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Metal-Ligand Cooperation Facilitates Bond Activation and Catalytic Hydrogenation with Zinc Pincer Complexes

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ABSTRACT: A series of PNP zinc pincer complexes capable of bond activation via aromatization/dearomatization metal-ligand cooperation (MLC) were prepared and characterized. Reversible heterolytic N-H and H-H bond activation by MLC is shown, in which hemilability of the phosphorus linkers plays a key role. Utilizing this zinc pincer system, base-free catalytic hydrogenation of imines and ketones is demonstrated. A detailed mechanistic study supported by computation implicates the key role of MLC in facilitating effective catalysis. This approach offers a new strategy for (de)hydrogenation and other catalytic transformations mediated by zinc and other main group metals.

INTRODUCTION

In moving towards a more sustainable future, it is imperative to develop "green" chemical transformations that are both economical and free of waste generation.¹ The most successful metals employed in catalytic reactions have historically been the noble metals, which typically suffer from high price, low abundance and toxicity.² Thus, in the past two decades, there has been a notable increase in efforts to develop both organocatalysts and catalysts based on main group metals, which are generally more abundant and cost effective alternatives to the noble metals.²⁻⁴ Furthermore, significant effort has focused on developing transformations that are atom-efficient or generate byproducts that are benign or useful in their own right (e.g. H₂O and H₂).⁵

With respect to utilizing molecular main group metal complexes for catalytic transformations, one common impediment is redox incoherence, often nullifying their ability to undergo the fundamental organometallic reactions of oxidative addition and reductive elimination (Figure 1).¹⁻⁶ For example, in homogeneous zinc, magnesium and calcium catalyzed reactions, the metal is almost exclusively limited to the M⁰ oxidation state, and thus productive cycles depend on only sigma bond metathesis and/or insertion steps which do not alter the oxidation state of the metal.⁵⁻⁶ Nonetheless, utilizing this paradigm, complexes of these metals and other main group metals have demonstrated versatile catalytic applications including hydroamination,⁷ polymerization,⁸ hydrolylation,⁹ hydroboration¹⁰ and hydrogenation¹¹⁻¹⁷ in which metal hydride intermediates are often speculated (and occasionally isolated).¹⁸⁻²⁰ Zinc, in particular, has shown activity for all of these transformations, and is a promising metal due to its low cost, relatively high abundance and low toxicity.¹²⁻¹⁴

Our group is interested in leveraging metal-ligand cooperation (MLC), in which bond activation occurs across both metal and ligand, to effect transformations in an atom-economical, waste-free fashion.¹⁵ The MLC approach has long been demonstrated for advancements with the noble metals, and more recently with more abundant first row transition metals, for reversible bond activation resembling oxidative addition and reductive elimination (Figure 1).¹,¹²⁻¹⁴,¹⁷⁻²⁷ Importantly, the metal center does not change oxidation state in this process, and as a result, this activation mode could also be potentially operative with redox-innocent main group metals.²⁸

![Figure 1. Top: Bond activation via oxidative addition/reductive elimination compared to bond activation by metal-ligand cooperation. Bottom: Nominal coordination modes of the PNP⁴ ligand to a generic metal (M) in which the ligand is an aromatized (L₃) neutral ligand versus a dearomatized (L₂X) anionic ligand.](image)

With respect to aromatization/dearomatization MLC with main group metals, Braunstein, Danopoulos and co-workers characterized a family of dearomatized lithium and potassium complexes, but bond activation with these complexes has not yet been demonstrated.²⁹ Most notably, Berben and co-workers have shown that aluminum complexes supported by a tridentate bis(imino)pyridine ligand can activate N-H and O-H bonds across the aluminum center and ligand.²⁸⁻³¹ Other examples with Group 13 metals have also been introduced and explored with similar application.³² In the case of zinc, we are only aware of reports in which the ligand itself is implicated as a proton or electron reservoir,³³,³⁴ and very recently,
MLC was proposed to facilitate methanol activation en route to a
caracterized zinc methylcarbonate species in a novel CO₂ reduc-
tion process. Nonetheless, direct observation of reversible H-X
bond activation across any main group metal and ligand via aro-
malization/dearomatization is unknown, and main group metal-ligand
cooperation remains an underexplored area.

Based on our previous efforts, we hypothesized that it should be
possible to synthesize pincer complexes of main group metals, such
as zinc, that could reversibly activate bonds by MLC in which the
oxidation state of the metal remains unchanged. If so, zinc-ligand
cooperation could be employed to catalyze useful transformations,
such as (de)hydrogenation reactions, which typically occur at a
transition metal center. Herein, we establish that both aromatized
and deaomeratized zinc complexes supported by the PNP ligand
(Figure 1) can be prepared and isolated in a straightforward man-
ner. We demonstrate the ability of this system to heterolytically
cleave and form H-H and N-H bonds. Finally, this new mode of
bond activation by zinc is applied towards the additive-free, catalyt-
ic hydrogenation of imines and ketones.

RESULTS AND DISCUSSION
Access to a deaomeratized zinc pincer complex is readily achieved
via the reaction of the PNP₄Bu pro-ligand with dimethylzinc at
140°C in toluene to generate PNP₄BuZnMe (1) concurrent with
loss of methane (Scheme 1). This simultaneous deprotonation and
complexation approach is analogous to the procedure employed to
prepare lithium and potassium pincer complexes, and is not un-
common in the synthesis of zinc alkyl and amido species. In
contrast to procedures employed in the preparation of traditional
daermatized transition-metal pincer complexes, in this ap-
proach, the addition of base is obviated by the basic nature of dim-
eethylzinc itself, which is capable of deprotonating the side arm of
the ligand. Upon mixing, the colorless ligand and dimethylzinc starting
materials form a bright yellow solution, which upon heating evolves
gas and exhibits an orange/red color, atypical of Zn²⁺ compounds
but quite typical of deaomeratized PNP pincer complexes. From
monitoring the reaction progress with ^1H and ^31P[^1H] NMR spec-
troscopy, we propose that the room temperature yellow intermediate
is formed by coordination of the PNP₄Bu ligand to ZnMe₂, and
subsequent the reaction process in the loss of methane and formation of the orange/red complex 1 (see Supporting Information). The
daomeratized compound, PNP₄BuZnMe, exhibits several character-
istic signals in solution by NMR spectroscopy. For example, in
toluene-d₈, multiplets at -0.02 ppm in the ^1H NMR spectrum and -
3.47 ppm in the ^13C[^1H] NMR spectrum indicate the presence of a
zinc methyl moiety coupled to two inequivalent phosphorus atoms.
In addition, the inequivalent arms of the pincer ligand are distin-
guishable by both ^1H (doublet at 3.53 ppm and broad singlet at
2.62 ppm) and ^13C[^1H] (doublet at 57.43 ppm and doublet of
doublets at 31.19 ppm) NMR spectra, associated with the deproto-
nated and protonated arms, respectively, as confirmed by HSQC
and DEPTQ NMR experiments. Most evidently, the ^31P[^1H] NMR
of 1 exhibits two distinct doublets (40.75 ppm and 5.74 ppm), with
JₚH coupling constants of 18 Hz, indicative of the inequivalent
phosphorus atoms, with similar shifts as the known lithium and
potassium compounds.

Utilizing the same protocol, a deaomeratized zinc ethyl compound,
PNP₄BuZnEt (2), was also prepared (Scheme 1). The zinc ethyl
complex forms via a similar pathway, and its spectroscopic features
effectively match that of 1 (see Supporting Information Table S2).
Most diagnostically, the ^31P[^1H] NMR also exhibits two doublets
(39.13 ppm and 4.53 ppm; JₚH = 15 Hz). The zinc amido complex,
PNP₄BuZnN(SiMe₃)₂ (3), is also isolable, and is prepared via the
reaction of PNP₄BuZnCl₂ (Scheme 1). As compared to 1 and 2,
PNP₄BuZnN(SiMe₃)₂ (4) also exhibits two resonances in the
^31P[^1H] NMR (35.20 ppm and -0.33 ppm), but unlike those of the
corresponding methyl and ethyl derivatives, the peaks are singlets
indicating no observable P-P coupling across the zinc center.

Scheme 1. Synthesis of Zinc Pincer Complexes

Single crystals of PNP₄BuZnR (R = Me, Et) and PNP₄BuZnN(SiMe₃)₂
were grown by cooling saturated pentane solutions to -32°C, and the molecular structures were determined by X-
ray crystallography (Figure 2), confirming the formation of a mon-
omeric, deaomeratized zinc pincer complex in each case. The zinc
center in 1 and 2 is pseudotetrahedral, distorting the PNP ligand
quite substantially from its typically planar conformation. Support-
ning the spectroscopic data, conclusive evidence of the deaomerat-
nature of the ligand is clear in each case: (i) the hydrogen atoms on
the pincer arms were found and refined, and (ii) the C-C distances are indicative of double bond character on one of the arms and
single bond character on the other arm (see Figure 2 and Support-
ing Information Table S1). Also in agreement with the spectro-
copic data, the Zn-P distance of the ligand arm that remains pro-
tonated increases 1 < 2 ≪ 4 (2.675Å, 2.965Å and 4.914Å, respec-
tively); in the case of 3, the second phosphorus arm is clearly un-
bound in the solid state, rendering the zinc center three-coordinate.
As such, it is understandable that the ^31P[^1H] NMR spectrum of 1
and 2 exhibit two doublets (from P-P coupling), whereas that for 4
exhibits two singlets, indicating an open arm in solution. Though a
coordination number of four is common for zinc, three-coordinate
zinc is less common but has been observed.

While the preparation of organozinc (RZnX) species is formally an
oxidative addition of an organic RX to Zn²⁺, these species are typi-
cally stoichiometric reagents; thus, in moving towards catalytic
applications, the development of molecular and recyclable zinc
compounds that can perform bond activation is significant. We
previously reported the activation of N-H bonds mediated by MLC
with a deaomeratized ruthenium complex. We found that electron-deficient aniline derivatives reacted via aro-
malization/deaomeratization MLC to afford ruthenium anilido complexes
Figure 2. Molecular structures of complexes (1), (2), (4) and (5). Selected hydrogen atoms omitted for clarity. Some groups displayed as wireframe for clarity. Select bond lengths (Å) and angles (°): (1): Zn1-C24 1.9969(18), Zn1-P1 2.4252(5), Zn1-P2 2.6750(5), P2-C7 1.8646(18), C7-C6 1.510(3), P1-C1 1.7608(18), C1-C2 1.387(2). (2): Zn1-C24 1.9731(14), Zn1-P1 2.4267(4), Zn1-P2 2.965, P1-C1 1.7491(15), C1-C2 1.394(2), P2-C7 1.8684(14), C7-C6 1.5043(19), N1-Zn1-P1 85.36(3). (4): Zn1-N2 1.8849(18), Zn1-P1 2.3369(6), Zn1-P2 4.914, P1-C1 1.746(2), C1-C2 1.402(3), P2-C7 1.866(2), C7-C6 1.508(3), P1-Zn1-N1 87.56(3), N1-Zn1-N2 127.36(7). (5): Zn1-N2 1.9954(14), Zn1-P1 2.4606(4), Zn1-C30 1.9872(18), P1-C1 1.8367(17), C1-C2 1.509(2), P2-C7 1.8648(18), C7-C6 1.510(2). See Supporting Information for molecular structure of (3).

irreversibly. In the case of ammonia, aniline and other amines, reversible addition was observed. Related palladium and copper chemistry has also been explored. We began our reactivity studies with the room temperature addition of the electron-poor aniline derivative, H2NAr (Ar = 2-chloro-4-nitrophenyl), to 1, which resulted in the immediate formation of the aromatized complex, PNPtBuZn(Me)NHAr (4), in which N-H activation has occurred across both the metal center and the ligand side-arm (Scheme 1). Notably, the oxidation state of the zinc center remains +2, in that the pincer ligand itself reassumes a neutral charge, with both the methyl and anilido moieties serving as X-type ligands. In solution, NMR spectroscopy provides conclusive evidence of the formation of 4, indicating symmetrization of the pincer side arms. Specifically, the 31P{1H} NMR changes drastically from two doublets for 1 (vide supra) to a broad singlet at 2.76 ppm for 4 and the 1H NMR displays a doublet for four hydrogen atoms at 2.99 ppm, demonstrating solution-state equivalence of the methylene side arms. NMR data suggests that the addition across the side arm is irreversible in the case of this weakly basic amine.

Single crystals of 5 suitable for X-ray diffraction were grown by slow diffusion of pentane into a toluene solution (Figure 2). The molecular structure confirms activation of H2NAr across both the metal center and ligand. In the solid state, one of the phosphorus arms of the PNPtBu pincer ligand is detached from the metal center, rendering complex 5 tetrahedral. A tetrahedral geometry is quite common for four-coordinate zinc centers, and the conformation also resembles the structure found for PNPtBuZnCl (see Supporting Information); however, the NMR spectroscopy data indicates an equivalence of the side arms in solution consistent with a 5-coordinate zinc center, hinting that there may be a difference between the solid and solution state behavior for both 3 and 5. To probe this difference, a variable temperature NMR experiment was performed for 5. At low temperature, inequivalence of the methylene and tert-butyl groups on the side arms by 1H NMR (Figure 3) and the phosphorus linkers by 31P{1H} NMR (see Supporting Information) could be observed. Decoalescence of the signals is observed around 253K and 238K in the 1H NMR and 31P{1H} NMR spectra, respectively. We also performed the analogous experiment with compound 3 and observe the same phenomenon (see Supporting Information). These experiments confirm the labile nature of the phosphorus linkers in solution and are significant in that the hemilability of the side arm of PNPtBu complexes has been proposed, but, to our knowledge, has never been demonstrated experimentally. This finding is meaningful in that hemilability in pincer complexes has been extensively studied and is believed to be significant in catalytic mechanisms of related compounds.

Most interestingly, addition of the more basic N-benzylaniline (PhN(H)Bn) to 1 under ambient conditions resulted in an observable equilibrium. Analysis of a mixture of PNPtBu*ZnMe (1) and PhN(H)Bn by 1H and 31P{1H} NMR spectroscopies indicates the formation of an equilibrium mixture containing three major species: free amine, deaeromatized zinc methyl complex with coordinated amine (6), and the N-H activated compound, PNPtBuZn(Me)NPhBn (7) (Scheme 2). Compound 7 is characterized as a component of the equilibrium mixture by NMR spectroscopy. Specifically, diagnostic signals at 23.19 ppm in the 31P{1H} NMR spectrum for the solution-state equivalent phosphorus atoms and at 4.33 ppm in the 1H NMR spectrum for the -CH2Ph moiety in the amido ligand are observed. In addition, a small amount (<5%) of a species tentatively identified as PNPtBu*ZnNPhBn is formed. This species exhibits 31P{1H} NMR characteristic signals similar to 1 and
is presumably formed from protolytic cleavage of the Zn-Me bond. The equilibrium between complexes 1, 6 and free amine and complex 7 could be probed by NMR spectroscopy via a variable temperature NMR study. Specifically, a d8-toluene solution of a roughly equimolar mixture of PNP/ZnMe and N-benzylaniline was heated in increments from room temperature to 120°C, allowing the overall equilibrium between 1 and 7 to be established at each temperature. Keq was determined by integration of the corresponding 1H NMR spectra and a Van ‘t Hoff plot permitted extraction of thermodynamic quantities (see Supporting Information). Keq over the temperature range was found to be between 1 and 100, with an experimentally determined Keq of 68.8 for the equilibrium mixture at 298K, associated with a ΔG of -2.4 kcal/mol, which agrees reasonably well with our computed results (+1.1 kcal/mol at 393.15K and 1M standard states, vide infra). Observation of this equilibrium provides evidence that (i) free amine can coordinate to and then react with 1 via MLC to rearromatize the ligand and generate 7, (ii) free amine can be released by MLC to regenerate 1 and (iii) that the reactants and product are quite similar energetically, such that the equilibrium is observable in solution by NMR spectroscopy. This unprecedented reversible N-H bond activation by MLC with a main group metal resembles transition-metal-like behavior.

Scheme 2. Reactivity of 1 Towards PhN(H)Bn, H2, and D2, and Trapping of a Proposed Zinc Hydride Complex

Subsequently, we turned our attention to the activation of a non-polar, environmentally relevant substrate, H2. Oxidative addition of H2 to a transition metal is very important in several transition-metal catalyzed processes,24 and we have observed reversible H2 activation by MLC with related transition metal systems with applications in (de)hydrogenation catalysis.24,58 Thus, we explored whether PNP/ZnMe could potentially activate hydrogen, a challenging non-polar bond, in the same fashion as the N-H bond. Treatment of a solution of 1 in toluene with 5 bar of H2 in a high-pressure Young tube resulted in no significant change, even upon gradual heating to 80°C. Heating the sample at 90°C, however, resulted in partial decomposition, with grey precipitation presumed to be Zn0, which was observed lining the walls of the NMR tube, and both CH3D and CH4 were detected by 1H NMR spectroscopy (vide infra). This result likely implicates insertion of the imine into a Zn-H bond and also hinted at possible catalytic hydrogenation applications.

Based on the unique activity of the main group metal zinc-based pincer complex towards H2 cleavage, insertion and reversible activation of N-H bonds (vide supra), we posited that leveraging MLC might permit hydrogenation of polar unsaturated bonds with this system. To our knowledge, zinc catalyzed hydrogenation has been demonstrated for imines under very high H2 pressures (68-100 bar)13,14 and ketones with limited scope and high H2 pressure (100 bar).58 Reductions catalyzed by molecular zinc compounds utilizing other hydrogen sources, specifically hydrosilanes and hydroboranes, have been demonstrated, including imines, ketones, aldehydes and nitriles.2,10,11,57 The lack of reports of hydrogenation, we believe, is related to the energetic cost of sigma bond metathesis to split hydrogen and release product (hence the success of other hydrogen sources with more favorable thermodynamic driving forces). Given the ability of the aromatization/dearomatization MLC approach to facilitate the reversible activation of H2 and N-H
bonds in this pincer system, we hypothesized that these alternate pathways could potentially bypass other more energetically demanding routes with less favorable thermodynamics, thus allowing hydrogenation at milder conditions compared to previously reported studies.

Indeed, PNP\textsuperscript{tBu\textasteriskcentered}ZnMe (1) is a moderately active catalyst for the hydrogenation of a model substrate, N-benzylideneaniline (Table 1, Entry 1), at substantially lower pressures (7 bars) than the previous reports (68-80 bars) of zinc-catalyzed imine hydrogenation.\textsuperscript{11,14}

Specifically, when 0.5 mmol of N-benzylideneaniline in 1.8 mL toluene was treated with 7 bars of H\textsubscript{2} in the presence of 1 (2.5 mol\%) at 120°C, the corresponding amine was observed by GC-MS and \textsuperscript{1}H NMR spectroscopy in up to 89% yield after 18 hours. Various substituted benzylideneaniline derivatives, with both electron donating and electron withdrawing groups on the phenyl ring, were also hydrogenated to their corresponding amines under similar conditions with high to excellent yields (Entries 2-6). Upon changing the R' group on nitrogen from phenyl to alkyl moieties, higher pressure is needed to obtain substantial conversion (Entries 7-10). Interestingly, N-benzylidene-t-butylamine was not amenable to hydrogenation under the reaction conditions, most probably due to the bulky tBu group (Entry 8). On the other hand, as the R' group was changed to a less bulky alkyl group (Me, Bn), hydrogenation to the corresponding amine products was observed (Entries 7 and 9). R' on carbon is not limited to aromatic substituents; while aldimines with aliphatic R' are relatively elusive, we also found that N-butylbenzylamine can be prepared from the corresponding imine, N-butyldienbenzylamine, in moderate yield with a somewhat longer reaction time (Entry 10). Finally with respect to imines, we demonstrate that 1 also catalyzes hydrogenation of a ketimine, specifically phenyl-(1-phenylethylidene)amine, in good yield (Entry 11).

While several main group metals exhibit activity for imine hydrogenation, homogeneous ketone hydrogenation by main group metals is exceptionally limited. Select examples exist requiring extremely high pressures,\textsuperscript{58,60,61} the use of additives\textsuperscript{60} or that exhibit narrow substrate scope.\textsuperscript{58,60,61} Thus, it is significant that we found that 1 can catalyze the hydrogenation of ketones with aromatic, aliphatic and mixed aromatic/aliphatic R and R' substituents under 65 bar of H\textsubscript{2} at 140°C. Specifically, benzophenone is hydrogenated to diphenylmethanol in up to 88% yield (Entry 12). Additionally, compound 1 catalyzes hydrogenation of 4-heptanone to 4-heptanol and propiophenone to 1-phenyl-1-propanol in good yield (Entries 13-14). With respect to green chemistry, utilizing zinc is inherently significant for these transformations, but also, it is important that (i) there is no need for any base or other additives and (ii) the process is 100% atom economical (as opposed to previously reported zinc reductions with hydrosilanes and hydroboranes).\textsuperscript{58,64}

Mechanistically, we propose a plausible cycle (Figure 4) accounting for the observations from the stoichiometric and catalytic experiments. In the first step, the arm of PNP\textsuperscript{tBu\textasteriskcentered}ZnMe (A), can open (B) allowing for the reversible activation of hydrogen by MLC to generate an aromatized zinc hydride intermediate (C). In the presence of imine or ketone, rather than decomposing, the zinc hydride can be trapped via an insertion pathway, generating the aromatized zinc amido or alkoxy complex (E) (vide supra, Scheme 2). Several pathways seem plausible for the insertion to proceed, but here we propose one concerted path (direct to E) and one stepwise path (via D, see Supporting Information). Insertion of imines or ketones into a zinc hydride bond has been previously proposed and observed.\textsuperscript{11,64} The aromatized zinc amido or alkoxy complex, per the stoichiometric experiments, can release product across the side arm

**Table 1. Hydrogenation of Imines and Ketones Catalyzed by 1**

| Entry | Product | Loading | Pressure | Temp | Time | Yield |
|-------|---------|---------|----------|------|------|-------|
| 1     |         | 2.5     | 7        | 120  | 18   | >95%  |
| 2     |         | 2.5     | 7        | 120  | 18   | 76%   |
| 3     |         | 2.5     | 7        | 120  | 18   | >95%  |
| 4     |         | 2.5     | 7        | 120  | 18   | 81%   |
| 5     |         | 2.5     | 7        | 120  | 18   | 93%   |
| 6     |         | 5       | 7        | 120  | 18   | >95%  |
| 7     |         | 5       | 30       | 120  | 18   | >95%  |
| 8     |         | 5       | 30       | 120  | 18   | 0%    |
| 9     |         | 5       | 30       | 120  | 18   | 74%   |
| 10    |         | 5       | 30       | 120  | 42   | 67%   |
| 11    |         | 5       | 30       | 120  | 42   | 79%   |
| 12    |         | 5       | 65       | 140  | 42   | 73-88%|
| 13    |         | 5       | 65       | 140  | 42   | 70%   |
| 14    |         | 5       | 65       | 140  | 42   | 80%   |

a) Standard Conditions: 0.5 mmol substrate, 1.8 mL toluene; % catalyst, H\textsubscript{2} pressure, temperature and time as specified b) Product confirmed by GC-MS c) Yield determined by \textsuperscript{1}H NMR spectroscopy of the crude reaction mixture with respect to mesitylene as an internal standard d) 3.6 mL of solvent used to improve substrate solubility e) no enantioselectivity observed f) Range for 3 independent trials
via MLC (through intermediate F), regenerating the dearomatized zinc methyl complex (A and B) to propagate the cycle. It is worth noting that the zinc amido or alkoxy intermediate (E) could also undergo sigma bond metathesis with hydrogen (a more typical mechanism for a main group metal) via a more energetically demanding pathway (vide infra), which would also be a productive route to regenerate (C).\(^{15}\)

DFT calculations at the \(\omega B97M-V/\text{def2-TZVPP} /\text{RIJCOSX/SMD}/\text{M06-L/def2-TZVP}/\text{GD3/W06}\) level of theory were performed on the model system (\(X = \text{Me}\); substrate = N-benzylideneaniline, 1 M standard states except \(H_2\); 7 atm) to provide insight into the plausibility of the proposed mechanism and to interrogate specifically whether product release via MLC (loss of amine from E to F to B) versus product release by hydrogenolysis (hydrogenation of E to C) is more favorable. In particular, computation indicates that the largest activation energy of the MLC pathway is the initial activation of hydrogen, which is overall 7.4 kcal/mol lower in energy than the highest energy barrier of the sigma bond metathesis pathway, which is the activation of hydrogen at the zinc amido complex (E to C; activation energy: 40.7 kcal/mol). Loss of amine via MLC has a barrier of 28.0 kcal/mol (E to F), which is 12.7 kcal/mol lower in energy than the hydrogenolysis product-forming step of the alternative mechanism. This difference supports the notion that both hydrogen activation and loss of amine through the MLC pathway is substantially more favorable than splitting hydrogen by sigma bond metathesis to generate product (see Supporting Information for full computational details).

To further probe these possible mechanisms, we also performed the hydrogenation experiments with zinc alkyl and amido species without the PNP\(^{16}\) ligand, which would be unable to proceed by a MLC pathway. Dimethylzinc alone shows no activity for imine hydrogenation under the standard conditions. Zinc bis(trimethylsilyl)amide, however, showed some activity across several experimental trials;\(^{16}\) however, a mercury test suppressed much of its activity for imine hydrogenation, and several trials of the same conditions led to variant results, leading us to believe that this activity is heterogeneous. Supporting this hypothesis, under the ketone hydrogenation conditions, zinc bis(trimethylsilyl)amide alone again gave varying results, and additionally suffers from selectivity problems (see Supporting Information). On the contrary, the presence of mercury had limited to no effect on the activity of I for both imine and ketone hydrogenation. Nonetheless, considering these computational and experimental findings, a contribution of the sigma bond metathesis pathway is unlikely but possible, and in addition, we can-
not rule out other possible outer sphere mechanisms or an FLP-like mechanism involving the labile arm, which was recently reported for a copper pincer complex.\textsuperscript{a}\textsuperscript{9} In that respect, it is interesting to note that the proposed pathway does not specifically imply the labile arm, indicating that PN complexes may also be suitable for such transformations.\textsuperscript{36,37}

Finally, with respect to the resting state and active catalytic species, we also note that during the course of the catalytic reaction, the zinc methyl moiety (denoted X in Figure 4) may be protonated with product (supported by the observation of the proposed complex, PN\textsuperscript{D~H}ZnNPhBn, in the equilibrium described above), especially as the concentration of amine or alcohol increases during the reaction. This substitution may or may not enhance the catalytic activity of the system. Indeed, monitoring the hydrogenation of 5 equivalents of N-benzylideneaniline in an NMR tube with 5 bar of hydrogen, in addition to free amine product, during the reaction we observed 1 with bound amine (6) and 7 in equilibrium as the major species, but also a species that may be the activation of the free imine across the side arm which forms initially (maximum observed concentration ca 30\%) and then decays as hydrogenation proceeds (depicted as G, but may be one of several isomers; See Supporting Information)\textsuperscript{40} and observable amounts of PN\textsuperscript{D~H}ZnNPhBn. Therefore, this finding, in conjunction with the aforementioned equilibrium experiment and Zn-H trapping experiment (outlined in Scheme 2) suggest that the formation of PN\textsuperscript{D~H}ZnNPhBn depends on the ratio of free amine to zinc complex in the system. We hypothesized that PN\textsuperscript{D~H}ZnNPhBn is likely also catalytically competent. In accordance, complex 4, prepared in situ from 3 and NaN(SiMe\textsubscript{3})\textsubscript{2}, is also active for imine and ketone hydrogenation. Regardless of the X substitution, in agreement with the computation, activation of hydrogen via MLC is likely the rate-determining step of the catalytic cycle. Further supporting this notion, we observe an approximate kinetically isotope effect of 1.71 when the model imine hydrogenation is performed in a high-pressure NMR tube with a mixture of H\textsubscript{2} and D\textsubscript{2} (See Supporting Information).

CONCLUSION

In conclusion, a series of dearmatized zinc pincer complexes supported by the PN\textsuperscript{D~H} ligand were prepared and characterized. The reactivity of PN\textsuperscript{D~H}ZnMe was explored, allowing for the unique observation of reversible N-H and H-H bond activation by MLC by a main group metal complex. Mechanistic studies indicate that hemilability of the phosphorus arms is key in allowing for this novel bond activation by zinc. Utilizing this zinc pincer system in catalysis, imines and ketones have been hydrogenated via a mechanism in which aromatization/dearomatization MLC was found to play a role in key steps of the catalytic cycle: H\textsubscript{2} activation and product release. Thus, leveraging MLC shows significant promise in advancing main group metal (de)hydrogenation catalysis. The study of further bond activations and catalytic applications of this system is currently underway, with the aim of broadening the capabilities of main group catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

General Information, Experimental Details, Computational Details (PDF)

X-Ray Data for Compounds 1-5 (ZIP/CIFs)

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Notes

The authors declare no competing financial interests.

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