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Zirconium-Mediated Imine Metathesis. Synthesis of 2,4-Diaza-1-zirconiacyclobutanes and the Mechanism of Their Reactions with Imines and Alkynes

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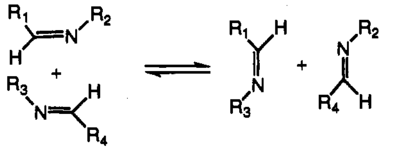
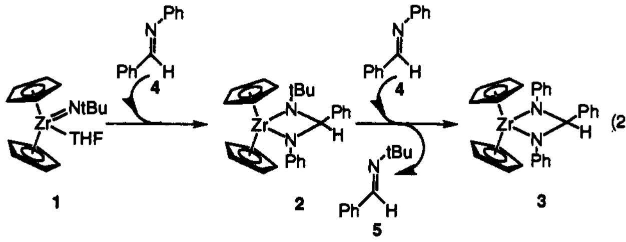
The study of alkylidene complexes and their role in olefin metathesis reactions are among the most active areas of organometallic research.[1-3] Although alkylidene complexes are known to react with imines,[4,5] few reports exist concerning the metathesis reactions that could occur upon reaction of imido complexes with imines (eq 1).[6-8] We have now found that Cp$_2$Zr(=N-*t*-Bu)(THF)[9] (1) undergoes a formal [2+2] cycloaddition reaction with benzaldehyde *N*-phenylimine (4) (eq 2) to afford the 2,4-diazametallacyclobutane 2. This is followed by reaction of 2 with a second molecule of *N*-phenylimine to give the related heterometallacycle 3 with release of benzaldehyde *N*-*tert*-butylimine (5). We report here the details of this reaction and a preliminary study of its mechanism.



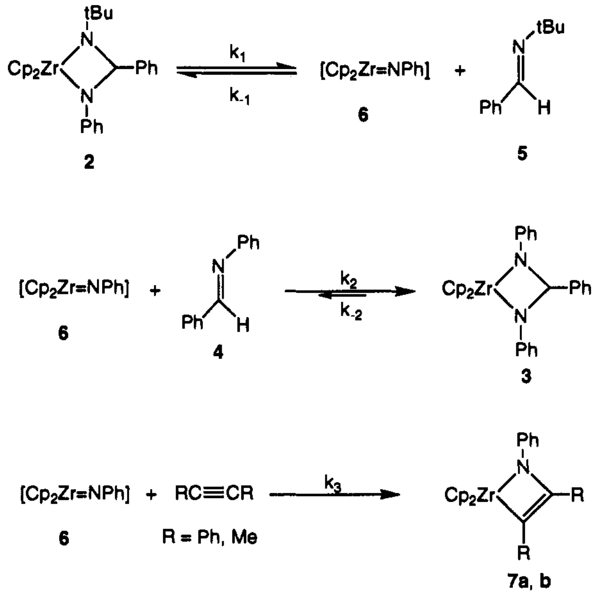
(1)



(2)

Treatment of zirconium imido complex 1 with benzaldehyde *N*-phenylimine at room temperature in toluene solution gave the red 2,4-diazametallacyclobutane product 2 in 91% yield after crystallization from the reaction mixture. Thermolysis of 2 at 85 °C with 1 equiv of the imine 4 resulted in stoichiometric metathesis that produced benzaldehyde *N*-*tert*-butylimine (5) and the new purple diazametallacycle 3 in 93% yield (eq 2). Both 2 and 3 are stable toward cycloreversion at 25 °C but undergo elimination of imine (5 in the case of 2 and 4 in the case of 3) at elevated temperatures to give dimeric [Cp$_2$Zr(NPh)]$_2$.[9,10]

Scheme 1



We believe that the formation of metallacycle 2 from 1 involves a pathway similar to that proposed earlier[11,12] for the reaction of 1 with alkynes: reversible dissociation of the THF ligand to generate the transient coordinatively unsaturated imido complex Cp$_2$Zr=N-*t*-Bu, followed by rapid reaction of this intermediate with the unsaturated organic compound to give metallacycle.[13] There are two reasonable mechanisms to describe the conversion of 2 to 3. The first is an associative process that involves direct attack of *N*-phenylimine 4 on diazametallacycle 2. This reaction should follow a rate law that is overall second order (first order in 2 and first order in 4). However, as summarized below this mechanism is inconsistent with our experimental observations.

An alternative dissociative mechanism (Scheme 1) involves a preequilibrium step in which *N*-*tert*-butylimine 5 is released and the transient imido complex 6 is formed (this intermediate is closely related to Cp$_2$Zr=N-*t*-Bu, but its THF complex does not appear to be isolable, presumably because of its propensity to dimerize irreversibly). Subsequent reaction of imido complex 6 with *N*-phenylimine 4 generates the new diazametallacycle 3. Experiments with both 3 and 5 showed that although the reaction is reversible (see below), if only modest concentrations of 5 are utilized in the kinetic study, the back reaction remains slow enough that the k_{-2} step can be ignored. Utilizing this assumption and applying the steady-state approximation to the concentration of 6 predicts the rate law shown in eq 3 ($A = k_2[\mathbf{4}]$). If this

$$\text{rate} = \frac{k_1[\mathbf{2}]A}{k_{-1}[\mathbf{5}] + A} \qquad (3)$$

mechanism controls the reaction, only under the conditions of $k_{-1}[\mathbf{5}] \gg k_2[\mathbf{4}]$ will the rate law give first-order behavior in [2] and [4], and under these conditions the rate should show inhibition by added *N*-*tert*-butylimine 5. As $k_2[\mathbf{4}]$ becomes much greater than $k_{-1}[\mathbf{5}]$, the reaction will reach saturation conditions. At this concentration of 4, the reaction order in both imines 4 and 5 should go to zero, and the observed rate will level off at $k_1[\mathbf{2}]A$.

Kinetic studies were carried out using excess concentrations of both imines in toluene-d_8 to maintain pseudo-first-order rate

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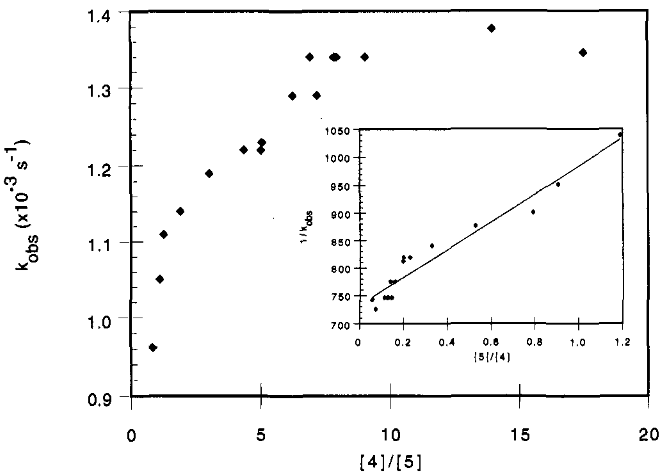

Figure 1. Dependence of k_{obs} on the concentration of added benzaldehyde *N*-phenylimine (**4**) and reciprocal plot of $1/k_{obs}$ vs [**5**]/[**4**] (inset). The linear fit gave a coefficient of $r = 0.97$.

behavior for **2**, and the disappearance of the starting metallacycle was monitored at 70 °C by ^{1}H NMR and UV–vis spectrometry. Under most conditions, the reaction gave complete and clean conversion to the metathesis product and excellent first-order behavior was observed. Only at very high concentrations of **5**, where the k_{-2} step becomes important, did we observe side reactions which led to small amounts of the dimer $[Cp_2Zr(NPh)]_2$. Rates measured using variable concentrations of both **4** and **5** demonstrated that at low concentrations of entering imine **4**, the rate was accelerated by added **4** and inhibited by extruded imine **5**. A plot of k_{obs} versus [**4**]/[**5**] was obtained (Figure 1) which clearly illustrates saturation kinetics at higher concentrations of *N*-phenylimine **4**, and a plot of $1/k_{obs}$ versus [**5**]/[**4**], although somewhat scattered, shows an essentially linear dependence on the imine ratio.

These data are consistent with the rate law given in eq 3, and we therefore favor this mechanism to describe the imine metathesis reaction. Values of $k_1 = (1.4 \pm 0.1) \times 10^{-3}\ s^{-1}$ and $k_{-1}/k_2 = 0.34 \pm 0.02$ were derived from the inverse first-order plot. The k_{-1}/k_2 ratio demonstrates that the transient imido complex is trapped more rapidly by the *N*-phenylimine than by the *N*-*tert*-butylimine. By carrying out the reaction in the presence of higher concentrations of **5**, so that the back reaction rate was increased, we were able to carry the reaction to equilibrium and determine that $K_{eq} = 4.6$. Thus, the higher thermodynamic stability of [**3** + **5**] over [**2** + **4**] is reflected to some extent in the transition states leading to the two metallacycles.

If the dissociative mechanism is correct, we reasoned that it should be possible to trap transient imido complex **6** generated from metallacycle **2** with alkynes.[9] Furthermore, these reactions should also demonstrate saturation kinetics, and the saturation rate constant k_1 should be identical to that measured in the imine metathesis study. We therefore examined the addition of diphenylacetylene and 2-butyne to diazametallacycle **2**. Monitoring these reactions at 70 °C by ^{1}H NMR spectrometry showed that metallacyclobutene products **7a** (89%) and **7b** (92%) were generated cleanly. As illustrated in Scheme 1, the phenylimido intermediate **6** identified as the first intermediate generated in the imine metathesis reaction can now be trapped by alkyne rather than by a second molecule of imine. This gives the rate law shown in eq 3 with term $A = k_3[\text{alkyne}]$.

A series of kinetic studies similar to those mentioned above demonstrated that the reaction was first order in [**2**] but zeroth order in [alkyne] even at the lowest concentrations of this reactant that we were conveniently able to reach while still maintaining pseudo-first-order conditions in [**2**]. Therefore, the reaction clearly does not involve initial attack of alkyne on the diazametallacycle. If the dissociative mechanism is presumed to occur, then under all of our conditions $k_3[\text{alkyne}] \gg k_{-1}[\mathbf{5}]$ (i.e., the alkynes trap imido complex **6** more rapidly than does *N*-phenylimine **4**), and the rate simplifies to $k_1[\mathbf{2}]$. Important support for this assumption is provided by the fact that the k_1 values determined from these rate studies are the same for both alkynes (for diphenylacetylene, $k_1 = (1.42 \pm 0.04) \times 10^{-3}\ s^{-1}$; for 2-butyne, $k_1 = (1.40 \pm 0.04) \times 10^{-3}\ s^{-1}$) and identical within experimental error to the k_1 value measured in the imine metathesis kinetic experiments. As expected from the reversibility studies mentioned above, heating **3** with diphenylacetylene also leads to **7a** but more slowly than this complex is formed from **2**.

To summarize, we have found a stoichiometric zirconium-mediated imine metathesis reaction that proceeds, in analogy to olefin metathesis, by an initial dissociative process that generates a transient imido complex intermediate. The imido complex is trapped even more efficiently by alkynes than by imines. The fact that identical values for the saturation rate constant k_1 are measured for the reactions of **2** with imine and two alkynes, at high imine or alkyne concentrations where diazametallacycle cleavage is rate determining, provides strong evidence for the mechanism illustrated in Scheme 1. In principle, imine interchange can also be catalyzed by protic acid or other electrophiles. It is somewhat suprising that only a few studies of the acid-catalyzed reaction have appeared in the literature,[14,15] indicating that metal-mediated metathesis may constitute a useful alternative method for carrying out this transformation. In preliminary experiments, we have found that both metallacycles **2** and **3** will catalyze the metathesis reaction of **4** and *N*-tolylanisaldehyde to give a statistical mixture of the four possible imine products (the two starting materials and both mixed products). Steric factors seem to be important in controlling the rates and thermodynamics of the zirconium-mediated metathesis, and conversion to dimer limits the lifetime of the catalyst. Further studies will be required to prevent dimer formation, determine the generality of the reaction, and evaluate the relative significance of steric and electronic factors in controlling its rate. These studies are presently under way.

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Supplementary Material Available: Spectroscopic and analytical data on complexes **2** and **3** and typical plots of absorbance versus time for the metathesis reactions (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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