Role of Trace Amine in the Metathesis of Imines by $CpTa(=NR)Cl_2$

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Tantalum imido compound $CpTa(=NBu^t)Cl_2$ (**1**) reacts with imines to give NR exchange (metathesis) products. Addition of <5 mol % of compound **1** to a 1:1 mixture of two different imines resulted in catalytic cross metathesis of the two imines to give an equilibrium mixture of imines. Kinetic studies of the reaction of **1** with excess imine $(Bu^t)HC{=}N(p\text{-tolyl})$ (**2a**) gave an average k_{obs} of 1.29×10^{-4} min^{-1} (σ 0.28). Pseudo-first-order behavior was observed for **1**. The dependence of k_{obs} on the concentration of **2a** was found to be nonlinear and dependent on catalytic amounts of contaminant amine *p*-tolylamine (**9**). Reaction of **1** with *tert*-butylamine (**6**) results in the formation of the imide/amide $CpTa(=NBu^t)(NHBu^t)Cl$ (**7**) and HCl. Compound **7** did not react with imines to give exchange products, so it is proposed that the reaction of **1** with imines is significantly accelerated by the presence of HCl.

Introduction

We have discovered that compounds of the general formula $CpTa(=NR)Cl_2$ represent a new class of imine metathesis catalysts. The impetus for these studies originated in our previous investigation of the imine reactivity of the group VI bis(imide) complexes $(DME)Cl_2Mo(=NR)_2$.[1−3] Although we had gained a significant understanding of the overall catalytic cycle, the complexity inherent in the dual-active site catalysts precluded the detailed mechanistic studies that are necessary to understand the system and enable the eventual application of the imine metathesis strategy to the catalytic synthesis of small molecules and polymers.

Interestingly, the two other examples of imine/imide exchange for which mechanistic data were reported apparently proceed by different pathways. The viability of a Chauvin-type[4] mechanism (Figure 1) was established by Bergman and co-workers in their observation of isolable diazametallacyclic intermediates in the reaction of $CpCp'Zr(=NR)(THF)$ (Cp′ = Cp, Cp*) with imines.[5−7] In contrast, Mountford and co-workers observed neither diazametallacycles nor kinetics consistent with a [2+2] mechanism and proposed an amine-catalyzed process to explain the reaction of $(py)_3Cl_2Ti(=NR)$ with imines.[8,9] Other examples of imine/imide and imine/carbodiimide metathesis are known, but little mechanistic data has been reported for these systems.[10−13] Given the variance in precedents, the determination of mechanism in our system is of particular importance to us as well as others.

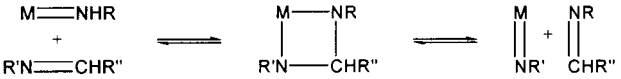

Figure 1. Chauvin-type mechanism for imine metathesis at an electrophilic metal center.

Since the dual-site molybdenum catalysts proved unsuitable for kinetic studies, we sought to discover a new single-site catalyst. Metal imides of the type $CpTa(=NR)Cl_2$ were selected because they possess a single imide functional group while being approximately isolobal with the molybdenum bis(imide) complex *sans* DME. Herein, we describe both the stoichiometric and catalytic metathetic reactions of these tantalum mono(imide) complexes with imines and, on the basis of kinetic analyses and ^{15}N-labeling studies, propose an acid-catalyzed mechanism.

Results

Imide/Imine Metathesis. $CpTa(=NBu^t)Cl_2$, **1**, reacted with 15 equiv of $(Bu^t)HC{=}N(p\text{-tolyl})$, **2a**, in C_6D_6 at 70 °C to yield imine $(Bu^t)HC{=}N(Bu^t)$, **4a**, as shown by comparison of the ^1H NMR spectroscopic resonances with those of an authentic sample (Scheme 1). A new Cp-containing compound, assigned as *p*-tolyl imide **3a**, was also produced, as evidenced by distinctive ^1H NMR resonances at δ 5.72 (Cp) and 2.19 (tolyl CH_3). No other species were observed. Within 3−4 days nearly all of the starting imide **1** was converted to the new product **3a**. No precipitates formed and integration versus an

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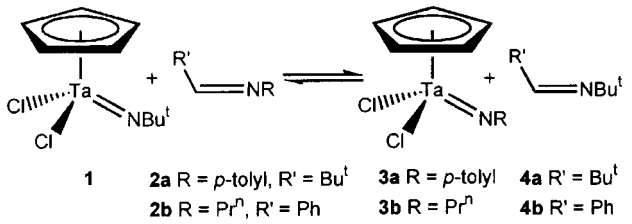
Scheme 1



1 **2a** R = *p*-tolyl, R' = Bu^t **3a** R = *p*-tolyl **4a** R' = Bu^t
2b R = Pr^n, R' = Ph **3b** R = Pr^n **4b** R' = Ph

internal standard confirmed that all species remained soluble.

Tantalum imide **1** also reacted metathetically in C_6D_6 with excess (Ph)HC═N(Pr^n), **2b**, to give imine (Ph)HC═N(Bu^t), **4b**, and a product assigned as CpTa(═NPr^n)-Cl_2, **3b**. Imine **4b** was identified in the reaction mixture by comparison with independently prepared compound. The assignment of the exchange product was made on the basis of the Cp resonance at δ 5.74 and a multiplet at δ 4.23 that is characteristic of the α-methylene of an N-alkyl group. The resonances for the hydrogens on the β- and γ-carbons of this new species appear to overlap with those of the starting material imide. After 1 day at 55 °C a third species, **5**, appeared. Compound **5** was identifiable only from a new Cp resonance at δ 6.10. Either this compound has no N-alkyl group or its resonances overlap with those of **1** and/or **3b**. We speculate that **5** may be the product of β-hydride elimination, which is unable to occur in the case of the *tert*-butyl imide, **1**, and the *p*-tolyl imide **3a**. After 10 days of heating there were no new species present by ^{1}H NMR spectroscopy, but precipitate was evident and the integration of all species against an internal standard showed a confirming decrease in the concentration of Cp-containing complexes.

Catalytic Imine Metathesis. CpTa(═NBu^t)Cl_2, **1**, acts as an imine metathesis catalyst. Addition of <5 mol % of **1** to a 1:1 mixture of imines **2a** and **2b** produces the metathesis products (Bu^t)HC═N(Pr^n) and (Ph)HC═N(*p*-tolyl) within hours at 70 °C (Scheme 2). The reaction is slow, reaching equilibrium after >1 week. The imines produced by imide/imine exchange and the imide products, **3a** and **3b**, were also observed in the reaction mixture. At longer reaction times (>2 weeks), precipitate was observed.

Kinetic Studies. The reaction of **1** with *N*-*p*-tolyl imine **2a** was monitored kinetically by ^{1}H NMR spectroscopy (Scheme 3). In the presence of excess imine, pseudo-first-order behavior was observed for **1**. The validity of a first-order analysis was confirmed by following several reactions for more than 5 half-lives and by the independence of the rate constant on the concentration of **1**. The observed pseudo-first-order rate constants, k_{obs}, were obtained by fitting the [Imide **1**]$_t$ − [Imide **1**]$_{eq}$ to a single-exponential function (Figure 2). An average K_{eq}, defined as {[Imide **3a**][Imine **4a**]}/{[Imide **1**][Imine **2a**]}, of 1.29 (σ = 0.28) was calculated from the data for experiments 2−9 (experiment 1 omitted because only a 6.3:1 excess was used).

To determine the order of the imine in the reaction, the dependence of k_{obs} on imine was examined. The plot of k_{obs} versus [Imine] for experiments 1−9 did not show a simple linear dependence (Figure 3). Moreover, two control experiments established that the reaction depended, at least partially, on a catalytic contaminant present in the imine. In the first control experiment, the original kinetic experiment (Scheme 3) was repeated with *doubly purified imine*; the k_{obs} obtained was significantly smaller than the rate constant that would have been predicted on the basis of data obtained from the singly purified imine (Table 1, experiment 10, Figure 2). In the second control experiment, the relative ratios of imine to imide were reversed such that there was an excess of imide **1**. The resulting reaction was extremely slow, with only trace amounts of product visible after 1 week at 70 °C (not included in table).

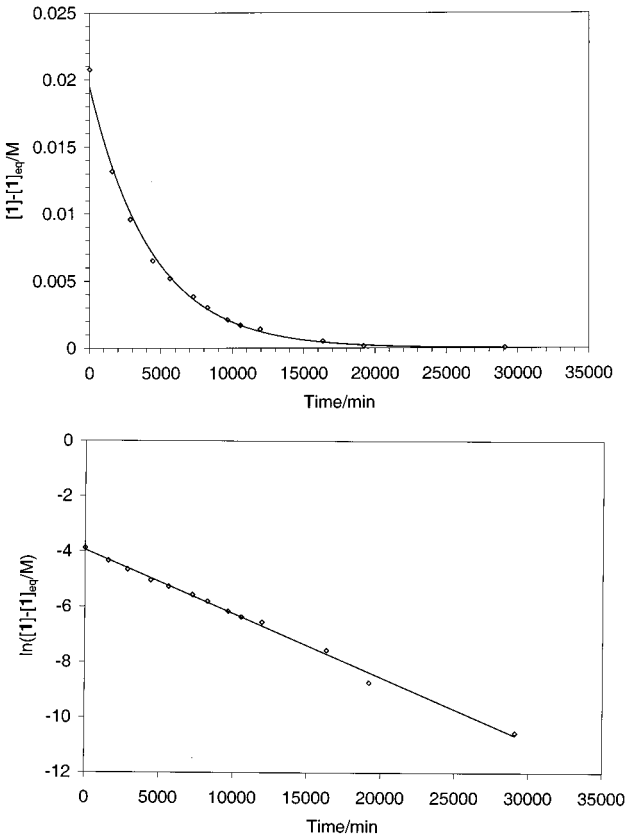


Figure 2. Pseudo-first-order disappearance of CpTa(═NBu^t)Cl_2, **1**, in the presence of 15 equiv of (Bu^t)HC═NTol, **2a** (k_{obs} = 2.6 × 10^{-4} min^{-1}). Corresponds to experiment 5 in Table 1.

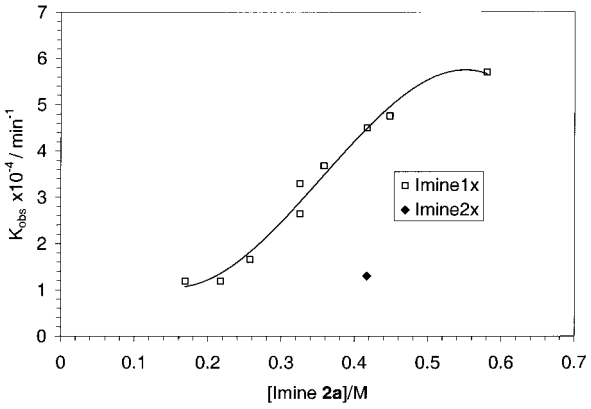
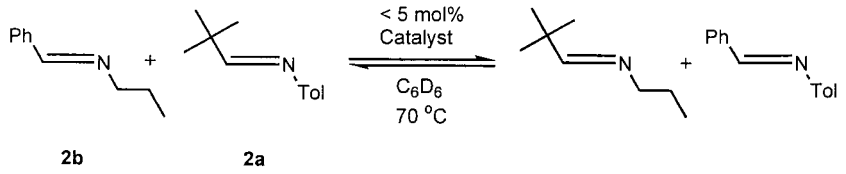


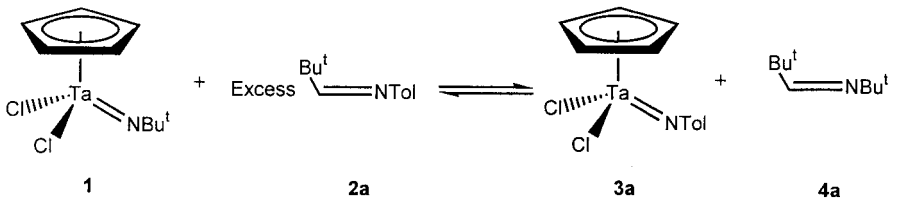
Figure 3. Dependence of the pseudo-first-order rate constant (k_{obs}) for the disappearance of **1** on imine concentration: Experiments 1−9 were performed with dried and distilled imine (Imine1×); experiment 10 used doubly purified imine (Imine2×). The imine1× data have been fitted with a polynomial to highlight the nonlinear trend. The curve does not represent a specific rate law.

Scheme 2



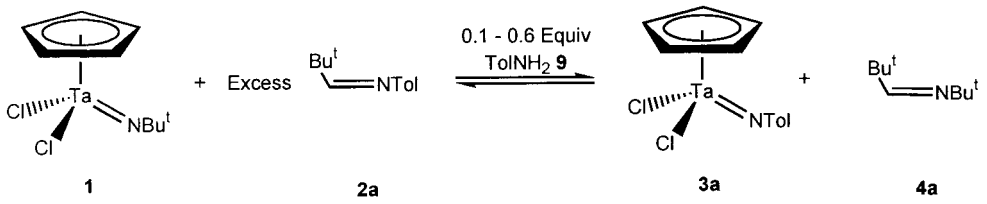
2b **2a**

Scheme 3



1 **2a** **3a** **4a**

Scheme 4



1 **2a** **3a** **4a**

Since the most likely catalytically active contaminant of the imine is amine, the reaction of **1** with excess *p*-tolylimine **2a** was repeated in the presence of added *p*-tolylamine **9** (0.1−0.6 equiv with respect to **1**, Scheme 4). A plot of the k_{obs} obtained from these experiments showed a direct dependence on amine concentration (Table 1, experiments 11−13, Figure 4). Although the trend appears linear, implying a first-order dependence on amine, the experiments covered a relatively small range of concentrations and the relationship is likely not one of simple proportionality. Experimental difficulties precluded studies of significantly lower or higher concentrations.

Several attempts to remove the amine from the reaction mixture failed. Any reagent sufficiently acidic or basic enough to completely sequester the amine also reacted in some fashion with the imide complex or with the imine. The amine must be accepted as a necessary component of any reaction mixture containing excess imine.

Amine/Imide Reactions. To probe the role of amine in the imide/imine metatheses, the direct reaction of *tert*-butyl imide **1** with *tert*-butylamine, **6**, was examined (Scheme 5). By ^{1}H NMR spectroscopy of the reaction mixtures, the instantaneous formation of a new imide/amide complex, CpTa(=NBu^t)(NHBu^t)Cl (**7**), was observed. Formation of the ammonium salt NH_3Bu^tCl (**8**) was also noted during the course of the reaction. The imide/amide was the only soluble product observed, independent of the ratio of amine to imide; addition of a single equivalent of amine gave 0.5 equiv of compound **7**. Although we could not isolate imide/amide **7** in analytically pure form nor could we obtain X-ray quality crystals, its formulation was consistent with all spectroscopic data and an analogous Cp* derivative is known.[11] A 2D heteronuclear multiple-bond correlation (HMBC) NMR spectrum showed the expected long-range coupling between the amide proton and the *ipso* carbon of the attached *tert*-butyl group. Also, the ^{15}N NMR spectra of the partially labeled and fully labeled derivatives CpTa(=NBu^t)(^{15}NHBu^t)Cl (**7N1a**) and CpTa(^{15}NBu^t)(^{15}NHBu^t)Cl (**7N2**) were consistent (vide supra).

Table 1. Kinetic Data for Imide/Imine Exchange Reactions

	[Imide **1**]/M	[Imine **2a**]$_{init}$/M	[Amine **9**]$_{init}$/M	k_{obs} (10^{-4}/min^{-1})
		Imide + Excess Imine[d]		
1	0.027	0.17	<0.002[b]	1.2[a]
2	0.022	0.22	<0.002[b]	1.2
3	0.026	0.25	<0.002[b]	1.7
4	0.022	0.32	<0.002[b]	3.3
5	0.022	0.32	<0.002[b]	2.6
6	0.022	0.36	<0.002[b]	3.7
7	0.028	0.42	<0.004[b]	4.5
8	0.039	0.58	<0.004[b]	5.7
9	0.022	0.43	<0.004[b]	4.7
		Imide + Excess Doubly Purified Imine[d]		
10	0.028	0.42[c]	<0.002[b]	1.2
		Imide + Excess Doubly Purified Imine + Amine[e]		
11	0.018	0.27[c]	0.0018	9.6
12	0.018	0.27[c]	0.0037	10.5
13	0.019	0.28[c]	0.0077	12.6
14	0.018	0.27[c]	0.011	14.5

[a] k_{obs} for this experiment is less certain due to an insufficient excess of imine to imide (6.3:1). [b] Upper limit based on NMR sensitivity and/or integration of observed baseline signals that are associated with trace amine. [c] Doubly purified imine. [d] Estimated uncertainty in $k_{obs} = \pm 0.6 \times 10^{-4}$ based on uncertainties in concentration, integration, and [Imine **2a**]$_{eq}$. [e] Estimated uncertainty in $k_{obs} = \pm 2.5 \times 10^{-4}$ based on uncertainties in concentration, integration, and [Imine **2a**]$_{eq}$. Amine **9** = *p*-tolylamine.

The reaction of *tert*-butyl imide **1** with *p*-tolylamine **9** was also examined by ^{1}H NMR (Scheme 6). The reaction mixture was significantly more complex than the reaction of **1** with *tert*-butylamine **6**. At equilibrium, at least five species were present including starting imide (20%) and the amine/imide exchange product, CpTa(=NTol)Cl$_2$ **3a** (15%). Significant precipitate, along with a broad resonance at δ 8.0, was consistent with the formation of ammonium salts. Although we were

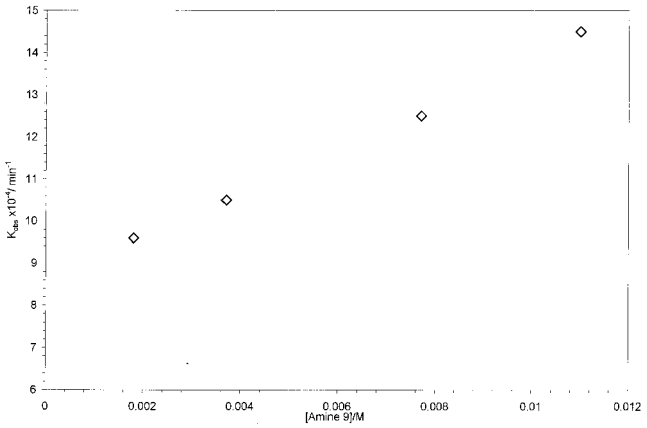
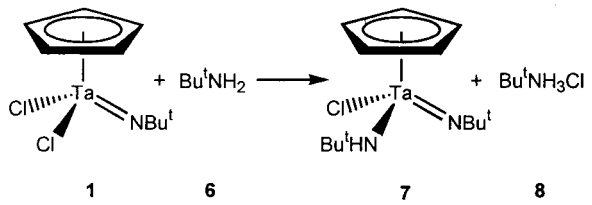


Figure 4. Dependence of the pseudo-first-order rate constant (k_{obs}) for the disappearance of **1** vs amine concentration for a ternary reaction of **1**, 15 equiv of imine **2a**, and *p*-tolylamine **9**.

Scheme 5



unable to identify all species in solution, by analogy to the *tert*-butylamine reactions, some or all of the imide/amide complexes are likely to be present: CpTa(=NBu^t)(NHTol)Cl (**10a**), CpTa(=NTol)(NHBu^t)Cl (**10b**), CpTa(=NBu^t)(NHBu^t)Cl (**7**), and CpTa(=NTol)(NHTol)Cl (**10c**). The ratios of all species were found to vary reversibly as a function of temperature.

The ternary reaction of tantalum imide **1**, *p*-tolylamine **9** (0.5 equiv), and *N*-tolylimine **2a** (15 equiv) was also studied by ^{1}H NMR and, initially, was found to contain all of the species seen in the binary imide/amine reaction (Scheme 7). After 6 days at 70 °C, the reaction had reached equilibrium and the spectrum was much simplified. Only three Cp-containing species remained: the product **3a** (87%), starting *tert*-butylimide **1** (4%), and a compound whose Cp resonance corresponded exactly with the one observed in the binary imide/tolyamine reaction (Scheme 6) for the most abundant of the putative imide/amide compounds **10a**−**c**. Imide/amide **7** can be ruled out on the basis of the known shift.

Reaction of Imide/Amide (7) with Imine. To determine if imide/amide **7** generated in situ might be responsible for the amine-accelerated rates of imine/imide exchange, we examined the reaction of *isolated* imide/amide **7** with 15 equiv of imine (Bu^t)CH=N(P-tolyl) (**2a**) (Scheme 8). Interestingly, no new imine product was detected after 2 days at 70 °C. The control, consisting of imide **1** and 15 equiv of the same imine, had proceeded to completion in the same period.

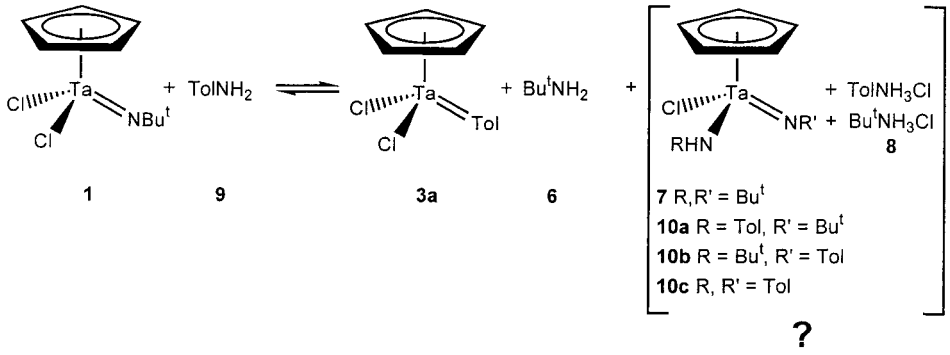
^{15}N-Labeling Studies. Studies involving ^{15}N-labeled substrates provided further insight into these complex reaction systems. We prepared $^{15}NH_2Bu^t$ (**6N**) and (Ph)HC=^{15}N(Bu^t) (**4bN**) using standard methods. The reaction of the labeled amine **6N** with imide **1** was studied over time by ^{1}H NMR and ^{15}N NMR spectroscopies (Scheme 9). Within a minute of the addition of a single equivalent amine **6N** to the imide in C_6D_6, a ^{1}H NMR spectrum showed that half of the starting material had been converted to the partially labeled imide/amide **7N1a**. The amine was completely consumed, and precipitate, presumably ammonium salt, was visible. Long-range $^3J_{NH}$ coupling of 2.2 Hz was observed from the amide nitrogen to the methyl peaks of the attached *tert*-butyl group. No such coupling was observed to the imide *tert*-butyl of **7N1a** or in the remaining starting material **1**. After heating for 2 h at 80 °C, the label began to wash into the imide positions, as evidenced by the broadening and splitting of the *tert*-butyl peaks. In the ^{15}N NMR spectra, parallel behavior was observed. Immediately after addition, only the amide resonance at δ 116.7 was easily detectable. *No resonance for the labeled free amine **6N** was observed*, indicating that it had been completely consumed. After heating, the resonances for the imide groups for both **7N2** and imide complex **1N** were easily visible. Presumably the monolabeled compound CpTa(^{15}NBu^t)(NHBu^t)Cl (**7N1b**) is also present, but it cannot be spectroscopically differentiated in mixtures containing **7N2**.

The ternary experiment involving stoichiometric imide **1**, (Ph)HC=N(Bu^t) (**4b**), and labeled amine **6N** was also followed by NMR. Initial ^{15}N NMR spectra showed only the partially labeled imide/amide **7N1a**. With heating, resonances for the imide functionalities of **1N** and **7N2** became visible, as did the imine nitrogen for **4bN**. Again, no free amine was observed. The ^{15}N spectra were collected with an NOE-suppressing pulse sequence in order to make it possible to integrate the peaks. Although the differences were not dramatic, it appeared as if the label washed into the imide positions faster than into the imine (Scheme 10). A control experiment with the imine **4b** and the labeled amine **6N** showed no scrambling of the isotopic label, even after heating at 80 °C for 1 h.

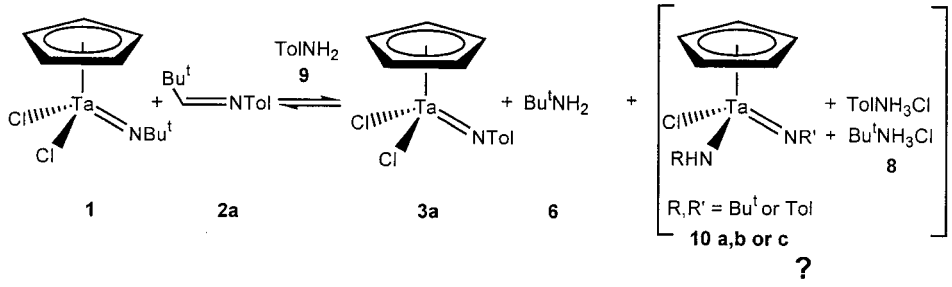
Reaction of the labeled imine **4bN** with imide **1** and unlabeled amine **6** was also followed by ^{15}N and ^{1}H NMR spectroscopy (Scheme 11). After initial formation of imide/amide **7**, the resonances associated with the imide **1N** and the imide/amide **7N1a** and **7N2** were seen to grow in, while the imine resonance for **4bN** was reduced. It appeared that the ^{15}N label was incorporated into the imide **1N** at a faster rate than into the imide/amide **7N2**. No free amine was seen at any point during the reaction.

To determine if the precipitated ammonium salt played a role in our reaction, or whether the nonpolar nature of the solvent excluded its participation, we conducted experiments to determine if NR exchange between solution phase species and the precipitated ammonium salt was possible (Scheme 12). We heated a sample of imide **1** in C_6D_6 with 2 equiv of solid, ^{15}N-labeled ammonium salt ^{t}BuNH$_3$Cl, **8N**. Although the solid did not appear to dissolve after several days of heating at 70 °C, a ^{15}N NMR spectrum of the sample clearly showed the presence of labeled imide **1N**. A similar experiment with the *tert*-butylamine **6** and the labeled ammonium salt **8N** also showed incorporation of the label despite the nonpolar nature of the solvent. As a comparison, a sample of unlabeled amine showed no detectable signal in the ^{15}N NMR spectrum after a similar period of data collection.

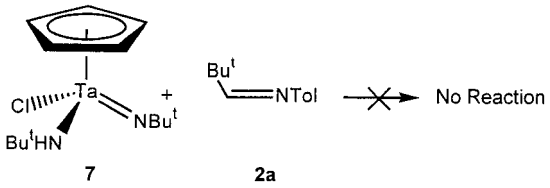
Scheme 6



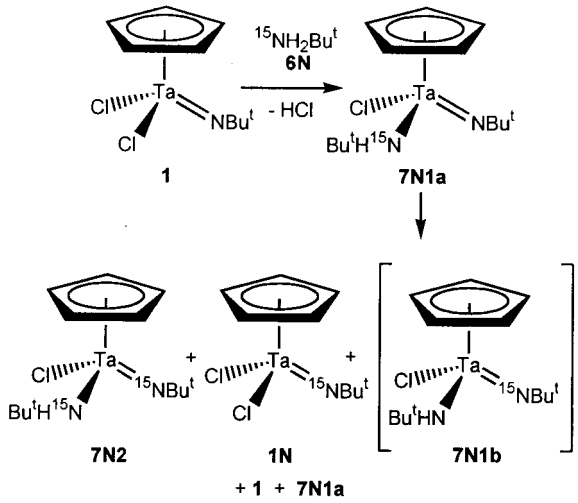
Scheme 7



Scheme 8



Scheme 9



Discussion

$CpTa(=NBu^t)Cl_2$, **1**, undergoes imide/imine exchange and catalyzes the metathesis of imines, but the primary mechanism appears to involve trace amine. The fact that the reaction is first order in **1** and that the rate depends on amine suggests that the reaction of these two components may be the rate-determining step of the reaction. These data rule out a Chauvin-type mechanism, which would be expected to be zero order in amine.

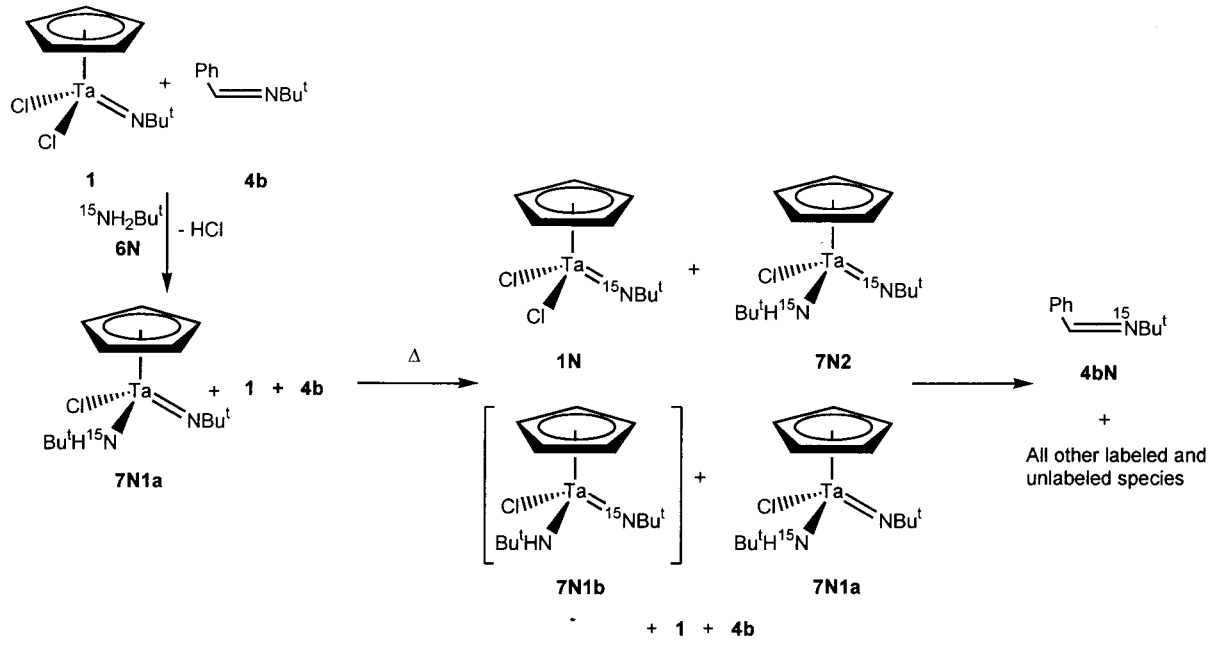
It is, at this point, relevant to discuss in more detail the mechanism proposed by Philip Mountford to explain the zero-order dependence on $(py)_3Cl_2Ti(=NBu^t)$ of the =NR exchange reaction with imine.[8] In the first step, Mountford postulates that a small amount of *tert*-butylamine reacts with the tolylimine to produce free *p*-tolylamine. Mountford and co-workers had previously established that *p*-tolylamine reacts with the butylimide titanium complex to regenerate the *tert*-butylamine and the product *p*-tolylimide complex (Scheme 13). If these two steps are combined, the overall reaction is catalytic in amine, and if the first step is rate determining, the zero-order dependence on imide complex is explained. In addition, the titanium complexes are available to act as Lewis acid catalysts for the amine/imine reaction.

An analogous mechanism can be proposed for the reaction of **1** with imine (Scheme 14). In this case, however, the relative rates of the two steps must be reversed in order to explain the first-order dependence of the reaction rate on **1**. It is also necessary to postulate that, in contrast with the Mountford system, step 2, the amine/imide exchange, is reversible.

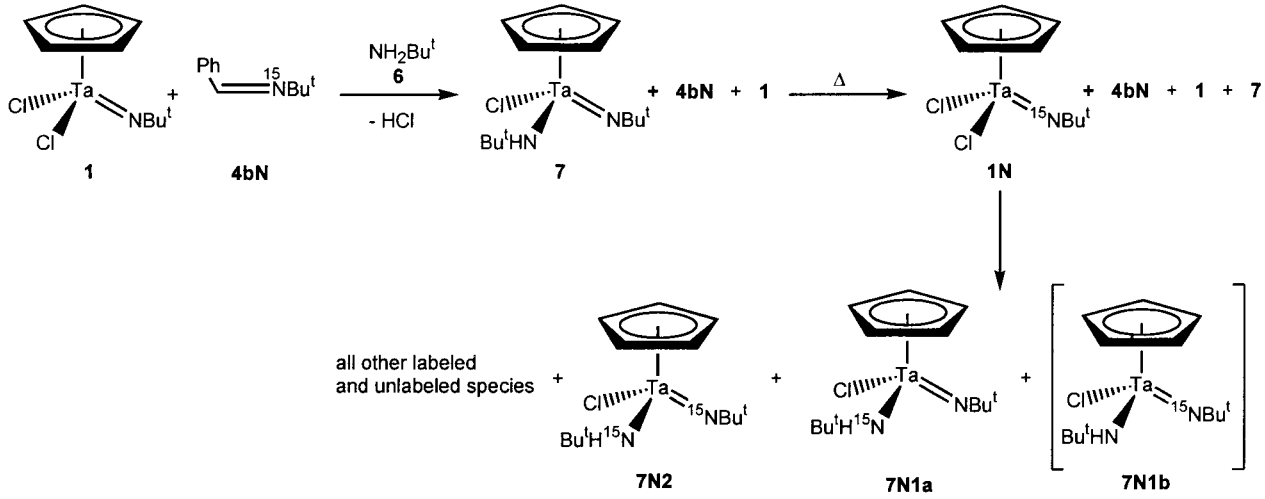
In addition to the amine-catalyzed pathway, two alternative mechanisms can be postulated if, instead of assuming that the amine acts as catalyst as depicted in Scheme 14, it is hypothesized that one of the products of the amine reaction with imide **1** is the mediator (Scheme 15). The two products from the reaction of *tert*-butylamine **6** with imide **1** are the imide/amide **7** and the HCl that is sequestered as the ammonium salt, NH_3-Bu^tCl **8**. The amide functional group of **7** could conceivably act as the mediator for the NR exchange reaction as shown in Scheme 16. The 1,3-proton transfer required could be intermolecular or intramolecular.

HCl as catalyst is also intriguing. Although it is mostly consumed by reaction with the basic *tert*-butylamine **6**, it is possible that some remains present in the broad reaction mixture. The observed exchange of ^{15}N

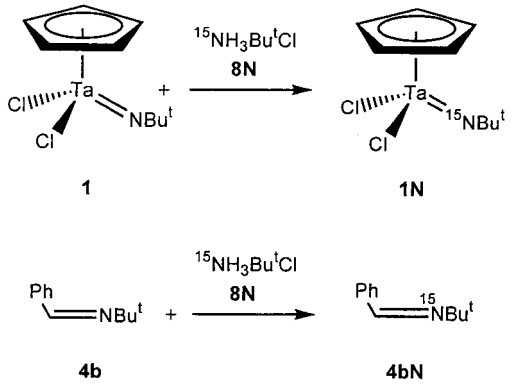
Scheme 10



Scheme 11



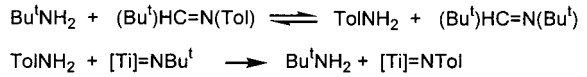
Scheme 12



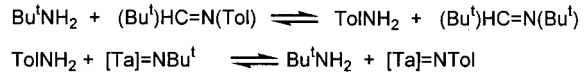
label from ammonium salt into soluble imide and imine suggests that the amine-bound HCl can interact with the other species in solution. Moreover, HCl could theoretically act as a catalyst for virtually any reaction combination in the mixture: imide/imide, imide/amide, imide/amine, amine/imine, imide/imide, amide/amine, and imine/imine (Scheme 17).

In considering these three mechanisms, we currently favor the third, HCl catalysis, as the most significant. The first mechanism, the amine-mediated pathway postulated by Mountford, is likely to occur at some rate in the reaction mixture. Both of the constituent reaction steps have been observed. However, this mechanism alone cannot explain some of our observations. First, the reactions of imide **1** with amines are not straightforward imide/amine exchanges. In contrast with the titanium complex studied by Mountford and co-workers, which gives simple amine/imide exchange, the reaction of amine with $CpTa(=NBu^t)Cl_2$, **1**, gives multiple products, including at least one stable imide/amide. Second, the strongly Lewis acidic **1** appears to nearly consume added amine. The concentration, therefore, of amine in solution when it originates as a trace contaminant must be very low. It is worth noting that the pyridine ligands coordinated to the titanium would be expected to diminish the Lewis acidity of the Mountford complex

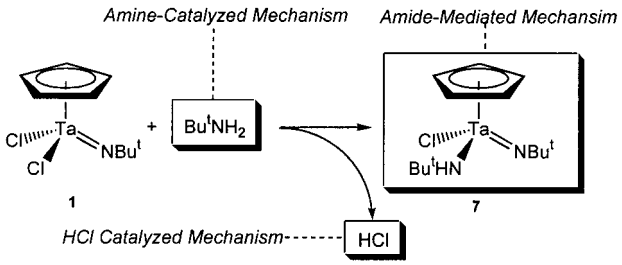
Scheme 13



Scheme 14



Scheme 15



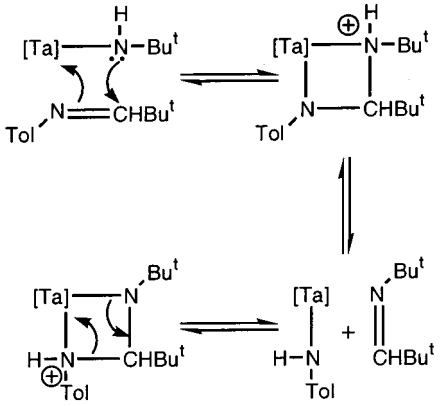
and may explain the divergence in behavior for the two systems. Finally, we observed that the ^{15}N label from added labeled amine moved more quickly to the imide positions than to the imine. This final observation is inconsistent with the fact that imide **1** is involved in the slowest rate-determining step. If we assumed the amine pathway dominates, then we would expect the label to move into the imine position faster. The second mechanism we postulated, mediation by imide/amide **7**, can be discounted. The imide/amide, when isolated, does not react with imines. Therefore, the compound cannot be the catalyst.

The third mechanism, mediation by HCl, is consistent with our data. The reaction of amine with imide **1** to produce HCl is rapid and quantitative in the case of *tert*-butylamine **6**. Although we are working in nonpolar solvents, the imide and imine functional groups are quite basic and could be protonated to a small extent. After protonation, one could postulate a catalyzed addition/elimination sequence that depends on original imide and also on imine. Concurrently, it must be assumed that some of the amine-catalyzed processes proposed in the first mechanism are occurring. As we stated earlier, the amine-mediated pathway does not explain all of our data, but it probably is active.

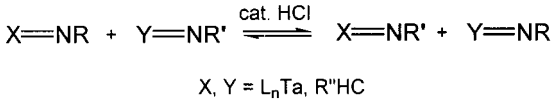
Although the idea of an acid-catalyzed stoichiometric addition/elimination reaction between an imide and an imine is intriguing and could be exploited, the presence of trace acid in any catalytic mixture of two imines and a transition metal catalyst is not tolerable. The acid-catalyzed imine exchange is quite facile and would compete with the metal-centered reaction. The benefits of metal catalysis, selectivity, and activation and the potential for metal-centered chain polymerization would be lost.

Our observations may have implications for other systems that have exhibited imine or carbodiimide metathesis activity. Royo, for example, reported imine and carbodiimide metathesis in the closely related pentamethylcyclopentadienyl system Cp*Ta(=NBu^t)-Cl$_2$.[11] The reaction of 1 equiv of imine, (Ph)HC=N(Ph), with the Cp* imide was found to be slow at 165 °C but proceeded at lower temperatures when an excess of imine was used. No diazametallacyclic intermediates

Scheme 16



Scheme 17



were observed, and Royo reported that switching solvent from C_6D_6 to $CDCl_3$ increased the reaction rate. All of these facts are suggestive of an HCl-catalyzed reaction similar to that observed in our system. Also analogous in composition and behavior are certain catalysts for NR exchange such as $Cl_3V(=NTol)$ and $(DME)Cl_3Nb(=NPh)$ reported by Birdwhistell[12] and Bruno,[10] respectively. In particular, these group V compounds are extremely electrophilic with potentially labile chloride supporting ligands. These similarities suggest that HCl catalysis could also be an important pathway for these systems. It is also possible that the $(DME)Cl_2Mo(=NR)_2$ system reported earlier by our group[1−3] is subject to this type of reactivity. Unfortunately, in this specific case the complexity of the dual active site catalyst precludes the detailed mechanistic studies necessary to confirm or deny this conjecture.

Conclusions. We have discovered that $CpTa(=NR)Cl_3$ reacts metathetically with amines to give the =NR exchanged products and that the mono(imide) can act as an imine metathesis catalyst. Kinetic analysis of the reaction suggests that amine plays a primary role in the reaction mechanism. ^{15}N-labeling studies are most consistent with a mechanism involving initial attack on the Lewis acidic metal center, giving an inactive metal complex and an equivalent of HCl. It is postulated that the HCl catalyzes a variety of processes in the reaction including imide/imine metathesis.

Experimental Section

General Procedures. All manipulations were performed under inert atmosphere using standard glovebox and Schlenk techniques. Solvents were distilled from appropriate purifying agents (noted in parentheses) prior to use: tetrahydrofuran (sodium/benzophenone ketyl), toluene (sodium/benzophenone), hexane (sodium/benzophenone), dichloromethane (P_2O_5), and 1,2-dichloroethane (P_2O_5). *tert*-Butylamine and *p*-tolylamine were distilled from CaH_2. The compounds $CpTaCl_4$,[14] trimethylsilylamines,[15] ^{15}N-labeled ammonium salt,[16] and imines[17] were prepared according to established methods. All other chemicals were used as received unless otherwise noted. ^{1}H,

(14) Cardosa, A. M.; Clark, R. J. H.; Moorehouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156−1160.

^{13}C, and ^{15}N NMR spectra were recorded with a Bruker AF500 or AF300 NMR spectrometer. Chemical shifts for ^{1}H and ^{13}C are referenced to the residual protio impurity in the deuterated solvent. ^{15}N chemical shifts are referenced to formamide used as an external standard. ^{14}N NMR spectra were recorded by Dr. M. Minelli, Grinnell College, Iowa. They were measured on a Bruker AC 300 MHz NMR spectrometer with a 10 mm broadband probehead (109Ag-31P) with digital tuning. Nitromethane neat was used as external reference (0 ppm).

CpTa(=NBu^t)Cl$_2$ (1) was prepared according to the method of Gibson for $CpCl_2Nb(=NBu^t)$ with slight modification.[18] To a stirred, room-temperature suspension of $CpTaCl_4$ (1.38 g, 3.57 mmol) in 1,2-dichloroethane (50 mL) in a 100 mL Schlenk flask was slowly added (TMS)NHBu^t (1.04 g, 7.17 mmol). The flask was fitted with a reflux condenser, and the suspension was refluxed under nitrogen overnight. The solvent was removed under vacuum, and the resulting yellow-brown solid was redissolved in hexane. The solution was filtered to remove an insoluble tan powder, and the filtrate was stored at −35 °C overnight. The product crystals were isolated as golden yellow needles by filtration in 72% yield (0.99 g, 2.55 mmol). ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C): δ 1.10 (s, 9H, C(CH_3)$_3$), 5.93 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 25 °C): δ 32.6 (C(*C*H$_3$)$_3$), 66.7 (*C*(CH$_3$)$_3$), 111.6 (C_5H_5). ^{14}N{^{1}H} NMR (21.69 MHz, CH_2Cl_2, 25 °C): δ 30 (*N*C(CH$_3$)$_3$). ^{15}N NMR of CpTa(=^{15}NBu^t)Cl$_2$ (**1N**) (50.68 MHz, C_6D_6, 25 °C): δ 292.4 (*N*C(CH$_3$)$_3$).

CpTa(=NBu^t)(NHBu^t)Cl (7). To a solution of CpTa(=NBu^t)Cl$_2$ (0.49 g, 1.27 mmol) in toluene (5 mL) was added H_2NBu^t (300 μL, 2.85 mmol). Precipitate formed immediately, and the solution was filtered through Celite to remove the ammonium salt. The solvent was removed from the filtrate under vacuum to give the product as an off-white powder in 86% yield (0.46 g, 1.09 mmol). Repeated recrystallizations did not give material suitable for chemical analysis nor for X-ray diffraction. ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C): δ 1.05 (s, 9H, NC(CH_3)$_3$), 1.13 (s, 9H, NHC(CH_3)$_3$), 5.88 (s, 5H, C_5H_5), 6.40 (s, 1H, N*H*C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 25 °C): δ 33.6 (NC(*C*H$_3$)$_3$), 34.5 (NHC(*C*H$_3$)$_3$), 56.5 (NH*C*(CH$_3$)$_3$), 65.5 (N*C*(CH$_3$)$_3$), 108.5 (C_5H_5). ^{15}N NMR of CpTa(=^{15}NBu^t)(^{15}NHBu^t)Cl (**7N2**) (50.68 MHz, C_6D_6, 25 °C): δ 116.7 (*N*HC(CH$_3$)$_3$), 267.0 (*N*C(CH$_3$)$_3$).

^{15}NH$_2$Bu^t (6N). To a slurry $^{15}NH_3Bu^tCl$ (0.30 g, 2.78 mmol) in 1.75 mL of C_6D_6 in a three-necked round-bottom flask under N_2 was added solid NaOH (0.2 g, 5 mmol, 1.8 equiv). Deionized water (250 μL) was added via syringe to help dissolve the solids. Some solid remained undissolved. The contents of the flask were stirred for 2 h and then vacuum transferred into a round-bottom flask containing CaH_2. After stirring for 24 h, the solution was vacuum transferred again into a clean flask containing more CaH_2 and stirred overnight before being vacuum transferred into a clean, dry flask. The dry C_6D_6 solution of the labeled amine was diluted to a total volume of 3 mL by addition of C_6D_6. An 80 μL aliquot was added to a solution of 50 μL of anisole (0.73 mmol) in C_6D_6 in an NMR tube. Integration of the ^{1}H NMR spectrum established that the concentration of the bulk solution was 0.626 M (68% yield). ^{15}N NMR spectroscopy determined that the label had been incorporated into the product. ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C): δ 0.98 (br, 2H, $^{15}NH_2$), 3.29 (d, 9H, CH_3, $^{3}J_{NH}$ = 2.3 Hz). ^{15}N NMR (50.68 MHz, C_6D_6, 25 °C): δ −53.6 (*N*H$_2$).

(Ph)HC=^{15}N(Bu^t) (4bN) was prepared by standard methods.[17] ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C): δ 8.12 (d, 1 H, ^{15}N=C*H*Ph, J_{NH} = 3.8 Hz), 7.80 (d, 2 H, CH*Ph*), 7.06−7.26 (m, 3 H, CH*Ph*), 1.23 (d, 9 H, ^{15}NC(CH_3)$_3$, J_{NH} = 1.3 Hz). ^{15}N NMR (50.68 MHz, C_6D_6, 25 °C): δ 244.1.

General Procedure for NMR Experiments. Imine and amine standard solutions were prepared by weighing the imine into a volumetric flask and diluting with C_6D_6. Likewise, standard solutions of the internal standards were prepared using volumetric flasks. The necessary amounts of these solutions were then transferred into an NMR tube equipped with a Teflon stopcock. The catalyst was either weighed into a vial, dissolved in 100 μL of C_6D_6, and transferred into the NMR tube or taken from a standard solution prepared in a volumetric flask. If needed, additional C_6D_6 was added to the NMR tube so that concentration remained constant between analogous experiments. When two imines were used, relative stoichiometry was checked by integration prior to heating.

Reaction of 1 and (Bu^t)HC=N(*p*-tolyl), 2a. Compound **1** (0.0066 g, 0.017 mmol, 1 equiv), (Bu^t)HC=N(*p*-tolyl) (0.171 mol, 10 equiv), and anisole internal standard were added to an NMR tube. The reaction was monitored at 55 °C for 45 days. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. Resonances for **3a** and **4a** were observed.

Reaction of 1 and (Ph)HC=N(Pr^n), 2b. Compound **1** (0.0066 g, 0.017 mmol, 1 equiv), (Ph)HC=N(Pr^n) (0.171 mol, 10 equiv), and hexamethylbenzene internal standard were added to an NMR tube. The reaction was monitored at 55 °C for 45 days. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. Resonances for **3b** and **4b** were observed initially. After 1 day resonances for compound **5** were observed.

Reaction of 1, (Bu^t)HC=N(*p*-tolyl), 2a, and (Ph)HC=N(Pr^n), 2b. Compound **1** (0.0066 g, 0.017 mmol, 1 equiv), (Ph)HC=N(Pr^n) (0.171 mmol, 10 equiv), (But)HC=N(*p*-tolyl) (0.171 mmol, 10 equiv), and hexamethylbenzene internal standard were added to an NMR tube. The reaction was monitored at 25 °C for 25 days, then 55 °C for 35 days. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. Resonances for the metathesis products (Ph)HC=N(*p*-tolyl) and (Bu^t)CH=N(Bu^t) were observed initially. After >2 weeks, precipitate was observed.

Reaction of Imide 1 and Labeled Amine 6N. A 20 μL portion of a 0.626 M (12.5 μmol) standard solution of labeled amine **6N**, in C_6D_6, was added to 100 μL of a 0.0912 M (9.12 μmol) standard solution of imide **1** in C_6D_6, in a screw top NMR tube. A fine precipitate of ammonium salt formed immediately. The progress of the reaction was monitored by ^{1}H and ^{15}N NMR spectroscopy at 80 °C for 3 days. Resonances for the labeled imide/amide **7N1a** were observed initially. Over the course of the reaction, resonances for **1N** and **7N2** were observed.

Reaction of Imide 1, Imine 4b, and Labeled Amine 6N. A 100 μL portion of a 0.626 M (62.5 μmol) standard solution of labeled amine **6N**, in C_6D_6, was added to a screw top NMR tube containing 400 μL of a 0.0912 M (36.5 μmol) standard solution of imide **1** and 100 μL of a 0.33 M (33.0 μmol) standard solution of imine **4b**. The progress of the reaction was monitored by ^{1}H and ^{15}N NMR spectroscopy at 80 °C for 3 days. Resonances for the labeled imide/amide **7N1a** were observed initially. Over the course of the reaction, resonance for **1N**, **4bN**, and **7N2** were observed.

Reaction of Imide 1, Labeled Imine 4bN, and Amine 6. A 200 μL portion of a 0.472 M (94.4 μmol) standard solution of amine in C_6D_6 was added to a screw top NMR tube containing 97.4 mg (251 μmol) of imide **1** and 200 μL of a 1.24 M (248 μmol) standard solution of imine **4bN**. The progress of the reaction was monitored by ^{1}H and ^{15}N NMR spectroscopy at 68 °C for 2 days. Resonances for the labeled imide **1N** were observed initially. Over the course of the reaction, resonances for **7N1a** and **7N2** were observed.

(15) TMS amines were synthesized by either (a) the addition of TMSCl to the parent lithium amine or (b) the reaction of TMSCl with the parent amine in basic solution.

(16) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041−2054.

(17) Imines were prepared by stirring a benzene solution of the corresponding amine and aldehyde over molecular sieves, followed by filtration, removal of solvent in vacuo, and vacuum distillation.

(18) Williams, D. N.; Mitchell, J. P.; Poole, A. D.; Siemeling, U.; Clegg, W.; Hockless, D. C. R.; O'Neil, P. A.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 739−751.

Reaction of Imide 1 with Labeled Ammonium Salt 8N. A 74.4 mg (0.19 mmol) portion of imide **1** and 42.9 mg (0.39 mmol) of labeled ammonium salt **8N** were added to a screw top NMR tube. Approximately 0.5 mL of C_6D_6 was added to give a yellow solution with a white precipitate. The sample was heated at 70 °C for 2 weeks. ^{15}N NMR spectroscopy revealed a resonance for labeled imide **1N**.

Reaction of Amine 6 with Labeled Ammonium Salt 8N. A 55.8 mg (0.50 mmol) portion of labeled ammonium salt was added to 0.5 mL of a 0.5 M (0.25 mmol) solution of amine **6**. The sample was heated at 70 °C for 2 weeks. ^{15}N NMR spectroscopy revealed a resonance for labeled amine **6N**.

Acknowledgment. This research was supported by NSF award CHE-0091400. We thank Dr. Martin Minelli and Dr. Fu-Tyan Lin for help in acquiring ^{14}N and ^{15}N NMR spectral data.

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