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Published on Web 08/17/2002

Catalytic Double-Bond Metathesis without the Transition Metal

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Received April 5, 2002

Abstract: Iminophosphoranes of the type $X_3P{=}NR$ (X = Cl, pyrrolyl; R = alkyl, aryl) catalytically metathesize C=N bonds of carbodiimides via an addition/elimination mechanism that, despite the lack of d orbital participation in P−N bonding, conserves the key features of metal-catalyzed olefin metathesis. Diazaphosphetidine intermediates, produced by the formal [2 + 2] addition of carbodiimides to the P=N bond, have been isolated and characterized. All phosphorus-containing species in the complex catalytic reaction mixtures have been identified and their origins explained. The kinetics of addition of diisopropylcarbodiimide to $Cl_3P{=}NPr^i$ and subsequent elimination were studied, and rate constants were determined: $k_{add} = 1.7 \times 10^{-3}$ ($\pm 0.1 \times 10^{-3}$) M s^{-1} and $k_{elim} = 4.0 \times 10^{-4}$ ($\pm 0.3 \times 10^{-4}$) s^{-1}. The rate of these reactions corresponds well with the observed catalytic TOF of 1.44 TO/P/h.

Introduction

Can a main group element do the job of a transition metal? There are in certain organic transformations, such as hydroformylation, sp^2-carbon coupling, and catalytic double bond metathesis, which conventional wisdom would say are practical only in the presence of elements that bear energetically accessible d-orbitals. Although in some cases one might find main group elements that accomplish the same overall reaction, they generally do so by acting as simple acids or bases, rather than following the same overall pathway as the transition metal catalyst they replace. It is tempting to assume that the main group versions will lack the specificity, activity, and potential for stereocontrol of their transition metal counterparts. There is, however, increasing evidence that certain main group systems are capable of activating substrates by pathways that, heretofore, were thought only accessible to transition metals. In particular, it is interesting to consider the recent reports of Ziegler−Natta-type polymerizations initiated by aluminum alkyls[1] and stereoselective ring-opening polymerizations catalyzed by single-site magnesium and aluminum alkoxide catalysts.[2]

We have been interested in the catalytic metathesis of C=N bonds. Not surprisingly, given the precedent of olefin metathesis,[3,4] early efforts, both in our group[5] and others,[6−8] focused on transition metal-based catalysts. Although C=N metathesis is possible in the presence of simple acids,[9] we hypothesized that a transition metal would be required to promote a controlled Chauvin-type mechanism that would allow us to exploit the reaction for materials synthesis via ring-opening metathesis polymerization (ROMP) and small molecule synthesis via ring-closing metathesis (RCM). In the course of studying the mechanisms of our own systems, however, the similarities between metathesis and the classic Wittig reaction became increasingly difficult to discount, despite our bias in favor of transition metals (Figure 1). In particular, we were struck by the fact that both reactions are proposed to proceed through a four-membered ring intermediate, the formal addition product of the unsaturated substrate and the catalyst.[10,11] These similarities prompted us to explore the potential of iminophosphoranes as C=N metathesis catalysts.

The major difference between a main group imide and a transition metal imide that would be expected to impact mechanism is the relative importance of d orbitals in bonding.

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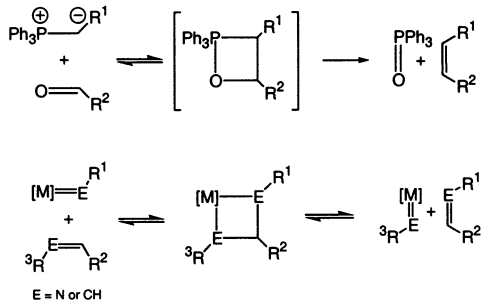


Figure 1. Similarities between the Wittig reaction and olefin/imine metatheses.

Both experimental observations[12] and theoretical studies[12−14] on transition metal imide complexes invoke a high degree of participation of d-orbitals in the multiple bond and the availability of empty d-orbitals for coordination of substrate. In contrast, modern calculations on main group hypervalent compounds suggest that although the presence of d-orbitals is necessary to successfully model any of the heavier main group elements, they do not play a significant role in bonding.[10,15,16] It has been proposed instead that negative hyperconjugation ($\pi_E \rightarrow \sigma^*_{PX}$, E = C, N) may be responsible for any π character in the P−C or P−N bonds.[16] These results have been upheld by recent calculations dealing specifically with the Wittig-type reactivity of phosphorus ylides[17] and iminophosphoranes.[18,19] Note that in this paper we will continue to represent the iminophosphoranes as doubly bonded for the sake of visual simplicity.

Another more directly observable difference between the known main group phosphorus ylide reactions and the transition metal systems is the stoichiometry. Traditional Wittig-type reactivity, in contrast with olefin metathesis, is stoichiometric and relies on the formation of thermodynamically stable phosphorus−oxygen bonds to drive the formation of C═C, C═N, or C═P bonds.[10,20] There are, however, some reports of phosphorus acting catalytically for example the disproportionation of isocyanates to give carbodiimides,[21] and anecdotal reports of stoichiometric metatheses of iminophosphoranes with carbodiimides.[22]

We have discovered that, despite these differences, iminophosphoranes of the type Cl_3P═NR can act as C═N metathesis

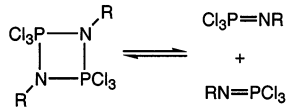
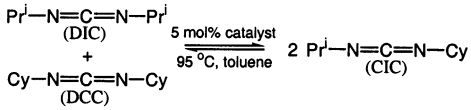


Figure 2. Iminophosphorane dimer/monomer equilibrium.

Scheme 1



catalysts. These main-group imide complexes[23] mediate the ═NR exchange between carbodiimides to give statistical mixtures of symmetric and unsymmetric carbodiimides (Scheme 1).[24] Herein, we explore the generality of the reaction, identify key intermediates, and provide mechanistic data consistent with an addition/elimination pathway that resembles, in most of its features, the Chauvin pathway proposed for olefin metathesis.

Results

Iminophosphoranes. Iminophosphoranes with chloride substituents on the phosphorus (Cl_3P═NR) have, thus far, proven to be the most successful carbodiimide metathesis catalysts. In contrast with ubiquitous P-phenyl-substituted iminophosphorane (Ph_3P═NPh), the trichloroiminophosphoranes naturally dimerize to form four-membered self-adducts (Figure 2). This tendency toward self-dimerization, which was reported previously by Becke-Goering,[25] Fluck,[26] and Zhmurova[27,28] and co-workers is facilitated by the relatively small size and electron-withdrawing nature of the chloride substituents.

To explore the generality of the dimerization reaction and to probe the correlation between dimer stability and catalyst efficiency, a series of iminophosphoranes with varying P- and N-substitution was prepared using adaptations of literature methods. In Table 1, we report the phosphorus NMR spectroscopic shifts for both monomer and dimer (if observable) forms and the percentage of material that is monomeric at 95 °C. Our NMR correlate well with those reported previously for compounds **1**, **4**, and **6**.[29]

The isolation of a pure sample of the isopropyliminophosphorane **2** from the standard reaction of lithium isopropylamide with PCl_5 proved difficult. Distillation did not separate the product from unreacted PCl_5. We were, however, able to obtain ^{31}P NMR spectral data and from that determine that **2** is monomeric in solution. The formulation of **2** was confirmed by derivatization with DIC to yield an isolable and well-characterized diazaphosphetidine derivative (diazaphosphetidine synthesis and characterization is discussed in detail later in this report).

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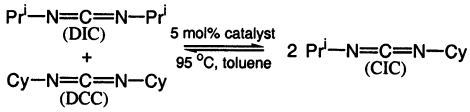
Table 1. Physical and Spectroscopic Information for Iminophosphoranes

cmpd	iminophosphorane	^{31}P NMR[a] (δ)	predominant species at rt	% monomer 95 °C
1	$Cl_3P{=}N{-}Pr^n$[b]	−67.8 (monomer)[e] −78.4 (dimer)	dimer	2
2	$Cl_3P{=}N{-}Pr^i$[c]	−70.6 (monomer)	monomer	>95[f]
3	$Cl_3P{=}N{-}Bu^t$[c]	−81.3 (monomer)	monomer	>95[f]
4	$Cl_3P{=}N{-}Ph$[d]	−48.6 (monomer) −77.0 (dimer)	dimer	78
5	$Cl_3P{=}N$-*p*-tolyl[d]	−53.5 (monomer) −78.1 (dimer)	dimer	50
6	$Cl_3P{=}N$-2-fluorophenyl[d]	−45.6 (monomer) −76.4 (dimer)	dimer	>95[f]
7	$Ph_3P{=}NPh$[d]	−1.2 (monomer)	monomer	>95[f]
8	(pyrrolyl)$_3$P=N-2-fluorophenyl	−32.4 (monomer)	monomer	>95[f]

[a] In toluene at room temperature, relative to 85% H_3PO_4. [b] Prepared via method A. [c] Prepared via method B. [d] Prepared via method C. [e]Measured at 100 °C. [f]Complete disassociation into monomer by ^{31}P NMR spectroscopy.

Scheme 2



The nature of the nitrogen substituent is an important determinant in the monomer/dimer equilibrium of a particular $Cl_3P{=}NR$ iminophosphorane. Hence, the basic, nonbulky *N*-alkyl iminophosphorane, **1**, is a strong dimer that does not readily dissociate significantly below ~90 °C. The more bulky *N-iso*- and *N-tert*-alkyl iminophosphoranes, **2** and **3**, in contrast, are monomeric at room temperature. Aryliminophosphoranes **4**−**6** form relatively weak self-adducts, dissociating significantly to monomeric form above 55 °C. The steric bulk and electronic nature of the phosphorus substituent also affects the monomer/dimer equilibrium. Both of the iminophosphoranes with phosphorus substituents other than chlorine, **7** and **8**, are monomeric, which is consistent with the increased steric bulk and the decreased electrophilicity at phosphorus.

Catalytic Carbodiimide Cross-Metathesis. All of the iminophosphoranes in Table 1 proved to be carbodiimide metathesis catalysts, except for **7**, which has phenyl substituents on the phosphorus. A standard cross-metathesis of carbodiimides involved heating a mixture of diisopropylcarbodiimide (DIC) and dicyclohexylcarbodiimide (DCC) at 95 °C in toluene in the presence of iminophosphorane (Scheme 2). ^{1}H NMR spectra indicated the presence of the new mixed cyclohexyl isopropylcarbodiimide (CIC), and the observation of additional ^{31}P NMR spectral resonances showed the presence of significant intermediates during the reaction. These intermediates are discussed in detail later. The reaction appears to be reasonably general—metathesis is observed for all combinations of DIC, DCC, and ditolylcarbodiimide (DTC).

The catalytic activities of iminophosphoranes **1**−**8** vary significantly. To determine what factors were responsible for these differences, the appearance of the mixed carbodiimide and the disappearance of the substrates were monitored as a function of time for each catalyst under a standard set of conditions. A sample plot for catalyst **1** is shown in Figure 3. The differences in activity as a function of N- and P-substituents can be illustrated by plotting the initial rate data for appearance of CIC for catalysts **1**−**8** on the same time axis (Figure 4).

Diazaphosphetidine Intermediates. As we reported in our preliminary communication, monomeric iminophosphoranes

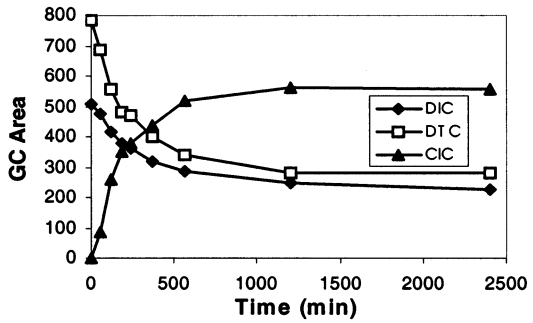


Figure 3. Sample GC catalysis data for carbodiimide metathesis catalyzed by $Cl_3P{=}NPr^n$.

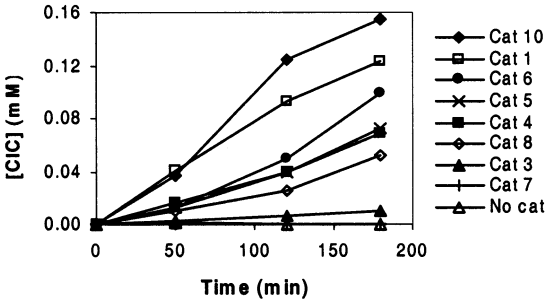
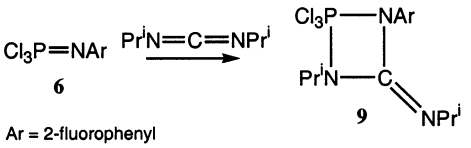


Figure 4. Comparison of the initial production of CIC for the catalysts used (data for catalyst **7** and "no catalyst" coincide on the baseline with no activity).

Scheme 3



react with carbodiimides to give diazaphosphetidine cycloadducts.[24] For example, stoichiometric addition of DIC to 2-fluorophenyliminophosphorane, followed by heating at 50 °C, yields a single product (Scheme 3). Analysis of ^{1}H and ^{31}P NMR spectral data supports formation of diazaphosphetidine adduct **9**. In particular, the ^{1}H NMR spectrum shows two inequivalent isopropyl resonances and a 31 Hz $^3J_{PH}$ coupling to only one of the isopropyl methynes that is indicative of C=N addition across the P=N bond, with N-to-P regiochemistry. This formulation was further supported by X-ray crystallography (Figure 5). The most noteworthy feature of the structure is that both nitrogens are bound to the phosphorus—there is no indication of ring-opened, betaine character. Details of the data collection and the structure can be found in the original communication.[24] Analogous aza-Wittig oxazaphosphetidine intermediates have been reported.[30]

The ease of formation of these diazaphosphetidines under stoichiometric conditions suggests that they are good candidates for the intermediates observed in the catalytic cross-metathesis mediated by iminophosphoranes. If, in particular, we examine the metathesis of DIC and DTC, we could expect to see up to six possible diazaphosphetidines (all those shown in Table 2).

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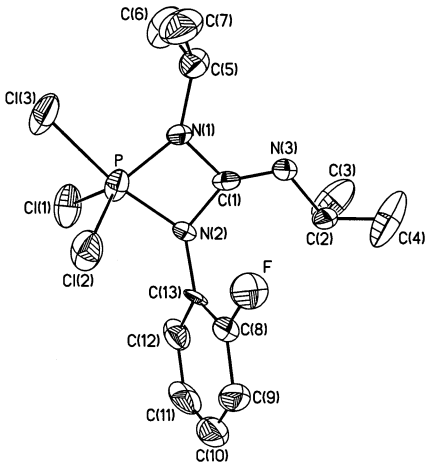
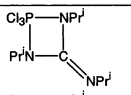
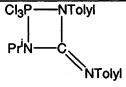
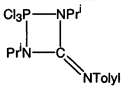
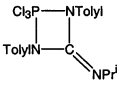
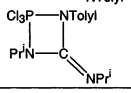
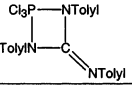


Figure 5. Molecular structure of **9**. Hydrogen atoms have been omitted for clarity, 50% probability ellipsoids.

Table 2. Spectroscopic Details for Diazaphosphetidines

Compound	Structure	^{31}P NMR (δ)	Compound	Structure	^{31}P NMR (δ)
10		- 60.3	**13**		- 55.2
11		- 59.3	**14**		---[a]
12		- 56.9	**15**		- 53.5

[a] ^{31}P NMR shift not determined due to coincidence with other resonances.

To determine if these proposed intermediates are present in catalytic reaction mixtures, we have measured ^{31}P NMR spectroscopic shifts for five of these six species. The diazaphosphetidines **10**, **12**, **13**, **15** were prepared and isolated by cycloaddition of either DIC or DTC to the appropriate iminophosphorane. The synthesis of the remaining two diazaphosphetidines was problematic, however, because two regioisomers are possible from addition of a mixed carbodiimide to an iminophosphorane. We, therefore, attempted to assign the ^{31}P NMR shifts for **11** and **14** by observing the ratios of all diazaphosphetidine species as we titrated **10** and **15** with DTC and DIC at sufficiently high temperatures that scrambling would occur. For example, a sample of diazaphosphetidine **10** was heated with 0.5 equiv of DTC. DIC was then added to shift the equilibrium back toward propyl-containing species. Since hysteresis was observed—the equilibrium ratios of certain adducts changed—it must be true that the dissociation of mixed diazaphosphetidines or the regiochemistry of addition of mixed carbodiimides to free iminophosphoranes or both favor certain species over others. The relative ratios are not simply governed by statistics. Subsequent incremental additions of DTC shifted the equilibrium toward diazaphosphetidines with multiple tolyl substituents. Interpolation of the data for a sequence of these experiments allowed us to assign the resonance for **11**. The diazaphosphetidine spectroscopic assignments were further confirmed by heating samples of isolated diazaphosphetidines **12** or **13** above 65 °C. Resonances were observed for the expected diazaphosphetidine scrambling products, **10**−**13** and **15**. It was not possible to assign a ^{31}P NMR shift for **14** using this methodology. We theorize that the resonance for **14** overlaps with that of another phosphorus-containing compound in these complex mixtures.

Table 3. Sample Catalysis NMR Data

diazaphosphetidine	^{31}P NMR shift (δ)	% of signal	diazaphosphetidine[a]	^{31}P NMR shift (δ)	% of signal
15	53.5	9.9	**16**	53.4	1.4
13	55.2	61.9	**17**	56.4	3.5
12	56.9	14.5	**9**	58.2	1.6
11	59.9	5.9	**18**	59.4	1.1
total % tolyl		92.2	total % fluorophenyl		7.8

[a] 2-fluorophenyl substituted diazaphosphetidines (Figure 6).

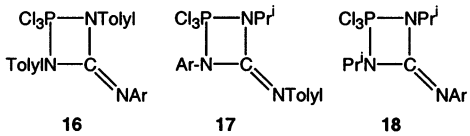


Figure 6. Proposed fluorophenyl-containing diazaphosphetidine intermediates (Ar = 2-flurophenyl).

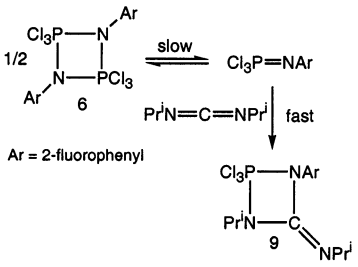
The isopropyl- and tolyl-containing diazaphosphetidines are, in fact, present in catalytic reaction mixtures. Specifically, an experiment involving 5 equiv each of DTC and DIC to 1 equiv of 2-fluorophenyliminophosphorane **6** exhibited resonances for **10**−**13**, and **15**. The spectrum also contained four additional peaks that comprised less than 8% of all the species present. One of these minor peaks corresponds to the 2-fluorophenyl-substituted diazaphosphetidine **9**. The other three resonances likely correspond to diazaphosphetidines that contain the original 2-fluorophenyl substituent (Table 3 and Figure 6). Tentative assignments of these minor products have been made on the basis of trends derived from the detailed study of the tolyl/isopropyl diazaphosphetidine series.

Significantly, the diazaphosphetidines are also catalysts for C═N metathesis. For example, diazaphosphetidine **10**, when added at a 5 mol % loading (the same conditions employed for the iminophosphorane catalysts), metathesized DIC and DCC at rates similar to those observed with pure iminophosphoranes. These reaction mixtures also contained resonances for the other diazaphosphetidines observed in the iminophosphorane catalytic mixtures. A turnover frequency (TOF) of 0.33 turnovers per phosphorus per hour (10800 s for a single turnover) was determined for **10** at 65 °C.

Kinetics. If the diazaphosphetidines are intermediates in the catalytic metathesis of carbodiimides, the rate of addition and elimination of carbodiimides to iminophosphoranes is of interest. However, initial attempts to observe the adduct formation by addition of DIC to 2-fluorophenyliminophosphorane **6** proved unsatisfactory. ^{31}P NMR spectroscopic data collected during the course of the experiment at 55 °C showed no monomer during the course of conversion from dimer to diazaphosphetidine adduct. Clearly, the rate-determining step was dissociation of the iminophosphorane dimer (Scheme 4). Using monomeric iminophosphoranes to directly observe the addition was not possible. Catalyst **2** could not be isolated in pure form and **3** would not form stable diazaphosphetidines.

The addition kinetic data were obtained instead by studying the equilibrium between diazaphosphetidine and dissociated iminophosphorane/carbodiimide using relaxation kinetic techniques (Scheme 5). We chose to study the equilibrium mixture

Scheme 4



Scheme 5

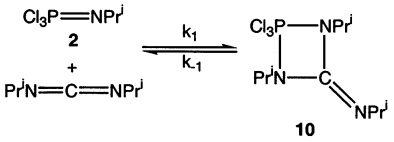


Table 4. K_{eq} for Cycloaddition/Cycloreversion of **10**

K_{eq}	temp (K)	K_{eq}	temp (K)
180	323	17.7	343
93.4	328	11.3	348
66.0	333	4.7	358
43.1	335	3.4	363
34.4	338	2.1	368

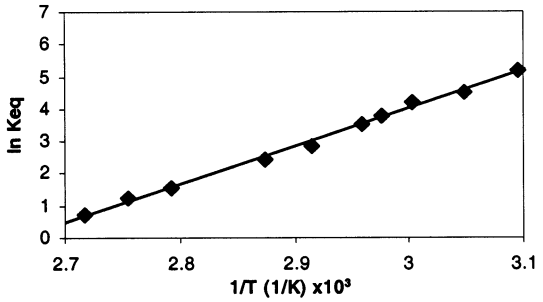
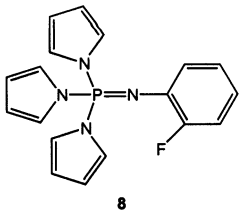


Figure 7. Temperature dependence of K_{eq} for cycloaddition-cycloreversion of **10**.

of addition/elimination products formed by dissolution of pure diazaphosphetidine **10** because the high symmetry eliminates the possibility of regioisomers or multiple products. Prior to undertaking the kinetic studies, equilibrium constants over a range of temperatures were obtained for the dissociation/association products of **10** (Table 4). A semilog plot of K_{eq} versus $1/T$ gave the thermodynamic parameters, $\Delta H = -97.6$ (± 8) kJ/mol and $\Delta S = -250$ ($\pm$ 20) J/(mol K) (Figure 7). The equilibrium data were used to determine the ideal conditions for the perturbation experiments.

To determine the kinetics of the dissociation, the sample was equilibrated to 338 K and then rapidly cooled to 335 K, resulting in a shift toward adduct. During the cooling process the concentrations of all the relevant species were monitored as a function of time. From a plot of $\ln(\Delta[\mathbf{2}]/\Delta[\mathbf{2}]_0)$ versus time the relaxation constant τ was determined to be 385 s. Using standard assumptions,[31] an expression for τ in terms of k_1 and k_{-1} can be derived. From the experimentally determined values for τ and K_{eq} at 335 K, k_1 and k_{-1} can be calculated as 1.7×10^{-3} ($\pm 0.1 \times 10^{-3}$) M s^{-1} and 4.0×10^{-4} ($\pm 0.3 \times 10^{-4}$) s^{-1}, respectively. A catalytic turnover frequency (TOF) of 1.44 turnovers per phosphorus per hour (2500 s per turnover) can be calculated. Calculation of the time for a single turnover assumes that metathesis is considered a simple sequence of addition (k_1), and elimination (k_{-1}) steps, with the elimination step being significantly slower and, thus, rate-determining.



8

Figure 8. Tris(pyrrolyl) iminophosphorane **8**.

Alternative Mechanistic Pathways. At higher temperatures there is a significantly increased risk of metathesis-induced byproducts of catalyst decomposition. Since a likely decomposition product in our system is HCl, a known catalyst for carbodiimide metathesis, we carried out several experiments to determine if it is a factor in these reactions. First, we produced a non-chlorine-containing iminophosphorane catalyst **8** (Figure 8). Pyrrolyl was chosen as a chlorine replacement based on Petersen's characterization of trispyrrolylphosphorus ligands.[32] Pyrrolyl is π-acidic, which allows replacement of chlorine without loss of electrophilicity at the phosphorus center—believed to be an important factor in the carbodiimide metatheses. In fact the P=N bond length was found to be similar to that of the analogous trichloroiminophosphoranes, indicating a similarity in electronegativity of the ligands.[33] Carbodiimide metathesis with the trispyrrolyl catalyst was successful, but was slower than with the trichloro catalysts. The increased time to equilibrium can be attributed to the bulk of the pyrrolyl groups. Although we cannot rule out the decomposition to produce pyrrole at trace levels, we see no evidence for it spectroscopically.

In addition, lowering the temperature should reduce the risk of catalyst decomposition and HCl formation for the trichloroiminophosphoranes. Although initially we ran the majority of our reactions at 120 °C, we found that successful carbodiimide metathesis occurred at 65 °C, and ^{31}P NMR spectra indicated the presence of the same intermediates as in the previous catalysis experiments. As would be expected, the time taken to reach equilibrium (20 h) was significantly longer at the lower temperature.

Finally, we were concerned about decomposition to produce amines, which could also have a role in metathesis. Amine-catalyzed processes for imine metathesis are implicated in transition metal systems.[34,35] The effect of amine on the iminophosphorane catalytic reactions was studied by running standard catalyses with trace amine. Although the amine contaminated catalyses reached equilibrium faster than those without trace amine added, we found no metathesis occurred with control reactions containing amine and no catalyst.

Discussion

Postulated Mechanism. The simplest proposed mechanism for this catalytic system is based on Chauvin's olefin metathesis

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(32) Moloy, K. G., Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 7696−7710.
(33) Bell, S. A.; Geib, S. J.; Meyer, T. Y. *Acta Crystallogr., Sect. C* **2001**, *57*, 1341−1342.
(34) Burland, M. C.; Pontz, T. W.; Meyer, T. Y. *Organometallics* **2002**, *21*. In press.
(35) McInnes, J. M.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1998**, *16*, 1669−1670.

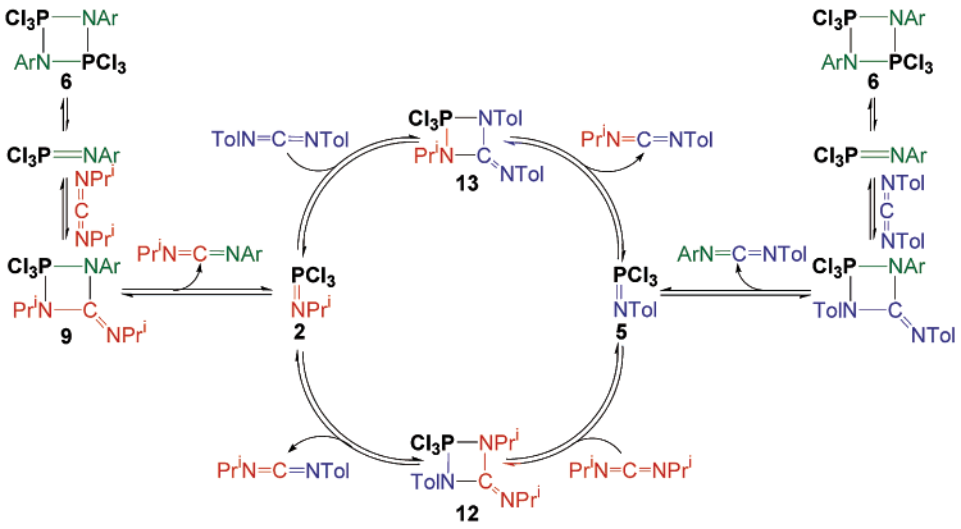

Figure 9. Iminophosphorane catalytic pathway.

mechanism[36] and the Wittig reaction pathway (Figure 9). Others have postulated a similar process for analogous transition metal systems.[6,7] In the proposed catalytic cycle, the iminophosphorane dimer dissociates; subsequent cycloaddition of a carbodiimide produces a diazaphosphetidine adduct. The new adduct can then undergo cycloreversion to produce the first catalytically relevant iminophosphorane. Repetition of the addition−elimination process completes the catalytic cycle, generating another equivalent of mixed carbodiimide. Only productive metatheses are illustrated in the catalytic cycle. It must be assumed that significant degenerate processes such as the reaction of isopropyliminophosphorane **2** with DIC are concurrent.

Our approach to studying this mechanism considered first the postulated catalytic intermediates. We were able to independently isolate and analyze the majority of the proposed adduct intermediates, and compare the resulting spectroscopic evidence with data collected during the catalysis experiments. The fact that all phosphorus resonances observed during the catalytic metathesis of DIC and DTC could be attributed to either iminophosphoranes or diazaphosphetidines that would be predicted to be present in such a reaction supports the addition/elimination pathway. Moreover, heating isolated samples of diazaphosphetidines that contained both alkyl and aryl groups (e.g., **12**) caused a scrambling of these substituents and produced an equilibrium mixture of the same diazaphosphetidines found during DIC and DTC cross-metathesis.

Changes in the relative number of the propyl and tolyl groups present should have a statistical effect on which diazaphosphetidines are present, and their approximate relative ratios. However, we have found that no matter which catalyst was used, adducts **12** and **13** were particularly prevalent, even when there was an excess of propyl or tolyl groups, respectively. The significant presence of **12** and **13** indicates that diazaphosphetidines with one endocyclic propyl and one endocyclic tolyl are likely more thermodynamically stable than other regioisomers.

A comparison of metathesis rate data gives us a qualitative understanding of each precatalyst's ability to convert into what we believe is the active catalyst, a dissociated iminophosphorane carrying a NR group from one of the carbodiimide substrates. There appear to be two factors that influence the activity of the precatalysts. First, it is clear that activity is affected by the tendency of iminophosphorane dimers to dissociate. Comparison of the tolyl- and phenyl- iminophosphoranes, **5** and **6**, in Figure 4 indicates that the fluorophenyliminophosphorane catalyst has a slightly higher initial reactivity than the tolyl system. This would be expected as the fluorophenyl system has a less stable dimer. Second, one must also consider the nucleophilicity of the iminophosphorane. We would expect the alkyl iminophosphoranes to be more nucleophilic than the aryl systems. This nucleophilic trend is clearly seen in Figure 4. The most reactive systems are the propyl (both isopropyl and *n*-propyl), followed by the aryl systems. Interestingly, the nucleophilicity difference between alkyl and aryl substituents is apparently more important than the monomer/dimer equilibrium effects, since the alkyl species are the fastest despite having the most stable dimers. The *tert*-butyl derivative is the slowest simply because of steric bulk inhibiting the formation of the diazaphosphetidines. We also found that the trispyrrolyl-substituted catalysts were slower than their chloro analogues. We believe that this is attributable to the steric bulk of the pyrrolyl groups. It is important to note that, while these pyrrolyl systems are slower, they do follow a reactivity pattern similar to that of the chloro systems. Carbodiimide metathesis did not occur when catalyst was not added nor when $Ph_3P{=}NPh$ **7** was present. The lack of reactivity **7** probably due to the steric bulk and poor electron-withdrawing ability of the phenyl groups on the phosphorus.

Further support for our postulated mechanism comes from the observed activity of diazaphosphetidines. As intermediates, they should be expected to act as catalysts with approximately the same reactivity as the "free" iminophosphoranes. This assumption was substantiated by experimental observations. We found that **10** is, in fact, one of the most active catalysts and is comparative in behavior to $Cl_3P{=}NPr^n$ **1**.

Alternative Mechanistic Pathways. Although there is significant evidence to support the diazaphosphetidine mechanism our experience with transition metal systems[34,37] led us to investigate minor pathways that could initiate carbodiimide metathesis. These include (i) decomposition of the catalyst to

(36) Herrison, J. P.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161−176.

(37) Jordan, A. Y.; Meyer, T. Y. *J. Organomet. Chem.* **1999**, *591*, 104−113.

produce HCl, which could subsequently propagate metathesis, and (ii) metathesis catalyzed by trace amine impurity.

Since HCl would also be a catalyst for the metathesis of carbodiimides, it is important that we determine that it is not a factor in these reactions. Although the decomposition of P-chlorinated iminophosphoranes to produce HCl is a reasonable postulate, our data are not consistent with its presence. First of all, our catalysts are extremely stable. Heating for weeks at >120 °C does not cause any detectable change. Also, the catalysis proceeds normally, but more slowly, when much lower temperatures are employed (65 °C). Moreover, trispyrrolyl iminophosphorane **8**, which cannot decompose to give HCl, shows reasonable catalytic activity. Although it could be argued that pyrrole, generated by an analogous decomposition, could serve as a catalyst as well, no pyrrole was observed in the reaction mixtures.

Our final and most convincing evidence against competing pathways, including HCl and amine-catalyzed processes, comes from the comparison of TOFs for overall catalyses (0.33 TO/P/h) and those determined from the kinetics of what we postulate is the rate-determining step, the elimination of carbodiimide from a diazaphosphetidines (1.44 TO/P/h). Although these two TOFs are not identical (they differ by a factor of 4.3), they are comparable given that the TOF calculated for the overall metatheses must necessarily be a lower limit since it does not account for the many redundant metatheses that must occur. On the basis of simple statistical arguments, we would predict a minimum factor of 3 underestimate of the TOF for the overall reaction. Since the addition/elimination reaction sequence is kinetically competent to explain the TOFs we observe, it appears unlikely that other competing pathways are contributing significantly to the rates.

We have shown that the mechanism of iminophosphorane metathesis does, in fact, conform to the Chauvin mechanism in that it consists of repeated addition/elimination steps. There remain two issues that have to be addressed before the degree of analogy can be fully established between the main group and transition metal pathways: precoordination and concertedness. Although precoordination of olefins is postulated and has been observed in transition metal-mediated olefin metathesis systems,[38] generally these adducts are not sufficiently stable to be observed.[4] The lack of energetically accessible d-orbitals would seem to preclude such an interaction for phosphorus. In recent theoretical studies on the aza-Wittig reaction, however, Koketsu et al. have found weak complexes that form by complementary interaction of the polar P−N and substrate C═O. These adducts exhibit some charge transfer from the nitrogen to the substrate but not sufficient to classify these intermediates as betaine-type structures.[19] An analogous approach would be likely for a C═N substrate although sterics (N-substituent) should destabilize the intermediate and may explain why such adducts are not observed.

The second issue, concertedness, could also be expected to be different in the metal and nonmetal systems. In the Chauvin-pathway for olefin metathesis, a high degree of concertedness is observed because, in contrast with olefin/olefin interactions, the π/π^* overlap required for a $[2_\pi + 2_\pi]$ between an alkylidene and an olefin is nonzero because d-orbitals are involved in M═C bonding.[14] Although the lack of betaine intermediates suggests that the P═N addition reactions are also highly concerted, it seems unlikely that the two systems can have identical pathways given the lack of π-bonding and d-orbital participation in the iminophosphoranes. Theoretical studies on this type of addition have shown, however, that the lowest-energy pathway for addition of unsaturated substrates to these dipolar compounds can involve a related, symmetry-allowed concerted process.[18,19,39] Although no calculations have been performed specifically on iminophosphorane-mediated C═N metathesis, a similar concerted pathway should be accessible.[40]

Conclusions

A metal is not required for a catalytic C═N metathesis involving a Chauvin-type addition/ elimination pathway. Iminophosphoranes with electron-withdrawing substituents have been shown to scramble ═NR substituents of carbodiimides via phosphetidine intermediates. Although turnover frequencies at 65 °C are relatively slow (1.44 TO/P/h), they compare favorably to that reported, 1.77 TO/Zr/h at 105 °C, for the only catalytic metal-based C═N metathesis system that has also been shown definitively to proceed by sequential addition/elimination, Cp*Cp(THF)Zr(═NBu^t).[7] We now plan to extend this work to imine metathesis with the aim of producing more diverse applications for these novel iminophosphorane metathesis catalysts.

Experimental Section

Solvents, Reagents, and General Data. Solvents were freshly distilled under nitrogen prior to use. Toluene and benzene were distilled from benzophenone/sodium. Chloroform, methylene chloride, and tetrachloroethane were dried over CaH_2 and fractionally distilled. All deuterated solvents used were purified in the same manner as the nondeuterated equivalent after being received from Cambridge Isotope Laboratories. Phosphorus pentachloride was used as purchased from Strem Chemicals. Solid carbodiimides were purified by sublimation, and liquid carbodiimides were purified by fractional distillation after stirring over sieves. All amines used were purified by fractional distillation after drying over CaH_2, and stored in darkness, under nitrogen.

Equipment. All manipulations of air- or water-sensitive compounds were performed using standard high-vacuum or Schlenk techniques. Solid organometallic compounds were transferred in a nitrogen-filled drybox and were stored at room temperature, unless otherwise stated. ^{1}H and ^{31}P NMR spectra were recorded with a Bruker AF300 spectrometer at 300 MHz and 121 MHZ, respectively. Chemical shifts were referenced to residual ^{1}H NMR signals of the deuterated solvents or external 85% phosphoric acid standards. The GC analyses were performed on a Hewlett-Packard 5890 chromatograph filled with a 30.0-m methyl siloxane capillary column (HP19091Z-413E) and a flame ionization detector.

Method A (Based on a Preparation by Fluck et al.).[26] *N*-4-Tolyl-*p*-trichloroiminophosphorane (5). In a three-necked flask equipped with a condenser, N_2-inlet and addition funnel, PCl_5 (3.90 g, 18.8 mmol) was added over a period of 10 min to toluidine (2.01 g, 18.8 mmol) in

(38) (a) Kress, J.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1585−1587. (b) Tallarico, J. A.; Bonitatebus, P. J., Jr.; Snapper, M. L. *J. Am. Chem. Soc.* **1997**, *199*, 77157-7158.

(39) Theory suggests that concerted [2 + 2] reactions are not forbidden for substrates that have signficant polarity. (a) Höller, R.; Lischka, H. *J. Am. Chem. Soc.* **1980**, *102*, 4632−4635. (b) Haller, J.; Beno, B. R.; Houk, K. N. *J. Am. Chem. Soc.* **1998**, *120*, 6468−6472. (c) Yamaguchi, K.; Fueno, T.; Fukutome, H. *Chem. Phys. Lett.* **1973**, 461−465. (d) Yamaguchi, K.; Fueno, T.; Fukutome, H. *Chem. Phys. Lett.* **1973**, *22*, 466−471.

(40) It has been suggested that heterocumulene additions to some unsaturated substrates may involve more than a [2 + 2] interaction. See, for example Deubel, D. V. *J. Phys. Chem. A* **2002**, *106*, 431−437.

1,2-tetrachloroethane (40 mL). The mixture was stirred for 25 min at room temperature and refluxed for a further 14 h. A white solid precipitated upon cooling. Recrystallization from toluene afforded white crystals (2.45 g, 56.2%). ^{1}H NMR (300 MHz, d_8-toluene) δ 7.10 (d/d, 4, aryl), 2.03 (s, 3, tolyl); ^{31}P{^{1}H} NMR (121 MHz, d_8-toluene) δ −78.1.

Method B (Based on a Preparation by Zhmurova et al.).[28] ***N*-*n*-Propyl-*p*-trichloroiminophosphorane (1).** A three-necked flask equipped with a condenser and N_2-inlet was charged with PCl_5 (2.98 g, 14.3 mmol), propylamine hydrochloride (1.36 g, 14.3 mmol), and chlorobenzene (15 mL). The resulting mixture was heated at approximately 90−100 °C for 4 h. White crystals formed upon cooling. Recrystallization from hexanes yielded white crystals (1.97 g, 70.3). ^{1}H NMR (300 MHz, d_8-toluene) δ 3.10 (m, 2, P−CH_2), 1.83 (m, 2, CH_2), 0.68 (t, 3, CH_3); ^{31}P{^{1}H} NMR (121 MHz, d_8-toluene) δ −78.4 (s).

Method C (Based on a Preparation by Schwesinger et al.)[41] ***N*-Isopropyl-*p*-trichloroiminophosphorane (2).** In a three-necked flask equipped with a condenser, N_2-inlet and addition funnel, PCl_5 (4.0 g, 19.0 mmol) was added over a period of 10 min to isopropylamine hydrochloride (1.83 g, 19.0 mmol) in 1,2-tetrachloroethane (40 mL). The mixture was stirred for 25 min at room temperature and warmed to 80 °C for a further 6 h. Vacuum distillation yielded a solution containing isopropyliminophosphorane and PCl_3. ^{1}H NMR (300 MHz, d_8-toluene) δ 4.35 (d/sept, 1, P−N−CH), 1.11 (dd, 7, CH−CH_3);^{31}P-{^{1}H} NMR (121 MHz, d_8-toluene) δ +220 (s, PCl_3), −70.6 (s, Cl_3P═NPr^i).

***N*-2-Fluorophenyl-*p*-trispyrrolyliminophosphorane (8).** Potassium pyrrolide (0.518 g, 4.93 mmol) was slowly added to a vigorously stirred solution of Cl_3P═NAr (0.405 g, 1.643 mmol) in hexanes (45 mL) at −78 °C. The mixture was stirred for 30 min at −78 °C, warmed to room temperature and stirred for an additional 14 h. Filtration yielded a colorless liquid that was reduced to 15 mL and cooled to −35 °C. The precipitate was removed by filtration. The filtrate was again reduced in volume and cooled to yield colorless crystals (0.231 g, 41.5%). ^{1}H NMR (300 MHz, d_8-toluene) δ 6.79 (m, 4, aryl), 6.67 (m, 6, pyrrolyl), 6.08 (m, 6, pyrrolyl); ^{31}P{^{1}H} NMR (121 MHz, d_8-toluene) δ −32.4; Analysis: 65.46 C, 5.12 H, 16.26 N; Calculated: 63.74 C, 5.01 H, 16.52 N.

Standard NMR Carbodiimide Metathesis. 2-Fluorophenyliminophosphorane **6** (18.4 mg, 0.074 mmol) and d_8-toluene (0.65 mL) were added to a screw-valve NMR tube. Initial ^{31}P and ^{1}H NMR spectra were acquired. Then diisopropylcarbodiimide (58.4 μL, 0.37 mmol) and ditolylcarbodiimide (82.8 mg, 0.37 mmol) were added. The mixture was heated overnight at 120 °C and further ^{31}P and ^{1}H NMR spectra were obtained. ^{1}H NMR (300 MHz, d_8-toluene) DTC δ 6.95 (m, 4, aryl), 2.06 (s, 3, CH_3C$_6$H$_4$N═C═Ntolyl); DIC − 3.38 (m, 1, CH$_3$CH(CH$_3$)N═C═NPr^i), 1.04 (d, 6, CH_3CH(CH$_3$)N═C═NPr^i); TIC 3.38 (m, 1, CH$_3$CH(CH$_3$)N═C═Ntolyl), 2.10 (s, CH_3C$_6$H$_4$N═C═N−Pr^i), 1.02 (d, 6, CH_3CH(CH$_3$)N═C═Ntolyl); ^{31}P NMR{^{1}H} (121 MHz, d_8-toluene) δ −46.0 (s), −53.4 (s), −53.6 (s), −54.4 (s), −55.3 (s), −56.4 (s), −57.0 (s), −58.2 (s), −59.5 (s).

3,4-Diisopropyl-1-tolyl-1,3-diazaphosphetidine (12). In a thick-walled reaction vessel diisopropylcarbodiimide (0.55 mL, 3.53 mmol) was added to a solution of tolyliminophosphorane **5** (0.775 g, 3.21 mmol) in toluene (25 mL) at room temperature. The mixture was heated at 65 °C in a closed system for 24 h. Filtration yielded a pale-yellow solution that was reduced to 2 mL. Cooling to −35 °C yielded white crystals (0.257 g, 21.8%). ^{1}H NMR (300 MHz, d_8-toluene) δ 6.95 (m, 4, aryl), 4.4 (d/sept, 1, P−N−CH(CH$_3$)$_2$), 3.45 (sept, 1, P−N−C−N−CH(CH$_3$)$_2$), 2.05 (s, tolyl), 1.53 (d, 7, P−N−C−(CH_3)$_2$), 0.95 (d, 7, P−N−C−N−CH(CH_3)$_2$); ^{31}P NMR (121 MHz, d_8-toluene) δ −56.9; Analysis: 45.08 C, 5.96 H, 11.37 N; Calculated: 45.51 C, 5.99 H, 11.22 N.

Diazaphosphetidine Scrambling. 3,4-Diisopropyl-1-tolyl-1,3-diazaphosphetidine **12** (18.0 mg, mmol) and d_8-toluene (0.65 mL) were added to a screw-valve NMR tube. The reaction mixture was heated to 95 °C and monitored for 48 h.^{31}P NMR{^{1}H} (121 MHz, d_8-toluene) δ −54.6 (s), −55.2 (s), −56.9 (s), −59.3 (s), −70.5 (s), −78.1 (s)

Incremental Carbodiimide Addition. 3,4-Diisopropyl-1-tolyl-1,3-diazaphosphetidine **12** (17.5 mg, 0.055 mmol), ditolylcarbodiimide (6.1 mg, 0.027 mmol), and d_8-toluene (0.65 mL) were added to a screw-valve NMR tube. The sample was heated to 95 °C for 24 h. At one-day intervals diisopropylcarbodiimide (9 μL, 0.027 mmol), ditolylcarbodiimide (12.2 mg, 0.055 mmol), ditolylcarbodiimide (12.2 mg, 0.055 mmol), ditolylcarbodiimide (12.2 mg, 0.055 mmol) were added. After each addition, the reaction mixture was heated to 95 °C for several hours before the next ^{31}P{^{1}H} NMR spectrum was acquired.

Comparison of Catalyst Rates. A stock solution of diisopropylcarbodiimide (8.90 mmol) and dicyclohexylcarbodiimide (8.90 mmol) in toluene (84 mL) was prepared. iminophosphorane **1** (24.8 mg, 0.128 mmol) was added to a 12-mL aliquot of this solution. The resulting solution was then divided further into 8 × 1.5 mL samples. One sample was used to determine the initial concentrations, and the other seven samples were placed in an oil bath at 95 °C. The samples were removed at set time intervals, immediately cooled in an acetone bath, and analyzed by GC (Figure 3). Using the same initial DIC/DCC stock solution this process was simultaneously performed with a control (no catalyst), diazaphosphetidine **10**, and catalysts **3**, **4**, **5**, and **7**.

***K*$_{eq}$ Studies.** 3,4-Diisopropyl-1-tolyl-1,3-diazaphosphetidine **12** (43.5 mg, 0.136 mmol) and d_8-toluene (0.70 mL) were added to a screw-valve NMR tube. The reaction mixture was heated to 45 °C and allowed to equilibrate for 30 min. ^{31}P{^{1}H} NMR (121 MHz, d_8-toluene, 318 K) δ −59.0 (s, diazaphosphetidine), −71.5 (s, Cl_3P═NPr^i). This process was repeated at 45, 50, 55, 60, 63, 65, 70, 75, 85, 95 °C.

Relaxation Kinetic Studies. 3,4-Diisopropyl-1-tolyl-1,3-diazaphosphetidine **12** (43.5 mg, 0.136 mmol) and d_8-toluene (0.70 mL) were added to a screw-valve NMR tube. The reaction mixture was heated to 65 °C and allowed to equilibrate for 1 h. This sample was then placed in a NMR spectroscopic probe equilibrated at 63 °C. ^{31}P NMR spectra were obtained over a 30-min period. Integration was then used in order to calculate the concentration of each of the species present. ^{31}P{^{1}H} NMR (121 MHz, d_8-toluene, 336 K) δ −59.0 (s), −71.5 (s).

Acknowledgment. This research was supported by NSF award CHE-0091400. T.Y.M. is a fellow of the Alfred P. Sloan Foundation. S.A.B. thanks the University of Pittsburgh for an Andrew Mellon Pre-Doctoral Fellowship.

Supporting Information Available: ^{31}P NMR spectral data for a typical carbodiimide cross-metathesis and a plot of relaxation kinetic data (PDF). This is material is available free of charge via the Internet at http://pubs.acs.org.

JA020494V

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