

Transition metal imide/organic imine metathesis reactions: *unexpected observations*

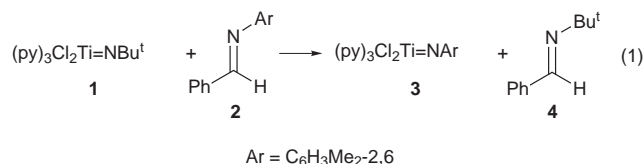
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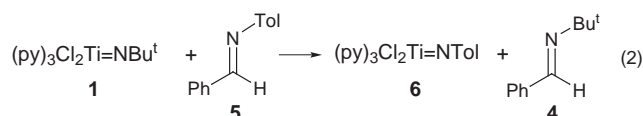
Mixtures of $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$ **1** and $\text{PhC}(\text{NAr})\text{H}$ (Ar = $\text{C}_6\text{H}_3\text{Me}_2$ -2,6 or $\text{C}_6\text{H}_4\text{Me}$ -4) gave quantitative conversion to $[\text{Ti}(\text{NAr})\text{Cl}_2(\text{py})_3]$ and $\text{PhC}(\text{NBu}^t)\text{H}$, the products of Ti=N-Bu^t/C=NAr transition metal imide/organic imine metathesis; examination of the kinetics for Ar = $\text{C}_6\text{H}_4\text{Me}$ -4 showed that the rate limiting step for this process is zero order in **1**, demonstrating that these reactions do not involve metal imide participation in the rate limiting step.

One attraction of transition metal imido compounds is their potential use in metal-mediated imido group (NR) transfer reactions. The addition of unsaturated substrates to M=NR linkages is now well documented, but examples of reactions resulting in complete removal (functional group transfer) of NR from metal to substrate are still somewhat more restricted, especially by comparison with the rich functional group transfer chemistry of metal oxo complexes.¹ Very recently there have been reports of transition metal imide/organic imine ($\text{L}_n\text{M}=\text{NR}/\text{R}_2\text{C}=\text{NR}'$) functional group metathesis reactions,² and these have been proposed in some instances to arise *via* metal imide-mediated processes, possibly involving cycloaddition of C=NR' to M=NR. Such processes appear to be the aza-analogues of the widely used metal alkylidene ($\text{L}_n\text{M}=\text{CR}_2$)/alkene ($\text{R}'\text{C}_2=\text{CR}'_2$) metathesis reaction³ and are therefore potentially hugely important transformations in stoichiometric and catalytic synthesis. Identification of the possible role(s) of the metal centre in such processes is clearly essential. As part of an ongoing study of early transition metal imido chemistry, we found that a number of titanium imido complexes undergo well characterised cycloaddition and other coupling reactions of the Ti=NR group (R = Bu^t or aryl) with organic substrates.⁴ In parallel studies we have observed reactions of $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$ ^{4b} with certain mono- and α -di-imines that yield the expected products of imide/imine functional group metathesis. The results herein show that examples of apparently metal-mediated imide/imine metathesis reactions must be subjected to mechanistic investigations before they can be properly authenticated.

Reaction of $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$ **1** with one equivalent of the *N*-2,6-dimethylphenylbenzaldehyde imine **2** at 60 °C for 96 hours in CDCl_3 gave (by NMR) quantitative and stoichiometric conversion to $\text{PhC}(\text{NBu}^t)\text{H}$ **4** and the arylimido compound $[\text{Ti}(\text{NC}_6\text{H}_3\text{Me}_2\text{-2,6})\text{Cl}_2(\text{py})_3]$ **3** [eqn. (1)].[§] Repeating the

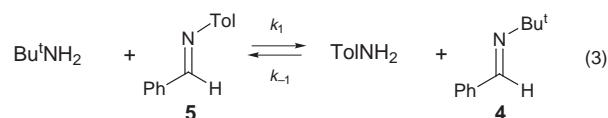


reaction on a preparative scale confirmed the exchange of *tert*-butylimide for the 2,6-dimethylphenylimide ligand. Similarly, reaction of **1** with one equivalent of the less bulky *N*-arylimine $\text{PhC}(\text{NTol})\text{H}$ **5** (Tol = $\text{C}_6\text{H}_4\text{Me}$ -4) gave a quantitative yield of **4** after only 4 hours at 60 °C in CDCl_3 , along with the tolylimido product **6** [eqn. (2)]. Products **3**, **4** and **6** were identified by comparison with authentic samples^{4b} and the reactions were

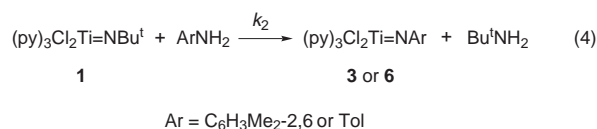


fully reproducible in both CDCl_3 and C_6D_6 . At first sight, eqns. (1) and (2) are apparently straightforward examples of metal-mediated imide/imine metathesis reactions. Furthermore, reaction of **1** with certain *N*-aryl- α -diimines also leads to the expected arylimido titanium products and the corresponding *N-tert*-butyl- α -diimines.

In a separate experiment [eqn. (3)] an equimolar mixture of



Bu^tNH_2 with **5** in CDCl_3 (no titanium imido compound added) gave an equilibrium mixture (K_{eq} ca. 1, *i.e.* $k_1 \approx k_{-1}$) containing the two starting compounds along with the products TolNH_2 and imine **4** after 8 hours at 30 °C. Similarly, starting with an equimolar mixture of pure TolNH_2 and **4** also gave an equilibrium mixture of TolNH_2 , **4**, Bu^tNH_2 and **5**. Since there is no thermodynamic driving force in eqn. (3) to account for the net quantitative reactions in eqns. (1) and (2), we infer that it is formation of the arylimido products **3** and **6** that causes these two reactions to go to completion. This hypothesis is supported by eqn. (4) which shows that addition of a stoichiometric



amount of arylamine to $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$ **1** gives quantitative formation of Bu^tNH_2 and the corresponding arylimido **3** or **6**.^{4b} This process is (qualitatively) very much faster than any of the other three [*i.e.* eqns. (1)–(3)]. Further evidence for the role of **1** as an effective trap for ArNH_2 came from NMR experiments in which **1** was added to a pre-equilibrated mixture of Bu^tNH_2 , **5**, TolNH_2 and **4** [eqn. (3)]: **1** and TolNH_2 were consumed and there was quantitative conversion of **5** to **4**.

Examination of the kinetics of eqn. (3) under pseudo-first order conditions established that this reaction [from left to right as shown in eqn. (3)] is first order in both Bu^tNH_2 and imine **5** and also allowed the direct deduction of k_1 . However, reaction of $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$ **1** with $\text{PhC}(\text{NTol})\text{H}$ **5** (10, 16.5 and 20 equivs.) under otherwise identical pseudo-first order conditions showed (Fig. 1) that the rate for eqn. (2) is zero order with respect to **1** and has no simple dependence on **5**. These observations are clearly not consistent with the expected titanium imide-mediated metathesis mechanism of the type illustrated in Scheme 1, in which a diazametallacycle **7** is formed in the rate limiting step. For such a process a rate dependency on **1** is required.¶ Indeed, to our knowledge, all

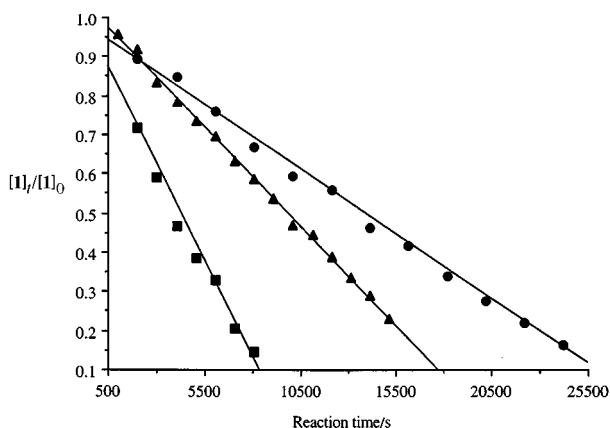
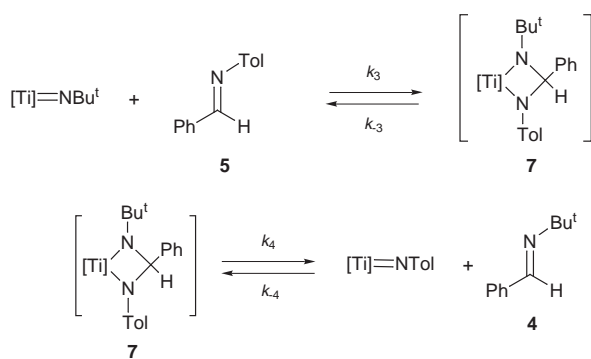


Fig. 1 Linear plots of $[1]/[1]_0$ versus time for the reactions with an excess of PhC(NTol)H **5** in CDCl₃ showing clearly the zero order dependence of rate on $[1]$. Legend: ● 10 equivalents of **5**; ▲, 16.5 equivalents of **5**; ■, 20 equivalents of **5**.



kinetically characterised examples of alkene metathesis by homogeneous metal alkylidene (carbene) complexes (which proceed *via* metallacyclobutane intermediates) show a first order dependence on metal concentration.⁵ Furthermore, studies by Lee and Bergman of cycloaddition reactions of the imido zirconium complex [Cp₂Zr(NR)(L)] (R = Bu^t or C₆H₃Me₂-2,6, L = THF, OPPh₃ or 4-*tert*-butylpyridine) have shown them to be first order in imido complex.⁶ Previously reported zirconium-mediated imine metathesis reactions also follow a first order relationship between reaction rate and metal complex, although in this instance the resting state of the complex is a diazametallacycle.^{2a}

The absence of a rate dependence on $[1]$ implies that one or more alternative mechanisms (to that shown in Scheme 1) must be operating in eqns. (1) and (2). At first sight, one possibility appears to be a tandem combination of eqns. (3) and (4) where traces of Bu^tNH₂ (in principle impossible to exclude for these very moisture sensitive systems, although we have no NMR evidence for its presence in mixtures of **1** and **5**) give rise to formation of imine **4**, the liberated TolNH₂ being scavenged by **1** forming the imido product **6**. However, the kinetic results do not support this mechanism since the rate law in this case requires a first-order dependence on $[5]$. Furthermore there is no evidence for significant enough concentrations of Bu^tNH₂ in these NMR mixtures to account for the observed rate of formation of **4** and **6** in these reactions.**

In summary we have demonstrated that apparently straightforward transition metal imide/organic imine metathesis reactions do not necessarily involve metal imide participation in the rate determining step. This is in sharp contrast to the well known metal alkylidene/alkene metathesis reactions. Cases of metal imide/imine metathesis must clearly be subjected to mechanistic scrutiny before conclusions concerning either the role of the metal centre or any structure–activity relationships can be

reached. Further investigations of these and other related reactions are currently under way.

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Notes and References

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§ For all the rate determinations the disappearance of [Ti(NBu^t)Cl₂(py)₃] **1** or Bu^tNH₂ was monitored over at least three half-lives under pseudo-first-order conditions with *p*-dimethoxybenzene as the internal standard. Both before and after each experiment the temperature in the NMR probe was calibrated using ethylene glycol (80%) in DMSO. The temperature did not vary by more than 1 °C. The samples were prepared in a dry-box using Teflon valve (Young's) 5 mm tubes, which had been rigorously dried. CDCl₃ and C₆D₆ were dried over calcium hydride and potassium respectively, at rt, then distilled under reduced pressure. ¹H NMR spectra were recorded on a Bruker DPX 300 spectrometer at 30 °C.

¶ For the process shown in Scheme 1, rate = $k_{\text{obs}}[\text{metal imide}][\text{organic imine}]$, where $k_{\text{obs}} = k_3k_4/(k_{-3} + k_4)$, assuming the k_{-4} step is not significant at low concentrations of product imine and a steady state approximation for **7**. In the reactions in eqns. (1) and (2), pyridine dissociation may be required before formation of hypothetical **7**. In this instance the rate should still be dependent on $[\text{metal imide}]$, but k_{obs} would show a dependence on $[\text{pyridine}]$. However, we have found that the five-coordinate bis(pyridine) complex [Ti(NBu^t)Cl₂(py)₂] also reacts with organic imines at a rate not significantly different from that of **1** under the same conditions and so the presence of the third pyridine molecule is not important.

|| Combining eqns. (3) and (4) and assuming a steady state approximation of [TolNH₂] leads to the expression: rate = $k_1[\text{Bu}^t\text{NH}_2][5]$ since, under the pseudo-first order conditions used here, $[5] \gg [4]$ and hence the k_{-1} back-reaction is negligible, especially since **1** is an effective trap for TolNH₂.

** From kinetic analysis of eqn. (3) we know independently the value of k_1 ($1.35 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$) under analogous reaction conditions. Therefore, if indeed rate = $k_1[\text{Bu}^t\text{NH}_2][5]$ then $[\text{Bu}^t\text{NH}_2]$ has to be approximately 0.10 to 0.43 M for the experiments shown in Fig. 1. From the NMR spectra the maximum possible value of $[\text{Bu}^t\text{NH}_2]$ in these experiments is < 0.005 M. However, it is possible that under the reaction conditions of eqns. (1) or (2), eqn. (3) is accelerated by Lewis and/or Brønsted acids. Indeed, tests of this hypothesis for eqn. (3) with added [Sc(OTf)₃] demonstrated a rate acceleration suggesting that Lewis acids (*e.g.* **1** and/or its trace decomposition products) may make a tandem combination of eqns. (3) and (4) a possibility. Toluene-*p*-sulfonic acid had no measurable effect on the rate of eqn. (3). We cannot directly determine the influence of additional Bu^tNH₂ on the rate of reaction of **1** with **5** [eqn. (2)]; any Bu^tNH₂ added would be rapidly scavenged by **5** [eqn. (3)] since $t_{1/2}$ for the consumption of **5** in eqn. (3) is *ca.* 25 times shorter than for **5** in eqn. (2) under otherwise identical conditions.

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