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# Iminophosphorane Mediated Imine Metathesis

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The iminophosphorane $Cl_3P{=}NAr$ (**1a**, Ar = 2-fluorophenyl) reacts metathetically with imines at 80 °C to produce =NR exchange products. Compound **1a** effectively catalyzes imine/imine and imine/carbodiimide cross-metathesis. The observation of =NR exchange products as well as spectroscopic evidence for the existence of diazaphosphetidine type intermediates suggests that a [2 + 2] addition/elimination mechanism is the primary pathway for substrates with N-alkyl substituents and a secondary pathway for N-aryl imines. In contrast to previously studied carbodiimide systems, the resting state of the catalyst is the iminophosphorane and not the diazaphosphetidine. For N-aryl imines, Lewis-acid catalysis appears to be the dominant mechanism, not addition/elimination. For N-alkyl imines, a decomposition pathway, involving HCl elimination from a phosphorus intermediate, is competitive in some cases.

## Introduction

Metal-catalyzed metathesis is an important C=C bond forming reaction that has been used extensively in both polymer and small molecule synthesis.[1] Thus far however, metathesis has been limited mainly to alkene metathesis reactions. Ongoing research in our group[2,3] and others[4] has been directed toward extending the metathesis methodology to the formation of double bonds containing heteroatoms. In particular, we have been studying the formation of C=N bonds in imines and carbodiimides. Previously, we reported imine metathesis catalyzed by molybdenum(VI) bis(imide) complexes[3] and tantalum(V) imide complexes.[2]

While transition metal catalyzed metathesis reactions are attractive, we have recently set about developing main group alternatives to traditional transition metal catalysts. Main group catalysts provide an interesting and underexploited alternative to transition metals.[5] The primary objective of this research is the development of new, highly effective catalysts that have functional group tolerances that are either greater than, or complementary to, current transition metal catalysts.

The similarities between the mechanisms of the Wittig reaction and transition metal catalyzed alkene metathesis lead us to investigate the catalytic properties of iminophosphoranes.[6] Recent work from our group has demonstrated the use of iminophosphoranes as carbodiimide metathesis catalysts.[7,8] We discovered that iminophosphoranes of the general formula $X_3P{=}NR$ (X = Cl, pyrrolyl; R = alkyl, aryl) can effectively catalyze the metathesis of carbodiimides via an addition/elimination mechanism that conserves the key features of metal-catalyzed olefin metathesis (Scheme 1). The

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(7) Bell, S. A.; Meyer, T. Y.; Geib, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 10698−10705.

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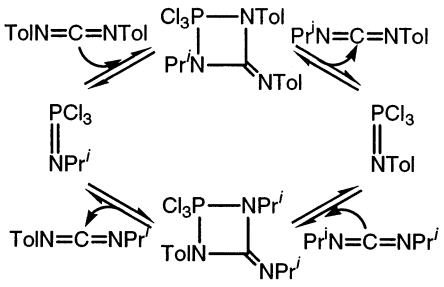
**Scheme 1**



isolation of the cyclic intermediates, diazaphosphetidines, from this reaction along with detailed studies of the kinetics of the addition/elimination steps provide strong evidence for a reaction mechanism that, in most aspects, is analogous to the Chauvin addition mechanism for olefin metathesis.[9]

The high yields and lack of byproducts that were characteristic of the carbodiimide metathesis made this system a good candidate for the activation of the less reactive C=N bonds of imines. Herein, we report the first evidence of imine metathesis by a main group iminophosphorane catalyst as well as discuss data that suggest that the metathesis of imines can proceed via an addition/elimination mechanism.

A variety of imines and iminophosphoranes were used in this work. They are summarized in Figure 1. It is important to note that iminophosphoranes with electron-withdrawing chloride substituents on phosphorus are known to self-dimerize and, depending on temperature and N-substituent, can be present as monomer, dimer, or a mixture of the two (Figure 2).[10]

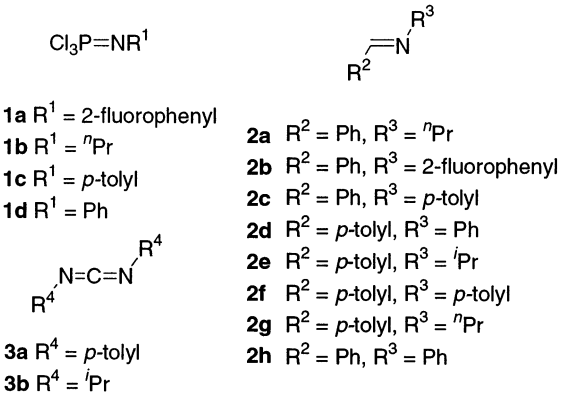



**Figure 1.** Iminophosphoranes (**1**), imines (**2**), and carbodiimides (**3**) relevant to the current studies.


**Figure 2.** Monomer/dimer equilibrium of iminophosphoranes.

## Experimental Section

**General Procedures.** All manipulations were performed under inert atmosphere using standard glovebox and Schlenk techniques. The following solvents were distilled from appropriate purifying agents (noted in parentheses) prior to use: toluene (sodium/benzophenone) and benzene (sodium/benzophenone). Imines[11] and iminophosphoranes[7] were prepared according to established methods. All other chemicals were used as received unless otherwise noted. $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded with a Bruker AF500 or AF300 NMR spectrometer. Chemical shifts for $^1$H and $^{13}$C NMR spectra are referenced to the residual protio impurity in the deuterated solvent. $^{31}$P NMR chemical shifts are referenced to 85% phosphoric acid used as an external standard. All imines were identified by comparison with spectra of authentic samples.

**Standard Iminophosphorane/Imine Reaction. Reaction of 1a with PhCH=N(*p*-tolyl) (2c).** A screw-valve NMR tube was charged with 2-fluorophenyliminophosphorane (**1a**) (33.5 mg, 0.136 mmol) and $C_6D_6$ (0.3 mL). The contents of the tube were heated to 80 °C for 1 h in an oil bath to dissolve the solid. The imine PhCH=N(*p*-tolyl) (**2c**) (119 mg, 0.609 mmol, 4.5 equiv) and $C_6D_6$ (0.2 mL) were added to the cooled NMR tube. Initial $^{31}$P and $^1$H NMR spectra were acquired. The tube was placed in an 80 °C oil bath, and NMR spectra were taken periodically over 6 days. $^1$H NMR (300 MHz, $C_6D_6$) **2c**: $\delta$ 8.21 (s, 1H, PhC*H*=NC$_6$H$_4$CH$_3$), 7.84 (d, 2H, PhCH=NC$_6$*H*$_4$CH$_3$), 7.14 (m, 5H, Ph), 7.00 (d, 2H, PhCH=NC$_6$*H*$_4$CH$_3$), 2.13 (s, 3H, PhCH=NC$_6$H$_4$C*H*$_3$). **2b**: $\delta$ 8.09 (s, 1H, PhC*H*=NAr), other peaks obscured by starting material. $^{31}$P NMR{$^1$H} (121 MHz, $C_6D_6$) $\delta$ 3.3 (s), −18.7 (s), −24.6 (s), −34.7 (s), −43.1 (s), −52.3 (s), −66.0 (s), −67.2 (s), −69.4 (s), −72.5 (s), −75.6 (s), −76.5 (s), −77.4 (s).

**Reaction of 1a with (*p*-Tolyl)CH=NPh (2d).** $^1$H NMR (300 MHz, $C_6D_6$) **2d**: $\delta$ 8.17 (s, 1H, CH$_3$C$_6$H$_4$C*H*=NPh), 7.78 (d, 2H, CH$_3$C$_6$*H*$_4$CH=NPh), 7.16 (m, 4H, Ph), 7.06 (m, 1H, Ph), 6.96 (d, 2H, CH$_3$C$_6$*H*$_4$CH=NPh), 2.03 (s, 3H, C*H*$_3$C$_6$H$_4$CH=NPh). $^{31}$P NMR{$^1$H} (121 MHz, $C_6D_6$) $\delta$ −19.3 (s), −34.2 (s), −35.3 (s), −43.1 (s), −50.2 (s), −68.1 (s), −69.2 (s), −70.8 (s), 75.6 (s), 77.0 (s), 77.1 (s), 78.5 (s).

**Reaction of 1a with PhCH=N$^n$Pr (2a).** Approximately 15% of the material was lost to decomposition after 3 days of heating at 80 °C. $^1$H NMR (300 MHz, $C_6D_6$) **2a**: $\delta$ 7.96 (s, 1H, PhC*H*=N$^n$Pr), 7.72 (m, 2H, Ph), 7.12 (m, 3H, Ph), 3.39 (t, 2H, NC*H*$_2$CH$_2$CH$_3$), 1.64 (m, 2H, NCH$_2$C*H*$_2$CH$_3$), 0.87 (t, 3H, NCH$_2$-CH$_2$C*H*$_3$). **2b**: $\delta$ 8.09 (s, 1H, PhC*H*=NAr), other peaks obscured by starting material. $^{31}$P NMR{$^1$H} (121 MHz, $C_6D_6$) $\delta$ −17.1 (s), −17.4 (s), −30.8 (s), −31.5 (s), −43.4 (s), −59.6 (s), −68.7 (s), −69.4 (s), −75.7 (s), −76.8 (s).

**Reaction of 1a with (*p*-tolyl)CH=N$^i$Pr (2e).** $^1$H NMR (300 MHz, $C_6D_6$) **2e**: $\delta$ 8.03 (s, 1H, CH$_3$C$_6$H$_4$C*H*=N$^i$Pr), 7.69 (d, 2H, CH$_3$C$_6$*H*$_4$CH=N$^i$Pr), 6.96 (d, 2H, CH$_3$C$_6$*H*$_4$CH=N$^i$Pr), 3.30 (sept, 1H, C*H*(CH$_3$)$_2$), 2.00 (s, 3H, C*H*$_3$C$_6$H$_4$CH=N$^i$Pr), 1.21 (d, 6H, CH-(C*H*$_3$)$_2$). $^{31}$P NMR{$^1$H} (121 MHz, $C_6D_6$) $\delta$ 3.1 (s), −27 (s), −43.4 (s), −75.7 (s).

**Standard Carbodiimide/Imine Cross Metathesis. Reaction of 1a with 2d and 3a.** A screw-valve NMR tube was charged with 2-fluorophenyliminophosphorane (**1a**) (41.0 mg, 0.166 mmol) and $C_6D_6$ (0.2 mL). The contents of the tube were heated to 80 °C for 1 h in an oil bath to dissolve the solid. The imine (*p*-tolyl)CH=NPh (**2d**) (95.5 mg, 0.489 mmol, 2.9 equiv), di(*p*-tolyl)carbodiimide (**3a**) (111.7, 0.502 mmol, 3 equiv), and $C_6D_6$ (0.2 mL) were added

(9) For a detailed discussion of iminophosphorane bonding and its relevance to the formally forbidden [2 + 2] reactions, see our previous work on iminophosphorane catalyzed carbodiimide metathesis, ref 7.

(10) Becke-Goehring, M.; Leichner, L.; Scharf, B. *Z. Anorg. Allg. Chem.* **1966**, *343*, 154−164. Fluck, E.; Wachtler, D. *Liebigs. Ann. Chem.* **1980**, 1651−1658. Zhmurova, I. N.; Drach, B. S. *Zh. Obsch. Khim.* **1964**, *34*, 1441−1446. Zhmurova, I. N.; Kisilenko, A. A.; Kirsanov, A. V. *Zh. Obsch. Khim.* **1962**, *32*, 2580−2586.

(11) 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, in the case of liquid imines, or recrystallization from hexane in the case of solid imines.

to the cold NMR tube. Initial $^{31}$P and $^{1}$H NMR spectra were acquired. The tube was placed in an 80 °C oil bath, and NMR spectra were taken periodically over 6 days. $^{1}$H NMR (300 MHz, $C_6D_6$) **2d**: 8.17 (s, 1H, $CH_3C_6H_4CH$═NPh), 7.78 (d, 2H, $CH_3C_6H_4$-CH═NPh), 7.16 (m, 4H, Ph), 7.06 (m, 1H, Ph), 6.96 (d, 2H, $CH_3C_6H_4CH$═NPh), 2.03 (s, 3H, $CH_3C_6H_4CH$═NPh). **3a**: $\delta$ 7.02 (d, 4H, $CH_3C_6H_4$), 6.82 (d, 4H, $CH_3C_6H_4$), 1.99 (s, 6H, $CH_3C_6H_4$). **2f**: $\delta$ 8.22 (s, 1H, $CH_3C_6H_4CH$═$NC_6H_4CH_3$), other peaks obscured by starting material. $^{31}$P NMR{$^{1}$H} (121 MHz, $C_6D_6$) $\delta$ 3.30 (s), −44.0 (s), −51.2 (s), −52.4 (s), −52.6 (s), −53.4 (s), −141.8 (s).

**Reaction of 1a with 2c and 3b.** $^{1}$H NMR (300 MHz, $C_6D_6$) **2c**: $\delta$ 8.21 (s, 1H, PhCH═$NC_6H_4CH_3$), 7.84 (d, 2H, PhCH═$NC_6H_4$-$CH_3$), 7.14 (m, 5H, Ph), 7.00 (d, 2H, PhCH═$NC_6H_4CH_3$), 2.13 (s, 3H, PhCH═$NC_6H_4CH_3$). **3b**: $\delta$ 3.30 (sept, 2H, $CH(CH_3)_2$), 1.01 (d, 2H, $CH_3$). After 2 days: $^{31}$P NMR{$^{1}$H} (121 MHz, $C_6D_6$) $\delta$ −25.5 (s), −46.2 (s), −55.8 (s), −56.3 (s), −57.5 (s), −58.4 (s), −58.8 (s), 59.6 (s), −69.1 (s). After 5 days, decomposition is serious (>50%) and masks the resonances of many identified species.

**Reaction of 1a with 2a and 3b.** $^{1}$H NMR (300 MHz, $C_6D_6$) **2a**: $\delta$ 7.96 (s, 1H, PhCH═N$^{n}$Pr), 7.72 (m, 2H, Ph), 7.12 (m, 3H, Ph), 3.39 (t, 2H, $NCH_2CH_2CH_3$), 1.64 (m, 2H, $NCH_2CH_2CH_3$), 0.87 (t, 3H, $NCH_2CH_2CH_3$). **3b**: $\delta$ 3.30 (p, 2H, $CH(CH_3)_2$), 1.01 (d, 2H, $CH_3$). After 1 h: $^{31}$P NMR{$^{1}$H} (121 MHz, $C_6D_6$) $\delta$ −57.6(s). Serious decomposition including phase separation observed immediately.

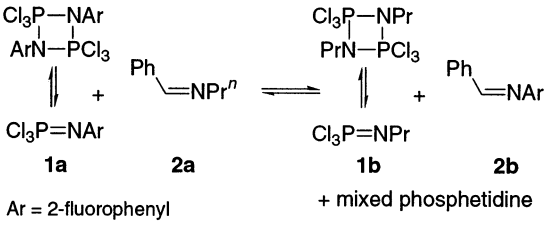
**Standard Imine Cross Metathesis. Reaction of 1a with 2c and 2d.** A screw-valve NMR tube was charged with 2-fluorophenyliminophosphorane (**1a**) (33.2 mg, 0.135 mmol) and $C_6D_6$ (0.3 mL). The contents of the tube were heated to 80 °C for 1 h in an oil bath to dissolve the solid. The imine PhCH═N(*p*-tolyl) (**2c**) (128 mg, 0.656 mmol, 4.9 equiv), (*p*-tolyl)CH═NPh (**2d**) (125 mg, 0.640 mmol, 4.7 equiv), and $C_6D_6$ (0.2 mL) were added to the cooled NMR tube. Initial $^{31}$P and $^{1}$H NMR spectra were acquired. The tube was placed in an 80 °C oil bath, and NMR spectra were taken periodically over 6 days. $^{1}$H NMR (300 MHz, $C_6D_6$) **2c**: $\delta$ 8.21, (s, 1H, PhCH═$NC_6H_4CH_3$), 7.84 (d, 2H, PhCH═$NC_6H_4CH_3$), 7.14 (m, 5H, Ph), 7.00 (d, 2H, PhCH═$NC_6H_4CH_3$), 2.13 (s, 3H, PhCH═$NC_6H_4CH_3$). **2d**: $\delta$ 8.17, (s, 1H, $CH_3C_6H_4CH$═NPh), 7.78 (d, 2H, $CH_3C_6H_4CH$═NPh), 7.16 (m, 4H, Ph), 7.06 (m, 1H, Ph), 6.96 (d, 2H, $CH_3C_6H_4CH$═NPh), 2.03 (s, 3H, $CH_3C_6H_4CH$═NPh). **2h**: $\delta$ 8.09, other peaks obscured by starting material. **2f**: $\delta$ 8.22, other peaks obscured by starting material. $^{31}$P NMR{$^{1}$H} (121 MHz, $C_6D_6$) $\delta$ 3.4 (s), −18.7 (s), −19.3 (s), −33.4 (s), −43.1 (s), −50.1 (s), −52.1 (s), −66.0 (s), −67.1 (s), −75.6 (s), −76.5 (s), −77.0 (s), −77.4 (s), −77.9 (s).

**Reaction of 1a with 2a and 2d.** $^{1}$H NMR (300 MHz, $C_6D_6$) **2a**: $\delta$ 7.96 (s, 1H, PhCH═N$^{n}$Pr), 7.72 (m, 2H, Ph), 7.12 (m, 3H, Ph), 3.39 (t, 2H, $NCH_2CH_2CH_3$), 1.64 (m, 2H, $NCH_2CH_2CH_3$), 0.87 (t, 3H, $NCH_2CH_2CH_3$). **2d**: $\delta$ 8.17 (s, 1H, $CH_3C_6H_4CH$═NPh), 7.78 (d, 2H, $CH_3C_6H_4CH$═NPh), 7.16 (m, 4H, Ph), 7.06 (m, 1H, Ph), 6.96 (d, 2H, $CH_3C_6H_4CH$═NPh), 2.03 (s, 3H, $CH_3C_6H_4CH$═NPh). **2h**: $\delta$ 8.09, other peaks obscured by starting material. **2g**: $\delta$ 7.98, other peaks obscured by starting material. After 8 days: $^{31}$P NMR-{$^{1}$H} (121 MHz, $C_6D_6$) $\delta$ 17.2 (s), 17.3 (s), −22.0 (s), −30.7 (s), −31.3 (s), −43.2 (s), −50.2 (s), −59.7 (s), −60.1 (s), −68.7 (s), −69.3 (s), −74.4 (s), −74.8 (s), −76.8 (s), −78.1 (s). Greater than 20% decomposition was observed after longer reaction times.

## Results

**Stoichiometric Reaction of Iminophosphoranes with Imines.** Since the key step of imine metathesis would be expected to involve the exchange of ═NR groups between

**Scheme 2**




a single imine and an iminophosphorane, we began by examining the stoichiometric reaction. When 2-fluorophenyliminophophorane (**1a**) is heated with an imine, ═NR exchange products are, indeed, formed (Scheme 2). For example, when **1a** is reacted with excess PhCH═N$^{n}$Pr (**2a**) and heated to 80 °C, peaks appear in the $^{31}$P NMR spectrum indicating the formation of new phosphorus containing species. Especially relevant is the peak at $\delta$ −76.7 that can be assigned, on the basis of our previous studies, as the *N*-*n*-propyliminophosphorane dimer **1b**. The presence of this new iminophosphorane confirms ═NR exchange has taken place. The monomeric form of **1b** is not seen because the *n*-propyl dimer is particularly stable and will not dissociate to any appreciable extent below 100 °C. $^{1}$H NMR data of the reaction mixture also show that the expected product imine (**2b**), carrying the 2-fluorophenyl substituent, is present in the reaction mixture.

In addition to the resonances for the products of metathesis, we also see other species in the NMR spectra of the reaction mixtures. Of particular note is a resonance at $\delta$ −59.6 that has all the characteristics that we would expect for a phosphetidine intermediate (Figure 3). The carbodiimide-derived phosphetidines that were isolated in our previous studies exhibited a characteristic phosphorus shift in this region. Furthermore, in proton-coupled $^{31}$P NMR spectra, the resonance becomes a complex multiplet as would be expected due to long-range P−H coupling with $H_a$ and $H_b$. Also present in the $^{1}$H NMR spectrum is a peak that can be assigned as $H_b$. Centered at $\delta$ 4.3, this resonance exhibits a $J_{PH}$ coupling constant of 18 Hz that is consistent with a 3-bond P−H coupling. The relatively low abundance of this intermediate made both the acquisition of a 2D P−H correlation spectrum and isolation impractical. Another intriguing peak in the $^{31}$P NMR spectrum at $\delta$ −17.4, which does not show $^{1}$H coupling, appears early in the reaction and persists as the most abundant phosphorus-containing species. Despite its relatively high concentration, repeated efforts to isolate the $\delta$ −17.4 species were unsuccessful.

It is important to note that there is decomposition occurring concurrently with the metathesis. Small amounts of a white crystalline compound precipitate from solution when the

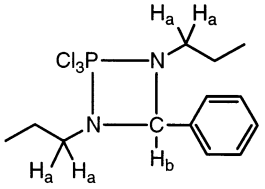
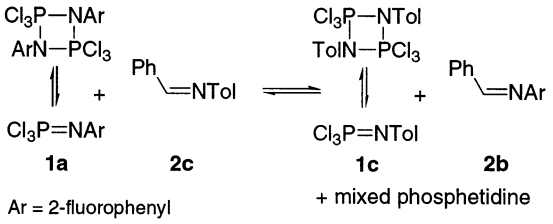
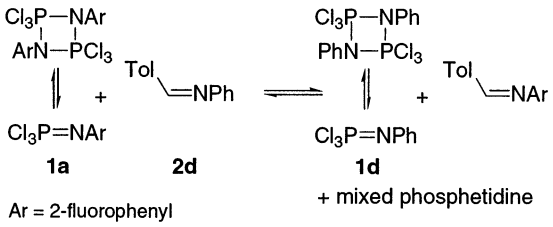



**Figure 3.** Structure of proposed phosphetidine intermediate.

**Scheme 3**




**Scheme 4**




reaction mixture is allowed to cool to room temperature after several days at 80 °C. This substance was isolated and identified as the hydrochloride salt of the original imine **2a**.

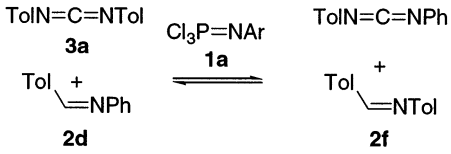
The stoichiometric reaction of an iminophosphorane with an imine is also observed for imines bearing N-aryl substituents. When **1a** is heated to 80 °C with excess PhCH═N(*p*-tolyl) (**2c**), metathesis occurs as is evidenced by NMR spectroscopy (Scheme 3). For this substrate, however, there is no accompanying decomposition; no salt precipitation is noted. Resonances are observed for both the monomeric and dimeric forms of *p*-tolyliminophosphorane product (**1c**). $^1$H NMR spectroscopy also confirms the production of the ═NR exchanged imine (**2b**). We cannot unambiguously identify any phosphetidine intermediates in the $^{31}$P NMR. Although there are signals present in the correct region of the spectrum, $\delta$ −50 to −70, and at least one is a doublet in the fully coupled $^{31}$P NMR spectrum, the concentrations are too low for definitive assignment. A correspondingly weak resonance at $\delta$ 4.0 in the $^1$H NMR spectrum, which could be assigned as a methine of a phosphetidine, is observed. Also of note in the $^{31}$P NMR spectrum is a resonance at $\delta$ −18.7 that is similar in shift to the $\delta$ −17.4 resonance observed in the case of the *n*-propyl imine **2a**. However, in this case, the peak is much smaller and never becomes the dominant phosphorus species.

The reaction of **1a** with another N-aryl imine, (*p*-tolyl)-CH═NPh (**2d**), gives very similar spectral data to that observed with the isomeric **2c**, although the peaks are slightly shifted as would be expected (Scheme 4). In contrast, iminophosphorane **1a** is unreactive with the sterically hindered aryl-N-alkyl imine (*p*-tolyl)CH═N$^i$Pr (**2e**). Even after days at 80 °C, there are no new signals in either the $^1$H or $^{31}$P NMR spectra.

When the *N*-*n*-propyliminophosphorane (**1b**) is used in place of **1a** in the reaction with imines **2a**, **2c**, or **2d**, no reaction occurs. Even after prolonged heating, the $^{31}$P NMR spectrum of the reaction mixture reveals that the iminophosphorane remains in its dimeric form; no new phosphorus species have been produced.

**Catalytic Carbodiimide/Imine Cross-Metathesis.** As an intermediate step to imine/imine metathesis, we explored the use of iminophosphoranes for the catalytic ═NR exchange between a carbodiimide and an imine. The 2-fluorophenyliminophosphorane (**1a**) proved to be an effective catalyst for carbodiimide imine cross-metathesis when the nitrogens of both substrates bear only aryl groups. For example, when (*p*-tolyl)CH═NPh (**2d**) is combined with di(*p*-tolyl)carbodiimide (**3a**) in the presence of **1a**, cross-metathesis products are formed as statistical mixtures (Scheme 5). Note that although catalysis occurs when less catalyst is present, throughout these studies a high catalyst loading (∼20%) was used so that intermediates could be observed. After heating overnight at 80 °C, $^1$H NMR spectroscopy reveals that the carbodiimide methyl peak has been reduced and new peaks have appeared in the tolyl methyl region. A resonance for methine of the product imine, (*p*-tolyl)CH═N(*p*-tolyl) (**2f**), can also be identified in the spectrum. The $^{31}$P NMR spectrum shows that the iminophosphorane starting material has been completely consumed. Two prominent new peaks for diazaphosphetidines resulting from addition of the di(*p*-tolyl)carbodiimide to an iminophosphorane are observed at $\delta$ −52.4 and −52.6. Figure 4 shows the phosphetidines that would be formed from the most likely combinations of iminophosphorane and carbodiimide. Although we have not assigned the individual resonances to specific structures in this case, our previous work on iminophosphorane mediated carbodiimide metathesis involved extensive studies of this type.[7] It should be noted that there are other, smaller resonances present in this region that could be assigned to minor phosphetidines. The catalytic reaction mixture requires >1 week at 80 °C to reach equilibrium. A control experiment consisting of the imine and carbodiimide without any added iminophosphorane showed no reaction after heating for the same period of time.

**Scheme 5**




The cross metathesis does not proceed when a carbodiimide bearing N-alkyl groups is used. When PhCH═N(*p*-tolyl) imine (**2c**) is reacted with diisopropylcarbodiimide (**3b**) in the presence of catalyst **1a**, no new imine products formed. The diazaphosphetidine arising from the addition of the carbodiimide to the starting iminophosphorane was observed, however. After 1 h of heating, all the starting iminophos-

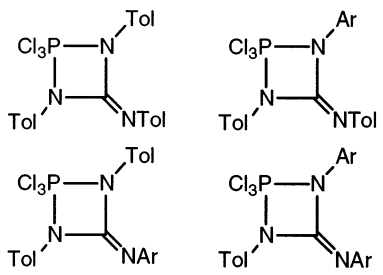
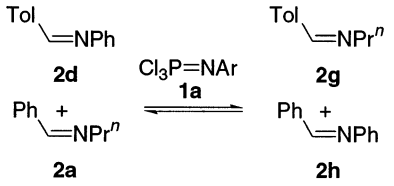



**Figure 4.** Possible phosphetidine intermediates from the cross-metathesis of di(*p*-tolyl)carbodiimide (**3a**) and (*p*-tolyl)CH═NPh (**2d**) (Ar = 2-fluorophenyl; Tol = *p*-tolyl).

**Scheme 6**




phorane has been converted to the diazaphosphetidine as determined by $^{31}$P NMR spectroscopy. Further heating leads to the formation of new diazaphosphetidines from the rearrangement of the initially formed species, but also a number of other new species form. After 5 days of heating, however, *no product imine* is seen in the $^{1}$H NMR spectrum. The large number of peaks in the $^{31}$P NMR spectrum and presence of solids suggested that significant decomposition has taken place.

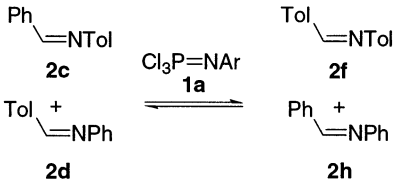
When an N-alkyl substituted imine such as PhCH═N$^{n}$Pr (**2a**) is reacted with diisopropylcarbodiimide (**3b**), the decomposition is even more dramatic: the solution separates into two phases after heating overnight. NMR spectra of the mixture showed extensive decomposition had taken place.

**Catalytic Imine Cross-Metathesis.** The N-aryl iminophosphorane **1a** also acts as a catalyst for imine cross-metathesis although competing reactions are a significant problem. The best-behaved system involves the combination of the imines (*p*-tolyl)CH═NPh (**2d**) and PhCH═N$^{n}$Pr (**2a**) with 2-flurophenyliminophophorane (**1a**). At room temperature, no reaction is seen. However, when the sample is heated to 80 °C, cross-metathesis products are seen both in the $^{1}$H NMR and $^{31}$P NMR spectra (Scheme 6). In particular, resonances are observed for both of the expected imine products **2g** and **2h**. Eventually, the imines equilibrate to give 1:1:1:1 statistical mixtures. The *N*-*n*-propyliminophosphorane dimer (**1b**), which should be produced during the course of the metathesis, can also be identified in the $^{31}$P NMR spectrum. Also present are a pair of $^{31}$P NMR resonances at $\delta$ −59.6 and −60.0 that are likely phosphetidines. It should be noted that these same peaks were also observed in the stoichiometric reactions of these imines with iminophosphorane **1a**. Also consistent with the stoichiometric reactions with imines **2a** and **2d**, resonances at $\delta$ −17.4 and −19.3 were observed. After 10 days at 80 °C, changes in the $^{1}$H NMR spectrum as well as the appearance of many new peaks in the $^{31}$P NMR spectrum suggest that decomposition has taken place. A control experiment consisting of the two imines without any added iminophosphorane showed no reaction after heating for the same period of time.

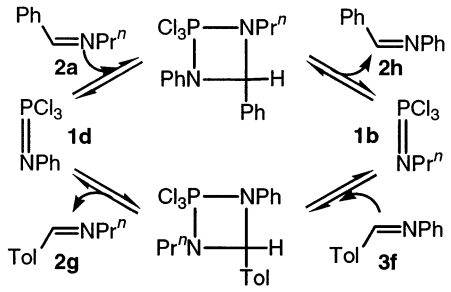
When the reaction was repeated using *N*-*n*-propyliminophosphorane (**1b**) in place of **1a**, no reaction occurred at room temperature. Even when the sample was heated to 95 °C, no evidence of reaction was seen in either the $^{1}$H or the $^{31}$P NMR spectra.

When two N-aryl imines, such as PhCH═N(*p*-tolyl) (**2c**) and (*p*-tolyl)CH═NPh (**2d**), are used as metathesis substrates in combination with the 2-fluorophenyliminophosphorane catalyst **1a**, significant amounts of ═NR exchange products are visible almost immediately at room temperature by $^{1}$H NMR spectroscopy (Scheme 7). After a few hours at room temperature, the imines can be seen to reach equilibrium. However, *no new phosphorus compounds are produced.* When these already metathesized reaction mixtures are heated to 80 °C, however, new phosphorus compounds are observed in the $^{31}$P NMR spectrum. After heating overnight, the first new peaks to form in the $^{31}$P NMR spectrum are at $\delta$ −18.7 and −19.2. After several days of heating, resonances corresponding to both the monomeric and dimeric forms of **1c** and **1d**, as well as resonances for putative phosphetidines intermediates, are observed in the phosphetidine region. Phosphorus mediated metathesis is obviously occurring at this point. It is important to note that decomposition was negligible and no iminium salt was observed. A control experiment consisting of the two imines without any added iminophosphorane showed no reaction after heating for the same period of time.

**Scheme 7**




**Scheme 8**




When substrate imines **2c** and **2d** were treated with the alkyliminophosphorane **1b**, a similarly fast initial metathesis to produce imine products **2f** and **2h** was observed. In contrast with the reaction using catalyst **1a**, however, no new phosphorus compounds were produced, even after days at 80 °C. As a control, imines **2c** and **2d** were also treated with catalytic $AlCl_3$ under the same conditions. Immediate ═NR exchange was observed at room temperature.

## Discussion

Iminophosphoranes catalyze the metathesis of imine substrates and imine/carbodiimide mixtures. Moreover, stoichiometric studies on the individual steps establish that imines react directly with iminophosphoranes to give ═NR exchange, consistent with a Chauvin-type addition/elimination mechanism (Scheme 8). There is also spectral evidence for the presence of phosphetidine intermediates formed by the addition of imines to iminophosphoranes, although the steady-state concentration of these intermediates is relatively low. In contrast with the carbodiimide system, the phosphetidine is not the resting state of the catalyst. Although the imine-derived phosphetidines (Figure 5, A) might be pre-

**Table 1.** Summary of Observed Reactions of Iminophosphoranes[a]

| imine 1 (R or Ar)[b] | imine 2 (R or Ar)[b] | carbodiimide (R or Ar)[b] | catalyst (R or Ar)[a] | observations | decomposition |
|---|---|---|---|---|---|
| R (**2a**) | | | Ar (**1a**) | metathesis after heating | minor (3 days) |
| R (**2e**) | | | Ar (**1a**) | no metathesis | no |
| Ar (**2c**, **2d**) | | | Ar (**1a**) | metathesis after heating | no |
| R (**2a**) | | | R (**1b**) | no metathesis | no |
| Ar (**2c**, **2d**) | | | R (**1b**) | no metathesis | no |
| Ar (**2d**) | | Ar (**3a**) | Ar (**1a**) | metathesis after heating | no |
| Ar (**2c**) | | R (**3b**) | Ar (**1a**) | no metathesis[c] | serious (5 days) |
| R (**2a**) | | R (**3b**) | Ar (**1a**) | no metathesis[c] | serious, phase separation (<1 day) |
| Ar (**2d**) | R (**2a**) | | Ar (**1a**) | metathesis after heating | serious (10 days) |
| Ar (**2c**) | Ar (**2d**) | | Ar (**1a**) | metathesis at room temp, new P species on heating | no |
| Ar (**2c**) | Ar (**2d**) | | R (**1b**) | metathesis at room temp, no new P species formed | no |

[a] Substrates and catalysts are categorized by nitrogen substituent. [b] Ar = N-aryl; R = N-alkyl. [c] Although carbodiimide scrambling was observed, no turnover of imine occurred.

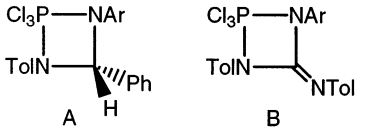



**Figure 5.** Phosphetidines formed from addition of PhCH═NTol (A) and TolN═C═NTol (B) to $Cl_3P$═NAr (Ar = 2-fluorophenyl).

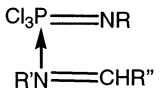



**Figure 6.** Imine adduct.

dicted to be more stable than the carbodiimide-derived phosphetidines (B) on the basis of only ring-strain arguments, the steric demands of the substrate substituents are more severe for the imine and are likely to destabilize addition products of type A. Moreover, the free carbodiimide is less stable than the imine, and it is probable that addition is simply thermodynamically more favorable for carbodiimides than imines.

There is also evidence in the reactions of imines with iminophosphoranes for another intermediate, an imine adduct, which is not observed when carbodiimide is the only substrate (Figure 6). Each of the reactions of iminophosphorane **1a** with imine, except **2e**, produces a phosphorus species with a $^{31}$P NMR resonance in the $\delta$ −17 to −19 region early in the reaction. The exact chemical shift is unique to each imine, and the prominence of the compound depends directly on the coordinating ability of the imine. Imine adducts of main group Lewis acids have been characterized extensively.[12] The adduct is a major component in the case of the N-alkyl imine **2a**, but only a minor component when the less basic N-aryl imines are used. Moreover, the only imine that does not make such an adduct is **2e**, the imine with a sterically demanding secondary alkyl substituent. The fact that these adducts are singlets in the $^1$H-coupled $^{31}$P NMR spectra suggests that they are fluxional at room temperature. It is not surprising that the less basic carbodiimides do not make similar adducts.

Although iminophosphoranes do react metathetically with imines, in examining the results as summarized in Table 1, it becomes immediately clear that the reactions of imines with iminophosphoranes are complex and that the course of the reaction depends on the substituents on nitrogen for both the catalyst and the substrates.

The *catalyst* substituent effects are thought to arise primarily from differences in their proclivity to dissociate into a monomeric form.[10] The position of the equilibrium is dependent on both electronic and steric factors. Under the conditions that the reactions were run, the 2-fluorophenyliminophosphorane (**1a**) is present mostly in its monomeric form while the *N*-*n*-propyliminophosphorane (**1b**) is nearly completely dimeric. To turn over, the imine must form a diazaphosphetidine with monomeric iminophosphorane (Figure 5, A). If the iminophosphorane itself forms a very strong dimer, as is the case for **1b**, the imine simply cannot compete effectively. Consistent with this argument is the fact that carbodiimides, which form more stable phosphetidines, can react catalytically with **1b**.

The *substrate* nitrogen substituent effects are more complex. There are three outcomes observed when iminophosphorane **1a** is combined with two imines: decomposition, instantaneous metathesis without intermediates, and catalytic iminophosphorane mediated metathesis. Decomposition, the first outcome, is observed when imines bear N-alkyl substituents. In some cases, the decomposition is minor and can be tolerated, while in others, the decomposition predominates. The exact pathway of decomposition is unclear at this point, but the isolation of hydrochloride salts of imines suggests that an HCl elimination from iminophosphorane may be involved. The presence of basic imines could clearly catalyze such a process. Our previous tantalum studies[2] showed that the presence of HCl is particularly troublesome since HCl can catalyze the metathesis of imines, hence adding more possible reaction pathways and complicating the process.

When an imine with an N-alkyl substituent is reacted with a N-aryl imine, we see what appears to be iminophosphorane mediated metathesis after heating. As was discussed earlier, all products and expected phosphorus intermediates are observed. Decomposition, although noted, is relatively slow and does not prevent the reaction mixture from completely metathesizing.

In the case of two N-aryl imines, evidence suggests that metathesis occurs by at least two mechanisms: Lewis acid catalysis and Chauvin-type addition elimination. At room

(12) Blackwell, J. M.; Piers, W. E.; Parves, M.; McDonald, R. *Organometallics* **2002**, *21*, 1400−1407 and references therein.

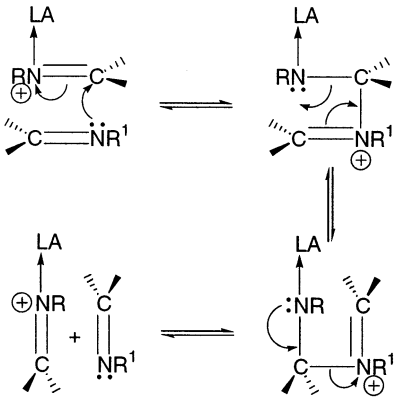



**Figure 7.** Metathesis of a Lewis acid (LA) coordinated imine.

temperature, the metathesis of the imine substrates proceeds without formation of the phosphorus intermediates that are characteristic of the stoichiometric reactions. When heated to the temperatures that were required to promote the stoichiometric reactions, however, these intermediates appear in the $^{31}$P NMR spectra.

Since the iminophosphoranes are quite Lewis acidic and since we know that N-aryl imines are very quickly metathesized in the presence of Brønsted[13] and Lewis acids such as $AlCl_3$, it seems likely that the room temperature behavior is due to a simple acid-catalyzed process (Figure 7). The fact that **1b**, the primarily dimeric iminophosphorane, promotes the room temperature exchange, but never gives intermediates, is consistent with this hypothesis since the dimer would not necessarily need to dissociate to act as a Lewis acid. Heating the reaction mixtures of **1a**, however, does produce the expected intermediates and phosphorus products, suggesting that while another pathway is dominant, the Chauvin mechanism is accessible at elevated temperatures. The Lewis acid pathway as well as a parallel Brønsted pathway (for decomposition reactions releasing HCl) must be considered as a factor for other substrate combinations.

(13) Toth, G.; Pinter, I.; Messmer, A. *Tetrahedron Lett.* **1974**, *9*, 735−738.

## Conclusion

This work has established that while the Chauvin mechanism for =NR metathesis is accessible to iminophosphorane catalysts, it is not always the most important pathway for reactions involving imines. It appears that a Lewis acid pathway may be important in certain cases and decomposition pathways are facile whenever N-alkyl groups are present. While the particular systems studied here do not appear to be well suited to controlled imine metathesis, they provide an important precedent for the development of a next generation of iminophosphorane-based catalysts. The apparent sensitivity of the iminophosphorane to the nature of the imine suggests that iminophosphorane catalysts can be produced that will exhibit high selectivity.

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