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Transition-Metal-Catalyzed Imine Metathesis

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*Summary: Mixtures of (n-Pr)N═CHPh (**3**) and PhN═CH(t-Bu) (**4**) undergo catalytic metathesis in the presence of 4 mol % of (DME)Cl_2Mo(═NR)$_2$ (R = t-Bu (**1a**), 2,6-diisopropylphenyl (**2**)) at 85−90 °C in C_6D_6 to form 1:1:1:1 equilibrium mixtures with PhN═CHPh (**5**) and (n-Pr)N═CH(t-Bu) (**6**).*

Metal-catalyzed metathesis is a valuable reaction, both in polymer[1] and small molecule synthesis,[2,3] but has been limited almost exclusively to C═C bond formation. Herein, we report the identification of a class of imide catalysts that effectively promote C═N bond formation via metathesis of imines. The development of a metal-catalyzed metathesis reaction is interesting from both a fundamental perspective and a practical one. Fundamentally, the comparison of the heteroolefin and alkene reactions will increase our understanding of both processes. Practically, the development of metal-catalyzed imine metathesis may offer important advantages over acid-catalyzed imine exchange,[4] including selectivity, mild reaction conditions, and varied functional group tolerances.

The only prior example of catalytic C═N bond formation via metal-mediated imine metathesis is the reaction of Cp_2Zr(═N-*t*-Bu)(THF) with *N*-phenyl imines, in a formal [2 + 2] addition, to give diazametallacycles that undergo further metathetical exchange with external imines.[5,6] The catalytic utility of this complex is limited, however, since it is inhibited by high imine concentrations and is subject to deactivation by irreversible dimerization. Several classes of related hetero-metatheses have also been reported: isocyanates and carbodiimides metathesize with group V and VI imide complexes,[7] imines react in a stoichiometric, Wittig fashion with alkylidenes,[8] metal imides react in a Wittig fashion with aldehydes,[9] and phosphinidenes metathesize P═P.[10]

We recently discovered that a class of bis(imide) complexes of the general formula (DME)Cl_2Mo(═NR)$_2$, originally prepared by Schrock and co-workers,[11] react

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(1) 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.

(2) Kim, S.-H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801−10802.

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

(4) Toth, G.; Pinter, I.; Messmer, A. *Tetrahedron Lett.* **1974**, *9*, 735−738.

(5) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 2669−2670.

(6) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 974−985.

(7) (a) Green, M. L. H.; Hogarth, G.; Konidaris, P. C.; Mountford, P. *J. Organomet. Chem.* **1990**, *394*, C9−C15. (b) Meisel, I.; Hertel, G.; Weiss, K. *J. Mol. Catal.* **1986**, *36*, 159−162. (c) Birdwhistell, K. R.; Boucher, T.; Ensminger, M.; Harris, S.; Johnson, M.; Toporek, S. *Organometallics* **1993**, *12*, 1023−1025.

(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*, 3077−3081. (c) Turner, H. W.; Fellmann, J. D.; Rocklage, S.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7809−7811.

(9) (a) Jolly, M.; Mitchell, J. P.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 1329−1330. (b) Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965−969. (c) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7808−7809. (d) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094−5095. (e) Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc., Chem. Commun.* **1978**, 579−580.

(10) Dillon, K. B.; Gibson, V. C.; Sequeira, L. J. *J. Am. Chem. Soc., Chem. Commun.* **1995**, 2429−2430.

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

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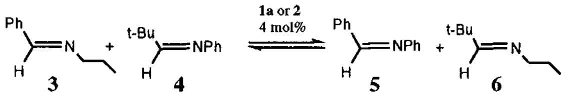
with a single imine to give a mixed bis(imide) complex and a new imine.[12] In contrast to the zirconium system, these bis(imide) complexes were not deactivated by dimerization. Since this type of *imide/imine* metathesis is the key step in the metathesis of multiple imines, we were optimistic that these complexes would be effective catalysts.

Both (DME)$Cl_2Mo({=}N\text{-}t\text{-}Bu)_2$ (**1a**) and (DME)$Cl_2Mo({=}NAr)_2$ (Ar = 2,6-diisopropylphenyl; **2**)[13] cleanly catalyze the metathesis of a mixture of two imines. The substrate imines (n-Pr)N=CHPh[14] (**3**) and PhN=CH(t-Bu) (**4**) were heated to 85−90 °C in the presence of 4 mol % of **1a** (mol % based on **3** + **4**) in C_6D_6. ^1H NMR spectra of the reaction mixture showed the presence of PhN=CHPh (**5**) and (n-Pr)N=CH(t-Bu) (**6**) (eq 1). After 22 h, imines **3**−**6** had attained an equilibrium ratio of 1:1:1:1.[15] The metathesis of imines **3** and **4** proceeded at a slower rate in the presence of bis(arylimide) **2**. Under identical reaction conditions this system required 4 days to reach equilibrium. The metathesis appears to be regiospecific for both catalysts; no olefin or diazene products are observed.

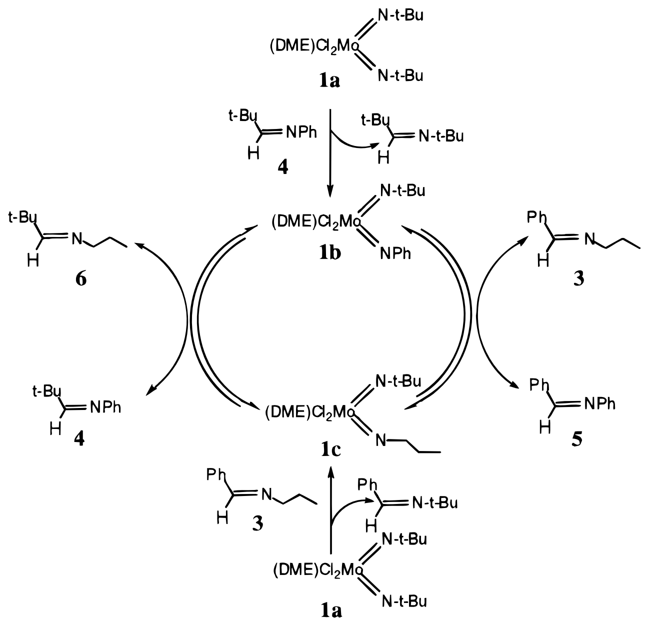


(1)

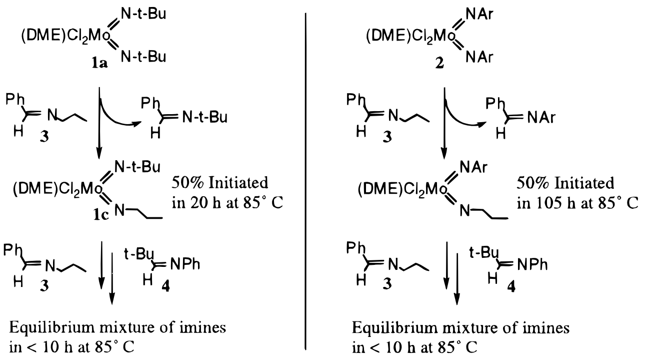
Imines **3** and **4** do not metathesize significantly in the absence of the bis(imide) catalysts. When these compounds were heated to 80 °C in C_6D_6 for 2 weeks, less than 5% of metathesis products **5** and **6** were detected. Given that imine metathesis is also promoted by H^+,[4] it is probable that the small amounts of products observed arose from trace acid on the glass NMR tube.

On the basis of these results and our prior report of the imide/imine metathesis activity of these bis(imide) complexes, we suggest that a probable catalytic sequence is as shown in Scheme 1. Bis(imide) **1a** could react with either imine **3** or **4** to form mixed bis(imide) complex **1c** or **1b**, respectively. Although the mixed bis(imide) complexes were not observed under these conditions (4 mol % catalyst), in previous stoichiometric experiments resonances for these complexes have been identified by ^1H NMR spectroscopy.[12] In the propagation step, the mixed bis(imide) reacts with the other imine to give product imine **5** or **6**. In order to produce the observed statistical mixture of imine products, all of the reactions must be reversible. Degenerate reactions, such as the reaction of **1b** with imine **4** to produce **1b** again, are not shown but must also occur.

Scheme 1



Scheme 2



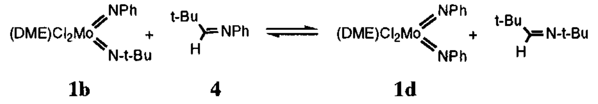
50% Initiated in 20 h at 85° C

Equilibrium mixture of imines in < 10 h at 85° C

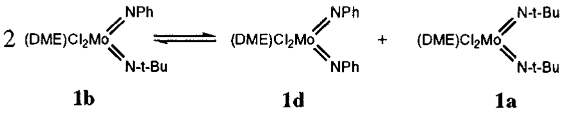
50% Initiated in 105 h at 85° C

Equilibrium mixture of imines in < 10 h at 85° C

For clarity, we have omitted from Scheme 1 two other processes that occur concurrently with the productive catalysis to produce homo-bis(imides). The first process involves the reaction of the second "spectator" imide with imine. We have previously established that this reaction does, in fact, occur.[12] For example, complex **1b** can react in a nondegenerate fashion with imine **4** to form a new bis(phenyl) imide, **1d** (eq 2). The second process that occurs in the metathesis reaction mixture is intermolecular imide exchange.[16] Complex **1b** can, for example, disproportionate to give homo-bis(imide) complexes **1d** and **1a** (eq 3). Although these two processes produce several species not shown in the pro-



(2)



(3)

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[12] Cantrell, G. K.; Meyer, T. Y. *Chem. Commun.* **1997**, 1551−1552.

[13] Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 2287−2289.

[14] 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 a different imine in: Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*; Academic Press: New York, 1986; Vol. II, p 302.

[15] **Typical Procedure: Catalytic Metathesis of (n-Pr)N=CHPh (3) and PhN=CH(t-Bu) (4) with (DME)$Cl_2Mo({=}N\text{-}t\text{-}Bu)_2$ (1a)**. Imines **3** (13 equiv) and **4** (13 equiv) were dissolved in 0.75 mL of C_6D_6 in an NMR tube equipped with a Teflon stopcock. Hexamethylbenzene (0.075 mL of a 0.05 M standard solution) and bis(imide) **1a** (0.004 g, 0.01 mmol, 1 equiv) were added. The sample was maintained for 24 h at room temperature to verify the stoichiometry and stability of the reaction mixture. The sample was heated and maintained at 85−90 °C for 3 days. The progress of the reaction was monitored by ^1H NMR. ^1H NMR (C_6D_6) of PhN=CHPh **(5)** (unisolated): δ 8.13 (s, 1, CHPh), 7.81 (m, 2, phenyl), 7.18−7.00 (m, phenyl). ^1H NMR (C_6D_6) of (n-Pr)N=CH(t-Bu) **(6)** (unisolated): δ 7.33 (s, 1, CH-t-Bu), 3.27 (t, 2, $NCH_2CH_2CH_3$, J_{CH}= 6.7 Hz), 1.61 (m, 2, $NCH_2CH_2CH_3$), 1.02 (s, 9, t-Bu), 0.85 (t, 3, $NCH_2CH_2CH_3$, J_{CH}= 8.6 Hz). Note: both **5** and **6** have been prepared independently for comparison.

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

posed catalytic cycle, the consequences are minimal if we assume that only one imide per metal center can react with an incoming imine at a time.

The observed differences in metathesis completion times for the two catalysts can be explained by differences in initiation rates. To model the initiation step, catalysts **1a** and **2** were each treated in parallel experiments with an excess of imine **3** (Scheme 2). After 20 h at 85 °C catalyst **1a** had reached 50% conversion to **1c**, based on production of (t-Bu)N=CHPh.[17] Catalyst **2** required 105 h to reach 50% conversion to (DME)Cl_2-Mo(=NAr)(=N-n-Pr). To these preinitiated reaction mixtures were added an excess of imine **4** and more imine **3** to make the imine concentrations approximately equal.[18] Both the reaction mixture that originally contained catalyst **1a** and the one that contained catalyst **2** reached equilibrium in under 10 h.[19] Clearly, the rate of initiation can have a significant effect on the overall metathesis reaction time.

The nature of the imide substituent is evidently the determining factor in imide/imine reactivity. From the relative initiation rates of catalysts **1a** and **2** we can conclude that t-Bu is faster than Ar. Moreover, the decreased overall metathesis time observed for preinitiated **1a** suggests that imides with n-Pr and Ph substituents react faster than either of the starting imides; the data are insufficient to rank the n-Pr vs Ph substituents. Upon initial consideration, steric demands of the imide nitrogen substituents appear to be the most significant factor in determining the reaction rates. Further studies are required to determine the role of electronic differences.

An estimate of the effective rate of catalysis can be made using the data from the preinitiated catalyst **2** (Scheme 2). A turnover frequency of ~3 imine Mo^{-1} h^{-1} was calculated,[20] assuming that the contribution to the catalysis by the 50% of uninitiated catalyst is negligible and that only one imide per metal participates at a time. This TOF represents a lower limit for the true catalytic rate, however, since the catalyst is also reacting in a degenerate fashion with starting imine and in an unproductive fashion with products.

Although it is clear that the imide is directly involved in the metathesis reaction, our preliminary studies do not permit definitive conclusions regarding the mechanism. We did not observe the diazametallacycle intermediates that might be expected by analogy to the zirconium imide system.[5,6] The absence of an observable metallacycle does not rule out a [2 + 2] mechanism, however, since the system could have an imide resting state. The preference for an unsaturated resting state has precedent in the closely related molybdenum olefin metathesis systems.[1b] We are currently investigating the heteroolefin metathesis mechanism as well as studying the effects of ligands on catalytic rate.

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Supporting Information Available: Text describing materials and methods (1 page). Ordering information is given on any current masthead page.

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[17] Under normal catalytic conditions (simultaneous addition of imines **3** and **4**), the imines produced in the initiation step are difficult or impossible to identify in the ^{1}H spectrum due to accidental overlap of imine resonances.

[18] A slight excess of **3** (16 equiv) over **4** (14 equiv) was present in the NMR tube.

[19] Catalyst **1a** reached equilibrium in ~5 h, while **2** required ~10 h. The difference in completion times is attributed to the continued initiation of the more reactive **1a** to produce additional active catalyst.

[20] TOF = (equiv of product imine at equilibrium)/(equiv of active catalyst)(time to equilibrium) = ~15/(0.5 (Mo))(10 h).