9092 *Inorg. Chem.* **2009**, *48*, 9092–9103
DOI: 10.1021/ic9005746

Inorganic Chemistry
Article

Combined Low Temperature Rapid Scan and ^{1}H NMR Mechanistic Study of the Protonation and Subsequent Benzene Elimination from a (Diimine)platinum(II) Diphenyl Complex Relevant to Arene C−H Activation

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Received March 24, 2009

A detailed kinetic study of the protonation and subsequent benzene elimination reactions of a (diimine)Pt^{II} diphenyl complex (denoted as (N−N)PtPh$_2$) has been undertaken in dichloromethane solution with and without acetonitrile as a cosolvent. Spectroscopic monitoring of the reactions by UV−vis stopped-flow and NMR techniques over the temperature range −80 to +27 °C allowed the assessment of the effects of acid concentration, coordinating solvent (MeCN) concentration, temperature, and pressure. Protonation of (N−N)PtPh$_2$ with HBF$_4$·Et$_2$O in CH$_2$Cl$_2$/MeCN occurs with a kinetic preference for protonation at the metal, rather than at a phenyl ligand, and rapidly produces (N−N)PtPh$_2$H(NCMe)$^+$ ($\Delta H^{\ddagger}$ = 29 ± 1 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −47 ± 4 J K^{-1} mol^{-1}). At higher temperatures, (N−N)PtPh$_2$H(NCMe)$^+$ eliminates benzene to furnish (N−N)PtPh(NCMe)$^+$. This reaction proceeds by rate-limiting MeCN dissociation ($\Delta H^{\ddagger}$ = 88 ± 2 kJ mol^{-1}, $\Delta S^{\ddagger}$ = +62 ± 6 J K^{-1} mol^{-1}, $\Delta V^{\ddagger}$ = +16 ± 2 cm^3 mol^{-1}). Protonation of (N−N)PtPh$_2$ in dichloromethane in the absence of MeCN cleanly produces the Pt(II) π-benzene complex (N−N)PtPh(η^2-C$_6$H$_6$)$^+$ at low temperatures. Addition of MeCN to a solution of the π-benzene complex causes an associative substitution of benzene by acetonitrile, the kinetics of which were monitored by ^{1}H NMR ($\Delta H^{\ddagger}$ = 39 ± 2 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −126 ± 11 J K^{-1} mol^{-1}). When the stronger triflic acid is employed in dichloromethane/acetonitrile, a second protonation-induced reaction also occurs. Thus, (N−N)PtPh(NCMe)$^+$ produces (N−N)Pt(NCMe)$_2$$^{2+}$ and benzene with no detectable intermediates ($\Delta H^{\ddagger}$ = 69 ± 1 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −43 ± 3 J K^{-1} mol^{-1}). The mechanisms for all steps are discussed in view of the accumulated data. Interestingly, the data allow a reinterpretation of a previous report on proton exchange between the phenyl and benzene ligands in (N−N)PtPh(η^2-C$_6$H$_6$)$^+$. It appears that the exchange occurs by a direct σ-bond metathesis pathway, rather than by the oxidative cleavage/reductive coupling sequence that was proposed.

Introduction

The selective, catalytic functionalization of hydrocarbons remains a golden target for contemporary chemists, with tremendous technological and industrial implications.[1−3] In the late 1960s, the groups of Garnett[4,5] and Shilov[6,7] established that Pt(II) salts in aqueous acidic solutions are capable of activating and even functionalizing hydrocarbon C−H bonds. Considerable mechanistic insight has been gained from detailed experimental studies in aqueous media, and on model systems in other solvents, and the activation and functionalization of hydrocarbons in the often-termed "Shilov system" are considered to take place by the general three-step mechanism[2,8−14] depicted in Scheme 1.

A considerable amount of mechanistic insight has been gained from studies of the microscopic reverse of the C−H activation step, that is, protonolysis of Pt-alkyl and Pt-aryl complexes. We and others have investigated relevant reactions

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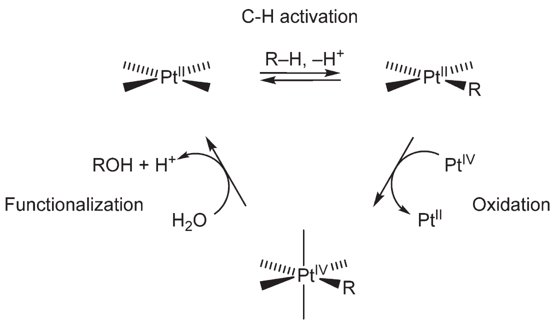
Scheme 1. Proposed Mechanism for Alkane Functionalization in the Shilov System



at (diimine)Pt(II) and Pt(IV) complexes.[8,15,16] One important finding has been that low-temperature protonation of (diimine)Pt(II) dialkyl and diaryl complexes leads to observable, but thermally sensitive, Pt(IV) hydridoalkyl and hydridoaryl complexes that eliminate the respective hydrocarbons upon heating.[17−23] Such Pt(IV) species have been proposed to be involved in arene C−H activation at (diimine)PtMe(solv)$^+$ species, where solv is a solvent molecule, in solution. Scheme 2 summarizes the mechanistic picture that has emerged for these reactions at (diimine)Pt(II) systems[16,18,24−27] and at related Pt species with bidentate ligands.[28−37] (It might be noted that some controversy concerning the finer mechanistic details of the introductory arene coordination at the diimine systems still remains.[27,38−40])

In Scheme 2, associative ligand substitutions (first of H_2O by TFE = trifluoroethanol, then of TFE by benzene) initially lead to a Pt(II) η^2-benzene complex. Oxidative C−H cleavage furnishes a putative Pt(IV) hydrido species which has not been directly observed under actual C−H activating conditions. Reversal of the latter process, encompassing the species enclosed in brackets in Scheme 2, facilitates the experimentally observed isotopic scrambling from C_6D_6 into the Pt-CH_3 group during benzene C−H(D) activation reactions.[16] Importantly, the η^2-arene Pt(II) species have been observed during low-temperature protonation of (diimine)PtMePh and (diimine)$PtPh_2$ complexes in poorly coordinating solvents such as dichloromethane.[18,23] Indeed, there is substantial evidence that oxidative addition of an arene at an unsaturated metal center usually, although not without exceptions,[41,42] proceeds via η^2-(C,C) pre-complexation of the arene.[9,43−52] This may be followed by an arene "slip" to an η^2-(C,H)[18,45,53] or even η^1-(C)[54] coordination mode from which the oxidative cleavage of the C−H bond occurs. We recently described that protonation of (diimine)$PtPh_2$ species in dichloromethane at low temperatures produced observable (diimine)Pt(C_6H_5)(η^2-C_6H_6)$^+$ species. By NMR exchange spectroscopy (EXSY), it was demonstrated that rapid site exchange of protons between the phenyl and π-benzene moieties occurred. The kinetics of the exchange processes were established by quantitative 2D EXSY measurements. A rapid proton exchange that involved oxidative cleavage to furnish a putative (diimine)$PtPh_2H(L)^+$ intermediate (L = loosely coordinated ligand or vacant site) originally postulated.[23] However, a direct proton transfer by a σ-bond metathesis (or a σ-complex assisted metathesis, σ-CAM[55]) pathway has been proposed to be more likely as suggested by recent density functional theory (DFT) calculations;[56] this possibility will be further elaborated in the Discussion section here.

In a recent contribution, we presented a detailed account of the kinetics of the rapid protonation of (diimine)$PtMe_2$ by $HBF_4\cdot Et_2O$ to provide the Pt(IV) complex (diimine)$PtMe_2$-$H(NCMe)^+$ and the subsequent elimination of methane

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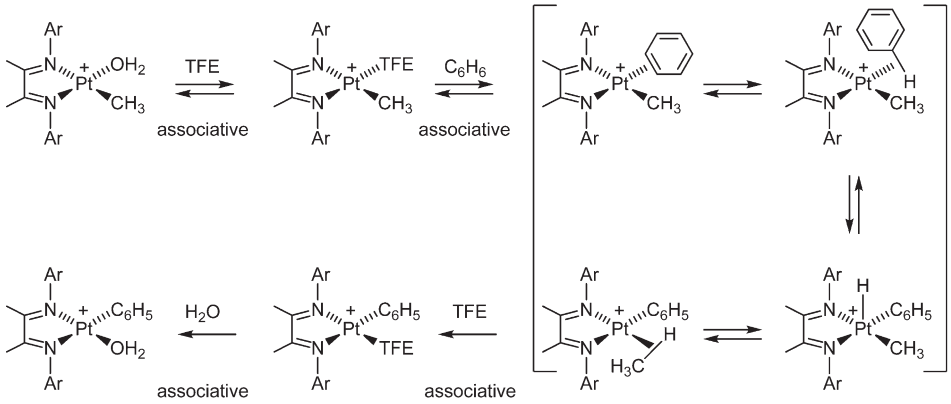
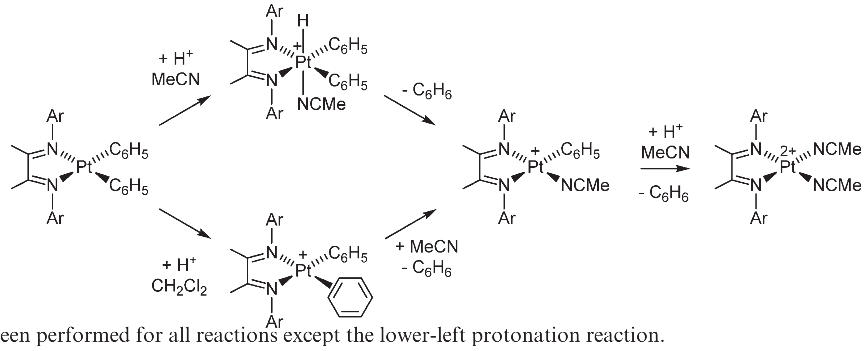
Scheme 2. Mechanism for Benzene C−H Activation, As Previously Proposed[16,18,25]



Scheme 3. Sequence of Reactions Studied in This Contribution[a]



[a] Kinetic studies have been performed for all reactions except the lower-left protonation reaction.

from this Pt(IV) species.[22] The latter reaction was found, by variable-temperature and variable-pressure kinetic measurements, to proceed by initial and rate-limiting MeCN dissociation. In the present contribution, we report the details of kinetic studies of protonation reactions and benzene-producing reactions at Pt(II) and Pt(IV) species that are derived from (N−N)$PtPh_2$, where N−N represents the specific diimine Ar-N=CMe−CMe=N−Ar; Ar = 2,6-$Me_2C_6H_3$. Concentration, temperature, and pressure-dependent kinetic measurements allow us to evaluate the kinetics for most of the reactions that are depicted in Scheme 3.

Results

1. Protonation of (N−N)$PtPh_2$ in the Presence of MeCN. The protonation of (N−N)$PtPh_2$ with $HBF_4 \cdot Et_2O$ in mixtures of CD_2Cl_2 and CD_3CN was previously studied by ^1H NMR spectroscopy,[23] and provides (N−N)$PtPh_2H(NCMe)^+$ as indicated in Scheme 3. While this Pt(IV) species is stable at −78 °C, benzene is released at about −40 °C with concomitant formation of (N−N)$PtPh(NCMe)^+$ with no detectable intermediates. Furthermore, we now find that when TfOH in MeCN (expected to be a stronger acid than $HBF_4 \cdot Et_2O$;[57] protonated Et_2O rather than HBF_4 is here the actual proton source) is employed, a second elimination of benzene is seen at ambient temperature conditions, producing the Pt(II) dication (N−N)$Pt(MeCN)_2^{2+}$. The same species was recently obtained from two successive protonation/methane elimination sequences from (N−N)$PtMe_2$ and TfOH.[58] This reaction sequence has now been subjected to a systematic kinetic investigation by time-resolved stopped-flow techniques with UV−vis monitoring of the reaction, with $HBF_4 \cdot Et_2O$ or TfOH as acids, in mixtures of dichloromethane/acetonitrile, in the temperature range −80 °C to +27 °C. To our satisfaction, the same three-step sequence was clearly observed by NMR and by UV−vis stopped-flow spectroscopic methods.

The first reaction step, the protonation of (N−N)$PtPh_2$, was carefully studied by ^1H NMR at −78 °C in MeCN/CH_2Cl_2 mixtures of different compositions. In all cases, (N−N)$PtPh_2$ reacted promptly to give mostly (N−N)$PtPh_2H(NCMe)^+$, with trace quantities (ca. 2−10%) of (N−N)$PtPh(NCMe)^+$ and benzene. There was no clear trend in the relative quantities of (N−N)$PtPh(NCMe)^+$ as a function of [MeCN] in the range 0.27−8.7 M. This contrasts with the findings from analogous experiments in which the protonation of (diimine)$PtMe_2$ complexes were studied: a consistent decrease in the yield of (diimine)$PtMe(NCMe)^+$, relative to (diimine)$PtMe_2H(NCMe)^+$, with increasing [MeCN] present was taken as evidence that the metal, rather than the methyl ligand, was the kinetically preferred site of protonation.[20,21] The lack of a clear-cut trend in the present system renders this question unresolved for the time being concerning the protonation of (N−N)$PtPh_2$. The presence of both products might indicate that two reaction channels are available. In the absence of other, more conclusive evidence, we surmise that the fact that (N−N)$PtPh_2H(NCMe)^+$ is the predominant product

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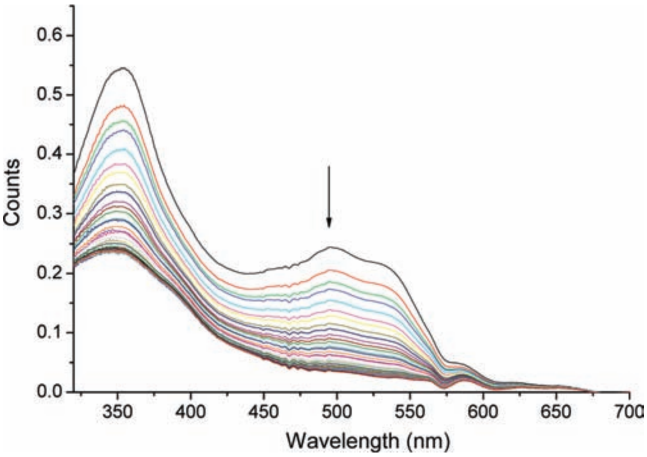

Figure 1. Time-resolved spectra for the protonation of (N$-$N)PtPh$_2$ with $\mathrm{HBF_4{\cdot}Et_2O}$ in $\mathrm{CH_2Cl_2}$ at -80 °C. Experimental conditions: [Pt] = 0.125 mM, [MeCN] = 5.74 M (30% v/v), [$\mathrm{HBF_4{\cdot}Et_2O}$] = 0.0124 M. The total duration of the experiment was 3.0 s.

suggests (but does not prove) that protonation at the metal is kinetically preferred. This assumption is supported by recent DFT calculations.[56] This subject will be further addressed in the Discussion section.

The protonation event was monitored in the temperature range -80 to -50 °C by time-resolved UV$-$vis stopped-flow spectroscopy. The concentrations of acid and acetonitrile in the dichloromethane solvent were systematically changed at -80 °C, always in a large excess relative to (N$-$N)PtPh$_2$ so as to ensure pseudo-first-order conditions. The protonation results in a characteristic decay in absorbance, and the changes observed in a typical time-resolved experiment are depicted in Figure 1. The spectral changes could in all cases be nicely fitted to a pseudo-first-order decay. The resulting pseudo-first-order rate constant was independent of [MeCN] in the range 0.95$-$5.7 M (5 to 30% v/v; see data in Table S1, Supporting Information). Lower [MeCN] could not be used because of the poor solubility of the acid in dichloromethane at low temperatures. The dependence of the pseudo-first-order rate constant on [$\mathrm{HBF_4{\cdot}Et_2O}$] (8.8$-$37.2 mM) at -80 °C in the presence of 30% (v/v) MeCN is shown in Figure 2 (data in Table S2, Supporting Information). Clearly, a first-order dependence is seen, and the calculated second-order rate constant by linear regression gives k (-80 °C) = 290 ± 20 M^{-1} s^{-1} (see Table S3, Supporting Information).

The temperature dependence of the rate constant for protonation was measured by monitoring the reaction of (N$-$N)PtPh$_2$ with a 12.4 mM $\mathrm{HBF_4{\cdot}Et_2O}$ solution in dichloromethane-30% MeCN (v/v; 5.74 M) in the temperature range -80 °C to -50 °C (data in Table S3, Supporting Information). The Eyring plot in Figure 3 shows an excellent linear fit, and the resulting kinetic parameters are $k(-80\ ^\circ\mathrm{C}) = 290 \pm 20$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 28.8 \pm 0.8$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -47 \pm 4$ J K^{-1} mol^{-1}.

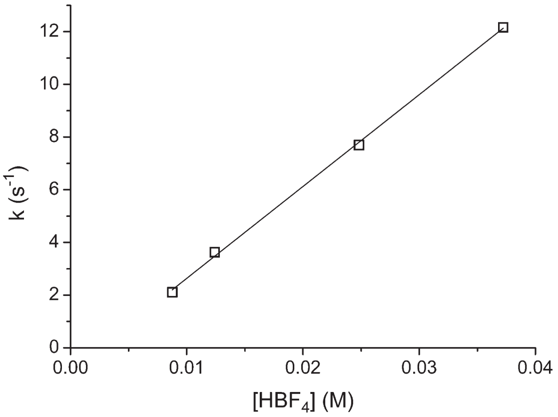

Figure 2. k_{obs} vs [$\mathrm{HBF_4{\cdot}Et_2O}$] for the protonation of (N$-$N)PtPh$_2$ in $\mathrm{CH_2Cl_2}$ at -80 °C. [Pt] = 0.125 mM, [MeCN] = 5.74 M (30% v/v).

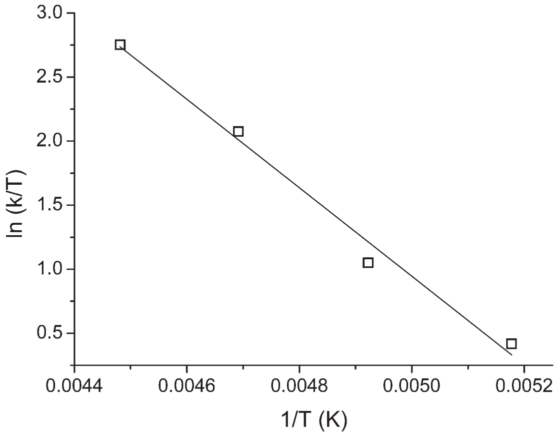

Figure 3. Eyring plot for the protonation of (N$-$N)PtPh$_2$ with $\mathrm{HBF_4{\cdot}Et_2O}$ in $\mathrm{CH_2Cl_2}$. Experimental conditions: [Pt] = 0.125 mM, [MeCN] = 5.74 M (30% v/v), [$\mathrm{HBF_4{\cdot}Et_2O}$] = 0.0124 mM.

The protonation has a rather small $\Delta H^{\ddagger}$ and substantially negative $\Delta S^{\ddagger}$ under the studied conditions. This is in accordance with the associative nature of the reaction. These data may be compared with our previously published data[22] on the protonation of (N$-$N)PtMe$_2$, namely, $\Delta H^{\ddagger} = 15$ kJ mol^{-1} and $\Delta S^{\ddagger} = -85$ J K^{-1} mol^{-1} were determined and are suggestive of an associative mechanism. The rate constant was reported as 15200 ± 400 M^{-1} s^{-1} at -78 °C. Protonation of the present (N$-$N)PtPh$_2$ system appears to be about 40 times slower than protonation of (N$-$N)PtMe$_2$ at -78 °C. This may reflect a combined effect of the relative electron withdrawing effect of Ph versus Me at the metal center and the increased steric bulk of Ph versus Me. It was suggested that (N$-$N)PtMe$_2$ underwent rate-determining protonation to yield a transient five-coordinate species which was rapidly trapped by the apical coordination of MeCN. We assume on the basis of the kinetic data and qualitative similarities (acid and MeCN dependence) that the same holds true for the current system, although a concerted protonation/acetonitrile addition cannot be ruled out on the basis of the available experimental evidence.

2. Elimination of Benzene from (N$-$N)PtPh$_2$H(NCMe)$^+$. Upon increasing the temperature to above about -40 °C, (N$-$N)PtPh$_2$H(NCMe)$^+$ starts to release benzene to cleanly furnish (N$-$N)PtPh(MeCN)$^+$ without detectable intermediates, as previously seen by ^{1}H NMR spectroscopy.[23] In the following, we describe the details of a kinetic investigation of this process in the temperature range -10 to $+27$ °C. The stopped-flow technique allows instant mixing of separately prepared solutions of (N$-$N)PtPh$_2$ and $\mathrm{HBF_4{\cdot}Et_2O}$ in

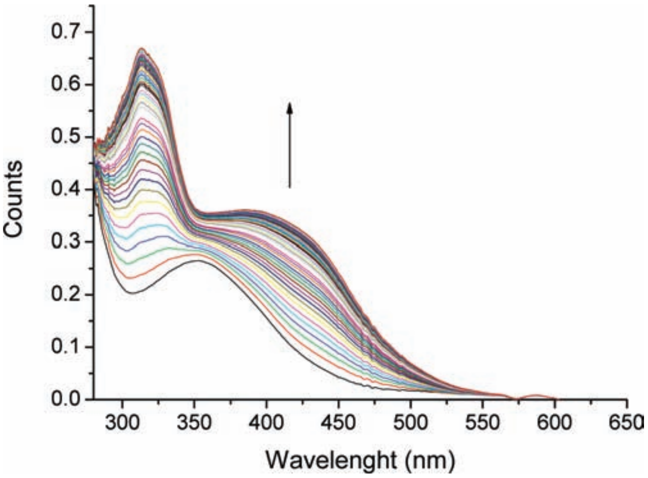

Figure 4. Time-resolved spectra for the elimination of benzene from (N−N)$PtPh_2H(NCMe)^+$ in CH_2Cl_2 at 0 °C. Experimental conditions: [Pt] = 0.125 mM, [MeCN] = 5.74 M (30% v/v), [$HBF_4\cdot Et_2O$] = 12.4 mM. The total duration of the experiment was 35 s.

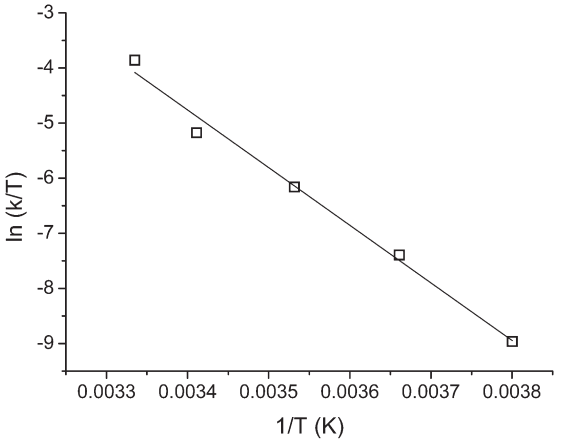

Figure 5. Eyring plot for the kinetic data for the elimination of benzene from (N−N)$PtPh_2H(NCMe)^+$ when $HBF_4\cdot Et_2O$ was the acid used to initially protonate (N−N)$PtPh_2$ (see text). Experimental conditions: [Pt] = 0.125 mM, [MeCN] = 5.7 M (30% v/v), [HBF_4] = 0.0124 M.

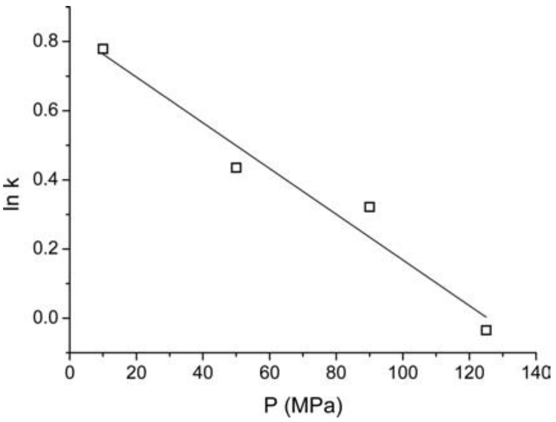

Figure 6. Pressure-dependent rate constants for the elimination of benzene from (N−N)$PtPh_2H(NCMe)^+$ at 20 °C. Experimental conditions: [Pt] = 0.125 mM, [MeCN] = 5.7 M (30% v/v), [$HBF_4\cdot Et_2O$] = 0.0062 M.

dichloromethane/acetonitrile mixtures to immediately furnish (N−N)$PtPh_2H(NCMe)^+$. The ensuing, much slower, benzene elimination can be conveniently monitored by UV−vis spectroscopy at varying [HBF_4], [MeCN], temperatures, and pressures. A typical time-resolved UV−vis spectrum of the reaction is depicted in Figure 4 and is characterized by an increase in absorbance in the selected wavelength region with time. The spectral changes are nicely described by first-order kinetics. The kinetic measurements were done by monitoring the spectral changes over the whole spectral range. The excellent first-order kinetic fits that were obtained suggest the smooth transformation of (N−N)$PtPh_2H(NCMe)^+$ to (N−N)$PtPh(NCMe)^+$ without any observable intermediates.

The rate of the reaction was studied at different acetonitrile concentrations. In the concentration range 0.95 to 5.7 M, only a slight effect of [MeCN] on the rate of benzene elimination was seen (ca. 20% rate increase in the concentration range; data in Table S4, Supporting Information). The kinetics of the benzene elimination were also evaluated at varying [$HBF_4\cdot Et_2O$] in dichloromethane containing acetonitrile (5.7 M, 30% v/v) at 27 °C (Table S5, Supporting Information). No significant effect of the acid concentration on the reaction rate could be discerned.

Variable-temperature kinetic measurements of the benzene elimination were done by recording the time-resolved UV−vis spectra during the elimination of benzene when the initial protonation was done with 12.4 mM $HBF_4\cdot Et_2O$ in dichloromethane containing 5.74 M MeCN (30% v/v) in the temperature range −10 to +20 °C. The kinetic data are summarized in Table S6, Supporting Information. Figure 5 shows an Eyring plot of the kinetic data, from which the following kinetic parameters were extracted: k (20 °C) = 2.3 s^{-1}, $\Delta H^\ddagger$ = 88 ± 2 kJ mol^{-1}, and $\Delta S^\ddagger$ = +62 ± 6 J K^{-1} mol^{-1}.

Finally, pressure-dependent kinetic measurements were performed for benzene elimination at pressures between 10 and 125 MPa at 20 °C. The volume of activation $\Delta V^\ddagger$ was calculated for the reaction from the slope of plots of ln k versus pressure (Figure 6) in the way that has been previously thoroughly described,[59] using a 0.125 mM solution of (N−N)$PtPh_2$ and 0.0062 M $HBF_4\cdot Et_2O$ in dichloromethane with 5.7 M MeCN (30% v/v). The measured rate constants are given in Table S7, Supporting Information. The good linear fit that is evident from Figure 6 provides an activation volume $\Delta V^\ddagger$ = +16 ± 2 cm^3 mol^{-1}.

In summary, the kinetics for the benzene elimination from (N−N)$PtPh_2H(NCMe)^+$ exhibit a rather high $\Delta H^\ddagger$, a large positive $\Delta S^\ddagger$, and a large positive $\Delta V^\ddagger$. The collective data strongly suggest a dissociative character of the rate-limiting step, believed to be MeCN dissociation, for the benzene elimination. The data are qualitatively similar to those determined[22] for the elimination of methane from (N−N)$PtMe_2H(NCMe)^+$, for which $\Delta H^\ddagger$ = 75 ± 1 kJ mol^{-1}, $\Delta S^\ddagger$ = +38 ± 5 J K^{-1} mol^{-1}, and $\Delta V^\ddagger$ = +18 ± 1 cm^3 mol^{-1}, and for which a mechanism that is dissociative with respect to MeCN was proposed.

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(59) van Eldik, R.; Hubbard, C. D. In *Chemistry at Extreme Conditions*; Manaa, M. R., Ed.; Elsevier: Amsterdam, 2005, pp 109−164.

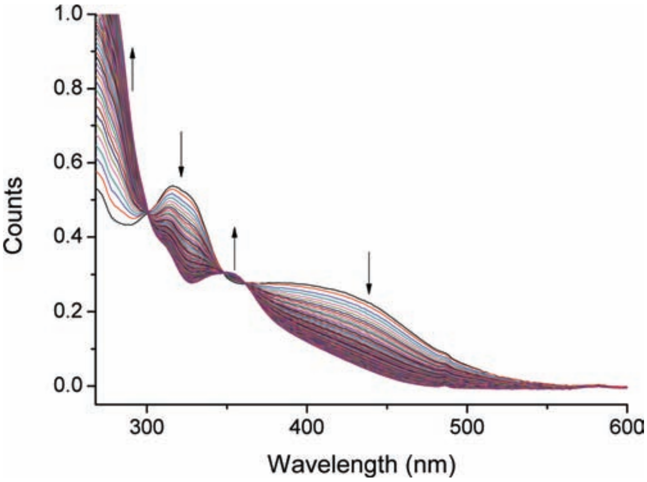

Figure 7. Time-resolved UV−vis spectra for the protonation/benzene elimination sequence from (N−N)$PtPh_2$ in dichloromethane/acetonitrile at 25 °C. Experimental conditions: [Pt] = 0.125 mM, [MeCN] = 5.74 M (30% v/v), [TfOH] = 0.013 M. The total duration of the experiment was 30 min.

3. Second Protonation and Benzene Elimination. As mentioned in the Introduction, (N−N)$PtPh_2$ reacts with TfOH in acetonitrile at ambient temperature to immediately furnish (N−N)PtPh(NCMe)$^+$ and then, more slowly, the (N−N)Pt$(NCMe)_2^{2+}$ dication. Analogous behavior has been reported for (diimine)$PtMe_2$ species, where treatment with TfOH can ultimately lead to the dicationic Pt complexes.[58]

The kinetics for this protonation/benzene elimination reaction was pursued with the stopped-flow UV−vis spectroscopic method in dichloromethane/acetonitrile mixtures. At 25 °C, the time-resolved UV−vis spectra (Figure 7) show characteristic absorption bands decaying in intensity at 320 and 430 nm, and bands of increasing intensity at 280 and 350 nm. Three well-defined isosbestic points are seen at 300, 346, and 360 nm. The first spectrum is that of (N−N)PtPh(NCMe)$^+$ and the last matches that of (N−N)Pt$(NCMe)_2^{2+}$, and the isosbestic points establish that no detectable intermediates build up during the reaction. The reaction rate was extracted from the changes in absorbance at 410 nm, and the data were nicely described by a single exponential decay suggestive of pseudo-first-order kinetic behavior in [Pt].

The kinetics were further evaluated by UV−vis monitoring of the reaction at 25 °C to study the influence of acid concentration on this step by varying [TfOH] in the range 0.013−0.13 M. In each case, the reaction exhibited pseudo-first-order kinetic behavior, and the observed rate increased linearly with [TfOH] (Figure 8; data in Table S8, Supporting Information). Thus, the reaction is first-order with respect to the acid, analogous to the first protonation of (N−N)$PtPh_2$ at low temperatures. From the slope of the plot in Figure 8, the second-order rate constant for the protonation was determined as 0.38 ± 0.03 M^{-1} s^{-1} at 25 °C. Interestingly, when $HBF_4 \cdot Et_2O$ was used as the acid (0.13 M), the pseudo-first-order rate constant was estimated to be as low as 3×10^{-5} s^{-1} corresponding to 2.3×10^{-4} M^{-1} s^{-1}. The significantly slower reaction is in accord with $HBF_4 \cdot Et_2O$ being a considerably weaker acid than TfOH.[57]

Variable-temperature kinetic measurements of the protonation/benzene elimination were done by recording the time-resolved UV−vis spectra for the reaction with 0.13 M TfOH in dichloromethane containing 5.74 M MeCN (30% v/v) in the temperature range 7−29 °C. The resulting kinetic data are provided in Table S9, Supporting Information. The Eyring plot in Figure 9 shows an excellent linear fit and gives the kinetic parameters: k (25 °C) = 0.033 M^{-1} s^{-1}, $\Delta H^{\ddagger}$ = 68.5 ± 1.0 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = −43 ± 3 J K^{-1} mol^{-1}.

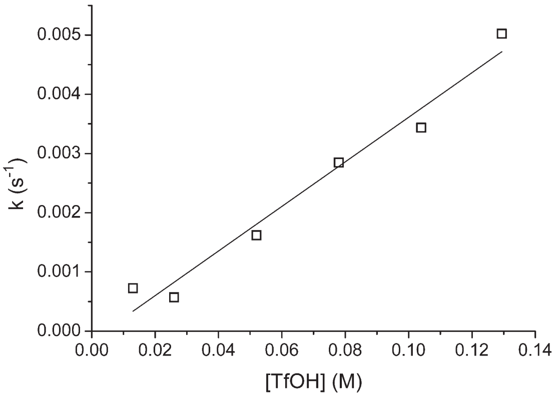

Figure 8. k_{obs} vs [TfOH] for the second protonation/elimination sequence in CH_2Cl_2. Experimental conditions: [Pt] 0.125 mM, [MeCN] = 5.74 M (30% v/v), and T = 25 °C.

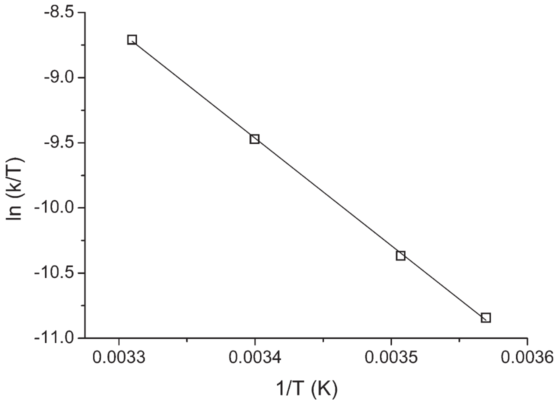

Figure 9. Eyring plot for the kinetic data for the second protonation/benzene elimination sequence from (N−N)$PtPh_2$. Experimental conditions: [Pt] = 0.125 mM, [MeCN] = 5.74 M (30% v/v), [TfOH] = 0.13 M in dichloromethane.

4. Substitution of Benzene on (N−N)PtPh(η^2-C_6H_6)$^+$ by Acetonitrile in Dichloromethane. We have recently reported that protonation of a series of (diimine)$PtPh_2$ complexes (diimine = Ar−N = CMe−CMe = N−Ar with differently substituted N-aryl groups) in dichloromethane at −78 °C results in the formation of (diimine)-PtPh(η^2-C_6H_6)$^+$ complexes that were characterized by ^1H NMR spectroscopy.[23] When Ar was a 2,6-dimethyl substituted phenyl group, these π-benzene complexes were relatively stable at temperatures up to about −40 °C. On the other hand, when Ar was unsubstituted at the 2,6-positions, the π-benzene complexes rapidly reacted by liberating benzene even at −78 °C. This might be a result of considerably faster associative substitution reactions at the π-benzene complexes that are 2,6-unsubstituted: For steric reasons, the N-aryl groups are oriented more or less perpendicular to the coordination plane at Pt.[23] Thence, substituents in the 2,6-positions will sterically block access to Pt from above and below the coordination plane for any incoming nucleophile. The substitution kinetics at the reasonably stable, N-aryl 2,6-dimethyl substituted π-benzene complex (N$-$N)PtPh(η^2-C_6H_6)$^+$ are described in the following.

A solution of the π-benzene complex (N$-$N)PtPh(η^2-C_6H_6)$^+$ in dichloromethane-d_2 was prepared in situ in an NMR-tube by addition of $HBF_4 \cdot Et_2O$ to a solution of (N$-$N)$PtPh_2$ at -78 °C. Controlled quantities of acetonitrile-d_3 in excess (to ensure pseudo-first-order conditions) were added at -78 °C, and the NMR tube was inserted into the precooled NMR probe so that the progress of the ensuing reaction could be monitored by ^{1}H NMR. At the temperatures investigated, smooth release of benzene and the formation of (N$-$N)PtPh-($NCCD_3$)$^+$ was observed. The rate of the reaction was determined by integration of the Pt-Ph signals in the NMR spectra using the residual proton signals of the solvent as an internal standard. The disappearance of the starting complex exhibited first-order kinetics for at least 3$-$4 half-lives of the reaction. The pseudo-first-order rate constant varied linearly with [acetonitrile-d_3], as illustrated in Figure 10. The near-zero intercept, $(-6 \pm 7) \times 10^{-5}$ s^{-1}, suggests that there is no MeCN-unassisted mechanism operating in parallel with the associative one implied by the data. The kinetic data are summarized in Table S10, Supporting Information. The average second-order rate constant was determined from these data as $k = (5.70 \pm 0.05) \times 10^{-4}$ M^{-1} s^{-1} at -55 °C.

Importantly, there was no evidence for formation of the Pt(IV) hydrido complex (N$-$N)$PtPh_2H(NCCD_3)^+$ in these experiments. This compound, if it were formed, would have been stable under the reaction conditions on the experimental time scale. In a separate experiment, EXSY spectra of (N$-$N)PtPh(η^2-C_6H_6)$^+$ were recorded in dichloromethane-d_2 in the absence of acetonitrile-d_3 and in the presence[60] of 54 mM acetonitrile-d_3 at -48 C. In both cases, EXSY correlation peaks between phenyl and π-benzene signals were seen, as described previously, and with intensities that were independent of the presence (or not) of acetonitrile. These findings provide compelling evidence that the exchange processes seen by EXSY cannot proceed via the intermediacy of (N$-$N)Pt-Ph_2H^+, which, if formed, should have been efficiently trapped by acetonitrile to furnish the stable, readily observable (N$-$N)$PtPh_2H(NCCD_3)^+$. (The acetonitrile concentration for this EXSY experiment, representing an about 2-fold excess relative to Pt, is considerably lower than that used for the substitution kinetics. Higher [MeCN] led to substitution of benzene, furnishing (N$-$N)PtPh(NCMe) exclusively, before significant EXSY peaks could be detected).

The temperature dependence of the substitution of benzene by acetonitrile was evaluated in the temperature range -55 to -70 °C. Figure 11 shows a linear Eyring plot of the kinetic data which are given in Table S11, Supporting Information. The derived activation parameters are $\Delta H^\ddagger = 39 \pm 2$ kJ mol^{-1} and $\Delta S^\ddagger = -126 \pm 11$ J K^{-1} mol^{-1}. The substantially negative entropy of activation and the first-order kinetic behavior of the rate on [MeCN] strongly imply an associative benzene substitution by acetonitrile. This is in agreement with recent DFT calculations which suggest a solvent-induced associative benzene elimination.[56]

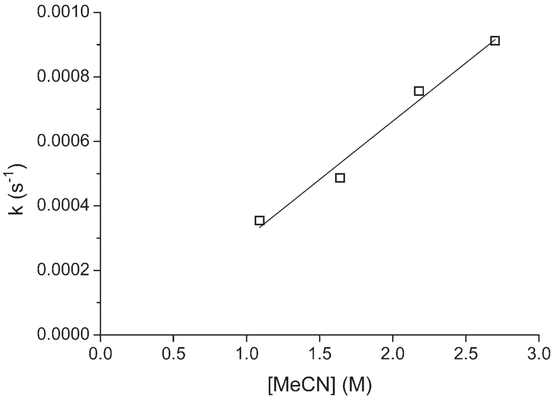

Figure 10. k_{obs} vs [CD_3CN] for the substitution of benzene at (N$-$N)PtPh(C_6H_6)$^+$ in dichloromethane-d_2. Experimental conditions: [Pt] = 0.023 mM, [MeCN] = 5.7 M (30% v/v), $T = -55$ °C. $HBF_4 \cdot Et_2O$ was used for in situ protonation of (N$-$N)$PtPh_2$ before addition of CD_3CN.

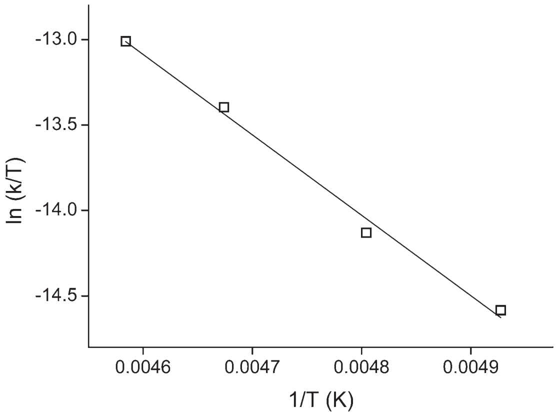

Figure 11. Eyring plot for the kinetic data for the substitution of benzene with acetonitrile at (N$-$N)PtPh(C_6H_6)$^+$ when $HBF_4 \cdot Et_2O$ was the acid used for the in situ protonation of (N$-$N)$PtPh_2$ before addition of CD_3CN to the solution in dichloromethane-d_2. Experimental conditions: [Pt] = 0.023 M, [MeCN] = 2.7 M, [HBF_4] = 0.10 M.

Discussion

The accumulated kinetic and mechanistic data that have been presented in the Results section are consistent with the overall reaction mechanism that is shown in Scheme 4 for the protonation of (N$-$N)$PtPh_2$ (**A**) and the following benzene-producing reactions. The details of this mechanism will now be the subject of discussion. It will be useful in this context to consult the data in Table 1, which lists rate constants for each step (where available). The data have been determined from the activation parameters described in the Results section or from data available elsewhere, at the temperatures -78, -40, 0, and $+30$ °C.

Low-Temperature Protonation of (N$-$N)$PtPh_2$. The protonation of complex **A** in dichloromethane/acetonitrile, observed as a fast reaction even at -80 °C, is postulated in Scheme 4 to occur as a two-step process that initially generates the unobserved five-coordinate intermediate (N$-$N)$PtPh_2H^+$ (**B**) followed by rapid capture of MeCN at the remaining vacant site. A concerted protonation and MeCN coordination cannot be ruled

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[60] We thank a reviewer for suggesting this experiment and for useful comments.

Scheme 4. Proposed Mechanistic Scheme for the Benzene Producing Reactions under Study

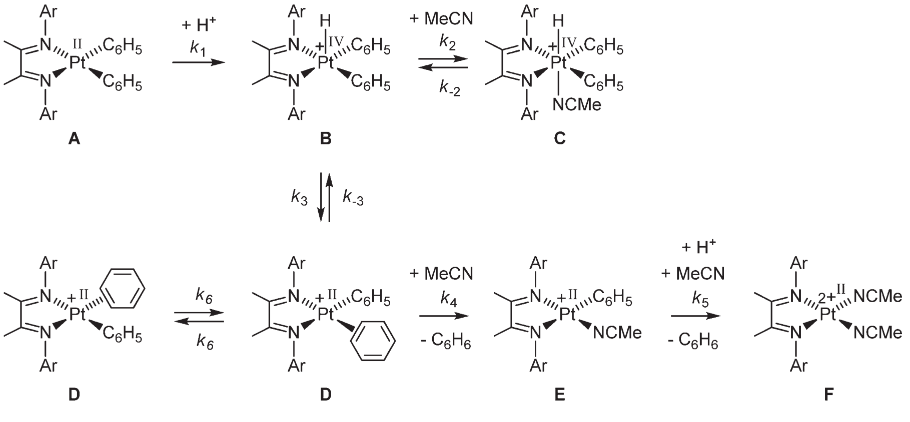


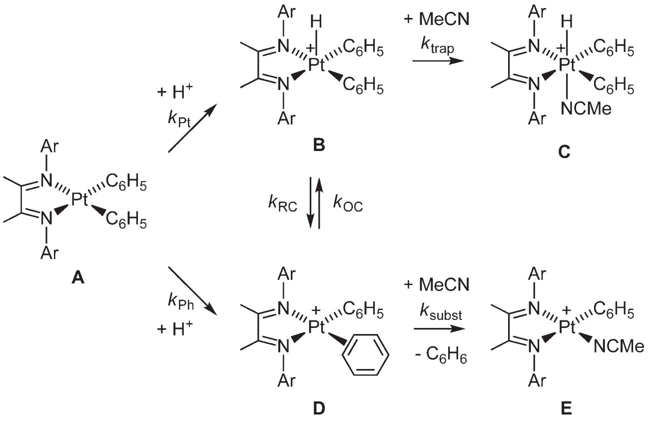
Table 1. Summary of Approximate, Available First-Order or Pseudo-First-Order Rate Constants (s^{-1}) for the Reactions in Scheme 4 at Selected Temperatures[a]

temperature	−78 °C	−40 °C	0 °C	+30 °C
$k_1[H^+]$[b]	3.5	75	770	3000
k_{-2}[c]	2.0×10^{-8}	0.00016	0.15	7.5
k_{-3}[d]	$< 5.6 \times 10^{-5}$	< 0.078	< 18	< 430
$k_4[MeCN]$[e]	0.00011	0.0063	0.14	0.85
$k_5[H^+]$[f]	1.0×10^{-9}	1.3×10^{-6}	0.00027	0.0060
k_6[g]	5.6×10^{-5}	0.078	18	430

[a] Data are derived from activation parameters determined in this study unless otherwise noted. [b] Second-order rate constant derived from the low-temperature protonation kinetics multiplied by $[HBF_4]$ taken as 0.0124 M. [c] First-order rate constant derived from the kinetics of benzene elimination from $(N-N)PtPh_2H(NCMe)^+$, assuming rate-determining MeCN dissociation. [d] An upper limit to the value for k_{-3} is given by k_6, see text. [e] Second-order rate constant derived from the benzene substitution kinetics multiplied by [MeCN] taken as 2.7 M. [f] Second-order rate constant derived from the high-temperature protonation kinetics multiplied by [TfOH] taken as 0.13 M. [g] First-order rate constant derived from kinetic data for H/H site-exchange between the phenyl and benzene ligands in $(N-N)PtPh(\eta^2-C_6H_6)^+$, see ref 23.

out, as stated in the Results section. The protonation is slower than that at the analogous $(N-N)PtMe_2$ complex by a factor of about 40 at −78 °C under comparable conditions. The difference may be attributed to a combination of the increased steric bulk and decreased donor power of the phenyl ligands versus the methyl ligands at Pt.

Scheme 5. Two Possible Sites of Protonation at $(N-N)PtPh_2$



One important question regarding the protonation event is whether the kinetically preferred site of protonation is the metal (rate constant k_{Pt}) or a phenyl ligand (k_{Ph}), see Scheme 5. A similar scheme was the basis for our analysis of the kinetically preferred site of protonation at $(diimine)PtMe_2$ complexes.[20,21] It was concluded that Pt protonation was preferred in that case. In the present context, protonation at Pt produces the five-coordinate intermediate **B**, which will furnish the observed product **C** when trapped by MeCN in the dichloromethane/acetonitrile medium. On the other hand, protonation at a phenyl group produces the π-benzene complex **D** which is the observed product in dichloromethane when the protonation is conducted in the absence of MeCN. Despite these observations, protonation at a phenyl group might be kinetically preferred even in the presence of MeCN, provided that the rate of interconversion between **B** and **D**, k_{RC} and k_{OC}, is fast relative to the rates of each of the product forming steps, k_{trap}[MeCN] and k_{subst}[MeCN], both of which are first-order with respect to [MeCN] (RC denotes "reductive coupling" and OC "oxidative cleavage" as suggested elsewhere[61]). As argued in the case of protonation at $(diimine)PtMe_2$,[20,21] the kinetically preferred site can be assessed provided that a [MeCN]-dependent product distribution is observed. Kinetic protonation at Pt should under such circumstances lead to a **C**/**E** ratio that increases with increasing [MeCN], whereas a kinetic preference for protonation at Ph should lead to a **C**/**E** ratio that decreases with increasing [MeCN]. The experimental results established that over the [MeCN] range 0.27−8.18 M, more than 90% of **C** was always produced at −78 °C; traces of **E** were always seen but there was no systematic trend in the **C**/**E** ratio with changes in [MeCN]. A **C**/**E** ratio that appears to be independent of [MeCN] can be explained by two possible scenarios based in Scheme 5: (i) Competing protonation at Pt and Ph with a strong preference for the former ($k_{Pt} > k_{Ph}$), combined with slow rates of interconversion k_{RC} and k_{OC}. The **C**/**E** ratio simply reflects the relative k_{Pt}/k_{Ph} rates. (ii) Protonation to give **B** and/or **D** followed by fast interconversion rates and much slower product-forming steps. The **C**/**E** ratio then depends on the relative k_{trap}/k_{subst} rates and the equilibrium constant for the **B**/**D** interconversion (Curtin−Hammett conditions[62]). The latter explanation can be readily ruled out in our case: The kinetic data in Table 1 clearly show that at −78 °C, an upper limit to the rate of interconversion, determined

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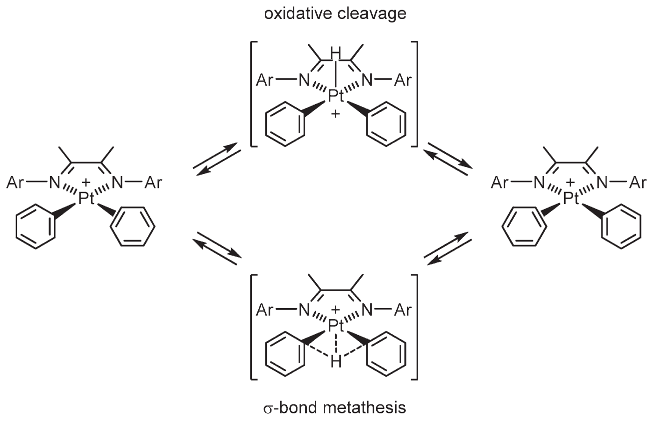
(61) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140–146.
(62) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83–134.

experimentally from the rates of proton exchange between phenyl and η^2-benzene ligands in (diimine)-$PtPh(\eta^2\text{-}C_6H_6)^+$ complexes (see next paragraph), is orders of magnitude slower than the rate of production of **C** in the protonation reaction. Therefore, **C** cannot be produced via protonation at Ph to give **D** followed by oxidative cleavage to furnish **B**. Consequently, we conclude that the kinetically preferred site of protonation in this system has to be the metal, furnishing the Pt(IV) hydride, rather than a phenyl ligand, to furnish the Pt(II) η^2-benzene complex. (An ipso protonation leading to an unobserved η^1-benzene structure, possibly resembling a Wheland-type intermediate, can however not be ruled out). Similar arguments were used to arrive at the same conclusion in a recent DFT study.[56] The trace quantities of **E** observed at −78 °C might suggest that protonation at Ph to furnish **D** is slightly competitive with the predominant protonation at Pt. On the other hand, the data in Table 1 suggest that substitution of η^2-C_6H_6 by MeCN in **D** should be exceedingly slow compared to the overall rate of protonation at −78 °C, and therefore **E** should not have time to form by this pathway at all on the experimental time scale. We must consider that the traces of **E**, which were observed by ^{1}H NMR but not under UV−vis kinetics conditions (under which traces would be difficult to detect), might be caused by experimental artifacts that are currently beyond our control.

In order that a clear trend can be observed in the product distribution when the trapping agent concentration is changed, a relatively delicate balance must exist between the relative rates of the two trapping reactions and the rates of interconversion between the intermediates that will be trapped. Apparently, the requirements concerning relative rates were met in our previous study on the protonation of $(N{-}N)PtMe_2$ species,[20] but not in the present case. An offset of one of the rates by an order of magnitude or so might be sufficient to prevent the observation of the sought-after trend. We note that in the present case, the steric bulk of the phenyl ligands may retard the trapping by MeCN, but would also similarly affect the rate of associative hydrocarbon substitution. Another significant difference is that benzene is associatively displaced in the present case versus methane in the former,[20] and that the barriers to reductive coupling/oxidative cleavage tend to be lower for sp^2 C−H bonds. Altogether, it is not obvious to us exactly which of the effects on the relative rates causes the difference in experimental outcome.

Reductive Coupling and Oxidative Cleavage. The kinetics of the proposed reversible interconversion between **B** and **D** in Scheme 5 has been described elsewhere,[23] but some comments need to be made here. It was seen by 2D EXSY ^{1}H NMR spectroscopic experiments on $(N{-}N)PtPh(\eta^2\text{-}C_6H_6)^+$ **D** in dichloromethane-d_2 that the protons of the C_6H_5 and η^2-C_6H_6 ligands underwent mutual site exchange. This was accompanied by exchange between the two non-equivalent halves of the diimine ligand. The kinetics of these exchange processes were evaluated by quantitative EXSY spectroscopy, and it was found that the diimine-based exchange occurred at the same rate as the $C_6H_5/\eta^2\text{-}C_6H_6$ exchange, with $\Delta G^‡$ about 61 kJ mol^{-1} in dichloromethane-d_2 at −40 °C. The underlying exchange mechanism that was originally proposed is the oxidative cleavage depicted in Scheme 6, top path. The five-coordinate species resulting from the oxidative cleavage of a C−H bond in the benzene ligand is crucial for the proton site exchange, as well as for the diimine symmetrization. Since **B** (whether a true intermediate or a transition state in this process) is expected to be a relatively high energy species compared to **D**, the rate constant k_{OC} can be taken as the rate constant for this exchange process. Recent DFT calculations[56] (computed $\Delta G^‡$ values at −40 °C) located **B** about 73 kJ mol^{-1} higher in energy than **D** and they are connected by a 86 kJ mol^{-1} barrier when going from **D** to **B**, that is, the barrier will be merely 13 kJ mol^{-1} in the reverse direction. (For these calculations, the polarized continuum model (PCM) was used to include *ether* as the solvent). Interestingly, the DFT results suggested that the $C_6H_5/\eta^2\text{-}C_6H_6$ exchange process is more likely to occur by a “direct σ-bond metathesis” in which the proton maintains a weak interaction with Pt as it passed along from one phenyl group to the other in the equatorial plane of the complex. We have now established that the EXSY correlation peaks are seen in spectra of $(N{-}N)PtPh(\eta^2\text{-}C_6H_6)^+$ even in the presence of acetonitrile. This provides strong evidence for the non-involvement of the putative intermediate $(N{-}N)Pt\text{-}Ph_2H^+$ in the exchange process, since it should have immediately formed $(N{-}N)PtPh_2H(NCCD_3)^+$ by trapping with acetonitrile under the reaction conditions.

Scheme 6. Oxidative Cleavage (top) and σ-Bond Metathesis (bottom) Pathways for the Proton Exchange between Phenyl and Benzene Ligands in $(N{-}N)PtPh(\eta^2\text{-}C_6H_6)^+$



The DFT-predicted direct σ-bond metathesis pathway now is an even more attractive alternative to the oxidative cleavage/reductive coupling pathway for exchange. Such a σ-bond metathesis process appears to nicely explain H/D exchanges between two phenyl groups, via a reasonably looking calculated transition-state structure.[56] (An analogous exchange mechanism is not necessarily involved in other reported, related exchange processes; it appears to us less likely to be involved in exchanges between two methyl groups,[17,20] or between phenyl and methyl groups[16,18]). The computed transition-state free energy for this process, which closely resembles the transition state in what Perutz and Sabo-Etienne[55] have termed a “σ-complex assisted metathesis” (σ-CAM), was 62 kJ mol^{-1}, that is, about 24 kJ mol^{-1} below that for the oxidative cleavage pathway. If these computational results give a true description of the mechanism, then one obvious implication will be that the numerical value that is used for k_{OC} is an *upper limit* to the real value: The EXSY kinetics represent the energetics for reaching the transition-state for the direct exchange process; the transition state for the oxidative cleavage must necessarily be higher in energy and thence the corresponding rate must be even slower—which strengthens the arguments that led to the conclusion in the previous paragraph: Pt is the kinetically preferred site of protonation. We note that kinetic isotope effects obtained by reactions with HX versus DX acids might shed further light on the nature of the initial protonation event, as demonstrated in a recent contribution by the Bercaw[63] and Romeo groups,[64] and we hope to report on this in a future contribution.

Elimination of Benzene from (N−N)PtPh$_2$H(NCMe)$^+$. The six-coordinate Pt(IV) hydride is quite stable on the time scale of all our experiments at −78 °C. When heated, the compound smoothly undergoes benzene elimination to furnish (N−N)PtPh(NCMe)$^+$. The kinetic parameters, notably the rather large $\Delta H^{\ddagger}$ and the substantially positive values for $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$, suggest that the rate-limiting step of this reaction must involve MeCN dissociation. The data in Table 1 show that at temperatures well below 0 °C, MeCN dissociation (k_{-2}) is considerably slower than benzene substitution (k_4[MeCN]), and within the framework of Scheme 4 the elimination of benzene from (N−N)PtPh$_2$H(NCMe)$^+$ to furnish (N−N)PtPh(NCMe)$^+$ is expected to proceed without the build-up of observable intermediates. At temperatures above 0 °C, benzene substitution is competitive with or even faster than MeCN dissociation. However, on the assumption that MeCN dissociation is reversible, the accumulation of the putative π-benzene intermediate (N−N)PtPh(η^2-C$_6$H$_6$)$^+$ would be negligible also under these conditions. Thus, the observations are readily reconciled with the notion that benzene elimination is dissociative and takes place without build-up of detectable intermediates. The mechanism is entirely analogous to that observed for the elimination of methane from (N−N)PtMe$_2$H(NCMe)$^+$.[22] It should be mentioned here that reductive eliminations of X−Y from octahedral L$_4$Pt^{IV}(X)(Y) compounds are usually found to be dissociative whenever a readily dissociable ligand is present; whether the overall process occurs in a concerted or stepwise fashion may strongly depend on the nature of the eliminating groups X and Y, as well as of the ancillary ligands L.[11,65−67] The five-coordinate species (N−N)PtPh$_2$H$^+$, a crucial intermediate that is postulated to be in common for the protonation as well as for the benzene reductive elimination processes, has not been directly observed, not even under the rapid-scan conditions utilized here. However, there are a few literature reports on isolable, five-coordinate Pt(IV) alkyl complexes.[68−74]

Substitution of Benzene by Acetonitrile at (N−N)PtPh(η^2-C$_6$H$_6$)$^+$. We have reported[23] that (diimine)PtPh(η^2-C$_6$H$_6$)$^+$ complexes are readily available by protonation of (diimine)PtPh$_2$ complexes in dichloromethane at about −78 °C. It was qualitatively seen that the stability of (diimine)PtPh(η^2-C$_6$H$_6$)$^+$ complexes with respect to benzene loss depended highly on the substituents at the N-aryl groups of the diimine ligand. Complexes that are 2,6-dimethyl substituted on the N-aryl groups slowly start to lose benzene at about −40 °C under these conditions, whereas 2,6-unsubstituted analogs start to lose benzene at a substantial rate even at −78 °C. These qualitative stability differences are readily understood if it is assumed that benzene loss occurs by an associative mechanism. Since the N-aryl groups are oriented more or less perpendicularly with respect to the coordination plane of Pt,[23] the N-aryl methyl substituents will serve to sterically protect the Pt center from nucleophilic attack by any incoming ligand that approaches from above or below the coordination plane. Experimental evidence suggests that substitution of methane by acetonitrile in (diimine)PtMe(σ-CH$_4$)$^+$ complexes,[19] and of toluene by acetonitrile in related (diimine)Pt(*o*/*m*/*p*-tolyl)(η^2-toluene)$^+$ species, are associative in nature. However, the kinetics of these processes have not been investigated in any detail.

The experimental results that have been presented herein leaves no doubt that substitution of benzene by acetonitrile in (N−N)PtPh(η^2-C$_6$H$_6$)$^+$ is an associative process. The first-order dependence of k_{obs} on [MeCN], with the near-zero intercept of the k_{obs} versus [MeCN] plot in Figure 10, as well as the substantially negative $\Delta S^{\ddagger}$, strongly support this notion. Thus, it appears that hydrocarbon loss from cationic diimine-supported complexes will generally proceed by an associative substitution mechanism in a good donor solvent like acetonitrile. It is noteworthy that addition of MeCN to (N−N)PtPh(η^2-C$_6$H$_6$)$^+$ produces only (N−N)PtPh(NCMe)$^+$ and not (N−N)PtPh$_2$H(NCMe)$^+$, which means that with reference to Scheme 5, it must be required that the rate constant for benzene substitution, k_4[MeCN], is expected to be substantially greater than that for oxidative cleavage, k_{-3}. This is based on the assumption that the trapping reaction k_2 is rapid, which is suggested by the fact that (N−N)PtPh$_2$H(NCMe)$^+$ is rapidly and cleanly produced from (N−N)PtPh$_2$ protonation in the presence of MeCN. The data in Table 1 show that the rate of site exchange in (N−N)PtPh(η^2-C$_6$H$_6$)$^+$ far outruns the rate of substitution by MeCN under typical experimental conditions; further evidence for this is provided by the observation of EXSY correlation peaks even in the presence of acetonitrile. This fact provides compelling experimental evidence that site exchange cannot occur by

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the oxidative cleavage/reductive coupling pathway. The combined data are most consistent with site exchange occurring by a separate pathway, that is, the concerted σ-bond metathesis pathway indicated in Scheme 6 and suggested by DFT calculations.[56] It should be mentioned here that directly observable equilibria between Pt(II) π-benzene and Pt(IV) hydrido phenyl complexes have been previously described.[75] For example, a dynamic equilibrium exists at low temperatures between $(\kappa^2\text{-HTp}')\text{PtH}(\eta^2\text{-C}_6\text{H}_6)^+$ and $(\kappa^2\text{-HTp}')\text{PtH}_2\text{Ph(NCMe)}^+$ (HTp'^- = N-protonated hydridotris(3,5-dimethylpyrazolyl)borate) in a dichloromethane-d_2 solution containing acetonitrile. These complexes are formally cationic at the pendant, uncomplexed, protonated pyrazole ring and, importantly, are neutral at Pt. The latter will tend to destabilize MeCN binding at Pt(IV) when compared to the situation in the cationic-at-Pt diimine systems that we describe here and therefore, a putative MeCN dissociation step should be much more facile in the HTp′ than in the diimine systems.

Protonation and Benzene Elimination at (N−N)PtPh(NCMe)$^+$. The second protonation of (N−N)PtPh_2 occurs at temperatures near ambient after the Pt(II) cation (N−N)PtPh(NCMe)$^+$ has been generated. This protonation is exceedingly slow when $\text{HBF}_4\cdot\text{Et}_2\text{O}$ is employed as the acid, but occurs much more rapidly when TfOH is used. This is in accord with the general notion that TfOH is a stronger acid than $\text{HBF}_4\cdot\text{Et}_2\text{O}$. The sluggishness of the reaction arises from the combined effect of a high $\Delta H^\ddagger$ (resulting from the necessity to protonate an already positively charged metal complex) and a strongly negative $\Delta S^\ddagger$. No intermediates have been observed for this reaction, perhaps not too surprising, considering the relatively high temperatures that are required for the protonation. These conditions are expected to lead to the instant elimination of benzene from a formally doubly charged Pt(II) π-benzene complex or a doubly charged Pt(IV) phenyl hydride complex. The kinetic data do not allow us to draw firm conclusions regarding the site of protonation, the involvement (or not) of Pt(IV) hydride species, the involvement (or not) of π-benzene intermediates, or the associative (or dissociative) nature of the benzene elimination or substitution. One difference is particularly striking when the first and second protonation are compared, in addition to the simple fact that the second protonation is much slower than the first: In the first protonation/benzene-forming sequence, the benzene-producing reactions are rate limiting reactions following a rapid protonation. In the second protonation/benzene-producing sequence, the benzene-producing reactions are rapid reactions following a rate-limiting protonation. This difference might be a consequence of the different temperature regimes of the two reaction sequences: The second protonation occurs at a temperature sufficiently high to dramatically accelerate the high-activation energy (as expressed through $\Delta G^\ddagger$) benzene-producing process relative to the lower-activation energy protonation event.

Summary and Concluding Remarks

In this contribution, we have described the combined results from NMR and stopped-flow UV−vis spectroscopic measurements on a well-defined sequence of reactions that is initiated by protonation of (N−N)PtPh_2. Detailed insight into the kinetics and mechanisms of a cascade of reactions that ultimately leads to the release of 2 equiv of benzene has been obtained within the temperature range of −80 to + 27 °C. The accumulated experimental data are in agreement with the mechanistic picture that is depicted in Scheme 4. At low temperatures (ca. −80 °C), protonation of (N−N)PtPh_2 with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ in dichloromethane/acetonitrile occurs at the metal to furnish an unobserved five-coordinate Pt(IV) complex (N−N)PtPh_2H^+ that is immediately trapped to furnish (N−N)$\text{PtPh}_2\text{H(NCMe)}^+$. This six-coordinate Pt(IV) hydride is stable under the low-temperature reaction conditions. At higher temperatures, (N−N)$\text{PtPh}_2\text{H(NCMe)}^+$ is kinetically less stable: The energetically costly MeCN dissociation occurs and under these conditions, the following reactions, namely, Ph-H reductive coupling to furnish (N−N)$\text{PtPh}(\eta^2\text{-C}_6\text{H}_6)^+$ and the subsequent associative substitution of acetonitrile for benzene, are quite rapid. Consequently, (N−N)$\text{PtPh}_2\text{H(NCMe)}^+$ produces (N−N)PtPh(NCMe)$^+$ without observable intermediates. The next protonation occurs at a reasonable rate only when the stronger acid TfOH is utilized and leads to benzene loss without observable intermediates. The (N−N)$\text{PtPh(C}_6\text{H}_6)^+$ complex can be independently prepared by protonation with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ in dichloromethane. Substitution of benzene by acetonitrile at this complex is clearly associative in nature and furnishes exclusively (N−N)PtPh(NCMe)$^+$ with no hints for (N−N)$\text{PtPh}_2\text{H(NCMe)}^+$. This observation provides indirect evidence that the previously reported exchange of protons between the phenyl and benzene ligands in (N−N)$\text{PtPh(C}_6\text{H}_6)^+$ probably occurs via a σ-bond metathesis pathway, also suggested by DFT calculations, rather than by an oxidative cleavage/reductive coupling sequence.

The diimine-Pt system offers rich opportunities to investigate the effects of substituents and other parameters on these and other reactions that are of relevance to C−H bond activation reactions that are of great practical and academic interest. Further studies are in progress and will be reported in due time.

Experimental Section

General Considerations. The solvents for UV−vis stopped-flow kinetics measurements, p.a. grade and ultra dry acetonitrile and dichloromethane, were supplied by Acros and were used without further purification. Deuterated solvents were used as received without further purification (CD_2Cl_2, CD_3CN, $\text{Et}_2\text{O-}d_{10}$). ^{1}H NMR spectra were measured on a Bruker DRX500 spectrometer. ^{1}H NMR chemical shifts (δ) are reported in ppm relative to TMS using the residual proton resonances of the solvent (δ 5.32 in CD_2Cl_2, 1.93 in CD_3CN). The temperature calibration for the low-temperature experiments was done using a thermocouple situated inside a thin glass tube that was inserted into an NMR tube with methanol.

The complex (N−N)PtPh_2 was prepared as described in the literature[23] from $\text{Ph}_2\text{Pt(SMe}_2)_2$[76] and the diimine.[77] ($\text{Ph}_2\text{Pt(SMe}_2)_2$ has been reported[78] to exist as mixtures of dimers and trimers).

Pt(II)/Pt(IV) Ratio vs [MeCN]. Competitive trapping experiments were conducted by adaptation of already published

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procedures.[20,21] A solution of (N−N)PtPh$_2$ (ca. 3 mg, 5 μmol) in CD$_2$Cl$_2$ (400 μL) in an NMR tube was cooled to −78 °C and layered with a mixture of HBF$_4$·Et$_2$O (3 μL) in MeCN-d_3 (x μL) and CD$_2$Cl$_2$ (300 − x μL.; x = 10−300 μL). The tube was capped and shaken to mix the reactants immediately before transfer to a pre-cooled NMR probe. A pale yellow solution was immediately obtained. The relative amounts of the Pt(II):Pt(IV) complexes were determined by integration of suitable non-overlapping ^{1}H NMR signals from the complexes. Thus, the Ar-Me signal at δ 2.13 from one-half of the diimine ligand was used for (N−N)PtPh(NCCD$_3$)$^+$, whereas the signal at δ 2.41 arising from the methyl groups at the backbone of the diimine ligand were used for (N−N)PtPh$_2$H(NCCD$_3$)$^+$. Characterization of the complexes has been already published.[23] The relative distribution of the two products was unaltered when the tube was kept for 3 h at the same temperature.

NMR Monitoring and Kinetics of Benzene Substitution by MeCN at (N−N)PtPh(η^2-C$_6$H$_6$)$^+$. The NMR investigation of the benzene substitution kinetics was performed by slight modifications of previously reported procedures.[20,22,23] In an NMR tube, (N−N)PtPh$_2$ (10 mg, 15 μmol) was dissolved in dichloromethane-d_2 (300 μL), and the tube was cooled to −78 °C on a dry ice/acetone bath. A solution of HBF$_4$·Et$_2$O (10 μL, 78 μmol) in a mixture of Et$_2$O-d_{10} (70 μL) and dichloromethane-d_2 (180 μL) was then added, the tube was shaken in the bath, and a ^{1}H NMR was recorded at −78 °C to ensure that all the starting material was consumed and that (N−N)PtPh(η^2-C$_6$H$_6$)$^+$ had formed (diagnostic signal at δ 6.85, s, 6 H, η^2-C$_6$H$_6$). The tube was removed from the NMR probe and returned to the dry ice/acetone bath. A solution of acetonitrile-d_3 (x μL) in dichloromethane (200 − x μL) was carefully layered on top of the contents in the NMR tube (x was in the range 40−100 μL, corresponding to acetonitrile concentrations in the range 1.0−2.7 M). The tube was then shaken to ensure complete mixing prior to transfer to the NMR probe and monitoring of the progress of the reaction at predetermined temperatures. A smooth conversion of (N−N)PtPh(η^2-C$_6$H$_6$)$^+$ to (N−N)PtPh(NCCD$_3$)$^+$ (δ 2.37, s, 6 H, Ar-*Me*) and benzene (δ 7.3, s, 6 H) was seen. The kinetic data were obtained by integration of the peak intensity for the phenyl ligand protons (δ 6.0−6.2) of the η^2-benzene complex versus the residual proton signal of the solvent dichloromethane-d_2 as an internal standard. A plot of ln(relative intensity) versus time was linear for 3−4 half-lives.

EXSY NMR Spectra of (N−N)PtPh(η^2-C$_6$H$_6$)$^+$ in the Absence and Presence of Acetonitrile-d_3. The sample preparation was identical to that of the benzene substitution kinetics experiments described above. The EXSY spectra were recorded at −48 °C without acetonitrile-d_3 or with 54 mM acetonitrile-d_3. The same experimental parameters were used as described in our previous contribution.[23] The EXSY correlation signals were of indistinguishable intensities in the two experiments.

UV−vis Stopped-Flow Measurements. In the stopped-flow kinetic studies the samples were prepared as follows. A mixture of acetonitrile and dichloromethane was prepared and used to dissolve the desired amount of platinum complex. With the same solvent mixture, the acid was diluted to the desired concentration. These two solutions were mixed in the UV−vis cuvette, providing a 0.125 mM solution of (N−N)PtPh$_2$. Using this procedure, different experiments were conducted in which the acid concentration was varied at constant acetonitrile concentration and vice versa.

UV−vis spectra were recorded on Shimadzu UV-2102 and Hewlett-Packard 8542A spectrophotometers. Low-temperature kinetic data were obtained by recording time-resolved UV−vis spectra using a modified Bio-Logic stopped-flow module μSFM-20 combined with a cryo-stopped-flow accessory (Huber CC90 cryostat) equipped with a J & M TIDAS high-speed diode array spectrometer with a combined deuterium and tungsten lamp (200−1015 nm bandwidth). Isolast "O" rings were used for all sealing purposes. Data were analyzed using the integrated Bio-Kine software, version 4.44, and the software package Specfit/32 global analysis program. Measurements under high pressure were carried out using a homemade high-pressure stopped-flow instrument,[79,80] for which Isolast "O" rings were also used for all syringe seals.

Four to nine kinetic runs were recorded under all conditions, and the reported rate constants represent the mean value. The UV−vis spectrophotometers and stopped-flow instrument were thermostatted at the desired temperature ± 0.1 °C. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from the slopes and intercepts of plots of ln(k/T) versus $1/T$, respectively, and values of $\Delta V^{\ddagger}$ were calculated from the slope of plots of ln(k) versus pressure in the usual way.[59]

Acknowledgment. We gratefully acknowledge generous financial support from the Norwegian Research Council (stipend to J.P.) and the Deutsche Forschungsgemeinschaft through SFB 583 "Redox-active metal complexes" (to I.I.B. and R.v.E.).

Supporting Information Available: One file containing kinetic data for the protonation of (N−N)PtPh$_2$ as a function of [MeCN], [HBF$_4$], and temperature; kinetic data for the elimination of benzene from (N−N)PtPh$_2$H(NCMe)$^+$ as a function of [MeCN], [HBF$_4$], temperature, and pressure; kinetic data for the protonation/benzene elimination of (N−N)PtPh(NCMe)$^+$ as a function of [TfOH] and temperature, and kinetic data for the substitution of benzene by acetonitrile at (N−N)PtPh(η^2-C$_6$H$_6$$^+$ as a function of [MeCN] and temperature, all in tabular form. This material is available free of charge via the Internet at http://pubs.acs.org.

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