Inorg. Chem. 2009, 48, 1808−1810

Inorganic Chemistry
Communication

Thermodynamic Investigations of the Staudinger Reaction of Trialkylphosphines with 1-Adamantyl Azide and the Isolation of an Unusual s-cis Phosphazide

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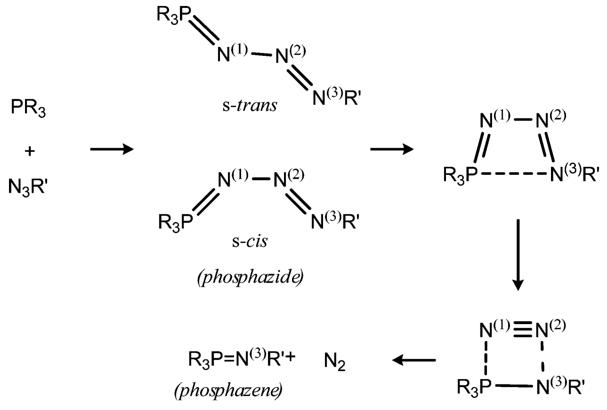
Received December 19, 2008

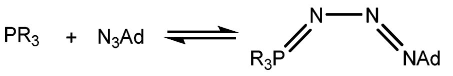
The reaction of PR_3 (R = Cy, ^{i}Pr) with 1-adamantyl azide (N_3Ad) in benzene results in an equilibrium of the starting material and the phosphazide R_3PN_3Ad. Thermodynamic and kinetic measurements were taken of the reaction of $P^{i}Pr_3$ with N_3Ad and yielded $\Delta H = -18.7 \pm 1.0$ kcal mol^{-1}, $\Delta S = -52.5 \pm 2.0$ cal mol^{-1} K^{-1}, $\Delta H^{\ddagger} = +12.0 \pm 1.0$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -25.3 \pm 1.2$ cal mol^{-1} K^{-1}. The phosphazides, R_3PN_3Ad, do not readily lose N_2 for R = Cy and ^{i}Pr; however, the reaction of PMe_3 with N_3Ad results in a smooth formation of the phosphazene $Me_3P{=}NAd$ with N_2 loss. Calorimetric investigations of this reaction led to an estimation of $\Delta H = -40 \pm 3$ kcal mol^{-1} for the loss of N_2 from the intermediate phosphazide R_3PN_3Ad and also yield an estimation of 72 ± 5 kcal mol^{-1} for the bond dissociation energy of the P=N bond in $R_3P{=}NAd$. The X-ray crystal structure of Cy_3PN_3Ad is reported.

First reported in 1919 by Staudinger and Meyer, the reaction of a tertiary phophine with an organic azide forms a phosphazene with the extrusion of molecular nitrogen.[1] The mechanism of this reaction is generally believed to proceed through an intermediate phosphazide, as shown in Scheme 1.[2] It has been speculated that the phosphazides are transient species in these reactions. It is now well-known that, under appropriate conditions and with the appropriate R and R′ groups, stable phosphazides can be isolated and characterized.[2,3] The majority of isolated posphazides are in the s-trans configuration. This communication reports the formation of a stable phosphazide with the unusual s-cis conformation. In addition, experimental thermodynamic and kinetic data for the formation of the P=NR bond are reported and compared to existing computational studies.

Scheme 1. Proposed Mechanism for Staudinger Reaction[2]



The reaction of equimolar amounts of PR_3 (R = Cy (cyclohexyl) and ^{i}Pr (isopropyl) with 1-adamantylazide (N_3Ad) in aromatic solvents at room temperature results in establishment of the equilibrium shown in reaction 1. ^{31}P and ^{1}H NMR clearly showed the presence of both the adduct and free reactants at room temperature. The existence of this equilibrium has been previously noted;[4,5] however, quantitative data have not been reported.



(1)

There is little apparent difference in the behavior of the isopropyl and cyclohexyl species since solutions of $^{i}Pr_3PN_3Ad$ with an equimolor amount of free PCy_3 at 298 K were observed to form an equilibrium, as shown in reaction 2. ^{31}P NMR showed that the resultant solution contained nearly equal amounts of both phosphazides, implying similar themochemical stabilities.

$$^{i}Pr_3PN_3Ad + PCy_3 \rightleftharpoons Cy_3PN_3Ad + P^{i}Pr_3 \qquad (2)$$

A toluene solution of Cy_3PN_3Ad allowed to evaporate slowly in a glovebox in an argon atmosphere afforded clear

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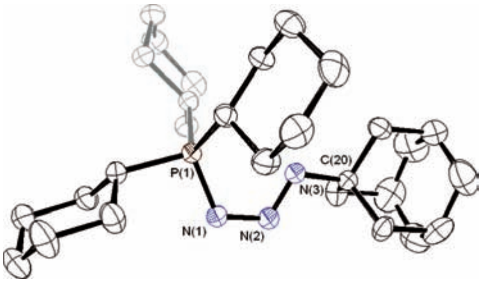

Figure 1. ORTEP diagram of Cy_3PN_3Ad with ellipsoid probability of 35%. Selected bond lengths (Å) and angles (deg): P(1)−N(1), 1.6534(14); N(1)−N(2), 1.345(2); N(2)−N(3), 1.261(2); N(3)−C(20), 1.488(2); P(1)−N(3), 2.720(1); P(1)−N(1)−N(2), 118.62(11); N(1)−N(2)−N(3), 116.55(14); N(2)−N(3)−C(20), 112.17(13).

colorless crystals. Its molecular structure in the solid state was determined by single-crystal X-ray diffraction (see Figure 1). This is only the second reported structure of an acyclic phosphazide in the s-cis configuration and the first containing all alkyl groups.

Betrand and co-workers reported the structure of 3-bis(diisopropylamino)-1,2,3,4-λ^5-phosphorinane-5,6-dicarboxylate, which is a cyclic phosphazide in which the phosphazide resides in the s-cis configuration when incorporated into six-membered ring.[6] Molina reported the first acyclic s-cis structure, $(C_6H_5)_3PN_3C(CN)(C_6H_5)(Me)$, in 1996.[7] The P(1)−N(1) bond distance of Cy_3PN_3Ad (1.6534(14) Å) is in accord with P=N, making the phosphorus formally P(V). The N(1)−N(2) distance (1.345(2) Å) and N(2)−N(3) distance (1.261(2) Å) in conjunction with the P(1)−N(1) distance are such as to suggest delocalization through the PNNN backbone. The bond angles of the N atoms are all consistent with sp^2 hybridization. The PNNN moiety is essentially planar with a torsion angle of approximately 2°.

The P(1)−N(1) distance in Cy_3PN_3Ad (1.6534(14) Å) as compared to that of Molina's phosphazide (1.641(2) Å) is slightly longer. Another difference of note is the distance between P(1) and N(3). The P(1)−N(3) distance of Cy_3PN_3Ad (2.720(1) Å) is shorter than that of $(C_6H_5)_3PN_3C(CN)(C_6H_5)(Me)$ (2.800(2) Å). This is most likely due to the greater steric bulk of the $C(CN)(C_6H_5)(Me)$ group over that of the Ad group of the azide. This same attribute is also observed in the smaller P(1)−N(1)−N(2) and N(1)−N(2)−N(3) angles of Cy_3PN_3Ad. Bond lengths and angles are also in good agreement with DFT calculations of Me_3PN_3Me.[8] The P(1)−N(3) distance is calculated to be 2.74 Å, and the P(1)−N(1) distance was calculated to be 1.66 Å.

Variable-temperature measurements of K_{eq} via NMR in C_6D_6 between the ranges of 298 and 328 K for the reaction of P^iPr_3 with N_3Ad were made as described in the Supporting Information. A van't Hoff plot, shown in Figure 2, yields thermodynamic data for reaction 1: $\Delta H = -18.7 \pm 1.0$ kcal mol^{-1} and $\Delta S = -52.5 \pm 2.0$ kcal mol^{-1} K^{-1}. The value of ΔH was also checked using calorimetric measurement of the reaction with N_3Ad as the limiting reagent and an approximate 10-fold excess of phosphine. The value of $\Delta H_{rxn} = -18.3 \pm 1.0$ kcal mol^{-1} is in good agreement with that determined from equilibrium data. The large negative entropy of reaction is attributed to "locking" of the phosphine substituents by the P=N bond formed in the highly crowded structure, as shown in Figure 1.

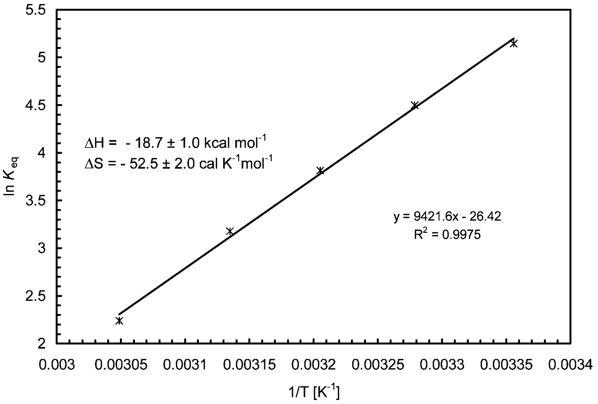

Figure 2. Van't Hoff plot of $P^iPr_3 + N_3Ad \leftrightarrow {}^iPr_3PN_3Ad$ in C_6D_6. Temperature ranges from 298 to 328 K.

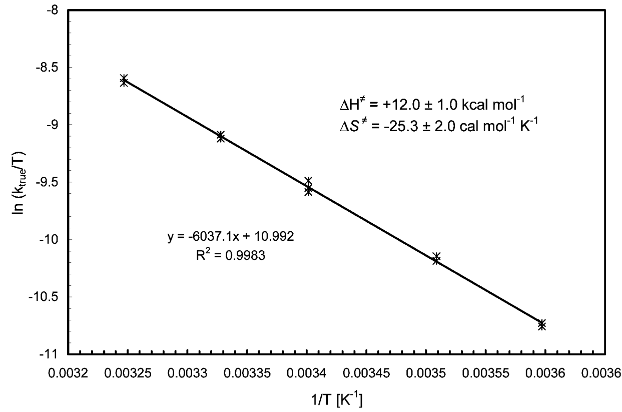

Figure 3. Eyring plot for the reaction of P^iPr_3 with N_3Ad. Experiments were carried out form 278 to 308 K.

The rate of reaction of P^iPr_3 with N_3Ad was studied using FTIR under pseudo-first-order conditions of excess P^iPr_3. The reaction gave excellent fits to first-order plots in ln $[N_3Ad]$, as shown in Supporting Information Figure S1a. Reducing the $[P^iPr_3]$ by half decreased the value of k_{obs} by half, and the rate law $d[{}^iPr_3PN_3Ad]/dt = k_{obs}[P^iPr_3][N_3Ad]$ is observed. Measurements of k_{obs} were taken in duplicate at five temperatures ranging from 278 to 308 K in toluene. An Eyring plot for this reaction is shown in Figure 3, from which activation parameters were derived: $\Delta H^{\ddagger} = +12.0 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -25.3 \pm 2.0$ cal mol^{-1} K^{-1}.

The phosphazide adducts R_3PN_3Ad are kinetically stable at ambient temperatures in the absence of light to N_2 loss, for R = Cy or ^iPr, but not for R = CH_3, for which the extrusion of N_2 occurs smoothly, as shown in reaction 3.

$$PMe_3 + N_3Ad \rightarrow Me_3P{=}NAd + N_2 \qquad (3)$$

Calorimetric measurements of this reaction determined ΔH_{rxn} to be -58.1 ± 2.5 kcal mol^{-1} with all species in solution. The data above can be used to derive an estimate of the $Me_3P{=}NAd$ bond strength, as shown in Scheme 2. Experimental data for a loss of N_2 from RN_3 could not be

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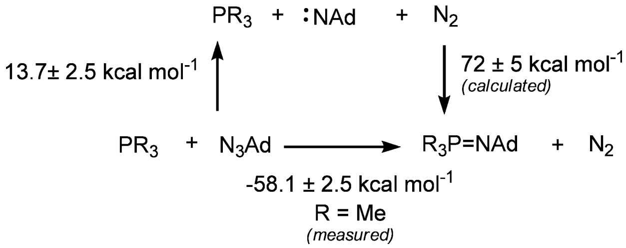
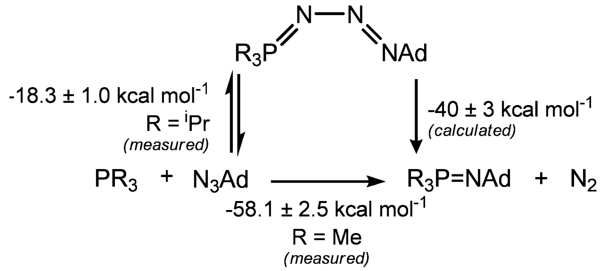
Scheme 2. Thermodynamic Cycle Used to Estimate the P═N BDE



Scheme 3. Thermodynamic Cycle Used to Estimate the Loss for N_2 from the Phosphazide R_3PN_3Ad



found; however, the conversion of HN_3 to NH and N_2 is endothermic by +13.7 kcal mol^{-1}.[9] This value was used as a model for RN_3 with an estimated uncertainty of ±2.5 kcal mol^{-1}. The derived bond strength estimate for AdN═PMe$_3$ of 72 ± 5 kcal mol^{-1} can be compared to that for E═PBu$_3$, E = O (140),[10] S (96),[11] Se (75),[11] and Te (52).[11] These data imply that the AdN═PMe$_3$ bond strength is roughly comparable to the Se═PMe$_3$ bond strength and considerably weaker than the O and S analogs. It is of interest to note that the Cp_2UO bond has been recently calculated to be 71 kcal mol^{-1} stronger than the Cp_2UNMe.[12] Additional calorimetric work to probe other Y═PR$_3$ bonds is in progress and may give insight into the relatively weak nature of the RN═PR$_3$ bond derived here.

Assuming that the heat of formation of the initial phosphazide Me_3PN_3Ad is similar to that of $^iPr_3PN_3Ad$, the heat of loss of N_2 from R_3PN_3Ad was estimated to be about −40 ± 3 kcal mol^{-1}. The thermodynamic cycle used to calculate this value is shown in Scheme 3 and summarizes the reaction energetics for phosphazide formation for alkyl group substituents. It is clear from the data in Scheme 3 that the elimination of N_2 (which should be entropically favored) is highly favorable.

Thermodynamic and kinetic data reported here can be compared to recent high-level theoretical calcultions.[8,13,14] Calculations at the B3LYP/6-31G(d) level show a significant substituent effect of the R group on both the P and N(3) atoms. (All of the following calculated values are in terms of Gibbs free energy at 298 K and 1 atm.) The s-cis conformation of the parent compound H_3PN_3H was calculated as +29.7 kcal mol^{-1} relative to the reactants, while Me_3PN_3Me is only +11.0 kcal mol^{-1} higher than the reactants. Thus, both adducts are computed to be thermodynamically unstable with respect to the reactants. For the reaction of P^iPr_3 with N_3Ad, the experimental ΔG was calculated to be −3.1 ± 1.5 kcal mol^{-1}. Due to reduced steric factors, Me_3PN_3Me would be expected to be more and not less stable than $^iPr_3PN_3Ad$, and so the calculations appear to underestimate the stability of the phosphazide. The discontinuity seen between the theoretical and experimental change in the overall change in Gibbs energy is not as pronounced in the activation parameters determined for their formation: $\Delta G_{\mathrm{exp}}^{\ddagger} = +19.5 \pm 1.2$ kcal mol^{-1} and $\Delta G_{\mathrm{calcd}}^{\ddagger} = +\ 23.7$ kcal mol^{-1}.

The apparent stability of Cy_3PN_3Ad in the s-cis confirmation may arise from interactions between the P and N(3) atoms. As noted by Wang and Tian,[8] the relative electronegativities of C (2.54), P (2.25), and N (3.07) result in the phosphorus carrying a slightly positive charge, while the N(3) carries a slightly negative charge. Electrostatic interactions would then serve to stabilize the s-cis isomer. The more stable nature of Cy_3PN_3Ad compared to Me_3PN_3Ad is attributed to the bulky substituents hindering further reaction, leading to N_2 loss and phosphazene formation.

The change in electronic energies for the reaction of PMe_3 with N_3Me was calculated as −45.1 kcal mol^{-1}.[8] This number corresponds to the experimentally determined ΔH_{rxn} for reaction 3 of −58.1 ± 2.5 kcal mol^{-1}, with the experimental value being considerably more exothermic. The value estimated for the loss of N_2 from the phosphazide (−40 ± 3 kcal mol^{-1}), as shown in Scheme 3, however, agrees well with Wang and Tian's calculated value of −43.7 kcal mol^{-1}. A surprising result of this study was the much weaker nature of the R$_3$P═NAd bond compared to R$_3$P═O. Additional investigations on the thermodynamics of the Staudinger reaction and related ylid-forming reactions are currently underway in our laboratory.

Acknowledgment. The authors thank the National Scientific Foundation (Grant No. CHE 0615742) for its financial support.

Supporting Information Available: Detailed experimental procedures, FTIR kinetics spectra, a calorimetric thermogram, FAB+ MS data, crystallographic data, and the CIF file for the structure of Cy_3PN_3Ad. This information is available free of charge via the Internet at http://pubs.acs.org.

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