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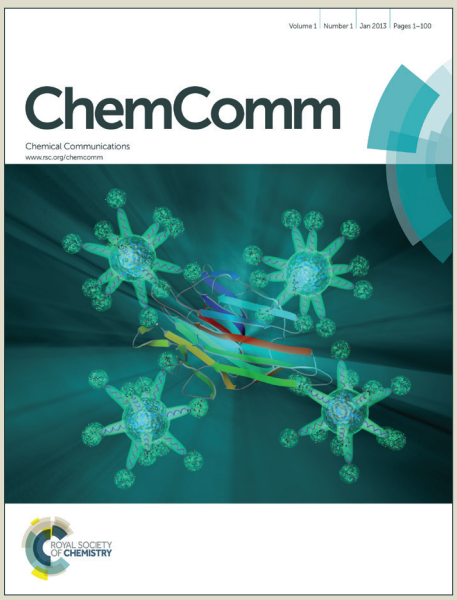

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FEATURE ARTICLE

Metal–ligand bifunctional reactivity and catalysis of protic N-heterocyclic carbene and pyrazole complexes featuring β-NH units

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Metal–ligand bifunctional cooperation has attracted much attention because it offers a powerful methodology to realize a number of highly efficient and selective catalysis. In this article, recent developments of the metal–ligand cooperative reactions of protic N-heterocyclic carbene (NHC) and pyrazole complexes bearing an acidic NH group at the position β to the metal are surveyed. Protic 2-pyridylidenes as related cooperating non-innocent ligands are also described.

1. Introduction

Metal–ligand bifunctional cooperation has been implicated in a number of catalysts including metalloenzymes in nature. The cooperating ligands therein impart superior substrate-activation and transformation ability as well as selectivity to the catalyst through non-covalent interactions such as hydrogen bonding. In [FeFe] hydrogenases, which catalyze reversible conversion of hydrogen gas into two protons and electrons, the bridging azadithiolato ligand serves as a Brønsted acid–base catalytic group to promote heterolytic cleavage of dihydrogen and proton relay involved in the catalysis (Fig. 1a).[1] Inspired by the prominent role of the amino group in the second coordination sphere, DuBois and co-workers developed metal–ligand bifunctional electrocatalysts for H_2 production and oxidation featuring uncoordinated amino groups, typified by the nickel complex shown in Fig. 1b.[2]

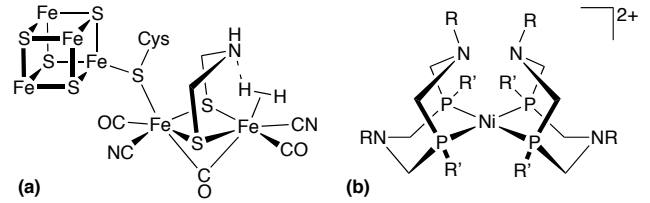
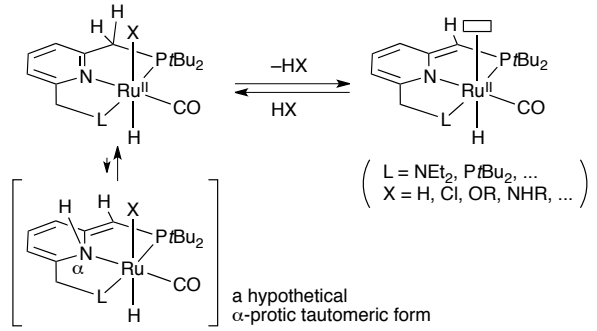
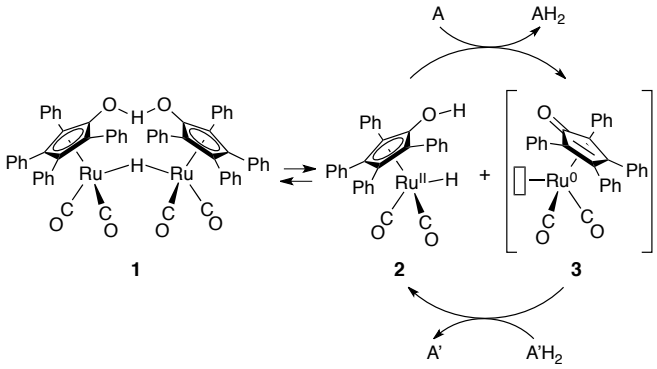


Fig. 1 (a) Active site of [FeFe] hydrogenase enzyme. (b) Metal–ligand bifunctional nickel complex that catalyzes electrochemical H_2 formation.

Provided that the remote cooperating ligand can tautomerize, at least formally, to an "α-protic" form where the Brønsted acidic hydrogen attaches to the donor atom in the position α to the metal, protonation/deprotonation of the cooperating unit in the second coordination sphere would be coupled with coordination/dissociation events on the metal center. For example, Milstein and co-workers demonstrated that a series of lutidine-based pincer-type complexes catalyze various hydrogenations and dehydrogenative transformations. These reactions are believed to proceed through addition and elimination of the substrates at the bifunctional platform containing the methylene group remote from the metal (Scheme 1),[3] as observed in the prototypical α-protic metal–amine bifunctional catalysts.[4] The hydroxycyclopentadienyl–hydrido Ru^{II} complex **2** derived from Shvo's catalyst **1** also undergoes reversible proton-coupled hydride transfer to the substrates, giving the coordinatively unsaturated cyclopentadienone Ru^0 species **3** as shown in Scheme 2.[5] It is to be noted that the interconversion, which leads to various transfer hydrogenation catalysis, involves formal redox of the metal and cooperating ligand in contrast to the corresponding transformation of the conventional metal–amine bifunctional catalysts as well as Milstein's catalyst. The bifunctional cooperation of a metal center and conjugated proton-responsive units placed at appropriate positions for substrate recognition, activation and transformation thus results in efficient and tunable catalysis owing to the structural diversity and electronic flexibility of the



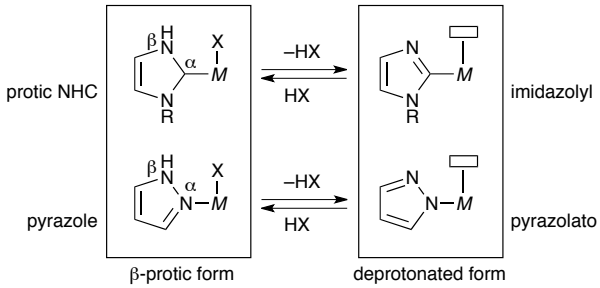
Scheme 1 Reversible deprotonation of the methylene group and metal–ligand bifunctional activation of substrates in Milstein's catalysts.



Scheme 2 Fragmentation of Shvo's catalyst **1** into a hydroxycyclopentadienyl–hydrido complex **2** and coordinatively unsaturated cyclopentadienone complex **3**, which are interconvertible with a hydrogen acceptor (A) and donor ($A'H_2$).

cooperating ligands.[6]

Among such bifunctional catalysts containing remote cooperating ligands, we focus here on the protic N-heterocyclic carbene (NHC)[7,8] and pyrazole[7,9,10] complexes featuring an NH group in the position β to the metal. The reasonable stability of the conjugate bases facilitates transfer of the nucleophilic group X to external substrates as well as the bifunctional activation of various pronucleophiles HX (Scheme 3). The metal–ligand cooperating reactivities and catalysis of these β-protic bifunctional complexes with different structures and Brønsted acidity will be described herein.



Scheme 3 β-Protic metal–ligand bifunctional catalysts and their reversible deprotonation.

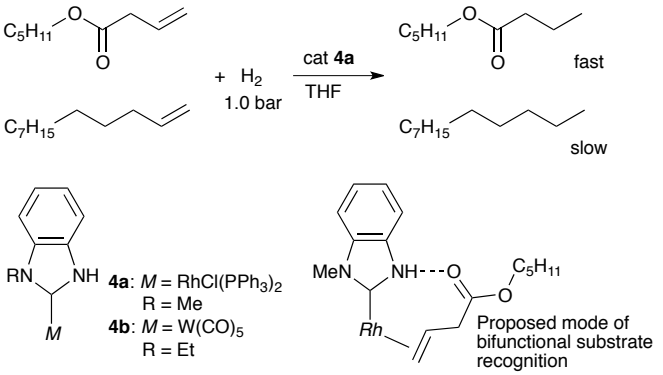
2. Protic NHC complexes

The NHCs have been used as auxiliary ligands in numerous homogeneous catalysts owing to their accessibility, robustness and σ-donating ability.[11] However, NHCs that have an NH-wingtip (protic NHC; also designated as NH-NHC, NR,NH-stabilized carbene, NH-functionalized NHC and so on) have been explored to a much less extent, at least partly because the protic NHCs are not generally obtained by simple deprotonation of the corresponding imidazolium salt with an acidic NH group and tend to isomerize to the corresponding imidazoles.[12] Protic NHC complexes thus have been synthesized as follows: (i) cyclization of isocyanides and amines on metal templates,[13] (ii) base/acid-promoted tautomerization of imidazole ligands, (iii) chelation-assisted formal tautomerization of imidazoles, (iv) oxidative addition of 2-haloimidazoles followed by N-protonation[14] and (v) deprotection of NH-masked NHC complexes. Readers can find the details in recent reviews.[7,8] In this article, we emphasize the metal–ligand bifunctional reactivity of protic NHC complexes.

2.1 Monodentate NHC complexes

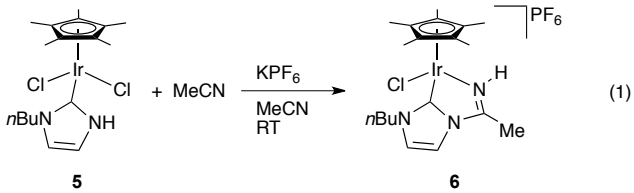
2.1.1 Substrate recognition and addition reaction

Hahn and co-workers demonstrated that the protic NHC complex **4a** catalyzes hydrogenation of an 3-butenoic acid ester more than two times faster than 1-dodecene.[15] The acceleration may be rationalized by the substrate recognition through a hydrogen bond between the protic NHC ligand and the carbonyl group of the alkenoic ester (Scheme 4). The ability of the NH group to form a hydrogen bond was evaluated by ^{1}H NMR titration experiments using the tungsten analogue **4b** and a urea derivative.



Scheme 4 Competitive hydrogenation of alkenes with/without a carbonyl group catalyzed by a protic NHC complex.

Chloride abstraction of the protic NHC complex **5** with KPF_6 in acetonitrile leads to *anti*-addition of the N–H bond to acetonitrile, giving the chelate imine complex **6** as shown in eqn. (1).[16] This transformation most likely occurs via a cationic acetonitrile complex, wherein the Lewis acidic iridium center activates the nitrile toward the intramolecular addition of the protic NHC ligand to the C≡N bond.[17]

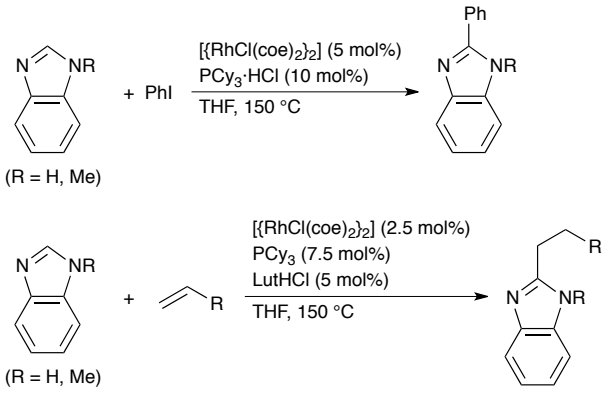


(1)

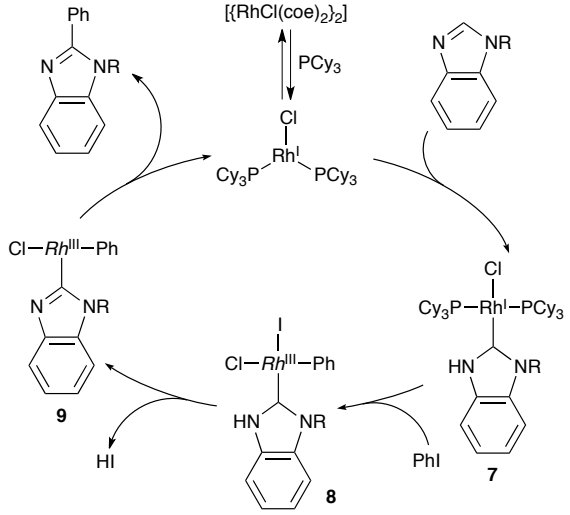
2.1.2 C–C bond formation

In the extensive work on Rh-catalyzed C–H bond functionalization of N-heterocycles,[18] Ellman, Bergman and co-workers described catalytic arylation[19] and alkylation[20] of imidazoles; typical examples are shown in Scheme 5. Scheme 6 illustrates a proposed mechanism of the catalytic arylation. Tautomerization of benzimidazole on the rhodium catalyst affords the protic NHC complex **7**, which has been

unambiguously characterized by an X-ray analysis (for R = Me). Complex **7** with the electron-donating NHC ligand then undergoes oxidative addition of iodobenzene. The Lewis acidic Rh^{III} center in the resultant complex **8** promotes deprotonation of the protic NHC ligand to give **9**, which yields the C-arylation product through reductive elimination. A related reaction of a six-membered dihydroquinazoline that proceeds via a protic NHC complex is also known.[21]



Scheme 5 Rh-catalyzed functionalization of benzimidazoles. coe = cyclooctene, LutHCl = 2,6-lutidinium chloride.



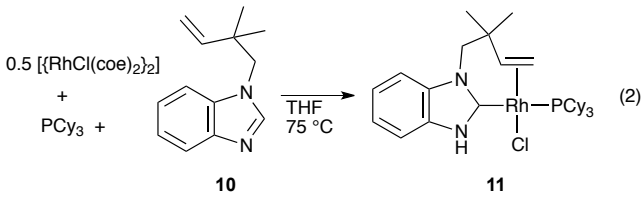
Scheme 6 A proposed mechanism for Rh-catalyzed arylation of benzimidazoles. *Rh* = $Rh(PCy_3)_n$.

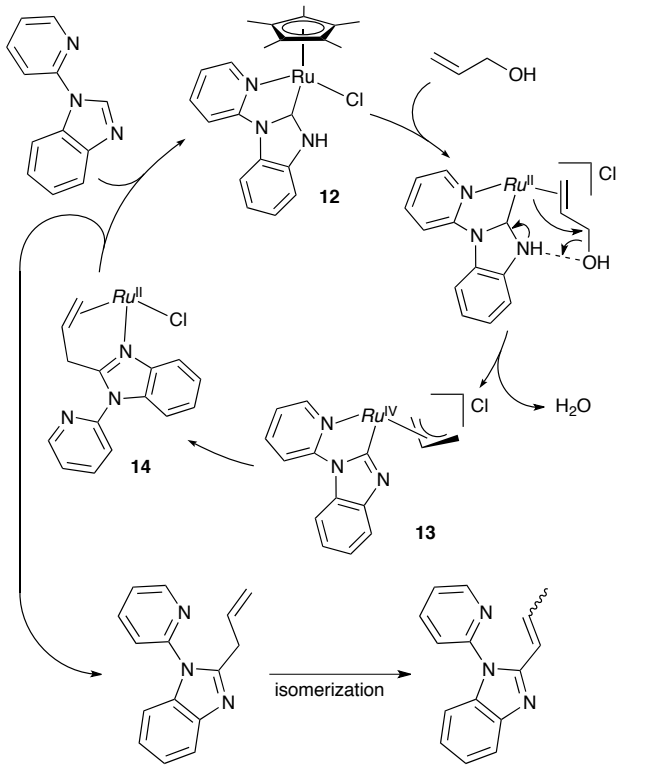
2.2. Chelate-stabilzed NHC complexes

The protic NHC ligand implicated in the catalysis shown in Scheme 5 originates in the substrate and is incorporated into the product. To expand the scope of the metal–ligand bifunctional catalysis of the protic NHC complexes, the cooperating ligand needs to be installed in the catalyst in advance and to be protected from dissociation. Chelate-stabilization of the protic NHC ligand offers a rational strategy for this purpose since such ligands are easily accessed by cyclometalation of imidazoles with appropriate anchoring groups.

2.2.1 C–C bond formation

Tan, Bergman and Ellman synthesized the chelation-stabilized protic NHC complex **11** through formal tautomerization of **10** on a rhodium complex as shown in eqn. (2).[22] They also demonstrated that **11** catalyzes cyclization of alkenyl-substituted imidazoles such as **10**, an intramolecular version of the reaction shown in Scheme 5,[22,23] in which the protic NHC ligand in **11** still comes from the substrate imidazole.





Scheme 7 A proposed mechanism for dehydrative coupling of pyridylbenzimidazole and allyl alcohol catalyzed by protic NHC complex **12**. *Ru* = Cp*Ru.

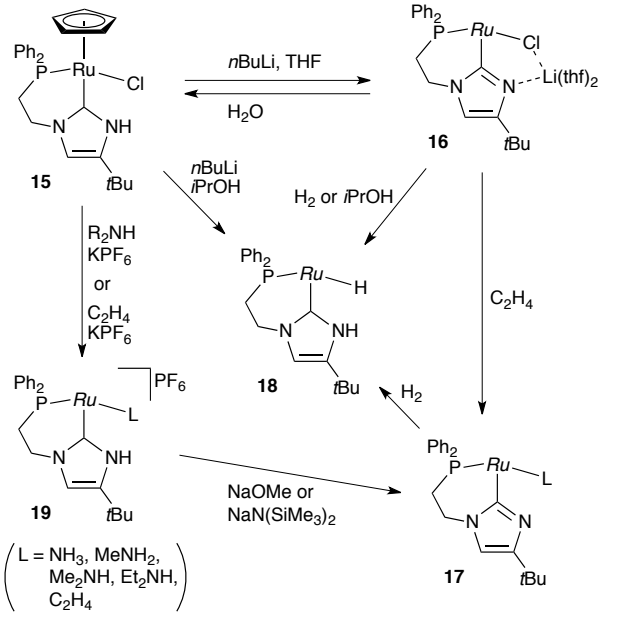
We have revealed the metal–ligand bifunctional cooperating reactivities of the C–N chelate protic NHC complex **12** prepared by cyclometalation of *N*-(2-pyridyl)benzimidazole. Complex **12** catalyzes dehydrative coupling of the benzimidazole and allyl alcohol.[24] The proposed mechanism is illustrated in Scheme 7. A two-point interaction between the protic NHC complex and the substrate would enables facile C–O bond cleavage of allyl alcohol to afford the π-allyl–imidazolyl Ru^{IV} species **13** under neutral conditions. In this dehydration step, the β-protic bifunctional complex **12** formally provides one proton and two electrons to the substrate. Reductive elimination easily occurs despite of the presence of the anchoring pyridyl group to yield the crystallographically

characterized 2-allylimidazole complex **14**. The involvment of **14** in the catalysis has been established by the facile formation of **14** in the reaction of **12** and allyl alcohol at room temperature. Replacement of the allylimidazole ligand in **14** by the pyridylimidazole substrate leads to tautomerization of the incoming imidazole to regenerate the protic NHC complex **12**.

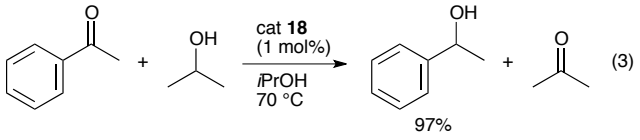
Proton migration from the NH unit in **12** to ligated substrates is also observed in the reaction of **12** and silver nitrite.[24] The resultant nitrosyl–imidazolyl complex undergoes reversible *N*-protonation to regenerate the protic NHC ligand. Structural changes of the imidazolyl ligand upon protonation have been scrutinized.[7,24]

2.2.2 H–H and H–X (X = O, C) bond cleavage

Grotjahn and co-workers reported the reactivities of the phosphine-tethered protic NHC ruthenium complexes as summarized in Scheme 8.[25] The protic NHC ligand in **15** is reversibly deprotonated with *n*-butyllithium or lithium diisopropylamide to afford the anionic imidazolyl complex **16**, which has been unambiguously characterized by an X-ray analysis as well as the ^{7}Li and ^{13}C NMR spectroscopy. Complex **16** can be regarded as a LiCl-masked coordinatively unsaturated imidazolyl complex. In fact, even ethylene instantaneously reacts with **16** to provide the imidazolyl–ethylene complex **17** (L = C_2H_4). The latent metal–ligand bifunctionality in **16** becomes more evident in the reactions with dihydrogen and 2-propanol, which result in heterolysis of H_2[26] and dehydrogenative oxidation of the alcohol to give the hydrido complex **18**. The hydrido complex is also obtainable in a one-pot reaction from **15**. In addition, the metal–ligand bifunctional hydrido complex **18** catalyzes transfer hydrogenation of acetophenone with 2-propanol in the absence of a base (eqn. (3)).

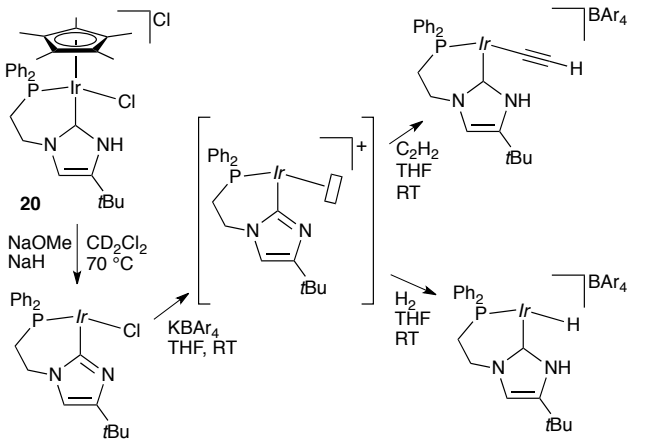


Scheme 8 Reactions of C–P chelate protic NHC ruthenium complexes. *Ru* = CpRu.

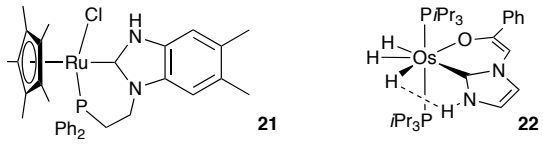


The reactions of **15** with protic amines as well as ethylene in the presence of hexafluorophosphate anion lead to the formation of a series of cationic complexes **19** (Scheme 8).[25] The protic NHC complexes **19** are converted to the imidazolyl complexes **17** upon treatment with a base. It is to be noted that the deprotonation occurs at the carbene site rather than the coordinated amine, indicating the stronger Brønsted acidity of the protic NHC ligand. The ^{15}N NMR study of the natural abundance samples using gHSQC technique revealed that deprotonation of the NH-wingtip results in significant downfield shift of the ^{15}N NMR signal.[25]

Stepwise dehydrochlorination of the isoelectronic iridium complex **20** shown in Scheme 9 also offers a bifunctional platform for heterolytic cleavage of dihydrogen as well as addition of acetylene.[27] The hydrogen bond between a related protic NHC ruthenium complex **21** and an external urea has been assessed by Hahn and co-workers.[28] Esteruelas and co-workers revealed the intramolecular dihydrogen bond between the protic NHC and hydrido ligands in the osmium complex **22** by an X-ray analysis.[29]



Scheme 9 Metal–ligand bifunctional reactions of protic NHC iridium complex **20**. *Ir* = Cp*Ir, BAr_4 = $B(C_6F_5)_4$.

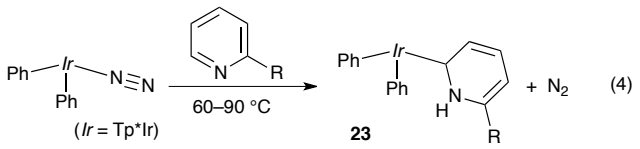


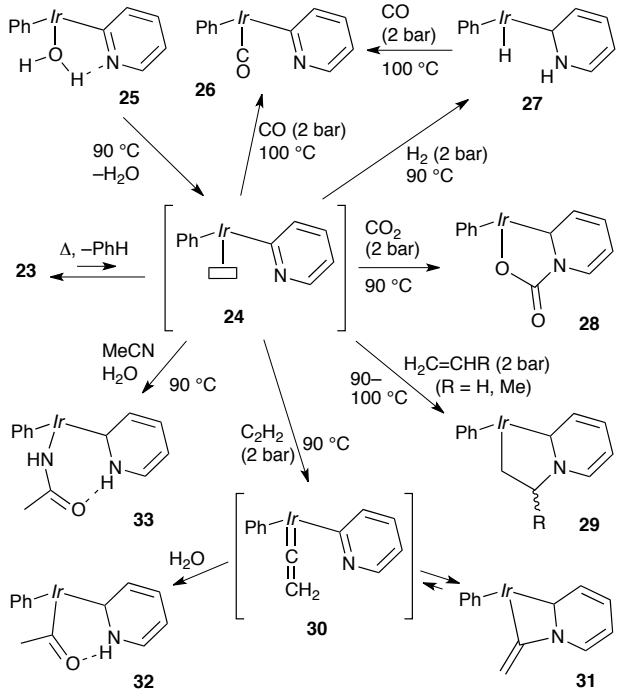
3. Pyridine-derived protic carbene complexes

Protic 2-pyridylidenes complexes[30] represent a subclass of β-protic NHC complexes. The synthesis have been achieved mainly through (i) formal tautomerization of pyridines on the metal center[31–37] and (ii) oxidative addition of 2-haloimidazoles followed by N-protonation.[38,39]

3.1 Reactions with H_2 and unsaturated molecules

Poveda, Carmona and co-workers demonstrated that the reaction of the dinitrogen complex [Tp*IrPh$_2$(N$_2$)] (Tp* = hydrotris(3,5-dimethylpyrazolyl)borato) with 2-substituted pyridines afford a series of protic 2-pyridylidene complexes **23** as shown in eqn. (4).[32,33] Theoretical calculations revealed that the tautomerization of pyridines most likely occurs through the σ-bond complex-assisted metathesis involving the phenyl ligand.[32] The parent 2-pyridylidene complex (R = H) can be obtained by alkaline hydrolysis of the trimethylsilyl derivative (R =SiMe$_3$).[32]

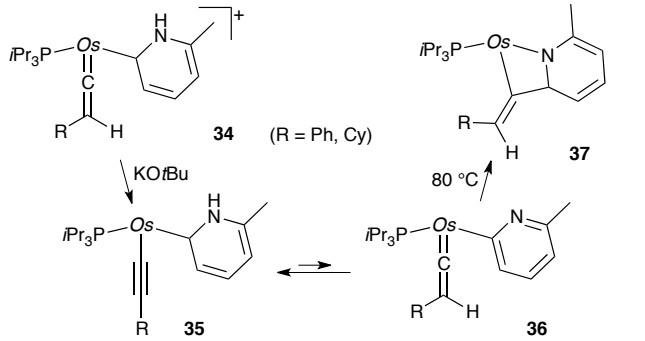




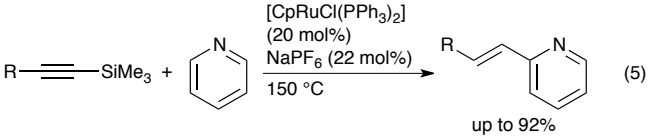
Scheme 10 Reactions of protic 2-pyridylidene iridium complex **23**. The 6-substituents on the pyridine ring are omitted. *Ir* = Tp*Ir.

When **23** is heated at 90 °C in C_6D_6, replacement of the phenyl ligands by C_6D_5 groups and deuteration of the NH unit take place.[32] This observation indicates that thermal elimination of benzene from **23** generates a coordinatively unsaturated pyridyl complex **24** (Scheme 10), which cleaves the C–D bond in the solvent C_6D_6 to give the deuterated **23**. In fact, **24** can be trapped as the carbonyl complex **26**.[40] Thermal liberation of water from the aqua (or hydroxo–pyridylidene) complex **25** also generates **24**, which subsequently reacts with benzene to give **23**.[32] The metal–ligand bifunctional platform in **24** undergoes additions of carbon dioxide and nonpolar alkenes to afford the iridacycles **28** and **29**, respectively.[40] The reaction of **23** with dihydrogen leads to heterolytic cleavage of H_2 on **24**,[26] giving the hydrido–carbene complex **27**.[40] Upon treatment with CO, this hydrido complex is converted to the carbonyl complex **26**, which may indicate the intermediacy of an η-H_2 complex in the H_2 heterolysis. Under strictly anhydrous conditions, **23** reacts with acetylene to provide an addition product **31** via intramolecular nucleophilic attack of the pyridyl ligand to the vinylidene moiety in the intermediate **30**, whilst attack of adventitious water to the vinylidene ligand yields the acyl complex **32**.[40] Similar hydration occurs in the reaction of **23** with acetonitrile and water, resulting in the formation of the acetamidato complex **33**.[40] The hydration appears to be aided by the neighboring Brønsted basic pyridyl ligand[41] because [Tp*IrPh$_2$(NCMe)] without the cooperating ligand does not react with water under the same conditions. The protic 2-pyridylidene ligand in related Tp*Ir complexes also undergo intramolecular C–N bond formation with the supporting phenyl,[42] alkyl[43] and diene[44] ligands.

As a part of their intensive study on protic 2-pyridylidene complexes,[34] Esteruelas and co-workers described C–C bond forming reactions on the protic carbene complex **34** obtained from tautomerization of 2-methylpyridine on [TpOs(P*i*Pr$_3$)(acetone)$_2$]BF$_4$ (Tp = hydrotris(pyrazolyl)borato) and a subsequent reaction with terminal alkynes (Scheme 11).[35] Deprotonation of **34** leads to the formation of an equilibrium mixture of the alkynyl–pyridylidene complex **35** and pyridyl–vinylidene complex **36**, the latter of which is converted to the 1,1-insertion product **37** instead of a C–N bond formation product as observed in a related Tp*Ir system (**31** in Scheme 10). Such a C–C bond forming step may be involved in the catalytic C–H functionalization of pyridines with alkynes exemplified by eqn. (5).[45] Berman, Bergman and Ellman proposed the involvement of a 2-pyridylidene complex in an Rh-catalyzed arylation of pyridines as the protic NHC complexes in the catalytic functionalization of imidazoles.[46]

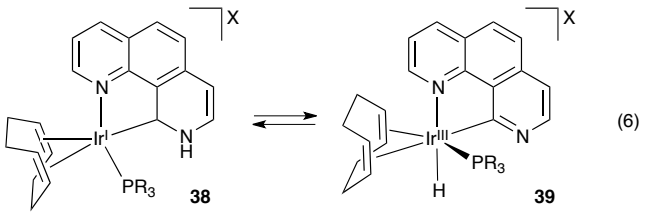


Scheme 11 C–C bond formation between protic 2-pyridylidene and acetylide ligands. *Os* = TpOs.

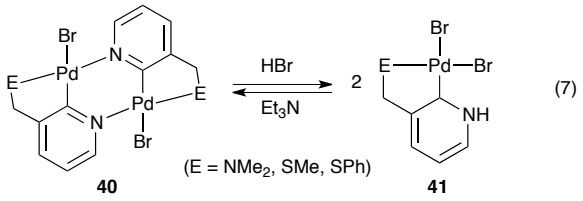


3.2 Reversible deprotonation

Chelation-assisted tautomerization of 2,3'-bipyridines and 1,9-phenanthrolines on $[Ir(cod)_2]BF_4$ yields a series of protic 2-pyridylidene complexes such as **38**.[36,37] These iridium(I) complexes are in equilibrium with the hydrido–pyridyl Ir^{III} complexes, represented by **39** (eqn. (6)). The equilibrium is significantly shifted to the protic 2-pyridylidene side by the counteranion X and solvent that can form a hydrogen bond with the NH group and thus stabilize the protic carbene ligand.[37,47] Similarly, Brønsted basic substituents at a appropriate position on the pyridine ring advantage the protic carbene isomer.[36,47] The 1,3-shift associated with formal redox of the metal center and umpolung of the hydrido ligand is accelerated by water, which participates in the proton transfer through a cyclic transition state.



Oxidative addition of 2-bromopyridines bearing nitrogen and sulfur donor tethers to $[Pd(dba)_2]$ (dba = dibenzylideneacetone) affords a series of dinuclear complexes **40**.[39] Subsequent protonation with HBr leads to the reversible formation of the protic 2-pyridylidene complexes **41** as shown in eqn. (7). Complexes **40** catalyze the Mizoroki–Heck reaction, although the catalysis appears heterogeneous on the basis of mechanistic studies.



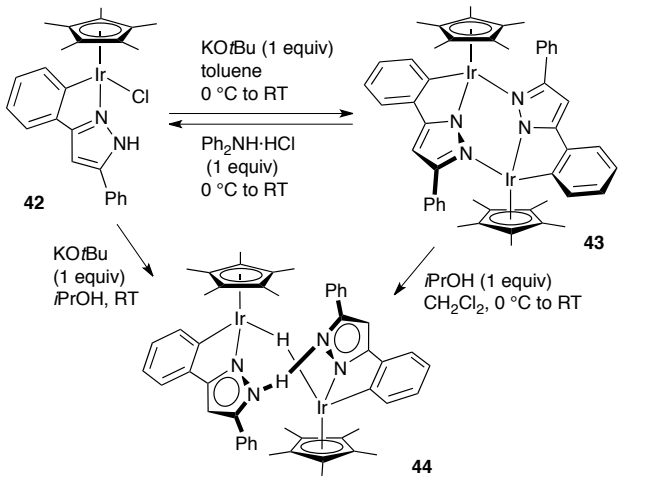
4. Protic pyrazole complexes

Having the structural similarity with the protic NHCs, protic pyrazoles provide the scaffolds for metal–ligand bifunctional cooperation.[48,49] In comparison with the protic NHCs, protic pyrazoles have an advantage of having no stable aprotic tautomer. The ease of the ligand synthesis and complexation allows more flexible design of the metal–ligand bifunctional platforms. In this section, we describe the metal–ligand cooperative reactions of the protic pyrazole complexes including those bearing two NH units in the second coordination sphere.

4.1 Mono(pyrazole) complexes

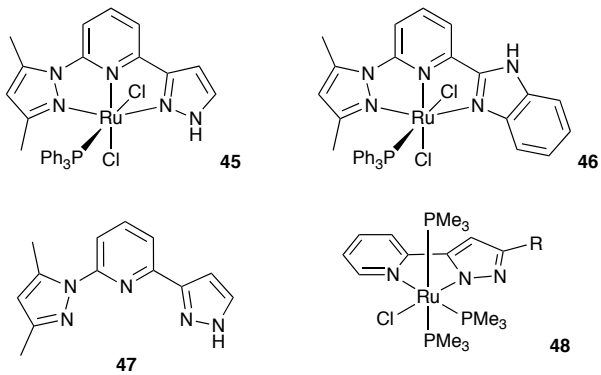
4.1.1 Deprotonation and hydrogen transfer

Given the proton-responsive nature of the N-unsubstituted pyrazole ligand,[7,50] coordinatively unsaturated pyrazolato complexes derived from the protic pyrazole complexes are expected to undergo hydrogenation and transfer hydrogenation through metal–ligand bifunctional cooperation as described in Schemes 8–10. We have demonstrated that the dehydrochlorination of the protic pyrazole complex **42** affords the pyrazolato-bridged dinuclear complex **43** in a reversible manner (Scheme 12).[51] The dimeric complex **43** is functionally equivalent to the expected coordinatively unsaturated mononuclear complex owing to the significant distortion of the pyrazolato bridge. In fact, transfer hydrogenation of **43** with 2-propanol smoothly takes place to produce the hydrido-bridged pyrazole–pyrazolato complex **44** whose structure is topologically related to Shvo's catalyst. This partially hydrogenated complex **44** is also obtained by dehydrochlorination of **42** in 2-propanol.

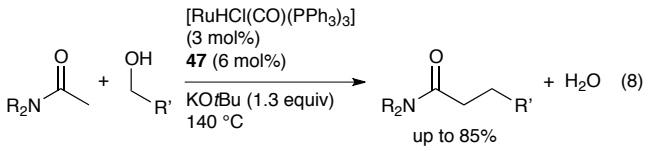


Scheme 12 Formation and transfer hydrogenation of pyrazolato complex **43**.

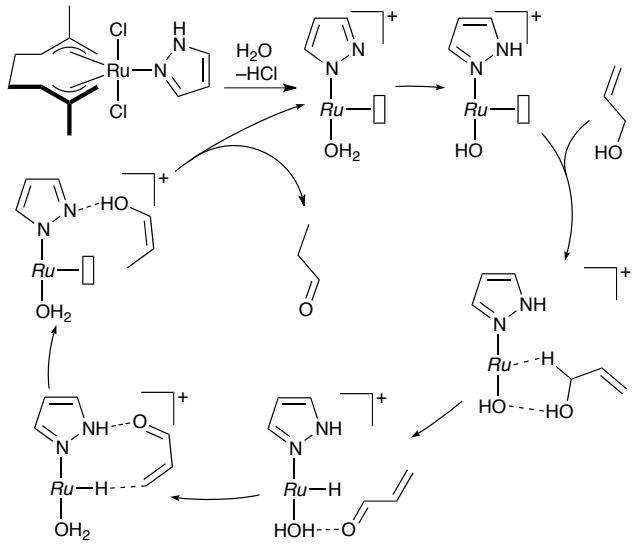
Yu and co-workers described catalytic transfer hydrogenation of ketones with pincer-type ruthenium complexes bearing a protic pyrazole arm such as **45**.[52] In this highly efficient catalysis, however, the NH unit does not appear to participate directly in substrate recognition and transformation because related imidazole complexes typified by **46** exhibit comparable catalytic activity despite that the NH unit lies at a more remote position γ to the metal.[53,54] The facile hydrogen transfer promoted by the protic pyrazole ligand **47** has also been applied to α-alkylation of amides with primary



alcohols shown in eqn. (8).[55] Thiel and co-workers disclosed that the N–N chelate pyridylpyrazolato complexes **48** catalyze transfer hydrogenation of acetophenone and hydrogenation of CO_2.[56] A mechanism without direct cooperation of the pyrazolato ligand has been proposed.



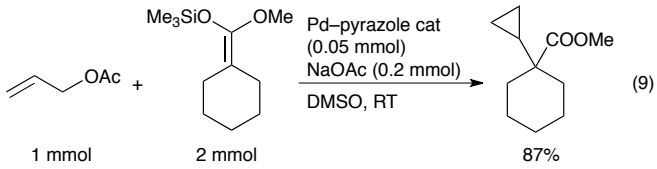
Gimeno, Lledós and co-workers have demonstrated that isomerization of allylic alcohols to carbonyl compounds is efficiently catalyzed by protic pyrazole Ru^{IV} complexes (Scheme 13).[57] The reaction occurs via bidirectional hydrogen transfer between the substrate and catalyst, which has been analyzed by DFT calculations. In the first half of the catalytic cycle, the hydroxo ligand derived from the water solvent participates in the hydrogen transfer. This step is also assisted by the pyrazolato ligand when the reaction is carried out in THF. On the other hand, the hydrogen transfer back to the substrate is achieved by the metal–pyrazole cooperation in both solvents. The same authors, however, also reported that a related γ-protic imidazole complex exhibits higher catalytic activity in water.[58]



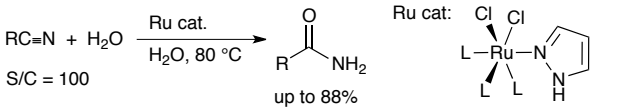
Scheme 13 A proposed mechanism for redox isomerization of allylic alcohols catalyzed by protic pyrazole complexes. Substituents on the pyrazole ligand and allylic alcohol are omitted. *Ru* = {bis(allyl)}Ru.

4.1.2 C–C and C–X (X = N, O, Si) bond formation

Some C–C bond forming reactions catalyzed by protic pyrazole complexes have been known. Satake and co-workers reported catalytic cyclopropanation of ketene silyl acetals with a cationic allyl–pyridylpyrazole Pd^{II} complex as shown in eqn. (9).[59] The active species is a deprotonated pyrazolato complex, and the secondary interactions of the β-NH unit with the substrates are not involved in the proposed mechanism. Protic pyrazole complexes and conjugate bases that catalyze the Mizoroki–Heck reaction,[60] Sonogashira reaction,[61] hydrosilylation of phenylacetylene[62] and oxidation of alkanes[63] are also reported.

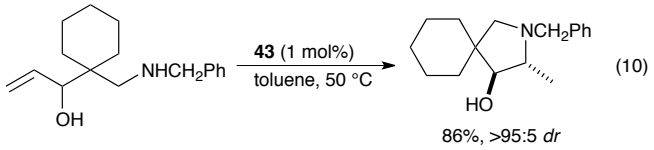


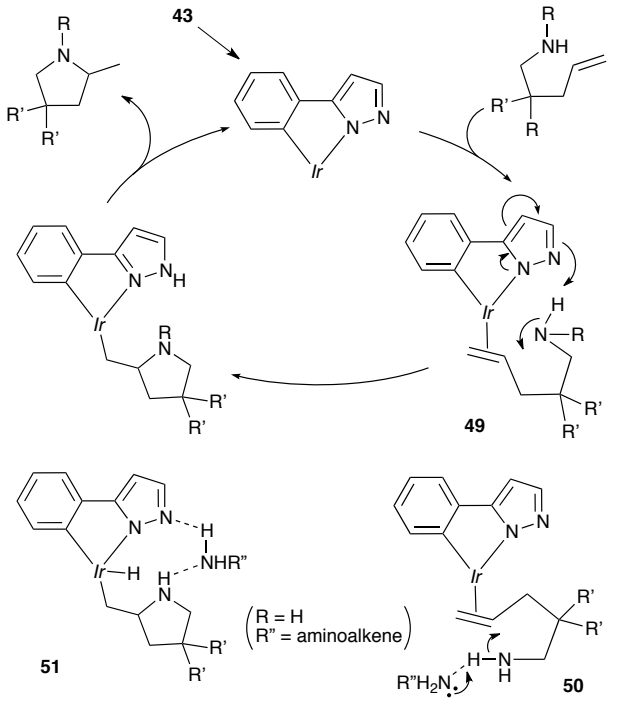
Nitriles undergo nucleophilic addition of pyrazoles in the coordination sphere to afford pyrazolylamidino complexes.[64] In addition, catalytic hydration of nitriles has been achieved by protic pyrazole complexes under neutral conditions (Scheme 14).[65] Although the detailed mechanism remains unclear, the catalysis may be explained by the metal–ligand bifunctional cooperation, wherein the Brønsted basic pyrazolato ligand activates the nucleophilic water molecule through hydrogen bonding.[41]



Scheme 14 Catalytic hydration of nitriles with protic pyrazole complex. L = Me_2SO.

The bifunctional nature of the protic pyrzole complexes would also be beneficial for simultaneous activation of two functional groups in one substrate molecule. We have disclosed that the iridium pyrazolato complex **43** catalyzes intramolecular cyclization of aminoalkenes as shown in eqn. (10).[51,66] This hydroamination reaction is tolerant of various functional groups such as ester, bromo, cyano and hydroxy groups. The catalyst is also applicable to less reactive aminoalkenes bearing a primary amino group or without *gem*-substituents on the linker chain. The low activity of *N*-methylated pyrazole complex as well as a related γ-protic imidazole complex indicates that the β-NH group is pivotal for the efficient catalysis. Scheme 15 illustrates a possible mechanism of the catalytic hydroamination. The olefin bond is activated by the Lewis acidic metal center toward nucleophilic attack of the amino group, which may be assisted by the hydrogen bond with the Brønsted basic pyrazolato ligand. The two-point interaction between the aminoalkenes and catalyst in **49** may rationalize the excellent catalytic activity and diastereoselectivity. Subsequent proton transfer from the pyrazole ligand would afford the cyclization product. An alternative mechanism, which features anti addition of the amino group (**50**) and rate-determining Ir–C bond protonolysis aided by a hydrogen bond network involving external protic amine molecules R"NH_2 (**51**), has also been proposed.[67]





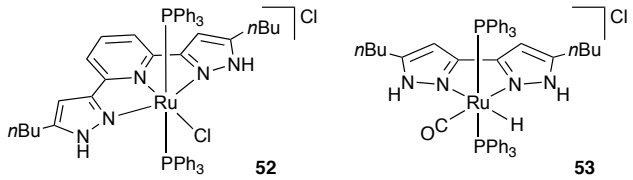
Scheme 15 A proposed mechanism for intramolecular hydroamination of aminoalkenes catalyzed pyrazolato iridium complex **43**. The phenyl group on the pyrazole ring is omitted. *Ir* = Cp*Ir.

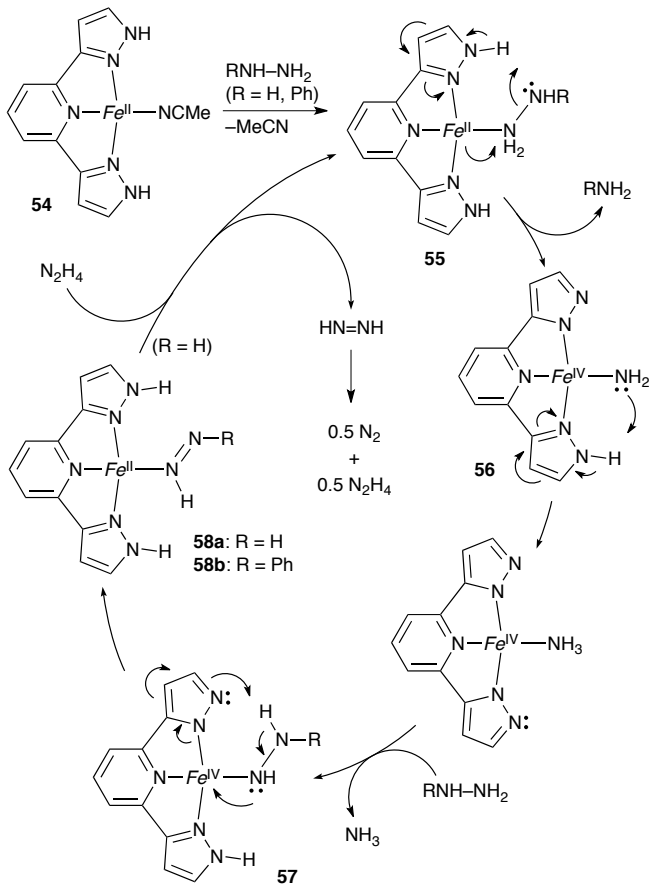
4.2 Bis(pyrazole) chelate complexes

The intriguing bifunctional reactivities of the protic pyrazole complexes described above prompted the exploration of poly(protic pyrazole) complexes bearing two or more NH groups, which would efficiently work in multipoint recognition of substrates and multiple proton transfer. In this context, the 2,6-di(1*H*-pyrazol-3-yl)pyridines are attractive components since this class of pincer-type ligands provides a unique metal–ligand multifunctional platform wherein the rigid chelate framework fixes the two coplanar β-NH units adjacent to a coordination site.[9,68]

4.2.1 Hydrogenation and polymerization catalysis

In the pioneering work, Thiel and co-workers revealed that the protic pincer-type bis(pyrazolyl)pyridine complex **52** along with the bis(pyrazole) complex **53** catalyzes hydrogenation and transfer hydrogenation of acetophenone.[69] As in the transfer hydrogenation with the related mono(pyrazole) complexes as well as bis(pyrazolyl)pyridine complexes,[70] however, cooperation of these NH units in the second coordination sphere has not been substantiated because an *N*-allylated derivative of **52** also exhibits comparable catalytic actvity.[71] Lang and co-workers described polymerization of methyl methacrylate[72] and ring-opening polymerization of ε-caprolactone[73] catalyzed by protic bis(pyrazolyl)pyridine copper and iron complexes. Application to Suzuki–Miyaura cross-coupling has also been reported.[74]





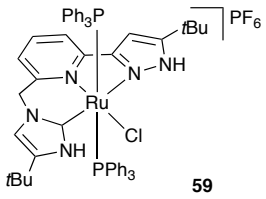
Scheme 16 A proposed mechanism for N–N bond cleavage of hydrazine catalyzed by protic bis(pyrazolyl)pyridine iron complex **54**. The total charges of the iron complexes (2+), triflate counteranions and tert-butyl groups in the pincer ligand have been omitted. *Fe* = $\{Fe(PMe_3)_2\}^{2+}$.

4.2.2 Multiple proton–electron transfer

We have recently described catalytic disproportionation of hydrazine to ammonia and dinitrogen promoted by the protic bis(pyrazolyl)pyrdine iron complex **54**.[75] Masking even one of the two β-NH units with a methyl group leads to a significant decrease in the catalytic activity, indicating that both of the two cooperating groups are indispensable. The proposed mechanism shown in Scheme 16 features multiple and bidirectional proton-coupled electron transfer (PCET) between the metal–ligand bifunctional platform and the substrate. A hydrogen bond between one of the β-NH unit and distal

nitrogen atom in the ligated hydrazine in **55** assists reductive N–N bond cleavage of hydrazine to give the $Fe^{IV}(NH_2)$ complex **56**. This step formally involves PCET from the bifunctional iron complex to the hydrazine. The remaining β-NH unit facilitates the substitution of the amido ligand by the second molecule of hydrazine to afford the hydrazido(1–) Fe^{IV} complex **57**. Subsequent PCET from the hydrazido ligand to the pyrazolato Fe^{IV} fragment leads to the formation of the Fe^{II} diazene complexes **58**. An X-ray analysis of the isolable phenyldiazene complex **58b** has revealed that the diazene ligand, a key catalytic intermediate, is stabilized by a hydrogen bonding network involving the two β-NH units and counteranions. Finally, the diazene ligand in **58a** liberates and disproportionates to dinitrogen and hydrazine.

We have also synthesized a pincer-type ruthenium complex **59** bearing both protic NHC and pyrazole arms.[76] Deprotonation of **59** afforded an NHC–pyrazolato complex, indicating that the pyrazole group is more acidic. The C_3-symmetric iron complex **60** has three protic pyrazole groups fixed by a hexadentate chelate ligand.[77] The NH units in the second coordination sphere are engaged in hydrogen bonds with the perchlorate counteranions.



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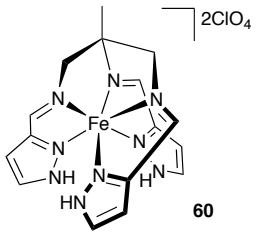

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5. Conclusion and perspective

Cooperation of the metals and NH functionality in the coordination sphere has been recognized as an attractive strategy for efficient catalysis. In α-protic amine complexes[4] the metal and NH group are in close proximity, whilst in β-protic NHC and pyrazole complexes the two functional groups are more separated yet electronically conjugated via π-electron systems, which allows the interplay between coordination and hydrogen bonds. A number of intriguing stoichiometic reactions of these β-protic complexes thus have been reported over the last decade. These findings also led to the development of the catalysis such as hydration of nitrile and intramolecular hydroamination along with simple hydrogenation and transfer hydrogenation. The direct cooperation of the β-NH unit to these catalysis is, however, not always evident. In some cases, N-alkylated derivatives and γ-protic imidazole analogues exhibit comparable or even better catalytic activity. More detailed mechanistic studies are obviously required to establish the bifunctional cooperative catalysis of the β-protic complexes. These studies should include quantitative assessment of the acidity of the NH units as well as the electron-donating ability of the proton-responsive N-heterocyclic ligands. The multiproton-responsive complex based on two or more β-protic moieties would also provide a promising research area. In particular, electron transfer triggered by multiple proton transfer from the β-NH units may facilitate transformation of chemically inert molecules such as carbon dioxide and dinitrogen.

Acknowledgements

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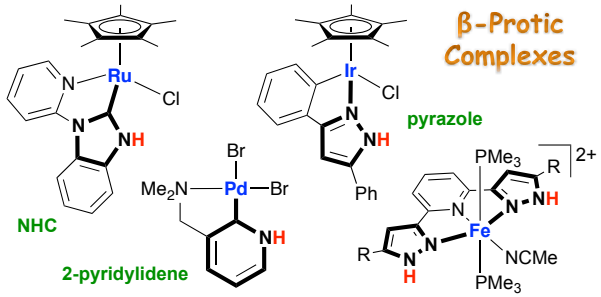
Table of contents entry:



The metal–ligand bifunctional cooperation of protic N-heterocyclic carbene and pyrazole complexes bearing an NH unit at the position β to the metal is surveyed.

Shigeki Kuwata was born in 1969 in Osaka, Japan. He received the Dr. Eng. degree from Department of Chemistry and Biotechnology at the University of Tokyo in 1997 under the supervision of Professors Masanobu Hidai and Yasushi Mizobe. Just after that, he was appointed as an Assistant Professor in the department. In 2002, he joined the Professor Ikariya's group at Tokyo Tech as an Associate Professor. He obtained Award for Young Scientists in Coordination Chemistry, Japan in 2002. His current research interests focus on the chemistry of "azametallics" featuring reactive metal–nitrogen units.

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