. Both the results of the initiation studies, which show the presence of imide/imine metathesis products, and the reproducibility of reaction times in independently prepared samples are inconsistent with this hypothesis. It is

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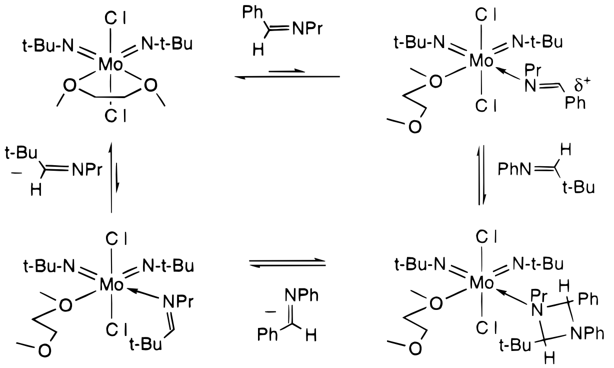
(25) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C.; Ratermann, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 1305−1306.

(26) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Raterman, A. L. *Inorg. Chem.* **1982**, *21*, 978−982.

Scheme 9



clear that the reaction does involve the metal center and is not due simply to external acid.

There does exist another potential Lewis acid-catalyzed pathway that cannot be as easily dismissed, however. In this other process, it is assumed that the molybdenum complex itself is the Lewis acid, activating the coordinated imine for nucleophilic attack by an external imine or trace amine (Scheme 9). Interestingly, imide steric bulk and alkoxide ancillary ligands would be expected to affect this pathway in a qualitative fashion similar to that of our proposed catalytic pathway. Which pathway the reaction follows, metal-mediated imide/imine metathesis or Lewis acid-assisted metathesis, should depend simply on the rate of internal imide vs external imine attack on the coordinated imine. Although at this point the data are insufficient to rule out some participation of this Lewis acid pathway, it is clear from the evidence presented above that our proposed imide-mediated catalytic pathway is competitive, if not dominant. Moreover, the apparently low disassociation constant for DME would be expected to favor the intramolecular imide attack over external imine attack. Future studies with cyclic imines should enable us to differentiate between the two pathways since the Lewis acid pathway would produce cyclic oligomers and would not be "living" in that there would be more chains than metal catalyst initiators.

═NR Group Transfer. In the course of these studies the relationships between the four types of ═NR transfer reactions have been established. For example, although imines react with both the molybdenum alkylidene and molybdenum imide functionality, the reactions have different ancillary ligand requirements. The imide/imine exchange apparently requires a more electrophilic metal center (only proceeds with Cl ligands) than alkylidene/imine metathesis. Earlier calculations by Rappé and Goddard on oxo/olefin metathesis suggest that the more electrophilic center may be necessary to stabilize the metallacyclic transition state.[27] Although that may be an important factor, we suggest that the electrophilicity is also necessary to activate the coordinated polar imine substrate and that this activation is likely to be important based on the known Lewis acid-catalyzed organic chemistry of heteroolefins.

We are also intrigued by the relationship of imine to olefin metathesis. In particular, the relatively slow speed of the imide/imine reaction compared with the alkylidene/olefin reaction is of interest if imine metathesis is to be used synthetically. Although arguments about the relative ground-state stabilization of molybdenum(VI) imides vs alkylidenes could be made and are probably relevant, we cannot judge the real reaction rate until we can factor out or remove competition from DME. More work is necessary before the relationship between ═NR transfer and ═CR transfer by metathesis will be understood.

Conclusion

The metathesis reaction can now be used to form C═N bonds catalytically. We have discovered that molybdenum bis(imide) complexes of the type $(DME)Cl_2Mo({=}NR)_2$ metathesize imines catalytically, but do not suffer from termination by irreversible dimerization. We can, therefore, begin to pursue the potential applications of this reaction to the synthesis of polymeric materials and small molecules. In addition, by studying alkylidene/imine, imide/imine, imine, and imide/imide metatheses, we have discovered that the catalytic reaction is part of a general class of reactions that involve the transfer of the ═NR group.

Experimental Section

General Methods. Unless otherwise noted, the following methods were utilized for all experiments described in this report. Manipulations were carried out under an inert nitrogen atmosphere in a Vacuum Atmospheres drybox or with standard Schlenk or vacuum line techniques. Reagent grade ether and toluene were distilled from sodium benzophenone ketyl under nitrogen. Reagent grade hexane was washed with sulfuric acid, passed through a column of activated alumina, and distilled from sodium benzophenone ketyl under nitrogen. Reagents were purified by standard methods unless otherwise noted. Benzene-d_6 was distilled from sodium benzophenone ketyl and stored in a glass vessel equipped with a Teflon stopcock. $(RO)_2Mo({=}CHR')({=}NAr)$[1] (Ar = 2,6-diisopropylphenyl; **1a**, R = $C(CF_3)_2CH_3$, R′ = *t*-Bu; **1b**, R = $C(CF_3)(CH_3)_2$, R′ = *t*-Bu), $(DME)Cl_2Mo({=}NR)_2$[1] (**3a**, R = 2,6-diisopropylphenyl; **4**, R = *t*-Bu), and $(RO)_2Mo({=}NAr)_2$[28] (**3b**, R = $C(CF_3)_2CH_3$; **3c**, R = *t*-Bu; **3d**, R = 2,6-diisopropylphenyl[2a]) were prepared as described in the literature. $(RO)_2Mo({=}CHR')({=}NAr)$ (Ar = 2,6-diisopropylphenyl; **1c**, R = *t*-Bu; R′ = $C(Ph)(CH_3)_2$)) was purchased from Strem Chemicals. ^1H NMR spectra were obtained on a Bruker AF 300 MHz spectrometer at 300 MHz. All spectra were obtained in benzene-d_6 at 25 °C. Mass spectroscopic data were obtained on a Hewlet Packard Series 5890 GC/5971A MS.

NMR Experiments. Reactions were monitored by NMR spectroscopy since equilibrium mixtures of starting materials and products were obtained in all cases. Isolation of organometallic products was not possible. NMR assignments are reported for significant species although phenyl region overlap prevents complete assignments in many cases. Hexamethylbenzene was used as an internal standard. With the exception of a few mixed bis(imide) complexes all species were identified by a comparison with authentic samples.

Typical Experimental Procedure for Alkylidene/Imine Metathesis. Reaction of $(CF_3(CH_3)_2CO)_2Mo({=}CH(t\text{-}Bu))({=}NAr)$ with PhHC═NPr. Complex **1b** (0.009 g, 0.015 mmol, 1 equiv) was dissolved in ca. 0.5 mL of C_6D_6 in an NMR tube equipped with a Teflon stopcock. Hexamethylbenzene in C_6D_6 and imine **I-Pr** (ca. 9 equiv) were added. The sample was heated for 4 d at 60 °C, 1 d at 70 °C, and 2 d at 85 °C. The progress of the reaction was monitored by ^1H NMR spectroscopy. ^1H NMR (C_6D_6) of *trans*-(Ph)HC═CH(*t*-Bu) (unisolated) δ 6.34 (d, 1, (Ph)*H*C, J_{HH} = 15.6 Hz), 6.19 (d, 1, C*H*(*t*-Bu), J_{HH} = 16.3 Hz), 1.03 (s, 9, CH(*t-Bu*)). The resonances for the phenyl group and for the mixed bis(imide) were not assignable in this case due to overlap with substrate and product resonances.

Typical Experimental Procedure for Imide/Imine Metathesis. Reaction of $(DME)Cl_2Mo({=}N\text{-}t\text{-}Bu)_2$ with (*t*-Bu)HC═NPh. Complex **4** (0.005 g, 0.012 mmol, 1 equiv) was dissolved in ca. 0.5 mL of C_6D_6 in an NMR tube equipped with a Teflon stopcock. Hexamethylbenzene in C_6D_6 and imine **II-Ph** (ca. 14 equiv) were added. The sample was maintained for 1 d at room temperature to verify the stoichiometry and stability of the reaction mixture. The sample was heated and maintained at 85 °C for 11 d. The progress of the reaction

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[27] Rappe, A. K.; Goddard, W. A., III, *J. Am. Chem. Soc.* **1982**, *104*, 448−456.

[28] Jolly, M.; Mitchell, J. P.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 1329−1330.

was monitored by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6) of *t*-BuN═CH(*t*-Bu) (unisolated) *δ* 7.41 (s, 1, C*H*(*t*-Bu), 1.15 (s, 9, *t*-BuN). The CH(*t-Bu*) resonance could not be assigned due to overlap with the *tert*-butyl resonance of **II-Ph**. ^{1}H NMR (C_6D_6) of Mo(NPh)(N-*t*-Bu)Cl_2(DME) (unisolated) *δ* 1.28 (s, 9, N-*t*-Bu), 3.35 (s, 6,*CH$_3$*OCH$_2$CH$_2$O*CH$_3$*), 3.24 (s, 4, CH$_3$O*CH$_2$CH$_2$*OCH$_3$). Phenyl resonances could not be definitively assigned due to the complexity of the spectrum in this region. DME resonances in the reaction mixture collapse to a very broad singlet at *δ* 3.25 by the end of the reaction.

Reaction of (DME)Cl$_2$Mo(═NAr)$_2$ with (*t*-Bu)HC═NPh. The experimental procedure was reported in ref 2a.

Typical Experimental Procedure for Imide/Imide Metathesis. Reaction of (DME)Cl$_2$Mo(NAr)$_2$ with (DME)Cl$_2$Mo(N-*t*-Bu)$_2$. Complexes **3a** (0.007 g, 0.017 mmol, 1 equiv) and **4** (0.010 g, 0.016 mmol, 1 equiv) were dissolved in ca. 0.5 mL of C_6D_6. Hexametheylbenzene in C_6D_6 was added as an internal standard. The sample was maintained for 15 h at room temperature to verify the stoichiometry and stability of the reaction mixture. The sample was heated and maintained at 70 °C for several weeks. The progress of the reaciton was monitored by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6) of (DME)Cl$_2$Mo(NAr)(N-*t*-Bu) (unisolated) *δ* 4.32 (sept, 2, C*H*Me$_2$, J_{HH} = 6.8 Hz), 3.41 (s, 6, *CH$_3$*OCH$_2$CH$_2$O*CH$_3$*), 3.19 (s, 4, CH$_3$O*CH$_2$CH$_2$*OCH$_3$), 1.42 (d, 12, CH*Me$_2$*, J_{HH} = 6.8 Hz), 1.26 (s, 9, N-*t*-Bu). Phenyl resonances could not be definitively assigned due to the complexity of the spectrum in this region. Resonances correspond to those reported by Copley and Gibson.[21]

Typical Experimental Procedure for Catalytic Imine Metathesis. Catalytic Metathesis of PhN═CH(*t*-Bu) and (*n*-Pr)N═CHPh with (DME)Cl$_2$Mo(═NAr)$_2$. Imines **I-Pr** (12 equiv) and **II-Ph** (12 equiv) were dissolved in ca. 0.75 mL of C_6D_6 in an NMR tube. Hexamethylbenzene (0.075 mL of a 0.5 M standard solution) and (DME)Cl$_2$Mo(═NAr)$_2$ (0.005 g, 0.008 mmol, 1 equiv) were added. The NMR tube was flame sealed. The sample was maintained for 48 h at room temperature to verify the stoichiometry and stability of the reaction mixture. The sample was then heated and maintained at 80−85 °C for 8 d. The progress of the reaction was monitored by ^{1}H NMR. ^{1}H NMR (C_6D_6) of imide/imine metathesis products: ArN═CHPh (unisolated) *δ* 8.0 (s, 1, C*H*Ph), 3.13 (sept, 2, C*H*Me$_2$, J_{HH} = 6.9 Hz), 1.16 (d, 12, CH*Me$_2$*, J_{HH} = 6.9 Hz); ArN═CH(*t*-Bu) (unisolated) *δ* 7.25 (s, 1, C*H*-*t*-Bu), 3.05 (sept, 2, C*H*Me$_2$, J_{HH} = 6.9 Hz), 1.17 (d, 12, CH*Me$_2$*, J_{HH} = 6.9 Hz). (Note that ArN═CH(*t*-Bu) is produced in smaller amounts than ArN═CHPh possibly due to differences in the rates of reaction of the starting material imines with the catalyst.) The aryl resonances could not be assigned due to overlapping resonances of the other products: ^{1}H NMR (C_6D_6) of imine metathesis products PhN═CHPh (unisolated) *δ* 8.12 (s, 1, C*H*Ph), 7.81 (m, 2, Ph), 7.0−7.18 (m, Ph); (*n*-Pr)N═CH(*t*-Bu) (unisolated) *δ* 7.33 (s, 1, C*H*(*t*-Bu), 3.26 (t, 2, N*CH$_2$*CH$_2$CH$_3$, J_{HH} = 6.9 Hz), 1.61 (m, 2, NCH$_2$*CH$_2$*CH$_3$), 0.86 (t, 3, NCH$_2$CH$_2$*CH$_3$*, J_{HH} = 7.5 Hz), 1.02 (s, 9, CH(*t-Bu*)).

Catalytic Metathesis of PhN═CH(*t*-Bu) and (*n*-Pr)-N═CHPh with (DME)Cl$_2$Mo(═N-*t*-Bu)$_2$. The experimental procedure was reported in ref 2b.

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