Organometallics **2000,** *19,* 4672−4674

Use of Niobium(III) and Niobium(V) Compounds in Catalytic Imine Metathesis under Mild Conditions

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Received July 17, 2000

*Summary: The niobium reagents $NbCl_3$(DME) (**1**) and mer-(DME)$Cl_3Nb{=}NPh$ (**6**) serve as effective catalysts or precatalysts in imine metathesis reactions with a variety of aldimines. These reactions are particularly convenient because they proceed at room temperature in a period of hours; noteworthy is the fact that **1** functions as a precatalyst even though it does not contain an imide ligand.*

Transition metals with multiply bonded ligands are extremely useful in processes such as oxidation[1] (M=O) and alkene metathesis[2] (M=CR_2). Although metal imides (M=NR) might be expected to exhibit chemistries similar to those of related oxides (with which they are isoelectronic), considerably less is known about =NR transfer and imine metathesis.[3] Early work showed that tantalum alkylidenes react with organic imines to give analogous tantalum imides:[4]

$$mer,cis\text{-}(THF)_2Cl_3Ta{=}CH^tBu \xrightarrow[Et_2O]{PhCH{=}NR} mer,cis\text{-}(THF)_2Cl_3Ta{=}NR \quad (1)$$

This process constitutes a stoichiometric metathesis reaction, and the alkylidenes have proven useful in a number of catalytic alkene metatheses.[2] Conversely, there are only two systems known to catalyze imine metathesis. Not surprisingly, both are imide complexes in which the metals are in their maximum oxidation state (Zr(IV)[5] or Mo(VI),[6] respectively), and both are effective at temperatures of ca. 85−100 °C. Indeed, related heteroatom metathesis systems are known,[7] and their reactions typically require elevated temperatures and/or long reaction times. In the course of some competition experiments involving two imines, we discovered that two different niobium compounds may be used to catalyze imine metathesis. Both systems proceed to equilibrium at room temperature, and typically do so within a few hours. This makes them the most active metathesis catalysts yet discovered, and we describe herein our preliminary studies on the chemistry of these two compounds.

Initial studies on this process were targeted at the use of formaldehyde imines.[8] These exist as cyclic trimers (hexahydrotriazines $(CH_2NR)_3$), which are presumably in equilibrium with the monomers. While pyrolysis of the trimers leads to the monomers,[9] the trimers are often used as an in situ source of imine; this latter approach was used here. The hexahydrotriazines were treated with the reagent $NbCl_3$(DME) (**1**); Pedersen has shown that this may be prepared in large quantitites, and it is a useful reagent for a variety of organic transformations.[10]

Reaction of the formaldehyde imine (**2**, as the trimer) with a second imine (**3**) and 5 mol % **1** (relative to the concentration of **3**) in THF[11] results in the conversion to the metathesis products shown in eq 2.[12] The process is easily monitored by gas chromatography−mass spectrometry, which confirms that the process is a true

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[11] Experimental details: in a typical procedure, a Schlenk flask was charged with 109 mg (0.35 mmol) of $(CH_2{=}NPh)_3$ and 5 mg (0.017 mmol, 5%) of $NbCl_3$(DME) in a nitrogen-filled glovebox. Using a Schlenk line, 10 mL of THF was added via nitrogen-flushed syringe. Finally, 68 μL (0.35 mmol) of $PhCH{=}NCH_2Ph$ was added via microsyringe. The resulting solution was stirred under nitrogen overnight. Small aliquots may be withdrawn for GCMS analysis to establish that the reaction has reached equilibrium. Product imines may be isolated via preparative thin-layer chromatography using ca. 15% ethyl acetate in hexane.

[12] Equation 2 is constructed to show the pairs of reactants tested. Hence, **2c** was reacted with both **3a** and **3c**.

10.1021/om000613k CCC: $19.00
Publication on Web 10/14/2000

$$\underset{\mathbf{2}}{R^1CH{=}NR^2} + \underset{\mathbf{3}}{R^3CH{=}NR^4} \overset{5\%\ \mathbf{1}}{\rightleftharpoons} \underset{\mathbf{4}}{R^1CH{=}NR^4} + \underset{\mathbf{5}}{R^3CH{=}NR^2} \qquad (2)$$

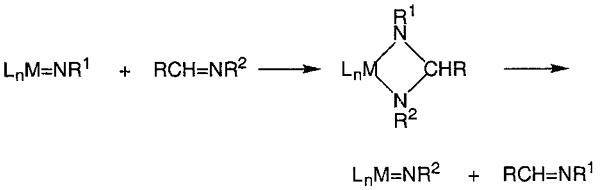
2a $R^1 = H, R^2 = Ph$	**3a** $R^3 = Ph, R^4 = Bz$	94 %
2b $R^1 = H, R^2 = {}^iPr$	**3a**	79%
2c $R^1 = H, R^2 = NNMe_2$	**3a**, **3c** $R^3 = {}^iPr, R^4 = Bz$	**5a**, 18% **5c**, 85%
2d $R^1 = H, R^2 = Bz$	**3d**, $R^3 = R^4 = Ph$	30%

metathesis reaction in which both **4** and **5** are produced. In most of the reactions represented in eq 2 we used equimolar amounts of **3** and the trimer of **2**, meaning that the formaldehyde imine was potentially present in 3-fold excess. Also apparent is the fact that **1** may be used in a mixed metathesis involving aldimines and hydrazones; the reaction of hydrazone **2c** (which is reportedly monomeric in solution)[13] proceeds with either **3a** or **3c**.

The reactions in eq 2 were run until equilibrium was established, a process typically requiring 4−12 h at ambient temperature. It is impossible to calculate equilibrium constants for most of the processes, since we do not know the equilibrium constants or rates governing the conversion of trimeric reagents to monomeric imines **2**. Hence, we have included in eq 2 the percent conversion of reactant **3** to product **5** at equilibrium; these were chosen because **3** is the limiting reagent in the reactions. It can be seen that the **3a**−**5a** conversion proceeds readily under the indicated conditions, presumably because the imine **5a** is stabilized by conjugation. To verify that this is an equilibrium situation, the reverse reaction between PhCH=NPh (**3d**) and $(CH_2{=}NBz)_3$ (**2d**) was also attempted. This reaction proceeded to a mixture of **4d** and **5d** in which the conversion was only ca. 30% (recall there is a 3-fold excess of formaldehyde imine used in both reactions; therefore, the equilibrium concentrations for the forward and reverse reactions will differ). In this reaction and in the reaction of **2c** and **3a** we also increased the starting concentration of **2** to confirm that this drove the reaction to higher levels of conversion (**3** → **5**). It should be noted that control reactions run without **1** showed no metathesis conversion in comparable time periods.

It is noteworthy that **1** does not contain an imide ligand yet still functions as a catalyst or precatalyst for metathesis reactions. We presume that the reactions in eq 2 involve conversion of **1** to an imide derivative. However, the lack of useful spectroscopic handles and poor solubility in most solvents make this difficult to verify. A closely related Nb(V) imide has been described in the literature;[14] therefore, we prepared and isolated *mer*-$(DME)Cl_3Nb{=}NPh$ (**6**). We verified that this is not a product of the reaction between $(CH_2{=}NPh)_3$ and **1**, and it is not surprising to learn that the imine does not have sufficient oxidizing power to effect the two-electron oxidation of **1** to **6**. Subsequently, **6** was screened for metathesis activity and found effective at the 5% catalyst loading level. It also functions at ambient temperature and operates on the substrates shown in eq 2. In addition, it proved more effective than **1** in the conversion of *o*-tolylCH=NPh and PhCH=NBz to the metathesis products, a process with an equilibrium constant near unity.

Although we are as yet unable to formulate a catalytic mechanism, we can offer some insights. Previous studies have established two mechanisms for imine metathesis with metal imides. The first involves a formal [2 + 2] addition of an imine to a metal imide. The resulting metallacycle may fragment in the opposite sense, giving the new imine (eq 3). This mechanism has been well-documented for zirconocene systems,[5] for which the metallacyclic species is the resting state, and it has been strongly implicated in $(DME)Cl_2Mo({=}NR)_2$ systems[6] in which the imide appears to be the resting state.



(3)

A second mechanism has recently been formulated on the basis of stoichiometric reactions of titanium imides.[15] Here it is observed that the overall reaction of metal imide with imine shows no kinetic dependence on the concentration of metal imide. Mountford has suggested that this involves the operation of eqs 4 and 5, which do comprise a sequence for the overall =NR exchange between metal and organic imine. The key here is that the first step involves amine/imine exchange, a process which provides the new amine (R^1NH_2) required for aminolysis of the metal imide $L_nM{=}NR^2$. If eq 4 is slower than eq 5, the overall metal imide/imine exchange will show no kinetic dependence on $L_nM{=}NR^2$.

$$ArCH{=}NR^1 + R^2NH_2 \rightarrow ArCH{=}NR^2 + R^1NH_2 \qquad (4)$$

$$L_nM{=}NR^2 + R^1NH_2 \rightarrow L_nM{=}NR^1 + R^2NH_2 \qquad (5)$$

In our studies of the catalysis by **1** we have eliminated the mechanism of eqs 4 and 5 from consideration. To do this, we compared the rate of conversion of PhCH=NBz to PhCH=NPh with both aniline and $(CH_2{=}NPh)_3$, and we set the starting concentrations of these latter reagents identical in the two separate reactions. This would correspond to the limiting scenario in which eq 4 is infinitely fast and provides for complete conversion of the imine to the new amine at the start of the reaction. Despite this, the reaction with $(CH_2{=}NPh)_3$ ($k_{obsd} = 0.14(2)\ h^{-1}$) proceeded at a faster rate than did that of aniline ($k_{obsd} = 0.016(3)\ h^{-1}$), meaning that the sequence (eqs 4 and 5) is not kinetically competent. Similarly, reactions with both **1** and **6** were run at 5% and 20% catalyst loadings, and the latter were considerably faster (too fast to get accurate kinetics data). Finally, the imine/metal imide metathesis reaction of **6**

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with excess PhCH═NBz was studied; two independent kinetics trials showed pseudo-first-order behavior with $k_{obsd} = 0.022(4)$ min^{-1}, confirming the first-order dependence of the metathesis process on **6**. All of these observations suggest that the mechanism in eqs 4 and 5 is not operating in these niobium-catalyzed reactions.

We attempted to gather evidence for a metallacyclic intermediate (as in eq 3) in the reactions of **6**. In this study ^{1}H NMR spectroscopy was used to study the chemistry of **6** in the presence of excess imine. NMR showed evidence for the presence of **6** and the metathesis product *mer*-(DME)Cl_3Nb═NBz, and these were the only niobium-containing species observed. From this observation it would appear that, if there is a metallacyclic species involved in catalysis, the imide is the resting state in the niobium systems. We are currently pursuing kinetics studies and seeking to prepare more tractable analogues of **1** for additional mechanistic studies.

In summary, we have described studies with Nb(III) and Nb(V) compounds which function as imine metathesis catalysts or precatalysts. The processes are noteworthy because they proceed readily at ambient temperature in a matter of hours, making these the most reactive such catalysts yet available. In addition, both **1** and **6** are conveniently accessible in one step from $NbCl_5$. While we have not seen metathesis with cyclic aldimines under these mild conditions,[6d] both compounds are active with acyclic aldimines and the one hydrazone we have considered. Further studies on the scope and mechanism of the process are in progress.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

OM000613K