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Highlight Review

Bifunctional Organometallic Catalysis and Reactivity Using Heterocyclic Phosphines and Metallated Heterocycles

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Abstract

Pyridyl- and imidazolylphosphines accelerate *anti*-Markovnikov alkyne hydration and alkene isomerization and deuteration by factors of 1000 to more than 10000. Evidence for proton transfer and hydrogen bonding in catalytic intermediates comes from computational, mechanistic, and structural studies. Related concepts are being applied to a novel class of protic N-heterocyclic carbene complexes which feature an unusual NH group.

♦ Introduction

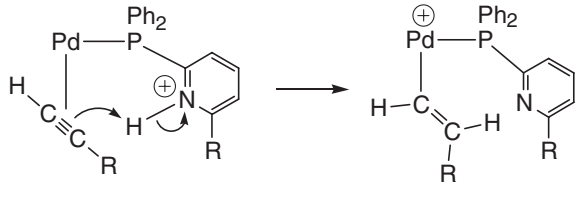
Improving catalysts and uncovering new mechanisms for catalysis could have a large practical impact in many areas, because it has been estimated that 35% of global gross domestic product depends on catalysis.[1] Our group has studied combining the ability of a transition metal to move electrons with ligands capable of proton transfer,[2,3] examples in the wider field of bifunctional catalysis.[4] Here we describe some fundamental studies of bifunctional catalysts and related complexes. Our starting point is phosphines bearing an imidazolyl or pyridyl group and the roles the basic nitrogen substituent can play, but we also consider imidazolyl–metal complexes as bifunctional organometallic fragments.

♦ Why Bifunctional Organometallic Catalysts?

Nature's enzymes are multifunctional, using several interactions in combination to accelerate reactions by factors of billions of times. Bifunctional organometallic catalysis seeks to improve reaction rates and selectivities by using not only the central transition metal, but also a pendant functional group on one (or more) ligands. Seminal examples include directed attack of nucleophiles on allyl–palladium intermediates (first reported in 1982 by Kumada[5]) and gold-templated aldol reactions (reported in 1986 by Ito, Sawamura, and Hayashi).[6] Famous subsequent examples are the transfer hydrogenation catalysts developed extensively by Noyori and co-workers,[7,8] and related Cp*M systems (M = Ru, Rh, and Ir).[9,10] These complexes appear to transfer hydrogen by a new, outer-sphere mechanism featuring cooperativity of a metal hydride M–H moiety and the N–H moiety of an amine ligand. Further studies by the Ikariya group showed the ability of the NH to deprotonate and activate various organic compounds.[11] Other notable cases are (a) the Shvo catalyst recently studied by Casey's group;[12,13] (b) Sigman's alcohol oxidation catalyst, for which he proposes alcohol binding involving proton transfer;[14,15] (c) nitrile hydration by $[Pt(L)_n(R_2P–OH)]$ complexes,[16–18] which are proposed to act by attack of the pendant hydroxy on coordinated and activated nitrile functionality; and (d) nitrile hydration by ruthenium hydride complexes, in which the hydride ligand may activate attacking water through hydrogen bonding.[19] In addition, there are a growing number of examples of bifunctional catalysis which are either strictly metal-free and organocatalytic, or which involve metals but probably not organometallic intermediates and changes in d-electron count: for some examples, see work of Shibasaki,[20] Lectka,[21] Whiting,[22] Maruoka,[23] and Saa.[24] Of course, this brief introduction cannot acknowledge all workers in the field of bifunctional catalysis; rather, it is the author's intent to convey some of the excitement and vibrancy of the field, as background for the following sections.

♦ Why Heterocyclic Phosphines?

Groundbreaking findings at Shell in the 1990s[25,26] showed that a pyrid-2-yl or 6-methylpyrid-2-yl phosphine significantly increased rate and selectivity for Pd-catalyzed methoxycarbonylation of propyne. As suggested in Scheme 1, a pyridinium species may be important in the catalytic cycle,[27,28] because a strong acid with weakly coordinating conjugate base (toluenesulfonic acid) was a necessary co-catalyst in this transformation. Despite the benefits of the novel use of pyridylphosphines noted above, until our work on imidazolyl- and pyridylphosphines there appeared to be no other reports of catalysis using these species. Instead, hundreds of pyridylphosphine complexes[29,30] and fewer imidazolylphosphine complexes (examples[31–38]) had been made for a variety of purposes other than catalysis.



Scheme 1. One proposed role for bifunctional heterocyclic phosphine.

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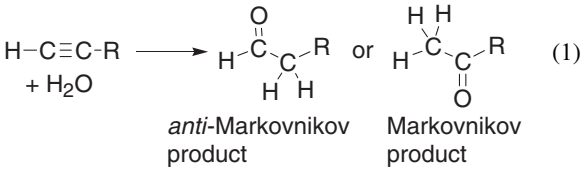
In addition to the work described above, since 2005, several notable reports of pyridylphosphine-enhanced catalysis from other labs have appeared, including in situ *anti*-Markovnikov alkyne hydration catalysts,[39] elegant applications of alkyne hydration to selective organic synthesis,[40–42] and enhanced nitrile hydration.[43] Here, hydrogen bonding or proton transfer in catalysis using heterocyclic phosphines and their complexes will be the focus.

♦ *Anti-Markovnikov Hydration of Alkynes to Make Aldehydes*

Catalyzed *anti*-Markovnikov alkyne hydration (eq 1) was completely unknown until the pioneering 1998 report by Tokunaga and Wakatsuki,[44] in which (arene)$RuCl_2$(phosphine) complexes were shown to either give Markovnikov or *anti*-Markovnikov selectivity, depending on which phosphine (and to some extent how much phosphine) was used. Even with the optimal catalyst, typical ratios of *anti*-Markovnikov to Markovnikov products were about 10 to 1, reaching 24 and 67 to 1 in the two most favorable cases; moreover, phenylacetylene was not hydrated to an appreciable extent.



(1)

Although we had begun to examine potential ligands for bifunctional catalysis in other contexts,[2,45,46] Tokunaga and Wakatsuki's report inspired us to examine the intriguing and challenging reaction of an alkyne and water, the prototypical polar reactant.

The Tokunaga and Wakatsuki team identified arene loss from (arene)$RuCl_2$(phosphine) early in the catalytic reaction, and like us, decided to focus on what should be more robust Cp analogs. However, they discovered[47] and solved a serious problem: the simple complex $CpRu(PPh_3)_2Cl$ as a catalyst suffered significant phosphine loss accompanied by inactivation through formation of $CpRu(PPh_3)Cl(CO)$. Preventing phosphine loss by using chelating or small phosphines led to use of **1**,[47] which as reported in 2001, afforded more than 90% yields of aldehydes uncontaminated by isomeric ketones, within 12 h at 100 °C.

Our alternative approach to overcoming the limitations of $CpRu(PPh_3)_2Cl$ was to increase the rate of attack on putative vinylidene intermediates by water (structure **A**, Figure 1), with the use of imidazolyl- or pyridylphosphines. Scheme 2 summarizes key relative rate data showing the benefits of heterocyclic phosphines. We compared complex **1**[47] which was the fastest and most selective catalyst for eq 1 with **2** and **3**;[3,48] unpublished data for aquo analog **4** show further improvement.

The *anti*-Markovnikov hydration of alkynes is clearly a multistep process, whether performed by traditional[49] or bifunctional catalysts. For many years, it was assumed that a key step in the process was movement of the terminal alkyne hydrogen in making a vinylidene intermediate. However, in 2001, Tokunaga and Wakatsuki gave compelling evidence inconsistent with this pathway, and proposed an intriguing alternative.[49] We have an ongoing program studying the mechanism of bifunctional catalysis, parts of which have already been reported.[48,50–53]

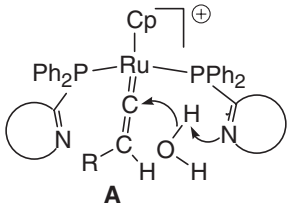
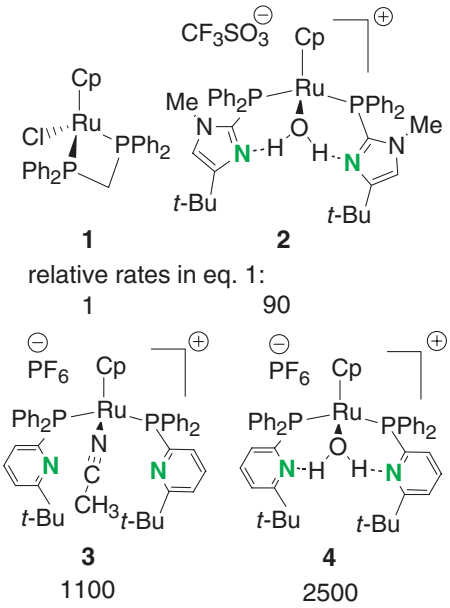


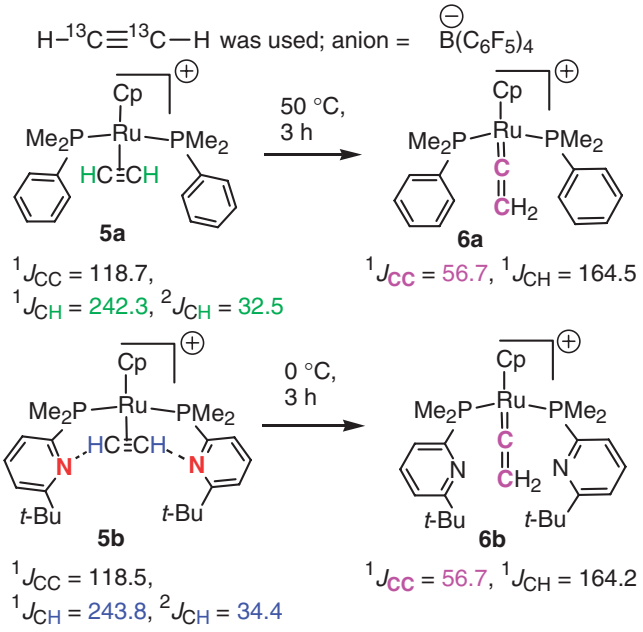
Figure 1.



Scheme 2. Relative rates of catalysts for *anti*-Markovnikov hydration of 1-nonyne using 2 mol % catalyst in acetone at 70 °C.

Nitrile dissociation on the $CpRu^+$ fragment is dissociative,[54] so loss of nitrile from **3** or of water from **2** or **4** followed by alkyne coordination is the likely start of alkyne hydration. In 2008,[50] we identified an intermediate alkyne π-complex (**5b**, Scheme 3) and its hydrogen bonding, and determined that our bifunctional ligands clearly facilitate alkyne-to-vinylidene transformation, since the temperatures needed for this reaction are 50 to 90 °C lower when heterocyclic ligands are used (**5b** to **6b**) rather than ligands without a pendant base (**5a** to **6a**). Further experimental and computational work is in progress to define the roles of the heterocycle in lowering activation energies of various steps.

Typically we conduct reactions in NMR tubes, so that we can determine the resting state and fate of the catalyst. Using either **3** or **4**, NMR spectroscopy showed resonances for catalyst **3** (when starting from **3**), **4**, vinylidene complexes like **11** (Scheme 4), and a fourth, unidentified species in varying amounts depending on how much alkyne had already been consumed.[51] By using acetylene and only a slight excess of water at 0 °C for several hours, we were able to increase the proportion of the fourth species such that its yield (based on **4**) exceeded 90%, which allowed us to study it in detail. At room temperature or above, the fourth species is consumed, acetaldehyde is formed, and **4** is regenerated.



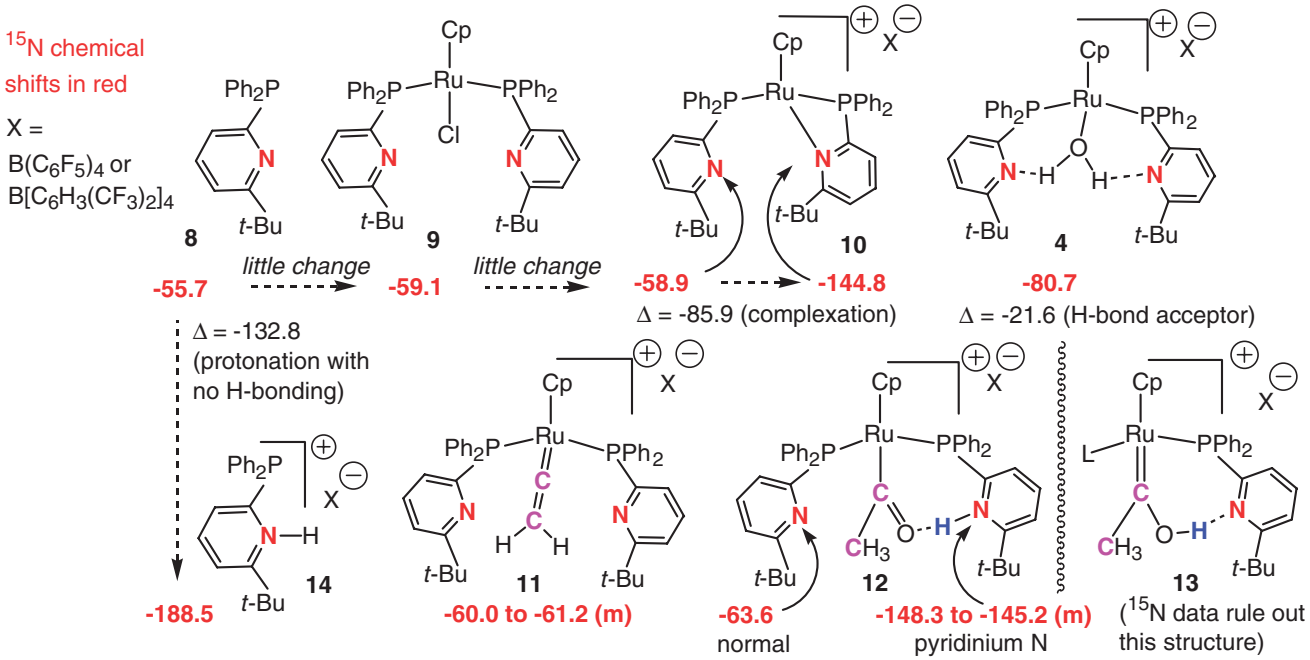
Scheme 3. Evidence for hydrogen bonding in intermediate alkyne π-complex: $^1J_{CC}$ and $^1J_{CH}$ are the same in vinylidene complexes **6a** and **6b**, showing same backbonding and same ligand electronics. In contrast, $^1J_{CH}$ and $^2J_{CH}$ are different in reactants **5a** and **5b**, which is not an effect of ligand electronics, rather of hydrogen bonding in **5b**.

To identify the new intermediate, we performed a series of experiments including ones with $H^{13}C^{13}CH$ and ^{15}N-labeled ligands as shown in Scheme 4. The data for the new intriguing intermediate are consistent with it being **12**, rather than its tautomer **13**. The difference between **12** and **13** is that **13** bears a hydroxycarbene ligand as hydrogen bond donor to one pyridyl substituent, whereas **12** features a pyridinium N–H as hydrogen bond donor to an acyl ligand. The pyridinium proton appeared as a very downfield ^1H resonance near 19 ppm. The acyl derived from $H^{13}C^{13}CH$ gave a downfield carbon resonance near 295 ppm and an upfield doublet at 51.4 ppm, with small C–C coupling (22.3 Hz) indicative of a single bond between the carbons. These data would fit either **12** or **13**; to decide which is the correct structure, ^{15}N NMR data[55] (Scheme 4) were necessary.

Before considering the effects of proton transfer or hydrogen bonding, it is useful to verify that changing bonding interactions or charge on atoms other than nitrogen have little effect. Indeed, it is very useful that the ^{15}N shift is almost insensitive to coordination at P (**8** to **9**), or ionization of a chloride ligand or presence of a π-acidic ligand, as seen by the chemical shift for the nonchelating ligands in **10** and **11**. In contrast, dramatic upfield shifts occur on coordination to a metal (chelating ligand in **10**) or N-protonation (model salt **14**), as seen for other metal–pyridine or –pyridinium species (for examples, see[56–59]).

The effects of hydrogen bonding or proton transfer in species **4** and **12** are clearly revealed by their ^{15}N NMR data. Hydrogen bonding in **4** is indicated by the fact that its ^{15}N chemical shift is 21.6 ppm upfield that of **9**. Turning to **12**-$(^{15}N)_2$, one ^{15}N resonance at −63.6 ppm reveals one pyridyl-phosphine ligand with no interaction at the nitrogen, whereas a second resonance centered at −146.7 ppm shows N-protonation rather than a nitrogen accepting hydrogen bond (**13**). Interestingly, these data had to be acquired at −100 °C to slow down a fluxional process involving transfer of the proton from one bifunctional ligand to another. Because the N-protonated nitrogen of **12** resonates near −146.7 ppm rather than near −188.5 ppm as in model pyridinium salt **14**, strong hydrogen bonding of the pyridinium N–H in **12** is proposed.

As added confirmation, the absolute value of the observed ^{15}N–H coupling constant for **12** (56.8 Hz) can be compared to that seen for model compound **14** in CD_2Cl_2 (92.3 Hz), which is not involved in hydrogen bonding.

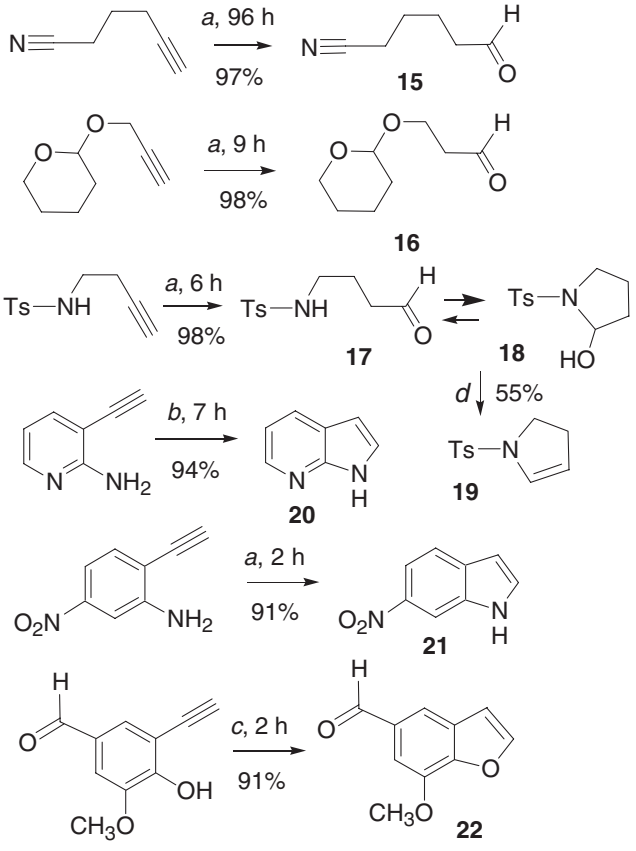


Scheme 4. ^{15}N chemical shifts are powerful tools for determining protonation and hydrogen bonding in **4** and **12**.

We now are using kinetics and theoretical calculations to probe the transition states between the spectroscopically observed species. As an example of the complexity of this endeavor, we find eight distinct reaction steps between water adding to the vinylidene ligand and acyl **12**. Significantly, each of the eight steps involves changes in hydrogen bonding or proton transfer,[60] showing the importance of the bifunctional ligands in this complex system.

♦ Use of Alkyne Hydration by (Heteroaryl)phosphine Complexes in Organic Synthesis

Selected examples of synthetically appealing alkyne hydrations are summarized in Scheme 5. We found that either acid-sensitive protecting groups (e.g., THP) or nitrile function are tolerated, allowing facile syntheses of **15** and **16**. A sulfonamide-substituted alkyne is readily hydrated, and the resulting equilibrium mixture containing mostly the aminal derivative **18** can be thermally dehydrated to produce cyclic enamine **19**. In more recent work,[61] we have applied **3** to a catalytic synthesis of both indoles and benzofurans, with representative syntheses of **20**–**22** shown. The closest approach to such versatility is shown by a Rh-based catalyst, and yet in that case efficient benzofuran synthesis required as much as 60 mol % of phosphine.[62] Hintermann's group has developed ways to make **3** and analogs in situ;[39] these catalysts have been used to make enantiomerically pure β-amino aldehyde derivatives,[41] as well as iterative approaches to both 1,3- and 1,4-polyalcohols.[40,42] Given the mild conditions for alkyne hydration, further applications to synthesis can be expected.



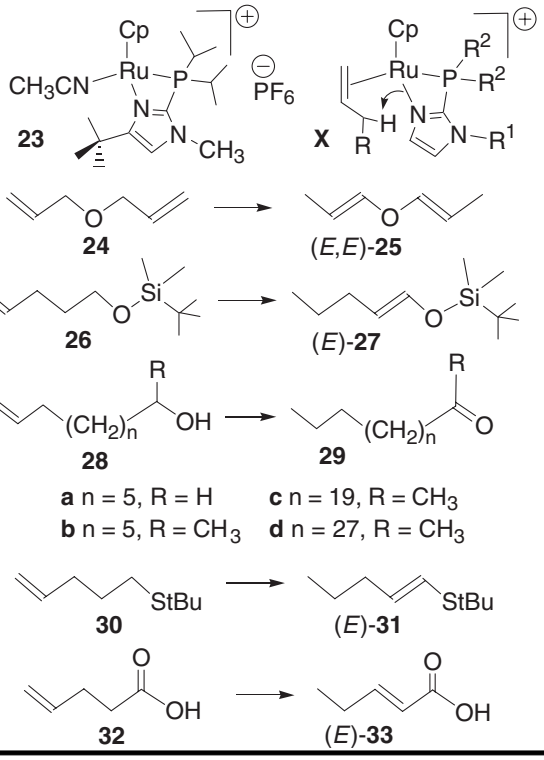
Scheme 5. Synthetic applications of alkyne hydration by bifunctional catalysts. Conditions: *a*, 2 mol % **3**, 5 equiv H_2O, acetone or acetone-d_6, 70 °C for the time indicated; *b*, same as *a* but without water and in dry THF-d_8; *c*, same as *a* but without water; *d*, toluene, no catalyst, reflux.

♦ Alkene Isomerization and Deuteration at Allylic Positions

Given the obvious importance of proton transfer in alkyne hydration, we considered alkene isomerization facilitated by a pendant heterocycle, as suggested by **X** (Table 1). After screening a variety of imidazolyl- and pyridylphosphines, complex **23** emerged as a superior catalyst[63,64] for a variety of reasons, including its ability to move an alkene over 30 positions on an unhindered carbon chain, and selectivity for forming and acting on (*E*)-substituted alkenes.

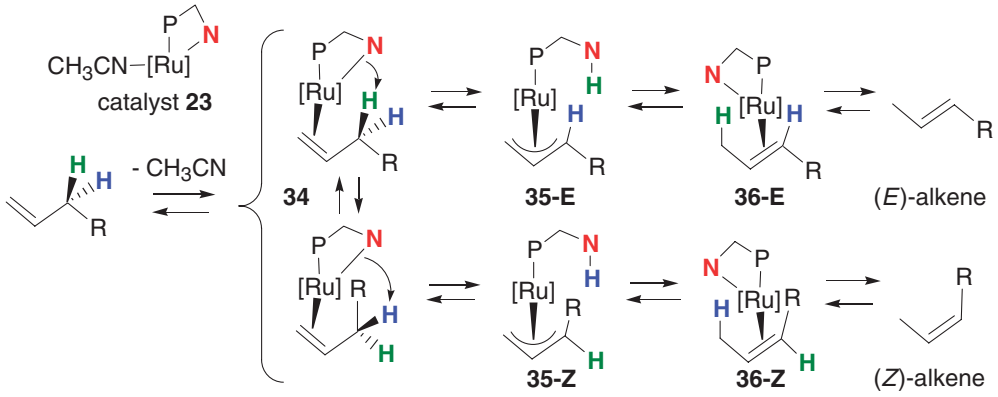
Catalyst **23** operates effectively between room temperature and 70 °C, where even the presence of a sulfide or carboxylic

Table 1. Examples of alkene isomerizations using **23**[a]



Entry	Reactant	Product	**23** /%	Temp /°C	Time /h	Yield /%
1	1-pentene	(*E*)-2-pentene	2	25	0.25	95
2	**24**	(*E*,*E*)-**25**	2	25	0.7	96
3	**26**	(*E*)-**27**	5	70	4	90
4	**28a**	**29a**	5	70	4	84
5	**28b**	**29b**	5	70	4	97
6	**28c**	**29c**	20	70	87	91[b]
7	**28d**	**29d**	30	70	72	81[b]
8	**30**	(*E*)-**31**	5	70	22	73
9	**32**	(*E*)-**33**	5	25	2	86

[a]Acetone-d_6 solvent; yields determined by ^{1}H NMR and internal standard unless otherwise indicated. [b]Isolated.



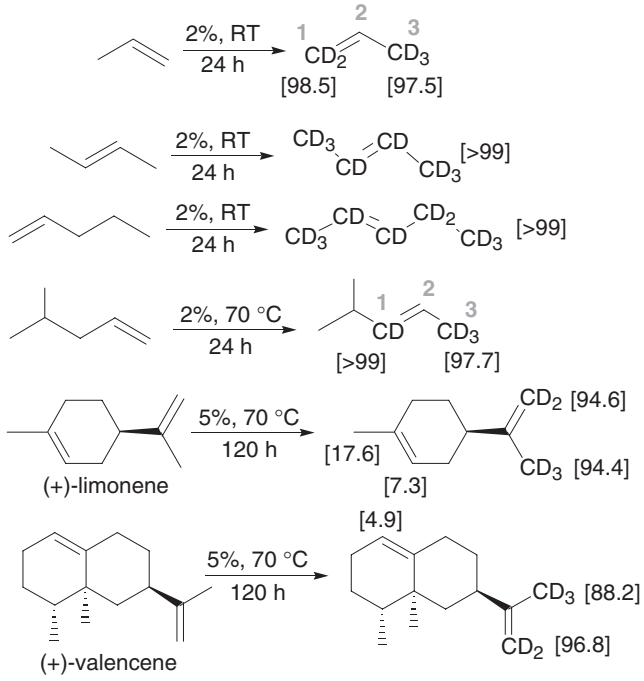
Scheme 6. Proposed mechanism of alkene isomerization by **23**.

acid are tolerated. Entries 6 and 7 indicate that significantly more catalyst and reaction time were needed, but in these cases the double bond was being moved 22 and 30 positions, respectively. The catalyst is likely performing a random walk up and down the chain, which would result in a great increase in time or catalyst needed.

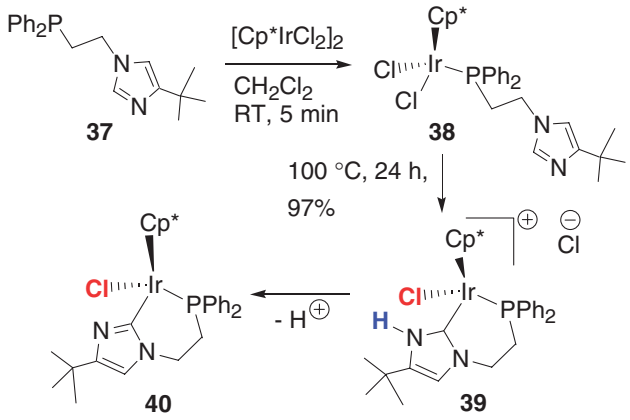
Our hypothesis (Scheme 6) for the mechanism by which **23** operates is based on several observations. First, adding ethylene to **23** gives one mole of free CH_3CN and a labile ethylene complex like **34**; surprisingly, the chelate remains intact. Larger nonpolar alkenes do not form detectable amounts of **34**, but we assume its presence given what was seen using ethylene. Proton transfer from either of the two diastereotopic allylic positions of **34** to the pendant base could give either **35-E** or **35-Z**. Diastereomer **35-Z** (with an endo-oriented alkyl substituent) is likely higher in energy than **35-E**. Moreover, the transition state between **34** and **35-Z** is likely higher in energy than the analogous transition state leading from **34** to **35-E**, thus explaining the high kinetic (*E*)-selectivity. Subsequent protonation by the imidazolium moiety at the other end of the allyl intermediate would generate an isomerized alkene ligand, which could dissociate. Calculations are underway to investigate this proposed process, with an eye to explaining the high kinetic selectivity.

Scheme 6 would predict H/D exchange and incorporation of deuterium in an alkene isomerization/deuteration process if D_2O were present. Most catalysts for H/D exchange are effective on arene and alkane C–H bonds,[65,66] rather than on alkene C–H positions. The smaller group of catalysts able to exchange at alkene C–H bonds usually do so with competing and poorly controlled alkene isomerization.[67–73] Hartwig's group recently reported an exceptional catalyst for exchange at vinylic positions, which does not isomerize alkenes.[73]

With such an extensive set of choices, it is rather surprising that none of these catalysts show selective H/D exchange at *allylic* positions. Therefore, we were pleasantly surprised[74] that **23** was very effective and selective in allylic H/D exchange. The results in Scheme 7 were obtained using sufficient D_2O to give 95% deuteration at accessible allylic positions. Propene is deuterated only at positions 1 and 3, in complete accord with Scheme 6. Longer alkenes such as 1-butene and 1-pentene however are completely deuterated and isomerized to form perdeuterated (*E*)-2-butene and (*E*)-2-pentene; here every position becomes allylic and exchangeable through isomerization up and down the chain. Useful steric control by branching impedes isomerization and hence also deuteration. The terpenes (+)-limonene and (+)-valencene both feature two double bonds, one within a ring and the other in an isopropenyl substituent, and our results[74] show that the latter can be fully pentadeuterated with little deuteration elsewhere. Thus, a variety of natural products containing an exocyclic isopropenyl group are expected to be selectively deuterated or even tritiated, affording standards for metabolism or pharmaceutical studies in a single, mild synthetic step.



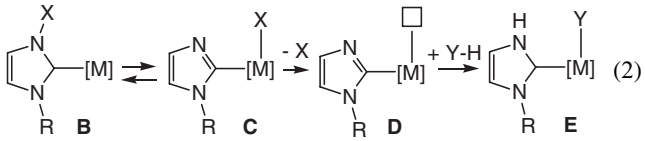
Scheme 7. Examples of selective and extensive alkene deuteration catalyzed by **23**.[74] Reactions were carried out in acetone-d_6 with enough D_2O so as to provide 20 D per exchangeable H present. The number in brackets indicates the percentage of the theoretical amount (95%) of deuterium at each position indicated. (*E*)-2-butene-d_8 was shown by ^{13}C NMR to be free of (*Z*)-isomer within limits of detection (10%).[74]



Scheme 8. Direct metallation of an imidazole at C-2 forming protic NHC complex **39**, and subsequent deprotonation to form conjugate base **40**.

♦ *Protic N-Heterocyclic Carbene Complexes and Metalated Heterocycles as Novel Bifunctional Species*

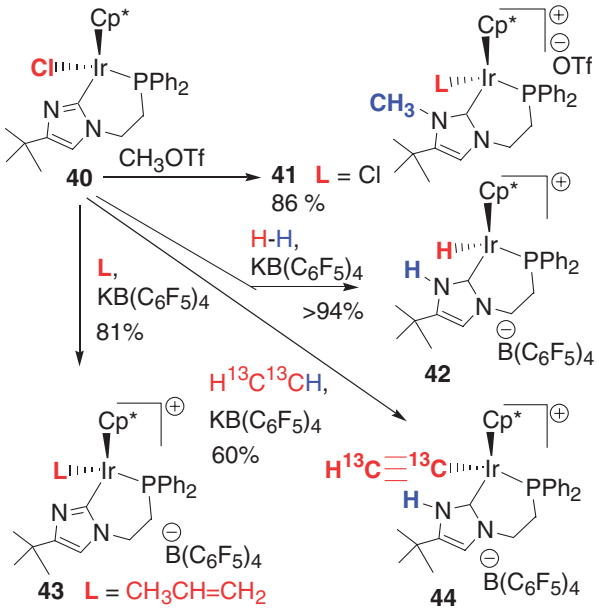
N-Heterocyclic carbene (NHC) complexes have become one of the most active and exciting areas of organometallic chemistry. The vast majority of reported NHC ligands are substituted at nitrogen(s) by alkyl, aryl, or other groups (structure **B**, X = R = alkyl or aryl) (eq 2). There are a few but increasing number of imidazole-derived NHC complexes bearing an NH (**B**, X = H), and a few cases of related NH-bearing carbenes derived from pyridines,[75] both of which may be aptly termed protic carbene derivatives. Little is known about the reactivity of protic NHC complexes containing an unusual free NH.



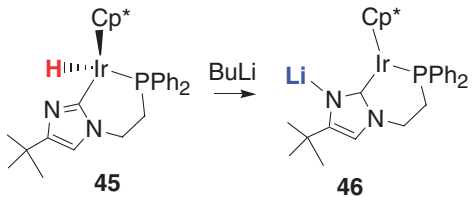
Given our research interests, we considered structure **B** (X = H) and its tautomer **C** with higher formal oxidation state at the metal. Ligand loss from **C** could form **D** with a vacant coordination site at the metal and a basic nitrogen in close proximity, which could facilitate breaking a bond, forming **E**. My group is actively researching a wide variety of complexes which allow us to conclude that structures **B**–**E** are indeed reasonable and interesting molecules with very useful properties. Here we illustrate some of our findings by focusing on derivatives of the Cp*Ir fragment (Scheme 8).[76]

Novel phosphine **37** readily coordinates through P to Ir at room temperature, and subsequent metallation at carbon is efficient at 100 °C. The resulting cationic complex can be readily deprotonated. Both **39** and its conjugate base **40** were successfully analyzed by X-ray diffraction; the structure of **40** showed a C2–Ir distance of 2.059(3) Å, whereas the same distance in **39** is shorter [2.026(2) Å], likely a reflection of the single Ir–C bond in **40** and the stronger Ir-carbene bond in **39**.

Ionization of the chloride ligand in **40** could allow formation of structure **D**, at least transiently. Adding CH_3OTf to imidazolyl complex **40** gave carbene **41** (Scheme 9), rather than formation of CH_3Cl. In contrast, chloride abstraction from **40** by $KB(C_6F_5)_4$ was observed, though not until other reactants were added. Propene coordinated to the metal, giving **43**. In the case of acetylene, the heterocyclic nitrogen acts as a base, forming acetylide carbene complex **44**, an example of **C** → **D** → **E**. Similarly, ionization of **40** in the presence of hydrogen led to heterolysis of the latter and formation of **42**.



Scheme 9. Results of treating imidazolyl complex **40** with ionizing reagents, including H–H and C–H activations.



Scheme 10. Conversion of Ir(III) species **45** into Ir(I) product **46**.

Treatment of a pale yellow solution of **45** (Scheme 10) with one equivalent of BuLi at room temperature gives a deep red solution. The single organometallic product is formulated as Ir(I) species **46** with a plane of symmetry because its ^1H and ^{13}C NMR spectra showed resonances for equivalent phenyl rings as well as only two signals for the $(CH_2)_2$ protons, even at −10 °C, whereas pseudotetrahedral complexes **39**–**44** showed more complex spectra. Conversion of **45** to **46** would be an example of transforming **C** to **B**, perhaps driven by the highly electropositive nature of X = Li in the latter species.

In summary, fundamental reactivity of NH-bearing NHC complex **39**, its conjugate base **40** and related species provide evidence for structures **B**–**E**. These results highlight new transformations made possible in an NHC complex by the presence of an NH group, as well as reactivity of the conjugate base at the free heterocyclic nitrogen.

♦ Summary

The role of pendant nitrogen-containing functional groups, whether as part of a heterocyclic phosphine, metallated heterocycle, or protic NHC complex, are examples of secondary interaction expected to expand the possibilities of organometallic chemistry and catalysis, with economic and societal benefits.

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55 A footnote in Table 2 of a recent article by the author[55a] gives the mistaken impression that the chemical shifts given are relative to formamide $\delta_N = 0$ when in fact they are relative to formamide $\delta_N = -267.8$. It should be emphasized that for ^{15}N NMR spectroscopy there is a wide variety of reference standards and even different assignment of positive and negative signs for chemical shift changes. Neat external CH_3NO_2 has been advocated as the most reliable standard;[55b] our data were acquired using a standard supplied by Varian (90% formamide in DMSO-d_6) and setting its observed chemical shift as -267.8 ppm, under which conditions the ^{15}N chemical shift of CH_3NO_2 would equal 0 ppm. a) D. B. Grotjahn, *Dalton Trans.* **2008**, 6497. b) J. Mason, L. F. Larkworthy, E. A. Moore, *Chem. Rev.* **2002**, *102*, 913.
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