CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200902827

# Metal–Pyrazole Bifunction in Half-Sandwich C–N Chelate Iridium Complexes: Pyrazole–Pyrazolato Interconversion and Application to Catalytic Intramolecular Hydroamination of Aminoalkene

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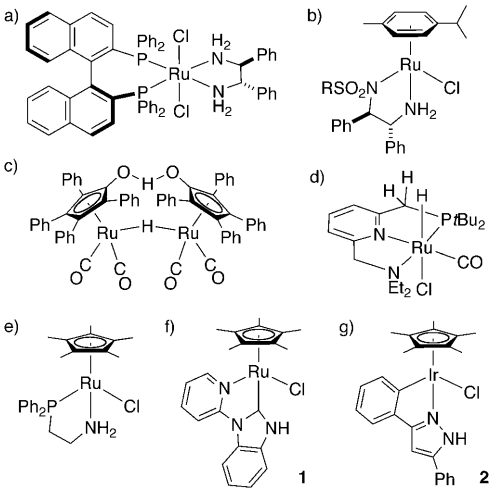
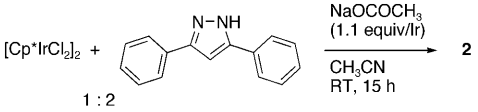
Metal–ligand bifunctional molecular catalysts, in which the ligand cooperates in the substrate binding and activation through secondary interactions, such as hydrogen bonding and proton transfer, have attracted increased attention in synthetic organic chemistry. Among the most successful examples are the Noyori's hydrogenation and Noyori and Ikariya's transfer-hydrogenation catalysts; these catalysts have chelate amine ligands to provide a protic NH group at the α-position to the metal (Scheme 1a,b).[1,2] The nitrogen ligand works as a hydrogen-bond donor to the substrate in the protonated amine form, and as an internal Brønsted base in the deprotonated amido form, to realize efficient catalytic reactions . Both amine and amido complexes are isolable in some cases, allowing for detailed mechanistic investigations. Shvo's catalyst[3] and Milstein's pincer-type complexes[4] (Scheme 1c,d) represent an additional class of bifunctional catalysts, in which an operationally protic group is situated at a place more distant from the metal. As an extension of our extensive studies on the bifunctional chelate amine complexes, such as Scheme 1b,e,[2,5,6] we recently synthesized a chelating N-heterocyclic carbene (NHC) complex, **1**, bearing a protic β-NH group and revealed facile C–O bond cleavage of allyl alcohol, which was ascribed to the metal–NH bifunction.[7] Still, bifunctional catalysis based on the β-NH group in ligated N-heteroaromatics remains in its infancy if compared with the α-NH analogues. For example, full characterization of interconvertible couples linked with the reversible addition of $H_2$ or pronucleophiles has rarely been achieved for the protic NHC complexes[7–9] and for the related, and more accessible, pyrazole-based chelate complexes.[10–12] We report here the C–N chelating protic pyrazole complex **2**, which is isoelectronic with **1**, as a new entry of β-NH-based bifunctional catalysts (Scheme 1g). The well-defined deprotonation–reprotonation network involving **2**, as well as catalytic hydroamination with **2** is described.[13]




Scheme 1. Examples of bifunctional transition metal catalysts with operationally protic ligands.

The chloro–pyrazole complex **2** was readily obtained by acetate-promoted cyclometalation[6,14] of 3,5-diphenylpyrazole [Eq. (1)]. The $^1$H NMR spectrum exhibits a low-field




(1)

NH singlet at $\delta = 11.58$ ppm, which disappears upon treatment with $D_2O$. The Brønsted acidity of the coordinated pyrazole in **2** was further indicated by X-ray analysis

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902827.

(Figure 1),[15] which revealed the presence of intermolecular hydrogen bonds between the pyrazole proton and the chloro ligand (Cl1···N1*, 3.215(7) Å) similar to those observed for complex **1**.[7]

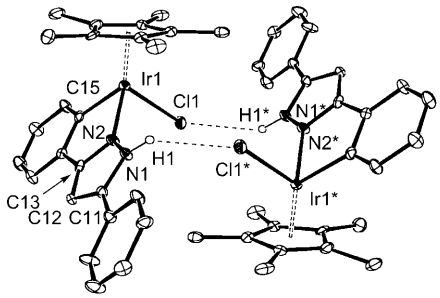
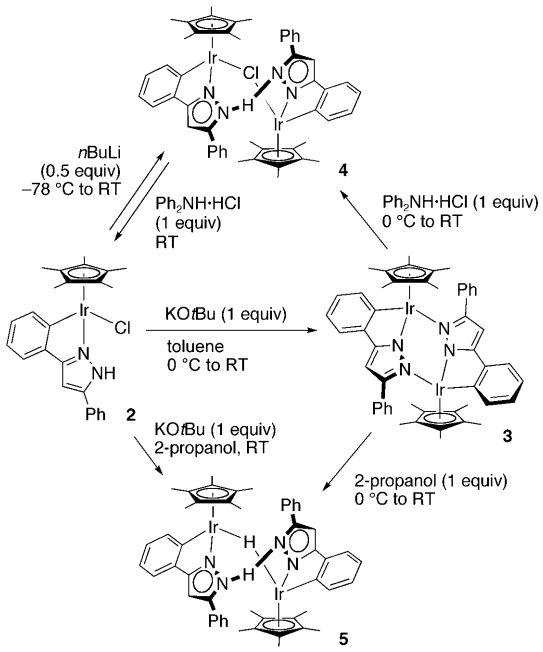



Figure 1. Dimeric structure of **2** connected with hydrogen bonds. Hydrogen atoms, except for the pyrazole proton, are omitted for clarity. Selected interatomic distances [Å]: Ir1–Cl1 2.417(2), Ir1–N2 2.065(7), N1–N2 1.363(9), Cl1–N1* 3.215(7), Cl1–H1* 2.495.

The chloro–pyrazole complex **2** underwent smooth dehydrochlorination with an equivalent amount of a base in toluene, similar to the C–N chelate amine complexes $[Cp^*IrCl(C_6H_4CR_2NH_2)]$ (R = Ph, $CH_3$), which contain an α-NH group.[6] Product **3** is a dimer of the expected 16-electron, coordinatively unsaturated pyrazolato complex, as shown in Scheme 2. The X-ray analysis of **3** revealed a pyrazolato-bridged dinuclear structure with a crystallographically imposed inversion center (Figure 2a).[15] The Ir-N-N-Ir linkage is significantly twisted with the torsion angle of 85.4(3)° to give the chair-form $Ir_2N_4$ six-membered ring. The Ir–N bond lengths outside the chelate ring (Ir1–N1*, 2.195(4) Å) are much longer than those in the chelate (Ir1–N2, 2.072(3) Å). The severe deviation from symmetric and planar μ-pyrazolato structures[17] is ascribed to the three-legged piano-stool configuration of the metal centers with the rigid chelate ligand.




Scheme 2. Interconversion between pyrazole and pyrazolato complexes.

When the chloro complex **2** was treated with only 0.5 equiv of base, partial dehydrochlorination took place to afford the chloro-bridged pyrazolato–pyrazole complex, **4**, exclusively (Scheme 2). Formally, **4** is an adduct of the saturated complex **2** and the coordinatively unsaturated dehydrochlorinated pyrazolato complex; however, electronic delocalization is suggested by the X-ray analysis of **4**, which revealed a symmetrical structure with an approximate $C_2$ axis passing through the bridging chloride and the midpoint of the two non-coordinated N atoms (Figure 2b).[15] Although the NH proton linking the two chelate ligands with a hydrogen bond[18] could not be found in the difference Fourier map, its presence is supported by the short N1–N3 distance of 2.736(10) Å as well as the $^1$H NMR spectrum of **4** at −90 °C, showing a broad singlet at $\delta = 16.04$ ppm.[19] A di-

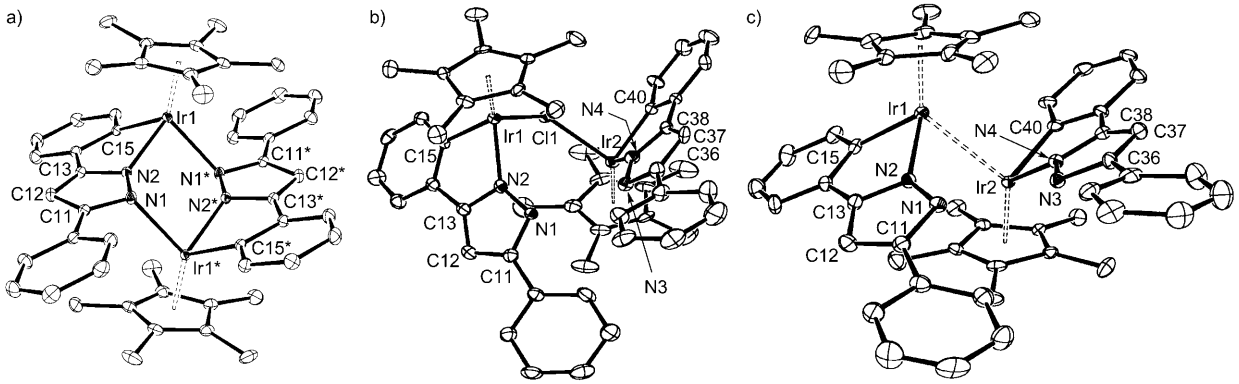



Figure 2. Structures of a) **3**, b) **4**, and c) **5**. Hydrogen atoms except for the pyrazole proton and bridging hydride are omitted for clarity. Selected interatomic distances [Å] for **3**: Ir1–N1* 2.195(4), Ir1–N2 2.072(3), N1–N2 1.374(4). For **4**: Ir1–Ir2 4.2737(5), Ir1–Cl1 2.419(2), Ir1–N2 2.095(9), Ir2–Cl1 2.427(2), Ir2–N4 2.084(7), N1–N2 1.365(12), N3–N4 1.383(11), N1–N3 2.736(10). For **5**: Ir1–Ir2 3.0372(2), Ir1–N2 2.080(5), Ir2–N4 2.084(6), N1–N2 1.352(8), N3–N4 1.359(8), N1–N3 2.799(7).

nuclear complex topologically related to **4**,[12a] and a mononuclear Cp*Ir complex[12b] bearing hydrogen-bonded pyrazolato and pyrazole ligands has been reported.

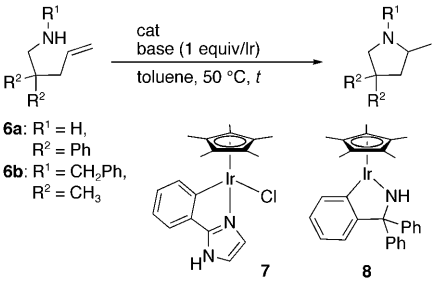
Notably, dehydrochlorination of **2** with base in 2-propanol as a hydrogen donor solvent resulted in the formation of the hydrido-bridged pyrazolato–pyrazole complex **5** (Scheme 2). The crystal structure shown in Figure 2c[15] closely resembles that of the chloro-bridged complex **4** except for the bridging hydrido ligand associated with the shorter Ir–Ir distance (3.0372(2) Å). The μ-hydride and hydrogen-bonded NH proton, which have not been located crystallographically but would lie on the approximate $C_2$ axis, give rise to high- and low-field resonances at $\delta = -19.75$ and 18.21 ppm in the $^1$H NMR spectrum at −50 °C.[19] The two Cp*Ir(C–N chelate) moieties are again equivalent in both $^1$H NMR and crystal-structure criteria.

The partially or fully deprotonated pyrazolato ligands in **3** and **4** were found to undergo reprotonation coupled with ligand coordination to the metal (Scheme 2). Stepwise addition of diphenylamine hydrochloride to the unsaturated pyrazolato dimer **3** sequentially afforded the chloro-bridged complex **4** and mononuclear chloro–pyrazole complex **2**. Complex **3** also reacts with 2-propanol to afford the hydrido-bridged complex **5**. The reactivities summarized in Scheme 2 are comparable to those found in the Shvo's complex,[3] as well as those of chelate amine complexes bearing an α-NH group.[1,2,20] It should be pointed out that the transformations in Scheme 2 are not associated with any formal redox of the metal center unlike the Shvo's catalyst.

Having established the protic pyrazole and basic pyrazolato interconversion linked to the metal-centered reactivities, we next applied the bifunctional nature of these complexes to the catalytic hydroamination of alkenes. The binary catalyst composed of an equimolar mixture of the chloro–pyrazole complex **2** and KO*t*Bu proved to promote intramolecular hydroamination of the ω-alkenic primary amine, **6a**, to give the cyclization product (Table 1). Yields as high as 98% were achieved after 15 h (entry 2), whereas the reaction rate significantly decreased in the absence of the external base (entry 3). As expected, the dehydrochlorinated pyrazolato dimer **3** catalyzed the reaction with almost the same efficiency as the binary catalyst (entry 4). The secondary amine **6b** was also quantitatively converted to the corresponding cyclic amine under the same conditions (entry 5). Notably complex **7**[21] bearing a γ-NH group, as well as the amido complex **8**,[6] have a much lower or no catalytic activity, suggesting that the catalysis is affected by the relative orientation of the metal and NH functionalities, as well as the ligand basicity (entries 6 and 7).

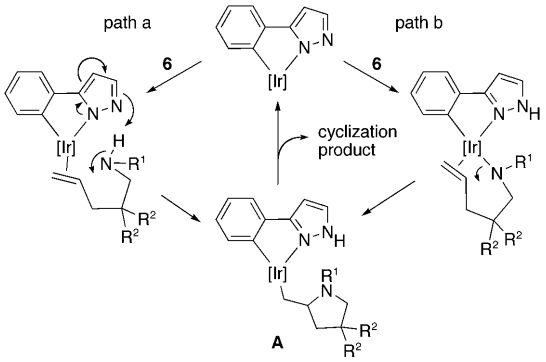
Hydroamination of alkenes and alkynes catalyzed by late transition metals provides an practical and atom-economical access to nitrogen-containing compounds with functional-group tolerance.[22] However, only a few successful examples of the addition of simple primary and secondary amines to unactivated alkenes have been reported.[23] For the catalytic hydroamination of alkene with late transition metals, mechanisms initiated by either olefin coordination or amine activation have been established.[22] Following the olefin activation mechanism, the reaction would involve the nucleophilic attack of the amine to the coordinated olefin, which is assisted by the secondary interaction with the basic pyrazolato ligand (Scheme 3, path a). Subsequent proton transfer from the pyrazole nitrogen in **A** would lead to Ir–C bond cleavage and the consequent release of the cyclization product. Whereas, initial addition of the amino group to form an amido–pyrazole intermediate in a bifunctional manner (path b) appears less plausible, because the next step would need an vacant site for olefin on the saturated metal center,[24] and hence require additional processes such as Cp* ring slippage. It is to be emphasized here that the β-nitrogen group in the bifunctional pyrazole/pyrazolato complexes should play significant roles in the present hydroamination regardless of which mechanism is operative.

Table 1. Intramolecular hydroamination catalyzed by C–N chelate complexes.[a]




| Entry | Substrate | Cat. | Base | $t$ [h] | Yield [%][b] |
|---|---|---|---|---|---|
| 1 | **6a** | **2** | KO*t*Bu | 6 | 75 |
| 2 | **6a** | **2** | KO*t*Bu | 15 | 98 |
| 3 | **6a** | **2** | none | 6 | 29 |
| 4 | **6a** | **3** | none | 15 | 96 |
| 5 | **6b** | **3** | none | 15 | 96 |
| 6 | **6a** | **7** | KO*t*Bu | 6 | 20 |
| 7 | **6a** | **8** | none | 15 | 0 |
| 8 | **6a** | none | KO*t*Bu | 6 | 0 |

[a] Reaction conditions: **6**:Ir = 20:1, [**6**] = 0.2 M. [b] Determined by $^1$H NMR spectroscopy.




Scheme 3. Possible mechanisms for cyclization of **6** catalyzed by pyrazolato complexes. [Ir] = Cp*Ir.

In summary, we have unequivocally characterized a series of pyrazole and pyrazolato complexes (**2**–**5**) with structural diversity and revealed their bifunctional addition–elimination chemistry, which is essential to realize the efficient catalysis. The intramolecular hydroamination of unactivated aminoalkenes catalyzed by **2** and **3** also suggested the importance of the acidic β-NH functionality. Further elucidation of the mechanism and substrate scope of the catalytic hydroamination is under way.

## Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 18065007, "Chemistry of Concerto Catalysis") from Ministry of Education, Culture, Sports, Science and Technology, Japan.

**Keywords:** catalysts · cooperative effects · hydrogen bonds · iridium · N ligands

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[13] Details of the syntheses and characterization are described in the Supporting Information.

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[15] Crystal data for **2**: $C_{25}H_{26}ClIrN_2$, $M_r=582.17$, crystal dimensions $0.2\times0.1\times0.1$ mm, monoclinic, $P2_1/n$, $a=8.4629(11)$ Å, $b=22.439(2)$ Å, $c=11.3728(11)$ Å, $\beta=93.830(5)°$, $V=2154.9(4)$ Å$^3$, $Z=4$, $\rho_{calcd}=1.794$ g cm$^{-3}$, $F_{000}=1136$, $\mu=6.351$ mm$^{-1}$, reflections measured 19706, independent reflections 4905, $R_{int}=0.081$, $R1=0.038$ [$I>2\sigma(I)$], $wR2=0.135$ (all data), residual electron density 2.38/−2.62 e Å$^{-3}$. For **3**: $C_{50}H_{50}Ir_2N_4$, $M_r=1091.41$, crystal dimensions $0.3\times0.2\times0.05$ mm, triclinic, $P\bar{1}$, $a=9.517(2)$ Å, $b=10.894(2)$ Å, $c=11.288(3)$ Å, $\alpha=65.774(6)°$, $\beta=89.253(9)°$, $\gamma=71.762(7)°$, $V=1004.5(4)$ Å$^3$, $Z=1$, $\rho_{calcd}=1.804$ g cm$^{-3}$, $F_{000}=532$, $\mu=6.677$ mm$^{-1}$, reflections measured 7463, independent reflections 4254, $R_{int}=0.030$, $R1=0.026$ [$I>2\sigma(I)$], $wR2=0.078$ (all data), residual electron density 1.24/−1.85 e Å$^{-3}$. For **4**: $C_{50}H_{51}ClIr_2N_4$, $M_r=1127.87$, crystal dimensions $0.3\times0.2\times0.1$ mm, triclinic, $P\bar{1}$, $a=10.812(3)$ Å, $b=13.866(4)$ Å, $c=14.830(4)$ Å, $\alpha=83.457(11)°$, $\beta=81.461(9)°$, $\gamma=74.813(8)°$, $V=2115.3(10)$ Å$^3$, $Z=2$, $\rho_{calcd}=1.771$ g cm$^{-3}$, $F_{000}=1100$, $\mu=6.406$ mm$^{-1}$, reflections measured 16730, independent reflections 9224, $R_{int}=0.052$, $R1=0.052$ [$I>2\sigma(I)$], $wR2=0.142$ (all data), residual electron density 2.91/−2.25 e Å$^{-3}$. For **5**·0.5$C_6H_{14}$: $C_{53}H_{59}Ir_2N_4$, $M_r=1136.52$, crystal dimensions $0.2\times0.2\times0.2$ mm, triclinic, $P\bar{1}$, $a=10.463(2)$ Å, $b=10.938(3)$ Å, $c=19.844(5)$ Å, $\alpha=87.060(6)°$, $\beta=84.563(6)°$, $\gamma=80.218(6)°$, $V=2226.3(9)$ Å$^3$, $Z=2$, $\rho_{calcd}=1.695$ g cm$^{-3}$, $F_{000}=1118$, $\mu=6.029$ mm$^{-1}$, reflections measured 17530, independent reflections 9689, $R_{int}=0.045$, $R1=0.037$ [$I>2\sigma(I)$], $wR2=0.112$ (all data), residual electron density 1.74/−1.24 e Å$^{-3}$. Data were collected at 193 K by using a Rigaku Saturn CCD area detector with graphite-monochromated $Mo_{K\alpha}$ radiation

  

($\lambda = 0.7107$ Å) to a maximum $2\theta$ value of 55°. Intensity data were corrected for Lorentz polarization effects and for absorption. Structure solution and refinements were performed with the CrystalStructure program package.[16] The structures were refined against $F^2$ with anisotropic temperature factors for all non-hydrogen atoms. The carbon atoms in the solvating *n*-hexane molecule in **5**·0.5$C_6H_{14}$ were refined with constraint geometries and fixed isotropic parameters. The hydrogen atoms except for the hydride and pyrazole hydrogen atoms in **4** and **5**·0.5 $C_6H_{14}$ were included in the refinements by using a riding model. CCDC-743358 (**2**), 743359 (**3**), 743360 (**4**), 743361 (**5**·0.5$C_6H_{14}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Received: October 29, 2009
Published online: November 27, 2009

  