Contribution from the Department of Chemistry,
Howard University, Washington, D.C. 20059

Extraplanar Ligand-Exchange Dynamics in (Tetraphenylporphinato)zinc(II) and the Conformation of Zinc(II) Porphyrins in Solution

CARLYLE B. STORM,* ANNE H. TURNER, and MADELINE B. SWANN

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The extraplanar ligand-exchange dynamics of (tetraphenylporphinato)zinc(II) with pyridine and *N*-methylimidazole have been studied at 21 °C in $CDCl_3$. For the ZnTPP–py system we find $k_{on} = 4.90 \times 10^8$ M^{-1} s^{-1}, $k_{off} = 1.98 \times 10^5$ s^{-1}, and $K = 2300 \pm 400$ M^{-1}. For the ZnTPP–*N*-MeIm system we find $k_{on} = 1.67 \times 10^8$ M^{-1} s^{-1}, $k_{off} = 4.78 \times 10^4$ s^{-1}, and $K = 10\,200 \pm 600$ M^{-1}. An analysis of the steric limitations of ZnTPP and the ligands (pyridine and *N*-methylimidazole) suggests that k_{on} is close to, if not at, the diffusion-controlled rate limit. Since the ZnTPP–L complexes are known to have the Zn(II) displaced some 0.3 Å out of the mean plane of the porphyrin ring, a diffusion-controlled k_{on} requires that the unligated ZnTPP also be nonplanar.

Introduction

(Tetraphenylporphinato)zinc(II) (ZnTPP) binds pyridine, and other nitrogen bases, in a 1:1 complex with the extraplanar ligand perpendicular to the plane of the porphyrin ring and the Zn(II) displaced some 0.3 Å from the mean plane of the porphyrin toward the ligand.[1-4] The complexing of the ligand to ZnTPP causes a large upfield shift of the ligand protons due to shielding by the porphyrin-ring current.[2] Because of the large shifts induced by the ring current, ZnTPP has been used as a diamagnetic shift reagent and the chemical shift of the pyridine protons in the 1:1 complex have been used to determine the geometry of the complex in solution.[5-7] As the mole ratio of L:ZnTPP increases above 1, the high-field shift of the ligand protons decreases to the limiting value of the free ligand.[2] This is consistent with a system in rapid exchange, the observed chemical shift being the mole fraction weighted average of free and bound ligand.

Earlier attempts to determine exchange rates by observing exchange line broadening in pyridine protons at 60 MHz were unsuccessful for both ZnTPP and MgTPP.[2,8] At 200 MHz the protons on pyridine and *N*-methylimidazole are visibly broadened at room temperature, corresponding to moderately fast exchange on the NMR time scale. We report here an analysis of the dynamics of the ligand exchange and relate it to the probable conformation of ZnTPP in solution.

Experimental Section

Tetraphenylporphine (Aldrich) was purified and converted to ZnTPP by the method of Fuhrhop and Smith.[9] Pyridine (Baker) and *N*-methylimidazole (Aldrich) were distilled from calcium hydride and stored over molecular sieves. Chloroform-*d* (Merck) and tetramethylsilane (Aldrich) were used as received.

Samples of ZnTPP (2–8 mg) were weighed on a microbalance directly into clean dry 5-mm NMR tubes, and 0.50 mL of $CDCl_3$ was added. A 10% (v/v) solution of ligand in $CDCl_3$ was prepared and the calculated amount required to achieve the desired ZnTPP:L ratio added to the ZnTPP solution with a 10-μL syringe, along with a small amount of Me_4Si. A second tube containing the same amount of ligand, chloroform-*d*, and TMS, but without ZnTPP, was prepared as a standard. The paired samples were run in succession after which 0.50 mL of $CDCl_3$ was added to each tube and the samples were rerun. This was continued until the total volume reached 2.0 mL for each tube, giving four concentrations per sample.

Spectra were run on a Nicolet NT-200 spectrometer equipped with a fixed-frequency 200-MHz proton probe using a 90° pulse angle and a 8.45-s pulse to pulse delay time. A sweep width of 2400 Hz was used and the free induction decay accumulated in a 16K memory block. Temperatures were measured by the method of Van Geet[10] as modified by Raiford et al.,[11] using a methanol sample at various times before, during, and after the kinetic runs. The equation, corrected to 200 MHz, is T (K) = $429.2 - 0.3113\Delta\nu - (3.463 \times 10^{-4})\Delta\nu^2$, where $\Delta\nu$ is the separation (in Hz) between the methyl and hydroxyl protons of methanol. The average of the temperatures was 293.9 ± 0.7 K.

Chemical shifts, coupling constants, and proton line widths for the ligand spectra and the ligand portion of the ZnTPP–L spectra were obtained by computer fitting using the NTCSIM program in the Nicolet 1180 software. The spectra were calculated and plotted to the same scale as the corresponding experimental spectrum until the calculated spectrum could be superimposed on the experimental.

Data Analysis

The spectra were treated as approaching the rapid-exchange limit. Meiboom et al.[12] have derived an approximation for the exchange-broadened line width whenever $(\tau_A + \tau_B) \ll (\omega_A - \omega_B)^{-1}$:

$$\frac{1}{T_2''} = \frac{1}{T_2'} + P_A^2 P_B^2 (\omega_A - \omega_B)^2 (\tau_A + \tau_B) \qquad (1)$$

where $1/T_2''$ and $1/T_2'$ are the line widths ($\times\pi$) $\Delta_i/[\text{ZnTPP}]_{total}$ the exchanging and nonexchanging systems, respectively, P_A and P_B the mole fractions of free and bound ligands, and ω_A and ω_B the corresponding chemical shifts (in radians).

In order to determine the chemical shift of the completely bound pyridine it is necessary to obtain spectra from solutions having large concentrations of free ZnTPP. In aromatic systems this can lead to errors caused by what Stamm et al. call "additional unspecified shielding" (AUS), from the unsuccessful collisions between the ligand and ZnTPP.[13] To determine the magnitude of the problem, a modified Scatchard treatment has been developed that simultaneously determines ω_B and tests each set of data for errors in dilution, measurement, etc.

For any ZnTPP–L sample, the chemical shifts of the ligand change with each dilution as the complex dissociates: ZnT-

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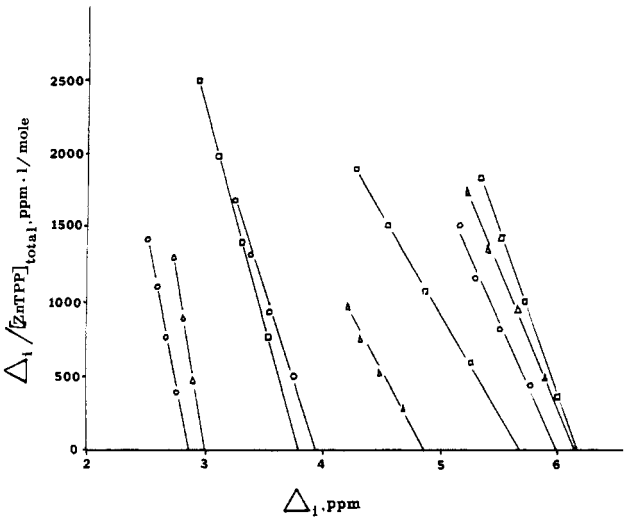

Figure 1. Example of the modified Scatchard plot used to determine the ω_B and mole fraction parameters for the α protons of the ZnTPP–py system. The ZnTPP/pyridine ratio and amount of ZnTPP for each series are as follows, from left to right: 2.50, 3.93 mg; 2.17, 4.05 mg; 1.39, 4.63 mg; 1.09, 3.06 mg; 0.85, 5.86 mg; 0.69, 2.61 mg; 0.68, 1.60 mg; 0.50, 2.14 mg; 0.48, 2.39 mg. See text for definition of symbols.

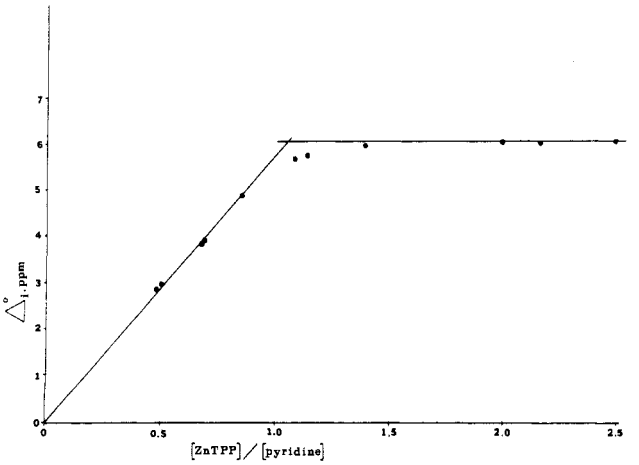

Figure 2. Δ_i° values obtained from the modified Scatchard plot vs. $[ZnTPP]_{total}/[py]_{total}$.

PP–L $\rightleftharpoons$ ZnTPP + L. In order to determine what the chemical shifts would be if the ligand were completely bound (i.e., if the ZnTPP–L complex had an infinitely high association constant), a plot of $\Delta_i/[ZnTPP]_{total}$ vs. Δ_i, where $\Delta_i = \nu_{free} - \nu_{obsd}$ for ligand protons, is useful. If the dilutions and chemical shift analyses have been done correctly, the plot is a straight line (Figure 1). The x intercept of the line is Δ_i°, the average chemical shift of the fully bound complex. Plots were done on all ligand resonances for mixtures having ratios of ZnTPP to ligand between 1.0:0.2 and 1.0:2.0 (at ratios much above 1:2, the ligand peaks being to run into the peaks from ZnTPP, making accurate analysis difficult). A second plot of Δ_i° vs. $[ZnTPP]_{total}/[ligand]_{total}$ (from the spectrum integrals) produces a straight line with a sharp break at $[ZnTPP]_{total}/[ligand]_{total} = 1$ (Figure 2). Above $[ZnTPP]_{total}/[ligand]_{total} = 1$, this line may have a small slope, the value of which can be used to correct the observed chemical shift for any additional unspecific shielding. For ZnTPP–py this correction is marginally significant, for ZnTPP–*N*-MeIm there is no correction, but the method is general and could prove more significant for less tightly bound complexes.

The value of ω_B for each ligand resonance is the Δ_i° at $[ZnTPP]_{total}/[ligand]_{total} = 1$. With ω_A determined by the

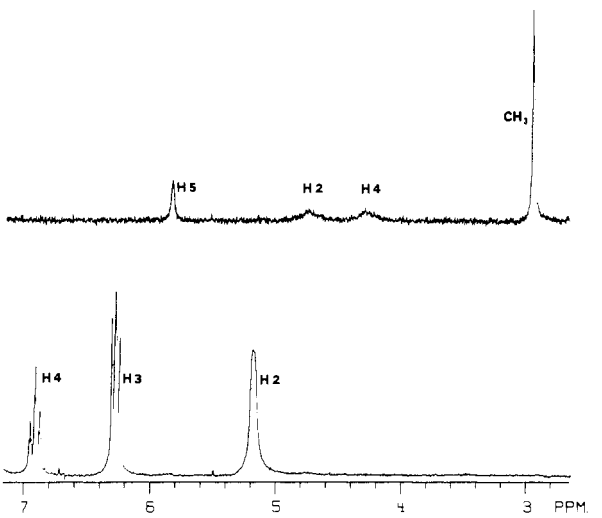

Figure 3. ^1H NMR spectrum of pyridine (lower) and *N*-methylimidazole (upper) in the presence of ZnTPP.

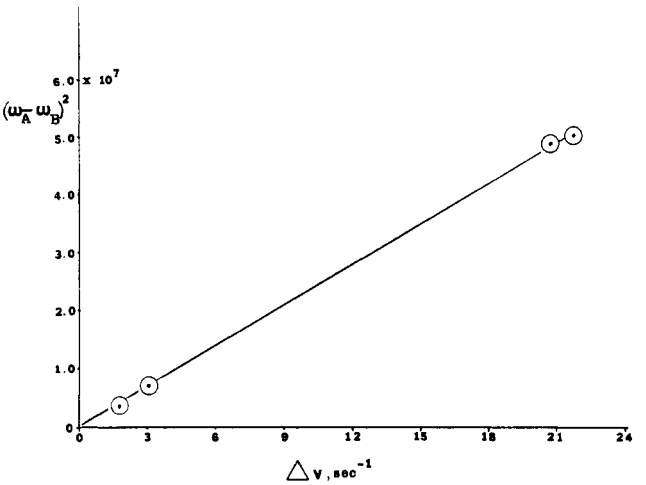

Figure 4. $(\omega_A - \omega_B)^2$ vs. the line width for the four resonances in *N*-methylimidazole in the presence of ZnTPP.

NTCSIM computer fitting for free pyridine, the mole fraction equations for pyridine are

$$\nu(\alpha_{obsd}) = 8.61P_A + (1 - P_A)2.48$$

$$\nu(\beta_{obsd}) = 7.28P_A + (1 - P_A)5.48$$

$$\nu(\gamma_{obsd}) = 7.67P_A + (1 - P_A)6.32$$

The average P_A from the three pyridine resonances was used as the mole fraction of free pyridine; $P_B = 1 - P_A$. This permits the calculation of $\tau_A + \tau_B$ from eq 1.

The data from *N*-MeIm–ZnTPP were treated in the same way.

The concentrations of all species in solution can be determined from the weight of the original ZnTPP, the average of the four integrals for each series, the mole fractions, and the volumes. This permits the calculation of the equilibrium constant $K_c = [ZnTPP–L]/[ZnTPP][L]$. A plot of $\tau_A + \tau_B$ vs. $1/([ZnTPP] + [L])$ gives a straight line, with the intercept giving $1/k_{off}$ and the slope $1/k_{on}$.

Results and Discussion

At 200 MHz the protons on pyridine and *N*-methylimidazole are visibly broadened in the presence of ZnTPP at room temperature (Figure 3), corresponding to moderately fast exchange on the NMR time scale. The chemical shifts are still averaged, but the line broadening is measureable. The resonances having the largest $\omega_A - \omega_B$ will be the first to move into the intermediate exchange region on the NMR time scale.

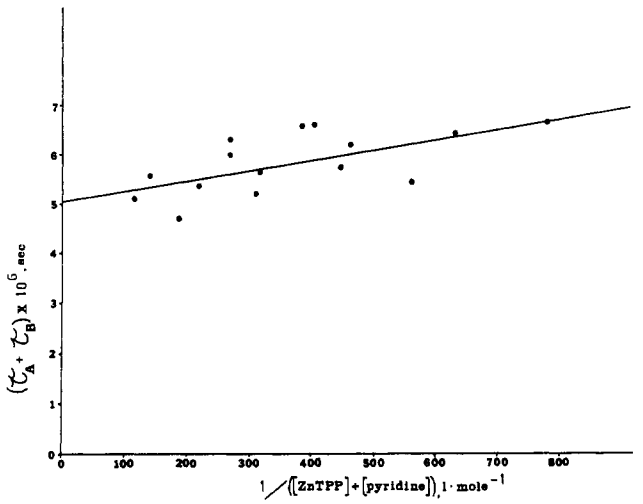

Figure 5. $\tau_A + \tau_B$ obtained from eq 1 vs. $1/([ZnTPP] + [py])$.

Table I. Rate and Equilibrium Constants for the Reaction of Pyridine and *N*-Methylimidazole with (Tetraphenylporphinato)zinc(II)

	k_1, s^{-1}	k_2, M^{-1} s^{-1}	K
ZnTPP-py	1.98×10^5	4.90×10^8	2300 ± 400^a 2477^b
ZnTPP-*N*-MeIm	4.78×10^4	1.67×10^8	$10\,200 \pm 600^a$ 3500^b

[a] Calculated from the concentrations, as determined in the data analysis. [b] Calculated from k_2/k_1.

In Figure 4, $(\omega_A - \omega_B)^2$ is plotted against $\Delta\nu$ for the four resonances in *N*-methylimidazole. The direct relationship of line width to $(\omega_A - \omega_B)^2$ for all of the lines in the spectrum demonstrates the rapid exchange limit appropriate for the use of eq 1.

In this system $\tau_A = 1/k_1$ and $\tau_B = 1/k_2([ZnTPP] + [L])$ (note—these are the free ZnTPP and free L concentrations at equilibrium).

$$\tau_A + \tau_B = 1/k_1 + 1/k_2([ZnTPP] + [L]) \qquad (2)$$

A plot of $\tau_A + \tau_B$ (calculated from eq 1) vs. $1/([ZnTPP] + [L])$ gives a straight line (Figure 5) with an intercept of $1/k_1$ and a slope of $1/k_2$, where k_1 and k_2 are the rate constants of the dissociation and association reactions, respectively:[14]

$$\text{ZnTPP-L} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{ZnTPP} + \text{L}$$

The rate constants and association constants obtained for ZnTPP-py and ZnTPP-*N*-MeIm are given in Table I.

The modified Scatchard treatment we have used in this study provides an accurate assessment of the high-field shifts of the coordinated ligand resonance (termed ΔP by Abraham et al.)[6,7] and an evaluation of any other process such as π-π interactions. The observed high-field shifts are somewhat larger than those reported previously: α protons, 6.13 (this work), 5.86 (6), 5.92 (5); β protons, 1.80, 1.77, 1.71; γ protons, 1.35, 1.40, 1.28. The accurate determination of these high-field shifts on ligand binding is important for the evaluation of the kinetic parameters and for the conformational analysis of the compounds in solution. The modified Scatchard treatment used here also provides accurate mole fractions used in the kinetic analysis and in determining the equilibrium constants.

A full explanation of the lability observed for metalloporphyrin–ligand complexes requires a detailed knowledge of their electronic properties, including both bonded and non-bonded (steric) interactions. The Zn(II)–porphyrin systems are excellent candidates for providing the basic structure and activity relationships for understanding this lability. The equilibrium only involves the addition of one extraplanar ligand, and a linear correlation has been observed between the logarithm of the formation constant of ZnTPP–L complexes and the pK_a values of 3- and 4-substituted pyridines.[2]

Pyridines substituted in the 2-position deviate from this relationship because of steric interactions. The influence of axial ligands on the ZnTPP visible spectrum has been studied[15] and interpreted as depending on the charge and polarizability of the ligand, rather than the strength of the Zn–L bond.

There have been a number of reports on the dynamics of ligand exchange in metalloporphyrins.[16-22] In the Ru(II)–carbonyl systems the lifetimes of the bound and free pyridine ligand are about equal.[16,17] The k_1 is around 0.09 s^{-1}, and a k_2 of 1.03 M^{-1} s^{-1} may be estimated from the published data.

The situation with iron porphyrins is much more complex. There are possibilities for both five- and six-coordinate species, multiplicities of spin states, and ion pairing. Attempts have been made to resolve the participation of five- and six-coordinate species and to define a dissociative mechanism.[18,19] Quantitative comparisons have been made between equilibrium constants measured by optical spectroscopy and NMR.[21] Values for k_1 for axial ligands vary between 60 and 2000 s^{-1}. Second-order rate constants for the exchange of the axial ligand in FeTTP-Cl and FeTTP-I are 5.6×10^2 and 5.9×10^3 M^{-1} s^{-1}, respectively. For similar In(III) systems the second-order rate is also about 10^4 M^{-1} s^{-1}.[22]

The rates observed here for ligand exchange in the ZnTPP–py and the ZnTPP–*N*-MeIm systems are much higher than any previously reported for a metalloporphyrin–ligand system lacking substantial steric hindrance. These rates are consistent with the exchange-labile nature of Zn(II) complexes. The k_2 observed here ($(2\text{–}6) \times 10^8$ M^{-1} s^{-1}) is probably close to the diffusion-controlled limit for this system. The rate constant for a diffusion-controlled reaction between two neutral species in chloroform is predicted to be 1.05×10^{10} M^{-1} s^{-1}.[22] There are severe steric restrictions on the attack of these ligands on ZnTPP in that only the area above and below the plane of the porphyrin ring is available for coordination addition and only the unshared pair of electrons on the ligands will coordinate. A simple surface area calculation suggests that compared to a sphere of radius 2.1 Å the potential reactive area for coordination to Zn(II) is reduced by 50% and compared to a sphere of 2.5-Å radius the unshared pair on pyridine or *N*-methylimidazole only provides for a reactivity on 16% of the surface. The steric restrictions would reduce the expected diffusion limit to around 8.5×10^8 M^{-1} s^{-1}, quite close to the rate we observe. Pyridine, and presumably *N*-methylimidazole, will hydrogen bond to chloroform,[23] and this would further reduce the theoretical maximum rate.

The high observed rate constant for k_2 argues in favor of a simple associative mechanism where the pyridine is entering an unoccupied coordination position on the four-coordinate ZnTPP. This in turn would argue that the k_1 is determined

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by the pK_a of the coordinated ligand and will correlate with K_{eq}. It is known that K_{eq} correlates very well with the basicity of nonhindered pyridines,[2] which is entirely consistent with these observations.

In 1966 Hoard suggested[24] that the alteration in the coordination geometry of protoheme on binding dioxygen was the probable starting point for a mechanism to account for the cooperative nature of reversible oxygenation in hemoglobin. There has been a great deal of interest in the systematic study of the conformation of the first-row transition-metal metalloporphyrins with the goal of understanding the electronic and structural contributions to the equilibrium geometries.[3,4] Zn(II), being an end member of the series (d^{10}), has received considerable attention.

The early expectation was that Zn(II) would be too large to fit into the central hole of the porphinato ligand.[25] Crystal structures of several five-coordinate Zn(II) porphyrins found the Zn(II) some 0.3 Å out of the mean plane of the porphyrin ring.[25-28] Solution NMR studies also found the Zn(II) displaced some 0.3 Å from the mean plane of the porphyrin ring.[5] In 1978 Scheidt and co-workers[29] reported the structure of a bis(toluene)solvate of (tetraphenylporphinato)zinc(II) in which the Zn(II) ion is centered in the central hole of the core, with somewhat compressed Zn–N bonds.

If the geometry with the Zn(II) centered in the central hole of the core is indeed an energy minimum in solution, then the k_2 for the binding of L to ZnTPP should be lower than the diffusion-controlled rate limit by an amount reflecting the activation energy required to move the Zn(II) out of the plane. Since k_1 appears to be at or near the diffusion-controlled limit, given the steric restrictions of the system, we suggest that the equilibrium solution conformation for ZnTPP has the Zn(II) displaced out of the plane by an amount close to that found in five-coordinate complexes.

The idea that the Zn(II) is displaced from the plane of the porphyrin ring in ZnTPP in solution is supported by published ^{15}N NMR studies.[30] On binding an extraplanar pyridine to ZnTPP the porphyrin ^{15}N resonance shifts to low field, with the magnitude of the shift linearly dependent on the pK value of the substituted pyridine. The chemical shift of the 3-cyanopyridine complex is only 0.17 ppm to low field from the uncomplexed porphyrin, and the maximum observed shift is only 2.2 ppm.

The Zn–N bond length reported in the planar ZnTPP is 2.036 Å while the average Zn–n bond length in four nonplanar five-coordinate ZnTP–L systems is 2.070 Å. If there were a substantial change in the Zn–porphyrin geometry in going from ZnTPP to ZnTPP–L in solution, we would expect a larger porphyrin ^{15}N chemical shift change.

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Registry No. ZnTPP-py, 24389-79-5; ZnTPP-*N*-MeIm, 67820-10-4; py, 110-86-1; *N*-MeIm, 616-47-7.

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Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

Molecular Addition Compounds. 9. Effect of Structure on the Reactivities of Representative Borane–Amine Complexes in Typical Reactions Such as Hydrolysis, Hydroboration, and Reduction[1]

HERBERT C. BROWN* and LEO T. MURRAY[2]

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A number of borane–amine complexes with widely different structural features in the amine portion was prepared and their reactivities toward typical B–H reactions, such as hydrolysis, hydroboration of 1-octene, and reduction of cyclohexanone, were studied. BH_3–amine complexes containing an *N*-phenyl group are hydrolyzed by neutral hydroxylic solvents, while others require a strong acid medium for the hydrolysis. In hydroboration, BH_3–*N*-phenylamine complexes react rapidly with 1-octene in THF at 25 °C, while all other types require refluxing THF or toluene for reaction. Again, BH_3–*N*-phenylamine complexes reduce cyclohexanone in THF at 25 °C at reasonable rates, while others require acetic acid solvent or mineral or Lewis acids to achieve the desired reduction. Thus, among such borane–amine addition compounds, the BH_3–*N*-phenylamines emerge as unique hydroborating and reducing agents. The results of the present study provide insights into the mechanisms of the hydroboration and reduction reactions. The rates of hydroboration of alkenes with BH_3–amine complexes are inversely related to the stability of the adduct, arguing for a prior dissociation of the adduct, followed by the reaction of BH_3 with the alkene. The reduction of cyclohexanone with BH_3–amine complex in THF proceeds by an analogous dissociation mechanism. In acetic acid or in the presence of mineral or Lewis acids, a bimolecular attack of the BH_3–amine complex on the protonated carbonyl group has been considered to be the most viable mechanistic pathway. However, this does not account for the effect of acids on hydrolytic behavior. Consequently, caution is urged in considering possible interpretation of the acid-enhanced reactions of amine–boranes.

Subsequent to the initial report by Köster[3] that alkenes can be hydroborated by borane–triethylamine complexes, the hydroborating ability of several other BH_3–amine complexes, such as with pyridine,[4] trimethylamine,[5] and *tert*-butylamine,[4]

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