Table VI. ^{1}H NMR Data for **6**, **6a**, and **6b** in C_7D_8 at 24.8 °C

	$Co(NPhBMes_2)_2$ (**6**)	$Co(NPhBXyl_2)_2$ (**6a**)	$Co[N(C_6D_5)BMes_2]_2$ (**6b**)
$-BMes_2$	46.1 (*m*-H)	47.2 (*m*-H)	46.2 (*m*-H)
	36.8 (*p*-Me)	−112.6 (*p*-H)	36.9 (*p*-Me)
	23.4 (*o*-Me)	23.1 (*o*-Me)	23.4 (*o*-Me)
−NPh	~24.5	31.2	
	0.2	0.4	
	49.9	−48.6	

Unambiguous assignment of the peaks in the spectra of **6** and **6a** is possible with the use of the deuterated derivative **6b**. Inspection of the data in Table VI reveals peaks due to the $-BMes_2$ group that are common to the three compounds. In addition, the deuterated phenyl group confirms the assignment of the remaining peaks in **6** and **6a** to the phenyl substituent.

In summary, a series (Cr → Ni) of transition-metal borylamides have been described. Though they are nominally two-coordinate, they will intramolecularly associate through a boron–mesityl ipso-carbon if permitted by either less sterically demanding nitrogen substituents or larger metallic radii. The intramolecular association is caused by the electron deficiency of the metals and the availability of electron density elsewhere in the molecule. The energy of this association is about 10 kcal in the case of cobalt species **6** and presumably **5** and **7**. With bulkier mesityl groups on nitrogen, two-coordination is observed for the metal series Mn → Ni. The chemistry of these interesting compounds is currently under investigation.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8618739) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supplementary Material Available: Full tables of crystallographic data, summary of data collection and refinement, positional parameters for non-hydrogen atoms, bond distances and angles, anisotropic thermal paramaters, and hydrogen coordinates (51 pages). Ordering information is given on any current masthead page.

Metal Template Assisted Schiff Base Condensations: An Evaluation of Thermodynamic versus Kinetic Control

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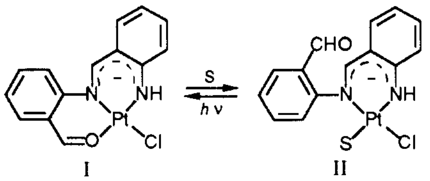
Abstract: The influence of kinetic and thermodynamic template effects has been examined for a unique platinum(II) complex, Pt(AAA)Cl (I) (AAA = *N*-(*o*-aminobenzylidene)anthranilaldehyde), resulting from the Schiff base condensation of two molecules of *o*-aminobenzaldehyde with $PtCl_4^{2-}$. The photochromic behavior of the terminal aldehyde of the dimeric condensate, I, which is replaced by coordinating solvents in the absence of light, allowed for the examination of the role of the metal ion in Schiff base condensations. New compounds were synthesized from I and 1,2-diaminobenzene, 1,2-diaminoethane, 1,3-diaminopropane, *o*-aminobenzylamine, *o*-toluidine, *o*-methylbenzylamine, methylamine, and *n*-propylamine. The kinetics of the reactions of three monoamines and two diamines with both I and solvated I (II) were examined. The Schiff base condensation did not occur to an appreciable extent in II, in which the aldehyde was not coordinated to the metal. The k_{obs} of the condensation with I when the aldehyde was coordinated ranged from 0.000165 s^{-1} for *o*-toluidine to 0.172 s^{-1} for methylamine at 25 °C, with aliphatic amines consistently faster than aromatic amines and bidentate amines faster than monodentate amines. Activation parameters were indicative of a bimolecular reaction. Significant secondary deuterium isotope effects were observed, with k_H/k_D ranging from 1.10 to 1.13. The kinetic results are consistent with an initial attack of the amine on the aldehyde carbon, isomerization to an N-coordinated carbinolamine, and a subsequent dehydration step.

Metal ion template assistance has been a boon to the rational design of complex multidentate ligand systems.[1] These reactions are often complicated by undesirable features such as polymerization or multiple product formation. The synthetic utilization of metal ions has been particularly valuable in Schiff base and related condensations.[2] In these reactions an amine and carbonyl react to form a carbinolamine intermediate followed by dehydration, giving an imine product. Unfortunately, these condensations are not normally "well-behaved", and unwanted side reactions often interfere with the isolation of the desired product. It is in this type of situation that metal ions have been so useful in providing a template for directing the course of the reaction. Examination of mechanistic pathways has been undertaken by a number of researchers.[3-7] Nonetheless, the opportunity to study

Scheme I[a]



[a] S = solvent.

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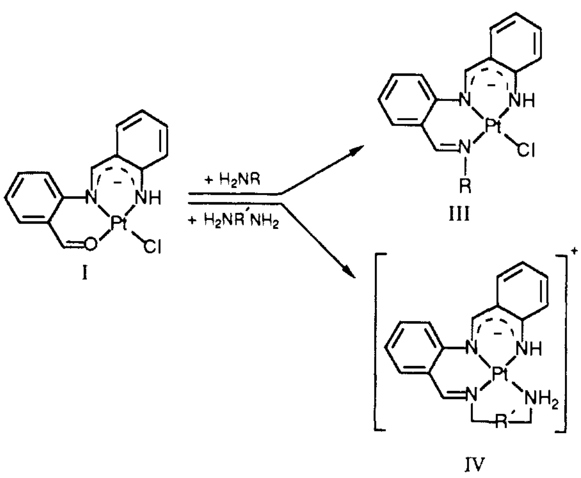
Scheme II[a]



[a] R = CH_3, R′ = CH_2CH_2, $CH_2CH_2CH_2$.

the influence of metal ion coordination has been rather limited, due to the general complexity of competing reactions.

A classic example of the template effect is the self-condensation of *o*-aminobenzaldehyde. A variety of different polycyclic species are obtained depending on reaction conditions.[8-10] In the presence of first-row metal ions a triaza- or tetraazamacrocycle can be obtained.[10] In the presence of platinum(II) under aqueous conditions, however, an intermediate, Pt(AAA)Cl (I) (AAA = *N*-(*o*-aminobenzylidene)anthranilaldehyde), in the self-condensation of *o*-aminobenzaldehyde on the route to the tetraazamacrocycle has been isolated in this laboratory.[11] This tridentate ligand also exhibits a photochromic effect, whereby the coordinated aldehyde in I is replaced by coordinating solvents (Scheme I, S = solvent) in the absence of light to give Pt(AAA)(S)Cl (II) and recoordinates in the presence of light in the visible and ultraviolet spectral regions.[12] Furthermore, I can undergo Schiff base reactions with monoamines and diamines to give III and IV, respectively (Scheme II).[13]

The chemical behavior of this novel photochromic system provides the unique opportunity to examine the role of the metal ion in Schiff base–template condensation reactions. Scheme II presents a clean, straightforward reaction without the hindrance of competing reactions and side products. Hence, the reactivity of the aldehyde when coordinated (I) as well as not coordinated (II) to platinum(II) can be examined in order to probe the relative influence of kinetic and thermodynamic template effects.

Two basic questions surface. First, how important is the coordination of the aldehyde in the nucleophilic attack of the amine? Thermodynamic control could be exerted by the metal ion in this step by stabilization of the carbinolamine intermediate. This can be examined by comparing the reactions of amines with I, with the aldehyde coordinated, and II, with the aldehyde not coordinated. The second question concerns kinetic control. If the metal ion plays an important role as a docking site for the incoming amine, the rates of condensation of bidentate amines should be greatly enhanced compared to those of monodentate amines.

Table I. Elemental Analyses and Mass Spectral Data of the Schiff Base Products[a]

complex		% C	% H	% N	parent ion *m/e*
[Pt(AAA)(dab)]Cl	calcd	44.16	3.13	10.31	506–510[b]
	found	43.80	3.40	10.20	
[Pt(AAA)(en)]Cl·H_2O	calcd	37.40	3.73	10.90	459–463[b]
	found	37.30	3.50	10.83	
[Pt(AAA)(tmd)]Cl·H_2O	calcd	38.68	4.01	10.61	471–475[b]
	found	38.90	4.10	10.20	
[Pt(AAA)(aba)]Cl	calcd	45.22	3.41	10.04	520–524[b]
	found	45.59	3.60	10.11	
Pt(AAA)($MeNH_2$)Cl	calcd	38.60	3.00	9.00	465–469
	found	38.30	3.70	8.70	
Pt(AAA)($PrNH_2$)Cl	calcd	41.27	3.64	8.49	493–499
	found	41.89	3.75	8.30	
Pt(AAA)(tol)Cl	calcd	46.45	3.32	7.74	541–547
	found	46.20	3.40	7.49	
Pt(AAA)(mba)Cl	calcd	47.41	3.59	7.54	555–560
	found	47.79	3.81	7.30	

[a] Abbreviations: AAA = *N*-(*o*-aminobenzylidene)anthranilaldehyde, dab = 1,2-diaminobenzene, en = 1,2-diaminoethane, tmd = 1,3-diaminopropane, aba = *o*-aminobenzylamine, tol = *o*-toluidine, mba = *o*-methylbenzylamine, $MeNH_2$ = methylamine, $PrNH_2$ = *n*-propylamine. [b] Parent ion isotope cluster corresponds to M − HCl.

Experimental Section

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 421 or 710B grating spectrophotometer as KBr disks or in $CHCl_3$ solutions. NMR spectra were obtained on a Varian EM-360 or XL-300 spectrometer using TMS as an internal standard. Chemical shifts are reported in ppm relative to TMS. Electronic spectra were recorded on a Perkin-Elmer 555 spectrophotometer. Mass spectral data were obtained by Dr. Charles Judson of the Mass Spectrometer Laboratory at the University of Kansas on a Hitachi CH-5 spectrometer. Elemental analyses for carbon, hydrogen, and nitrogen were performed at the Microanalytical Laboratory, University of Kansas, by Dr. Tho Nguyen.

All solvents used in the kinetic studies were spectral grade and were stored over activated 3A powder. THF was distilled, from either LAH or sodium benzophenone ketyl. Acetonitrile was distilled from CaH_2 and P_2O_5 through a 40-cm column packed with glass beads. Both CH_2Cl_2 and $CHCl_3$ were stored over $CaCl_2$ for several days and distilled from P_2O_5. Anhydrous ethanol was obtained by refluxing a commercial grade absolute ethanol over CaH_2 for several hours and distilling.

Synthesis. Commercially obtained 1,2-diaminobenzene was recrystallized twice from $CHCl_3$. Technical grade *o*-toluidine was converted to its hydrochloride salt by the addition of HCl to a 10% acetone/*o*-toluidine mixture. The salt was collected and extracted with ethyl ether. The free base was regenerated by shaking with $SnCl_2$ for 1–2 h (to remove traces of sulfur) followed by vacuum distillation. The 1,2-diaminobenzene and 1,3-propanediamine were placed over KOH for 24 h and distilled under nitrogen.

o-Aminobenzaldehyde was prepared by a modification of the method of Smith and Opie.[14]

o-Aminobenzyl alcohol-d_2 was prepared by previously published methods from ethyl anthranilate, substituting LAD for LAH.[15]

o-Aminobenzaldehyde-*d* was prepared from *o*-aminobenzyl alcohol-d_2 by oxidation with MnO_2 "A"[16] in THF at 10–15 °C for 3 days. The reaction mixture was filtered, and the MnO_2 was washed with several 25-mL portions of ether followed by 2 × 20 mL portions of $CHCl_3$. The filtrates were combined and evaporated. Water was added and the oil was steam-distilled. The cold distillate was extracted with CH_2Cl_2. After the combined extracts were dried over Na_2SO_4 and the solvent was removed, a yellow green oil was obtained which solidified on standing.

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Table II. ^{1}H NMR Chemical Shifts for the Neutral Schiff Base Adducts[a]

complex	δ, ppm
Pt(AAA)($MeNH_2$)Cl	8.8 (s, *H*C=N), 8.5 (s, *H*C=N), 7.8–6.5 (m, HC_{phen}), 2.9 (s, H_3C)
Pt(AAA)($PrNH_2$)Cl	8.8 (s, *H*C=N), 8.5 (s, *H*C=N), 7.8–6.5 (m, HC_{phen}), 4.56 (NCH_2), 2.04 (m, CH_2CH_3), 0.93 (t, CH_3)
Pt(AAA)(tol)Cl	9.1 (s, *H*C=N), 8.7 (s, *H*C=N), 7.9–6.6 (m, HC_{phen}), 2.3 (s, CH_3)
Pt(AAA)(mba)Cl	8.8 (s, *H*C=N), 8.5 (s, *H*C=N), 7.8–6.5 (m, HC_{phen}), 5.9 (s, CH_2NH_2), 2.3 (s, CH_3)

[a] Abbreviations: AAA = *N*-(*o*-aminobenzylidene)anthranilaldehyde, $MeNH_2$ = methylamine, $PrNH_2$ = propylamine, tol = *o*-toluidine, mba = *o*-methylbenzylamine.

Yield: 286 mg of *o*-aminobenzaldehyde-*d* (47%).

o-Methylbenzylamine[17] and *o*-aminobenzylamine[18] were prepared according to previously published procedures.

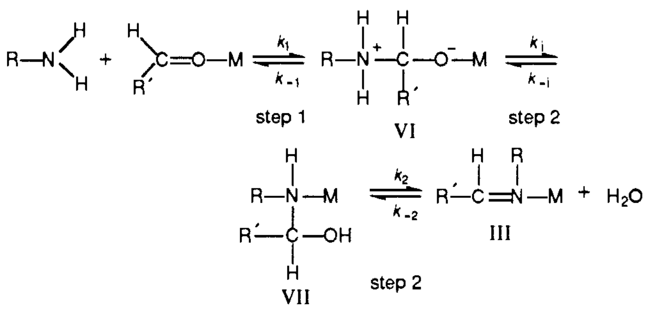
Pt(AAA)Cl (I) and Pt(AAA)Cl-d_2 (AAA = *N*-(*o*-aminobenzylidene)anthranilaldehyde) were prepared as reported previously,[11] the latter utilizing *o*-aminobenzaldehyde-*d*.

Pt(AAA)Cl Adducts. New compounds were synthesized by condensing 1,2-diaminobenzene (dab), 1,2-diaminoethane (en), 1,3-diaminopropane (tmd), *o*-aminobenzylamine (aba), *o*-toluidine (tol), *o*-methylbenzylamine (mba), methylamine ($MeNH_2$), and *n*-propylamine ($PrNH_2$) with I. Pt(AAA)Cl (I) (15 mg, 0.033 mmol) was dissolved in 10 mL of $CHCl_3$ with stirring. The appropriate (di)amine (0.070 mmol) was added dropwise in $CHCl_3$ (if solid) or neat (if liquid) and the resulting solution was refluxed for 1 h, during which time the color of the solution changed from purple to red. After the solution cooled to room temperature, hexane was added, and the product precipitated. Due to the high solubility of the monoamine products in $CHCl_3$, the volume was reduced to 3 mL and hexane was added, followed by cooling. Elemental and mass spectral analyses for the compounds agree with the proposed structures (Table I). In the ^{1}H NMR spectra of the neutral adducts (III) (Table II) the imine carbon protons appear as singlets at about 8.5 and 8.8 ppm. The spectra of the cationic complexes (IV) have the same general features in the downfield regions, but are not reported due to strong solvent and water absorptions that obscure the upfield regions. The infrared spectra (Table III) are similar to that of the starting complex. A variable absorption in the 3340–3320-cm^{-1} region is assigned to the N–H stretch of the deprotonated amine of the *o*-aminobenzylidene portion of the chelate. The diamine adducts also exhibit a variable absorption in the 3260–3235-cm^{-1} region, assigned to the N–H stretch of the coordinated terminal amine function. Bands in the 1700–1490-cm^{-1} region correspond to conjugated C=C, delocalized C=N, and N–H vibrations. The major feature of the electronic spectra (Table IV) is the distinct shifting of the 574-nm absorption ($CHCl_3$, ϵ = 12000) of I to the 520–490 nm region (ϵ = 10000). For the 1,2-diaminoethane condensate an additional strong absorption is observed in the visible region at 482 nm.

Kinetics. All rate measurements were performed under pseudo-first-order conditions with minimally a 10 M excess of amine. In a typical experiment, 3.00 mL of (di)amine was pipetted into a cuvette, which was then placed in one of five thermostated cell holders and allowed to equilibrate for 5 min. Temperature was maintained to ±0.1 °C with an attached Perkin-Elmer digital controller. An external water circulating bath was used in conjunction with the controller for temperatures below 25 °C. A cuvette containing a solution of either I or II (~5 × 10^{-4} M) was similarly stored in one of the cell holders of the PE 555. Once the solutions were thermally equilibrated, 500 μL of the complex solution was added to the (di)amine solution. The solution was mixed and then placed in the optical path of the spectrophotometer, and data collection was initiated. Absorbance changes were monitored as a function of time at a fixed wavelength.

The progress of the reactions was followed by observing the decay of the peak of the major absorbance in the visible region of either I or II. Absorbance changes due to product formation (at 500–530 nm and, in some cases, 340–400 nm) were also monitored as a function of time when possible. In acetonitrile solutions it was necessary to photolyze the sample in order to obtain maximum complex with the aldehyde coordinated. A 60–75% mixture of desired reactant could be obtained by photolyzing with a 250-W lamp for 10–15 min prior to kinetic runs. The reactions performed in $CHCl_3$ consisted of 100% reactant species I.

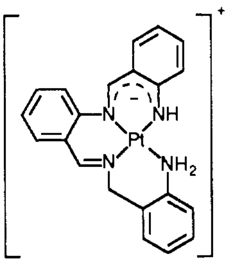
Scheme III



Rate data were collected either on a strip chart recorder or on a diskette interfaced with a Zenith Z-100 computer with interface and software package SPECTRO-555 supplied by the Instrument Design Laboratory, University of Kansas. Data were collected for 6–7 half-lives and analyzed according to the Guggenheim method.[19] Linear regressions using CREG1[20] and nonlinear regressions using CLK[21] were performed on the Zenith Z-100 computer. First- and sencond-order rate constants were obtained with BREG1.[21] The k_{obs} values as reported were obtained by extrapolation for a given kinetic run to 0.015 M amine concentration. Runs were repeated 2–4 times and were reproducible to within ±5%.

Results and Discussion

Synthesis and Characterization. The syntheses were all straightforward and analyzed correctly for the expected products. The only ambiguity in the condensation was for that with *o*-aminobenzylamine, which could condense via either the benzyl amine or the aromatic amine. The proton NMR was analogous to that of the *o*-methylbenzylamine adduct, which by necessity condenses via the benzyl amine. Thus, it is surmised that *o*-aminobenzylamine condenses in an analogous fashion (V), rather than with the aniline nitrogen forming the imine. This supposition is supported further by the mass spectral pattern, which does not show *m*/*e* of X − NH_2 − CH_2.



V

Mechanism of the Schiff Base Condensation. The mechanism proposed for a general Schiff base condensation reaction involves formation of a carbinolamine intermediate followed by dehydration to give the imine. These reactions are subject to general-acid catalysis, operative in the first equilibrium step.[22]

In the case of a metal ion assisted reaction, metal ion substitution is also involved. Substitution reactions of square-planar complexes are well documented and occur via an associative mechanism in which two pathways are operable. One involves nucleophilic attack by the ligand, while the other consists of initial solvation, followed by replacement of solvent by the incoming ligand.[23]

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Table III. Infrared Spectra of the Schiff Base Products (cm^{-1})^{a,d}

complex	NH	CH^{b}	C=C	C=N/C=C^{c}
[Pt(AAA)(dab)]Cl	3260 w		1600 sh, 1550 sh, 1490	1620 s
[Pt(AAA)(en)]Cl	3230 br, m, 1492		1602 sh, 1560 sh	1618 s
[Pt(AAA)(tmd)]Cl	3250 br		1600 w, 1568 w	1620 s
[Pt(AAA)(aba)]Cl	3239 s	3020 w, 2975–2970 w	1605 m, 1598 m, 1498 m	1628 s
Pt(AAA)(MeNH$_2$)Cl	3344 w	2990–2930 w	1605 sh, 1560 m, 1498 w	1628 s
Pt(AAA)(PrNH$_2$)Cl	3350 w		1602 sh, 1570–1560 m, 1492 w	1626 s
Pt(AAA)(tol)Cl	3340 m		1601 w, 1558 m, 1495 m	1623 s
Pt(AAA)(mba)Cl	3340 w	2985–2955	1603 sh, 1568–1555 m, 1498 w	1625 s

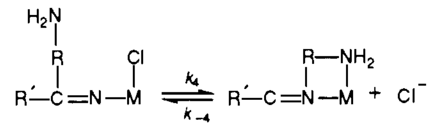
[a] Spectra recorded as KBr disks. Abbreviations: AAA = *N*-(*o*-aminobenzylidene)anthranilaldehyde, dab = 1,2-diaminobenzene, en = 1,2-diaminoethane, tmd = 1,3-diaminopropane, aba = *o*-aminobenzylamine, MeNH$_2$ = methylamine, PrNH$_2$ = propylamine, tol = *o*-toluidine, mba = *o*-methylbenzylamine. [b] Aromatic and aliphatic C–H stretch. [c] Unresolved C=N stretch and phenyl ring vibration. [d] Key: s, strong; m, medium; w, weak; br, broad; sh, shoulder.

Table IV. Electronic Spectra of the Schiff Base Adducts^{a}

complex	λ_{max}, nm ($\epsilon \times 10^4$)	solvent
[Pt(AAA)(dab)]Cl	526 (1.17), 379 (1.41)	MeOH
[Pt(AAA)(en)]Cl	507 (1.18), 482 (1.13), 355 (1.07), 325 (1.25), 304 (1.42), 271 (2.15)	MeOH
[Pt(AAA)(tmd)]Cl	511 (0.978), 354 (0.875), 304 (1.13)	MeOH
[Pt(AAA)(aba)]Cl	510 (1.20), 355 (1.12), 305 (1.41), 270 (2.74)	MeOH
Pt(AAA)(MeNH$_2$)Cl	530 (0.488), 368 (sh) (0.371), 315 (0.661), 274 (1.26)	CH$_3$CN
Pt(AAA)(PrNH$_2$)Cl	529 (0.913), 367 (0.631), 317 (1.10)	CHCl$_3$
Pt(AAA)(tol)Cl	530 (1.02), 318 (1.27), 276 (2.37)	CH$_3$CN
Pt(AAA)(mba)Cl	536 (1.06), 319 (1.38), 280 (2.35)	CHCl$_3$

[a] Abbreviations: AAA = *N*-(*o*-aminobenzylidene)anthranilaldehyde, dab = 1,2-diaminobenzene, en = 1,2-diaminoethane, tmd = 1,3-diaminopropane, aba = *o*-aminobenzylamine, MeNH$_2$ = methylamine, PrNH$_2$ = propylamine, tol = *o*-toluidine, mba = *o*-methylbenzylamine.

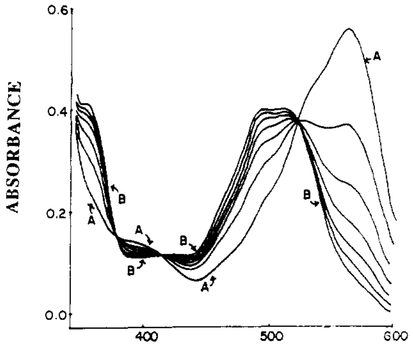
Scheme IV



VIII III

The mechanistic pathway proposed for these types of reactions is shown in Scheme III.[6,7,24] The initial step is reversible formation of the carbinolamine precursor (step 1). Structural evidence for carbinolamine intermediates has been obtained by other workers for the reaction of 2,6-diformylpyridine and 6,6′-bis(1-methylhydrazino)-2,2′-bipyridyl in the presence of Zn(II).[24] The initial attack is followed by deprotonation of the amine and protonation of the oxygen to give an N-coordinated carbinolamine, VII (step 2, where i stands for isomerization). The prerequisite proton transfer from nitrogen to oxygen before the isomerization step 2 is not shown for purposes of simplification. The next and final step in the case of monoamines is dehydration with imine formation (step 3).

For bidentate amines, an additional step is rapid substitution of the coordinated chloride by the other amine terminus (Scheme IV).



WAVELENGTH (nm)

Figure 1. Spectral sequence for the reaction of excess *o*-aminobenzylamine with Pt(AAA)Cl (I) (6.08×10^{-5} M) in CH$_3$CN at 25 °C: (A) initial spectrum of Pt(AAA)Cl; (B) final spectrum of the product [Pt(AAA)(aba)]Cl (V).

Table V. Rate Constant Data for the Condensation of Pt(AAA)Cl (I) with Monoamines and Diamines^{a}

amine	temp, °C	solvent	k_{obs},^{a} s^{-1}	k_1',^{b} M^{-1} s^{-1}
o-toluidine	25	CHCl$_3$	0.000165	0.0017
1,2-diaminobenzene	25	CHCl$_3$	0.000253	0.068
o-methylbenzylamine	25	CHCl$_3$	0.0186	1.44
o-aminobenzylamine	25	CHCl$_3$	0.0754	5.10
o-toluidine	30	CH$_3$CN	0.0000920	0.00161
1,2-diaminobenzene	30	CH$_3$CN	0.000957	0.0662
o-methylbenzylamine	25	CH$_3$CN	0.109	7.31
o-aminobenzylamine	25	CH$_3$CN	0.134	8.53
methylamine	25	CHCl$_3$	0.170^{c}	
methylamine	15	CHCl$_3$	0.0803	4.66

[a] The pseudo-first-order rate constants, k_{obs}, for a number of amine concentrations were obtained on solutions 5×10^{-4} M in Pt(AAA)Cl and at least a 10 M excess of amine. The k_{obs} values reported in the table are for amine concentrations of 0.015 M. [b] The k_1' values were obtained from plots of k_{obs} versus amine concentration according to eq 1. [c] Calculated from an Arrhenius plot.

Kinetics of the Schiff Base Condensation of Pt(AAA)Cl (I). The condensation of three monoamines (*o*-methylbenzylamine, *o*-toluidine, and methylamine) and two diamines (*o*-aminobenzylamine and 1,2-diaminobenzene) with I was examined in CHCl$_3$ and CH$_3$CN. When the reactions were carried out with a 1:1 molar ratio of amine:Pt complex I, isosbestic points were observed in CHCl$_3$, but not in CH$_3$CN. When pseudo-first-order conditions were used, isosbestic points were evident in both solvents. A typical spectral sequence for the *o*-aminobenzylamine condensation with I in CH$_3$CN is shown in Figure 1. The k_{obs} values for 0.015 M amine concentrations are reported in Table V, along with k_1' (eq 1), as determined from the slope of the plots k_{obs} at a variety of amine concentrations versus amine concentration.

$$k_{obs} = k_1'[\text{amine}] \qquad (1)$$

$$k_{obs} = k_1'[\text{amine}] + k_2'[\text{amine}]^2 \qquad (2)$$

The observed rate law for the reaction of Pt(AAA)Cl (I) is essentially first order in amine concentration (eq 1) for all of the reactions except with monoamines in CHCl$_3$ at lower temperatures (20 °C and below). For the latter systems, the rate law takes the form of a second-order polynomial function, the second term dependent on [amine]^2 (eq 2, Figure 2). In related condensations this finding has been attributed to the formation of a ternary complex between the carbonyl, amine, and base.[25] The base then

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(23) (a) Wilkens, R. G. In *The Study of Kinetics and Mechanism of Reaction of Transiton Metal Complexes*, Allyn and Bacon: 1974; Chapters 4, 8. (b) Basolo, F.; Pearson, R. G. In *Mechanisms* of *Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967.

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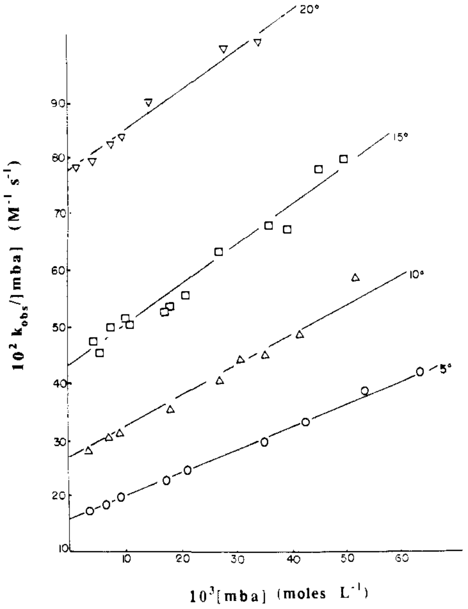

Figure 2. Plots of $k_{obs}/[o\text{-methylbenzylamine}]$ ($M^{-1}\ s^{-1}$) vs [*o*-methylbenzylamine] for the reaction of Pt(AAA)Cl (III) in $CHCl_3$ at 5 (○), 10 (△), 15 (□), and 20 °C (▽).

acts as a mediator in acquiring a proton from the carbinolamine nitrogen, as suggested by Sayer and Jencks for the reaction of 2-methyl-3-thiosemicarbazide with *p*-chlorobenzaldehyde at high pH.[26]

In each case the diamines were faster than the monoamine analogues. For example, for the aromatic amines, *o*-toluidine and 1,2-diaminobenzene, k_1' is 40 times larger for the latter compared to the former in both $CHCl_3$ and CH_3CN. The amines with aliphatic portions, *o*-methylbenzylamine, *o*-aminobenzylamine, and methylamine, were faster than the aromatic amines. The condensation of methylamine displayed the highest k_{obs} in $CHCl_3$ (0.172 min^{-1}) and was too fast to be followed in CH_3CN. Aliphatic diamines were so reactive that they could not be examined by routine kinetic methods, and suitable stop-flow methods were unavailable. Similar findings in salicylaldehyde condensations have been attributed to statistical effects (two amines vs one),[7] rather than an initial coordination followed by an anchimeric assistance mechanism.[7,27] That an initial associative substitution process is not occurring in the case of the bidentate amines is indicated by the mode of bonding of *o*-aminobenzylamine. The aliphatic, more nucleophilic nitrogen is bound to the newly formed imine (V). Additionally, the second amine in the bidentate ligands could also assist in the dehydration step via an internal catalysis mechanism as reported for non-metal-mediated imine formation reactions[26] or by aiding in the proton-transfer step prior to isomerization (step 2, Scheme III).

Kinetics of the Reaction of Pt(AAA)(CH_3CN)Cl (II) with Amines. Attempts to obtain the analogous Schiff base condensations using II, in which the aldehyde was not coordinated, were unsuccessful. These reactions were performed in the dark in CH_3CN as shown for *o*-methylbenzylamine in Figure 3. While a reaction did occur on a very slow time scale (4.40×10^{-5} and $1.38 \times 10^{-6}\ s^{-1}$ for methylamine and 1,2-diaminobenzene, respectively), as evidenced by the change in absorption spectra, the final spectra were not analogous to the Schiff base condensates. Isolation and characterization of the product were not achieved due to extreme light sensitivity. Samples exposed to any light immediately formed enough of the coordinated aldehyde complex, I, to allow the Schiff base condensation to occur. The finding that the Schiff base condensation occurs only when the aldehyde is coordinated is evidence to the crucial role of the metal ion in these reactions. While the reaction observed in the absence of light in acetonitrile may be merely a substitution reaction, no analytical data were obtained.

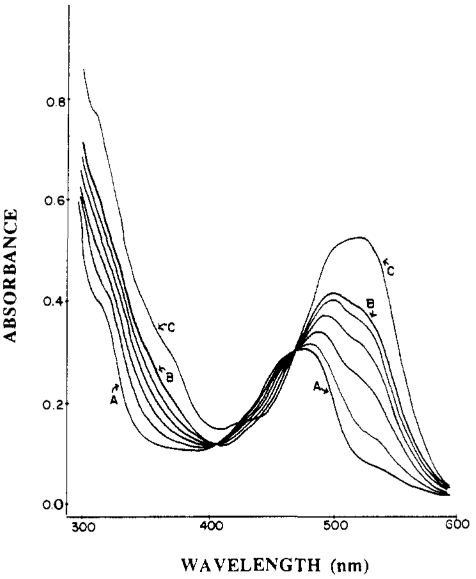

Figure 3. Spectral sequence for the reaction of excess *o*-methylbenzylamine with Pt(AAA)(CH_3CN)Cl (II) (6.08×10^{-5} M) at 25 °C: (A) initial spectrum (II); (B) spectrum of the solution after 3 h; (C) spectrum after irradiation with an incandescent lamp, which correlates with that of Pt(AAA)(mba)Cl.

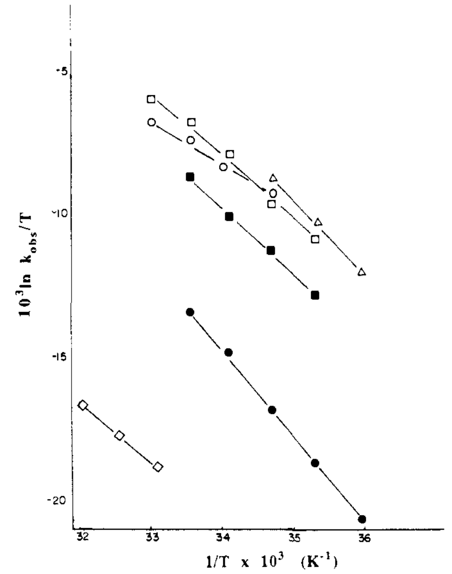

Figure 4. Plots of $\ln k_{obs}/T$ ($s^{-1}\ K^{-1}$) vs $1/T$ (K^{-1}) for *o*-aminobenzylamine in CH_3CN (□) and $CHCl_3$ (■), *o*-methylbenzylamine in CH_3CN (○) and $CHCl_3$ (●), methylamine in $CHCl_3$ (△), and 1,2-diaminobenzene in CH_3CN (◇).

Activation Parameters. Activation parameters were determined for the monoamine condensates, *o*-methylbenzylamine and methylamine, and diamine condensates, *o*-aminobenzylamine and 1,2-diaminobenzene, at a standard-state amine concentration of 0.015 M (Table VI, Figure 4) from k_{obs} values as a function of temperature. The rate constant k_1' from eq 1 was not used because of the complications from the higher order polynomial rate terms for the monoamines in $CHCl_3$. The activation parameters are as anticipated for the bimolecular metal-assisted Schiff base condensations and are in agreement with values reported for similar reactions.[5-7] In general, E_a, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$ are higher in $CHCl_3$ compared to CH_3CN. This is especially evident for *o*-methylbenzylamine (E_a = 60.9 kJ mol^{-1} in $CHCl_3$ and 31.5 kJ mol^{-1} in CH_3CN). The solvent dependencies observed, with higher rates in CH_3CN compared to $CHCl_3$, are reasonable considering that generation of the polar intermediate VI (Scheme III) would

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Table VI. Pseudo-First-Order Rate Constants and Activation Parameters[a] for the Condensation of Monoamines and Diamines with Pt(AAA)Cl

amine	temp, °C	solvent	$10^3 k_{obs}$, s^{-1}	E_a	$\Delta H^\ddagger$	$\Delta G^\ddagger$	$\Delta S^\ddagger$
o-aminobenzylamine	10	$CHCl_3$	26.4				
	15	$CHCl_3$	39.6				
	20	$CHCl_3$	51.9				
	25	$CHCl_3$	75.4	48.0	45.5	79.4	-114
	10	CH_3CN	47.6				
	15	CH_3CN	61.3				
	20	CH_3CN	99.2				
	25	CH_3CN	134	46.2	43.7	78.0	-115
	30	CH_3CN	162				
o-methylbenzylamine	5	$CHCl_3$	3.28				
	10	$CHCl_3$	5.14				
	15	$CHCl_3$	7.97				
	20	$CHCl_3$	13.2				
	25	$CHCl_3$	18.6	60.9	58.4	82.9	-82.1
	15	CH_3CN	67.6				
	20	CH_3CN	85.0				
	25	CH_3CN	109	31.5	29.0	78.5	-166
	30	CH_3CN	128				
1,2-diaminobenzene	25^b	CH_3CN	2.74	39.5	37.1	87.6	-169
	29	CH_3CN	3.40				
	34	CH_3CN	4.33				
	39	CH_3CN	5.63				
methylamine	5	$CHCl_3$	35.5				
	10	$CHCl_3$	53.4				
	15	$CHCl_3$	80.3				
	25^b	$CHCl_3$	172	54.4	51.9	77.4	-85.5

[a] The activation parameters were calculated from the following relationships: $E_a = \Delta H^\ddagger + RT$, $\Delta G^\ddagger = -RT \ln kh/Tk_B$, and $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, where h is Planck's constant, k_B is Boltzmann's constant, and k is the observed rate in s^{-1} for the reaction at a given temperature T and 0.015 M amine concentration. E_a, $\Delta H^\ddagger$, and $\Delta G^\ddagger$ are reported in kJ mol^{-1}, and $\Delta S^\ddagger$ is reported in J mol^{-1} K^{-1}. [b] Calculated from an Arrhenius plot.

Table VII. Secondary Deuterium Isotope Effects on the Rates of the Schiff Base Condensation Reactions of Pt(AAA)Cl (I) with Amines

amine	concn, M	temp, °C	solvent	$10^3 k_{H,obs}$, s^{-1}	$10^3 k_{D,obs}$, s^{-1}	k_H/k_D
mba[a]	0.0169	15	$CHCl_3$	8.76	7.80	1.12
mba	0.0343	15	$CHCl_3$	21.7	19.7	1.10
aba	0.00627	15	$CHCl_3$	14.3	12.7	1.13
dab	0.123	25	$CHCl_3$	7.04	6.38	1.10
aba	0.00303	20	CH_3CN	22.0	19.7	1.12

[a] Abbreviations: AAA = *N*-(*o*-aminobenzylidene)anthranilaldehyde, mba = *o*-methylbenzylamine, aba = *o*-aminobenzylamine, dab = 1,2-diaminobenzene.

be favored by the more polar solvent. The large negative $\Delta S^\ddagger$'s observed for *o*-methylbenzylamine and 1,2-diaminobenzene in CH_3CN are indicative of highly ordered transition states. Such an observation could be related to the propensity of CH_3CN to coordinate to the metal via an associative mechanism. Melson and co-workers also observed a large negative $\Delta S^\ddagger$ of -210 J mol^{-1} K^{-1} in the nickel-assisted condensation of a diamine with a coordinated ketone in reactions done in potentially coordinating ethanolic THF solution.[5]

Isotope Studies. Secondary deuterium isotope effects were determined for amine condensations using Pt(AAA)Cl (I) with a ^2H-labeled aldehyde coordinated to the platinum. The results show a k_H/k_D variation from 1.10 to 1.13 (Table VII). These effects normally reflect a change in geometry between the reactant state and transition state for a given reaction[28] and, in particular, depend on shifts in the frequency of the out-of-plane bending mode that accompanies $sp^2 \leftrightarrow sp^3$ hybridization changes.[29] With respect to a nucleophilic substitution at a carbonyl, a k_H/k_D of 1.10–1.13 is usually indicative of a change from sp^3 to sp^2 hybridization.[30] The only step in which an sp^3 to sp^2 change occurs in the reaction of **I** with amines is the final dehydration step. At first glance, therefore, the isotope data suggest that the dehydration step (Scheme III, step 3) is rate limiting, which means that the reactant state must be taken to be compound VII (Scheme III) and all prior steps must occur on a rapid time scale. If this were the case, either isosbestic points would not be observed in the reaction or the initial spectra observed in the condensations would correspond to that of the carbinolamine intermediate, VII. Experimentally, neither of these situations exist. Isosbestic points are evident for all of the condensations (Figure 1), and the initial spectra all correspond exactly to that of I in the absence of amine. Hence, some other factor or factors must be responsible for the observed isotope effects. While a definitive answer to this puzzle is not at the moment available, one possibility that has been cited in other reactions where anomalous isotope effects are found involves quantum mechanical tunneling.[31,32] Such a mechanism has been proposed for both proton transfer in elimination reactions[33] and hydride-transfer reactions.[33,34] Thus, while the secondary deuterium isotope results are indeed interesting and bear further

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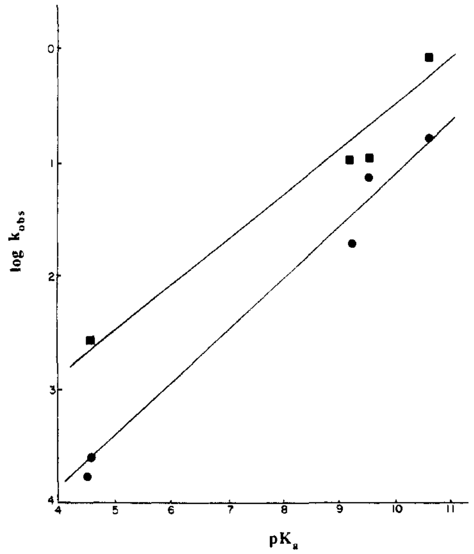

Figure 5. Plots of log k_{obs} vs pK_a of amine in $CHCl_3$ (●) and CH_3CN (■). The pK_a's for all of the amines except mba and aba were obtained from Martell and Smith (Martell, A. E.; Smith, R. M. In *Critical Stability Constants*; Plenum: New York, Vols. 2 (1975) and 5 (1982). The pK_a for mba was obtained from Carothers et al. (Carothers, W. H.; Bickford, C. F.; Hurwitz, G. J. *J. Am. Chem. Soc.* **1927**, *49*, 2908), and the pK_a for aba was estimated from that for mba. The pK_a's were taken as tol = 4.57, mba = 4.63, mba = 9.23, aba = 9.29, and $MeNH_2$ = 10.67.

investigation, they do not pinpoint the rate-limiting step.

Brønsted Plots. Of interest with respect to the relative magnitude of k_{obs} as a function of amine identity is the Brønsted plot of log k_{obs} vs pK_a of the amine (Figure 5). Brønsted plots such as these have been used widely in similar studies.[35] The log β_{nuc} values of the slope of the plots of k_{obs} vs pK_a of the amine indicate the degree of charge development on the amine at the transition state. A value of 0.5, for example, indicates that the change in charge on the amine is half that of the corresponding protonation reaction. While the reactions in this study are performed in nonaqueous solvents, where the pK_a's are not necessarily meaningful, a good linear fit is obtained for the condensation rates in $CHCl_3$ (slope of β_{nuc} = 0.48 (25)) and for four points obtained for the CH_3CN reaction (β_{nuc} = 0.42 (13)). Plots of log k_1' with pK_a's are also fairly linear but are not shown because of the higher polynomial terms observed for some of the condensations. A lower β_{nuc} has been correlated with a rate-limiting nucleophilic attack in a variety of aminolysis reactions by Jencks and co-workers, and β_{nuc} values usually range from 0.3 for a rate-limiting attack step to 1.0 for rate-limiting breakdown of the tetrahedral intermediate.[35] The presence of the metal ion tends to complicate these reactions as compared to the non-metal-assisted aminolysis reactions, since it is not possible in the scope of this study to predict the degree of charge on the nitrogen after step 1, VI, or step 2, VII (Scheme III), as well as in the product, III (Scheme III) or IV (Scheme IV). Nonetheless, the linear dependence of the log k_{obs} on the pK_a's of the amines points to a similar mechanistic pathway throughout the range of amines studied. Aliphatic bidentate amines, 1,2-diaminoethane and 1,3-diaminopropane, react too fast to be followed kinetically, and yet have pK_a's similar to that of methylamine, which would result in a change in slope of the plot. Generally, this is taken to mean a change in the rate-limiting step.[36] In this case, it could be related to a very strong internal catalytic influence of the second aliphatic amine in the dehydration or proton-transfer step, since these amines are sterically more flexible than their aromatic cousins.[35]

Conclusions

This system has provided a unique opportunity to examine metal ion influence on Schiff base condensation reactions and, particularly, the comparative importance of the kinetic and thermodynamic template effects. As a result of these studies, the major role of the metal ion was found to be as Lewis acid in stabilizing the carbinolamine intermediate via a thermodynamic template effect. Metal control in this manner is indeed critical to the reaction, since the reaction does not appear to occur to an appreciable extent in the absence of aldehyde coordination. The kinetic template effect is, therefore, not nearly as crucial in this sequence as in reactions that proceed to fully closed macrocyclic rings. The ligand substitution portion of the reaction appears to be considerably slower in the absence of the Schiff base condensation, as evidenced by the exceedingly slow reaction of IV with amines, which is thought to be a simple substitution reaction.

Acknowledgment. This work was supported by a grant from the University of Kansas General Research Fund (3229-XO-0038). The authors also thank Drs. R. L. Schowen, D. H. Busch, and D. Vander Velde for helpful discussions and W. G. Rohly for providing preliminary data for this study.

Registry No. I, 73920-56-6; III (R = *o*-MeC_6H_4), 124380-86-5; III (R = *o*-$MeC_6H_4CH_2$), 124380-87-6; III (R = Me), 124380-88-7; III (R = Pr), 124380-91-2; IV (R' = *o*-C_6H_4), 124380-84-3; IV (R' = CH_2CH_2), 124380-89-8; IV (R' = $CH_2CH_2CH_2$), 124380-90-1; V, 124380-85-4; dab, 95-54-5; aba, 4403-69-4; tol, 95-53-4; mba, 89-93-0; en, 107-15-3; tmd, 109-76-2; $MeNH_2$, 74-89-5; $PrNH_2$, 107-10-8; deuterium, 7782-39-0.

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