

Azaheteroalkene metathesis: reaction of imines with molybdenum(vi) bis(imide) complexes

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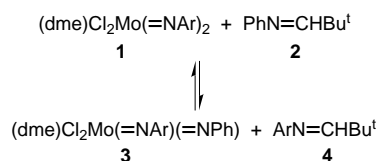
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Bis(imide) complexes $(dme)Cl_2Mo(=NR)_2$ ($R = Bu^t$, $C_6H_3Pr^i-2,6$) and $(Bu^tO)_2Mo(=NAr)_2$ ($Ar = C_6H_3Pr^i-2,6$) undergo imide/imine metathesis with $PhN=CH(Bu^t)$ or $(Pr^n)N=CHPh$.

Transition-metal-mediated reactions offer many potential advantages over traditional approaches to carbon–heteroatom bond formation including selectivity, mild reaction conditions, varied functional group tolerances, and increased reaction rates. A promising strategy for the development of these coupling reactions involves the extension of metal–alkylidene-mediated alkene metathesis, which is used extensively in polymer synthesis and increasingly in the preparation of natural products,^{1–3} to heteroalkenes. We are particularly interested in carbon–nitrogen bond formation through metal–imide-mediated imine metathesis.

Reports of catalytic metathesis of azaheteroalkenes are rare and no system of general utility has been described.^{4,5} Carbodiimides have been metathesized by $Cl_4Mo=NR^6$ and isocyanates by $[(\eta-C_5H_4Me)Mo(=NR)_2]_2$.⁷ Only one example exists, however, of the metathesis of the less activated, but more versatile imine substrates. The early transition-metal imide complex, $(\eta-C_5H_5)_2Zr(=NBu^t)(thf)$, reacted with *N*-phenylimines to give diazametallacycles that underwent further metathetical exchange with external imines, presumably *via* imide intermediates.^{8,9} Although this reagent is an imine metathesis catalyst, it suffers from significant limitations, the reaction is inhibited by high imine concentrations and the reagent is reported to undergo a competing dimerization that deactivates it towards further reaction. Herein, we identify a class of metal complexes that exhibit the key step of catalytic imine metathesis, imide/imine metathesis, without such substrate inhibition or terminal dimer formation.

Treatment of $(dme)Cl_2Mo(=NAr)_2$ ¹⁰ ($Ar = C_6H_3Pr^i-2,6$) **1**, with 0.8 equiv. of *tert*-butylanil **2**[†] in C_6D_6 at 100 °C produced metathesis product **4** over the course of several days as observed by ¹H NMR spectroscopy (Scheme 1). After 18 days the ratio of **2** to **4** was *ca.* 1 : 1.[‡] When the reaction was repeated with 12 equiv. of imine **2** to 1 equiv. of bis(imide) **1**, the reaction proceeded much more rapidly, producing 1.4 equiv. of imine **4** after 8 days at 85 °C.§ Inversion of the stoichiometry, 9 equiv. of **1** to 1 equiv. of imine **2**, slowed the reaction to the degree that only a trace of product imine **4** was observed after 8 days at 85 °C. Unambiguous identification of product imine **4** was achieved by comparison of the ¹H NMR spectrum with that of an authentic sample and by GC–MS analysis of the reaction mixture. Increasing the temperature results in a concomitant



Scheme 1

increase in rate; the optimum reaction conditions have not yet been determined.

These reactions proceeded cleanly. No evidence for pre-coordination or for metallacyclic intermediates was observed by ¹H NMR spectroscopy for any of the stoichiometric combinations;¶ nor were alkenes detected. Competing intermolecular imide/imide metathesis,¹¹ which in these systems equilibrates all bis(imide) complexes, prevented isolation and complete characterization of the mixed imide product $(dme)Cl_2Mo(=NAr)(=NPh)$ **3**. ¹H NMR resonances associated with **3** were, however, identified in the reaction mixture by comparison with those from a spectrum of an authentic sample.||,**

Imide/imine metathesis is remarkably general for this class of bis(imides). The reaction proceeds despite changes in substrate imine, imide-nitrogen substituent, or ancillary ligand (Table 1). Specifically, imides **1** and $(dme)Cl_2Mo(=NBu^t)_2$, **5**,¹⁰ react with imine **2**. Imides **1**, **5**, and $(Bu^tO)_2Mo(=NAr)_2$, **6**,¹² also react with *N*-propylbenzalimine **8**, to give the expected exchange products. Only the sterically crowded $(ArO)_2Mo(=NAr)_2$, **7**, is unreactive.†† The fact that imide/imine metathesis occurs in all but one of the examples investigated to date suggests that these catalysts can be ‘tuned’ by varying the ancillary ligands.

One goal of this work was to identify a catalyst that does not undergo significant termination reactions. Compelling evidence for a lack of such termination reactions in the systems we have described can be found by examining the ¹H NMR spectra; no significant amount of any species other than those described above was present. Specifically, we did not observe any stable

Table 1. Imide/imine metathesis

$$(dme)Cl_2Mo \begin{array}{l} \diagup NR^1 \\ \diagdown NR^1 \end{array} + \begin{array}{l} R^2 \\ \diagup \\ H \end{array} = NR^3 \rightleftharpoons \left[(dme)Cl_2Mo \begin{array}{l} \diagup NR^3 \\ \diagdown NR^1 \end{array} \right] + \begin{array}{l} R^2 \\ \diagup \\ H \end{array} = NR^1$$

Bis(imide)	Substrate imine	Product imine ^a
$(dme)Cl_2Mo(=NAr)_2$ 1	Bu^t H =NPh 2	Bu^t H =NAr
	Ph H =N-CH ₂ CH ₂ CH ₃ 8	Ph H =NAr
$(dme)Cl_2Mo(=NBu^t)_2$ 5	Bu^t H =NPh 2	Bu^t H =NBu ^t
	Ph H =N-CH ₂ CH ₂ CH ₃ 8	Ph H =NBu ^t
$(Bu^tO)_2Mo(=NAr)_2$ 6	Ph H =N-CH ₂ CH ₂ CH ₃ 8	Ph H =NAr
$(ArO)_2Mo(=NAr)_2$ 7	Ph H =N-CH ₂ CH ₂ CH ₃ 8	No reaction

^a Characterized by ¹H NMR spectroscopy and/or GC–MS analysis.

imide-bridged dimers, a particular concern since similar dimer formation limited the utility of $(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Zr}(=\text{NBu}^t)(\text{thf})$ as an imine metathesis catalyst.^{8,9} Previous workers, who have examined these molybdenum bis(imide) complexes for other applications, have also found them to be primarily monomeric in solution. In a particularly relevant and elegant study, Gibson and coworkers observed intermolecular imide/imide exchange of $(\text{Bu}^t\text{O})_2\text{Mo}(=\text{NBu}^t)_2$ with $(\text{Bu}^t\text{O})_2\text{Mo}(=\text{NAr})_2$.¹¹ Although the most likely mechanism for exchange would involve an imide-bridged dimer, no spectral evidence for a significant concentration of this intermediate could be found. Also germane is the observation by Chisholm *et al.* that an analogous bis(imide) dimer $[(\text{Bu}^t\text{O})_2\text{Mo}(=\text{NPh})(\mu\text{-NPh})]_2$,¹³ characterized by X-ray crystallography, exhibited a monomeric solution molecular mass.¹⁴ Based on our data and these reports we can conclude that, although imide-bridged dimers are likely to be present in our reaction mixture, they do not represent a termination step for imide/imine metathesis.

Although these preliminary studies do not provide a complete picture of the metathesis, the data do provide some insights into the mechanism. It is clear, for example, that the imine products do not arise from a pathway involving initial decomposition of the metal imide. In control experiments, catalysts **1** and **5** were observed to be stable for weeks at 100 °C in C_6D_6 . Moreover, integration of imide ^1H NMR resonances vs. an internal standard showed that there was very little diversion of metal-imide complexes to insoluble or unidentified species.

We also do not believe that the reaction we are observing is water catalyzed. No acceleration was observed when trace water was added to the reaction mixture, nor was the reaction retarded when the reaction mixture was pre-dried for 3 days over molecular sieves before it was decanted and combined with bis(imide) complex **1**.

Like many of the alkylidene catalysts, the bis(imide) catalysts described herein do not exhibit pre-coordinated nor metallacyclic intermediates in their reaction with unsaturated substrates.^{1c} Further studies are required to ascertain if, in fact, the metathesis proceeds through a [2 + 2] mechanism as would be expected by analogy to alkene metathesis systems. These studies are currently being pursued.

In summary, we have identified the first potential catalysts for imine metathesis. These bis(imide) catalysts undergo a general metathesis with imines without termination by dimer formation.

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Footnotes and References

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† Imines were prepared by condensation of the parent aldehyde and amine in benzene over molecular sieves, followed by purification by vacuum distillation. The procedure was analogous to that described for imine preparation by S. R. Sandler, and W. Karo, in *Organic Functional Group Preparations*, Academic Press, New York, 1986, vol. II, p. 302.

‡ The ratio of products reported reflects the equilibrium reached after complete metathesis of the first and partial metathesis of the second imide reactive site.

§ *Typical NMR experiment:* reaction of $(\text{dme})\text{Cl}_2\text{Mo}(\text{NAr})_2$ **1** and $\text{PhN}=\text{CH}(\text{Bu}^t)$ **2**. Complex **1** (0.005 g, 0.008 mmol, 1 equiv.) was dissolved in *ca.* 0.5 ml C_6D_6 in an NMR tube equipped with a Teflon stopcock. Hexamethylbenzene in C_6D_6 and imine **2** (*ca.* 12 equiv.) were added. The sample was maintained for 24 h at room temp. to verify the stoichiometry and stability of the reaction mixture. The sample was heated and maintained at 85 °C for 18 d. The progress of the reaction was monitored by ^1H NMR spectroscopy. ^1H NMR (C_6D_6) of $\text{ArN}=\text{CH}(\text{Bu}^t)$ (unisolated) δ 7.25 (s, 1, CHBu^t), 3.05 (spt, 2, CHMe_2 , J_{CH} 6.7 Hz), 1.17 (d, 12, CHMe_2 , J_{CH} 6.6 Hz), 1.07 (s, 9, Bu^t); mass spectrum (EI) m/z 245 (M^+), 188 ($\text{M}^+ - \text{Bu}^t$). ^1H NMR (C_6D_6) $(\text{dme})\text{Cl}_2\text{Mo}(\text{NAr})(\text{NPh})$ (unisolated) δ 4.40 (spt, 2, CHMe_2 , J_{CH} 7.1 Hz), 1.30 (d, 12, CHMe_2 , J_{CH} 6.8 Hz). Phenyl and aryl resonances could not be definitively assigned owing to the complexity of the spectrum in this region.

¶ The diazametallacycle, if present, exists only in trace amounts since the total imine concentration (substrate + product) remains nearly constant throughout the reaction.

|| Compound **3** was independently prepared by the reaction of bis(imide) **1** with phenyl isocyanate.

** $(\text{dme})\text{Cl}_2\text{Mo}(=\text{NPh})_2$ should be present as well, arising from metathesis of both imido groups and, also, from intermolecular imide/imide metathesis. The complexity of the phenyl region of the spectrum precludes the assignment of resonances for this species.

†† $(\text{ArO})_2\text{Mo}(\text{NAr})_2$ was prepared by analogy to $(\text{Bu}^t\text{O})_2\text{Mo}(\text{NAr})_2$ by reaction of $(\text{dme})\text{Cl}_2\text{Mo}(\text{NAr})_2$ with 2 equiv. of LiOAr . ^1H NMR (C_6D_6) δ 6.87–7.08 (m, 12, aryl), 3.82 (spt, 4, CHMe_2 , J_{CH} 6.8 Hz), 3.48 (spt, 4, CHMe_2 , J_{CH} 6.8 Hz), 1.25 (d, 24, CHMe_2 , J_{CH} 6.8 Hz), 1.00 (d, 24, CHMe_2 , J_{CH} 6.8 Hz); ^{13}C NMR (C_6D_6) δ 160.7 (C_{ipso} , OAr), 154.4 (C_{ipso} , NAr), 143.6, 138.2, 127.6, 124.3, 123.9, 123.1 (aryl), 29.4 (CHMe_2 , OAr), 28.0 (CHMe_2 , NAr), 24.5 (CHMe_2 , OAr), 24.2 (CHMe_2 , NAr). Anal. Calc. for $\text{C}_{48}\text{H}_{68}\text{N}_2\text{O}_2\text{Mo}$: C, 71.87; H, 8.56; N, 3.50. Found: C, 71.91; H, 8.74; N, 3.50%.

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