

Iminophosphorane-mediated carbodiimide metathesis

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Iminophosphorane $\text{Cl}_3\text{P}=\text{NAr}$ (Ar = 2-fluorophenyl) is an active carbodiimide metathesis catalyst and the cycloaddition product, a 1,3-diaza-2-phosphetidine, is an intermediate in the reaction.

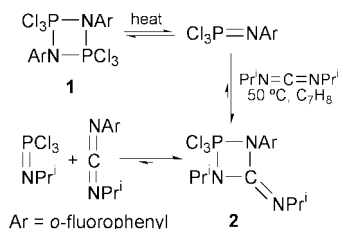
We study the metathesis of C=N bonds with the intention of developing the diverse synthetic and polymerization applications that depend on a single, well-defined reaction site. Until now, both our efforts^{1–3} and those of others⁴ have focused on metal-imide-mediated process. There are intriguing examples in the literature of stoichiometric metathesis of iminophosphoranes with carbodiimides as well as catalytic disproportionation of isocyanates using phosphine oxides.^{5–9} These examples of heterocumulene reactivity inspired us to extend our search for C=N metathesis catalysts to include phosphorus systems. Here, we describe our discovery that iminophosphoranes can act as catalysts for metathesis of carbodiimides, and we provide evidence for a diazaphosphetidine intermediate.

Trichloroiminophosphoranes can self-dimerize in solution, a behavior that should, theoretically, correlate with a potential for reactivity with the similarly polarized C=N bond. In particular, we have focused on the *o*-fluorophenyl derivative, **1** which is known¹⁰ to exist as an equilibrium mixture of dimer and monomer ($K_{\text{eq}} = 0.17 \text{ dm}^3 \text{ mol}^{-1}$ at 50 °C, Scheme 1). ³¹P NMR spectroscopy easily differentiates the two forms: –45.2 ppm (monomer) and –76.4 ppm (dimer).

The addition of an equivalent of diisopropylcarbodiimide to the iminophosphorane equilibrium mixture, followed by heating to 50 °C for 24 h gives a single product† by ³¹P NMR spectroscopy (–58.2 ppm). ¹H NMR spectroscopic data‡ are consistent with the formulation of diazaphosphetidine **2** arising from the addition of the C=N bond across the P=N bond, with the expected N-to-P regiochemistry. The observed 31 Hz phosphorus coupling of the methyne proton of one of the two inequivalent isopropyl groups is diagnostic for this product.

X-Ray diffraction studies of a single crystal,§ isolated from a preparative scale reaction, confirmed the guanidinate-type structure (Fig. 1). Complex **2** crystallized into a pseudo-*TBPY* geometry with one chlorine and the aryl-substituted nitrogen located in axial positions. Although electronegativity arguments would predict two axial chlorines, the small guanidinate ring size dictates that the more electronegative of the two nitrogens, the N-2-fluorophenyl, will occupy one axial site. The notably unsymmetric ring can then be explained by normal axial/equatorial bond length differences.

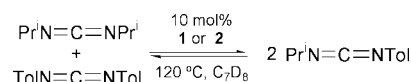
Although one example of a similar guanidinate-type structure was found in a search of the Cambridge Crystal Database,¹¹ the compound was not prepared by cycloaddition. Analogous urea-derived structures are more common.¹² It is interesting to note



Scheme 1

that Molina *et al.*, as part of their extensive studies on the preparation of heterocycles from carbodiimides, isocyanates and iminophosphoranes, isolated and characterized crystallographically an example of a zwitterionic, betaine form of this type of intermediate.¹³

Heating diisopropylcarbodiimide and di(*p*-tolyl)carbodiimide at 120–125 °C in toluene in the presence of iminophosphorane **1** (10 mol%) induced metathesis of the carbodiimides as indicated by the growth of ¹H NMR resonances associated with the mixed carbodiimide (Scheme 2). No =NR exchange was noted when the carbodiimides were heated without catalyst present. The reaction proceeded in < 24 h to give equilibrium mixtures of the carbodiimides. In an independent experiment, the same carbodiimides were metathesized at a similar rate in the presence of 10 mol% of the guanidinate complex **2**. The parallel activity of the guanidinate complex is consistent with its role as an intermediate in the catalytic process, although further studies will be required before other mechanisms, such as acid- or amine-catalyzed reactions,^{4a} can be ruled out.



Scheme 2

The similarities of Wittig chemistry and metal-catalyzed metathesis are interesting. Until now, however, phosphorus-ylide and -imine reactions have nearly always exploited the formation of a thermodynamically more stable P=E (E = O,S) bond as a driving force. In contrast, the preliminary results described here establish that truly catalytic metathetical processes are also possible for phosphorus. We are currently investigating the generality of these reactions.

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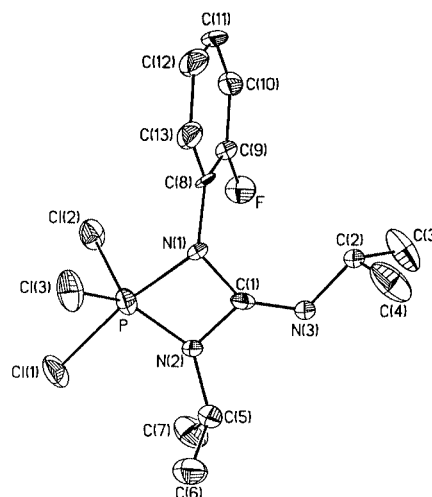


Fig. 1 Molecular structure of **2** indicating the atomic numbering scheme. Selected bond lengths (Å) and angles (°): P–Cl(1) 2.1029(12), P–Cl(3) 2.0352(12), P–N(1) 1.783(3), P–N(2) 1.6511(4), N(1)–C(1) 1.398(4), N(2)–C(1) 1.432(4); Cl(1)–P–Cl(3) 90.95(5), Cl(2)–P–Cl(3) 108.06(6), N(1)–P–Cl(1) 170.44(13), N(2)–P–Cl(1) 94.93(11), N(1)–C(1)–N(3) 138.5(3), N(1)–C(1)–N(2) 96.4(3), N(2)–C(1)–N(3) 125.1(3).

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Notes and references

† *Synthetic procedure for 2*: 1,3-diisopropylcarbodiimide (0.400 mL, 2.56 mmol) was added to a toluene solution (20 mL) of **1** (0.631 g, 2.56 mmol), in a reaction vessel equipped with a Teflon stopcock. After stirring for 48 h at 50 °C, the solvent was removed to give a white solid. Recrystallization from CH₂Cl₂–hexanes (1 : 6) at –35 °C gave a 50.2% yield of **2**. Anal. Calc. for C₁₃H₁₈N₃PFCl₃: C, 41.90; H, 4.88; N, 11.27. Found: C, 41.71; H, 4.93; N, 11.09%.

‡ *Spectral data for 2*: ¹H NMR (300 MHz, C₇D₈): δ 6.64–6.75 (m, aromatics), 4.35 (d/sept, PNCH), 3.35 (sept, NC=NCH), 1.49 (d, NC=NCHCH₃), 1.02 (d, PNCHCH₃), 0.91 (d, PNCHC'H₃). ³¹P{¹H} NMR (121 MHz, C₇D₈): δ –58.2 (s).

§ *Crystallographic data for 2* at 210(2) K: C₁₃H₁₈Cl₃FN₃P, *M* = 372.62, monoclinic, space group *P*2₁/*n*, *a* = 9.2930(19), *b* = 17.376(4), *c* = 10.822(2) Å, β = 93.02 (3)°, *V* = 1745.1(6) Å³, *D* = 1.418 g cm^{–3}, *Z* = 4, μ = 0.622 mm^{–1}. Of the 2503 reflections collected (2.22 ≤ 2θ ≤ 26.00°) with Mo-Kα radiation (λ = 0.71073 Å), the 2288 with *F*_o² > 2 σ(*F*_o²) were used in the final least-squares refinement to yield *R*(*F*_o) = 0.0360 and *R*_w(*F*_o²) = 0.0931.

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