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Facile N−H Bond Cleavage of Ammonia by an Iridium Complex Bearing a Noninnocent PNP-Pincer Type Phosphaalkene Ligand

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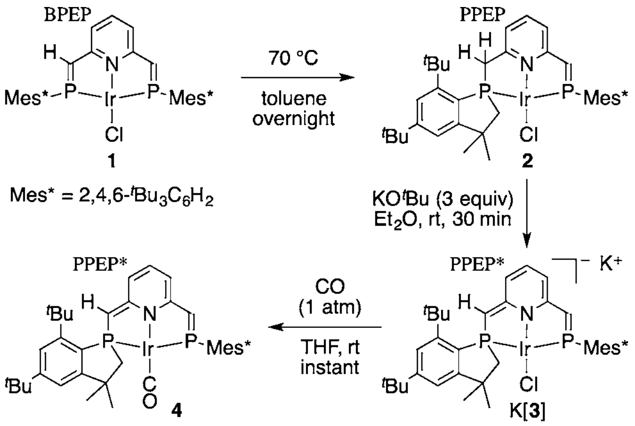
S *Supporting Information*

ABSTRACT: A novel PNP-pincer type phosphaalkene complex of iridium bearing a dearomatized pyridine unit (**3**) has been prepared. Complex **3** rapidly reacts with ammonia at room temperature to afford a parent amido complex in high yield. DFT calculations indicate that the phosphaalkene unit with a strong π-accepting property effectively facilitates the N−H bond cleavage of ammonia via metal−ligand cooperation.

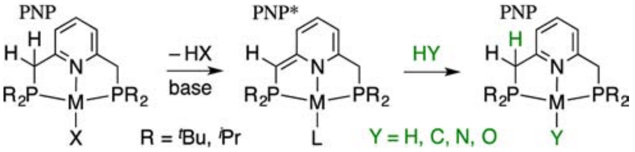
There has been continuous research interest in the catalytic conversion of inexpensive ammonia into higher-value nitrogen-containing compounds under mild conditions.[1] Although N−H bond cleavage by transition metal complexes may play a key role in such catalysis,[2] this process is not easily achieved with ammonia, mainly due to the preferential formation of ammine adducts.[1] In this context, complexes that undergo oxidative addition[3] or metathetical reactions with ammonia[4] have been investigated. In contrast, deprotonative N−H bond cleavage via metal−ligand cooperation, which may serve as an efficient route to parent amido complexes, remains almost unexplored.[5,6] Herein, we disclose that this novel bond activation process of ammonia readily proceeds with a PNP-pincer type phosphaalkene complex that exhibits noninnocent behavior (Scheme 1).

So far, PNP-pincer complexes have been studied for phosphine analogues.[6−8] In particular, Milstein et al. have nicely demonstrated that pyridine-based PNP complexes undergo deprotonation at the benzylic carbon to cause dearomatization of the pyridine ring (Scheme 2).[6,7] The dearomatized PNP* complex can cleave a variety of chemical bonds in a heterolytic manner, via metal−ligand cooperation accompanied by regeneration of the aromatic pyridine ring, where the metal center and the vinylic carbon serve as a Lewis acid and a Brønsted base, respectively. Recently, this bond activation process was tested for ammonia using [Ru(H)(CO)(PNP*)].[6a] Although the occurrence of N−H bond cleavage was indicated by deuterium-labeling experiments, the parent amido complex was not obtained.

Scheme 1. Synthesis of Dearomatized PNP-Pincer Complexes Containing a Phosphaalkene Unit



Scheme 2. Noninnocent Behavior of Pyridine-Based PNP-Pincer Ligands



In this study, we introduced a phosphaalkene unit into a dearomatized pincer system. Phosphaalkenes with a P═C double bond possess an extremely low-lying π^* orbital and, thus, exhibit strong π-accepting properties toward transition metals.[9−11] We expected that this particular ligand property would greatly enhance the Lewis acidity of the metal center, thereby facilitating the N−H bond cleavage of ammonia.

The desired complex **3** was synthesized in two steps from [IrCl(BPEP)] (**1**)[10d,12] (Scheme 1). Heating a toluene solution of **1** at 70 °C overnight formed unsymmetrical complex **2** quantitatively, via intramolecular C−H addition of a ^{t}Bu group to the P═C bond.[13] Treatment of **2** with ^{t}BuOK in Et$_2$O caused deprotonation at the benzylic position instantly, to afford the potassium salt of **3** (K[**3**]) with the dearomatized PPEP* ligand, which was isolated as [K(18-crown-6)][**3**] in 73% yield. The ^{31}P{^{1}H} NMR spectrum exhibited two sets of doublets at δ 234.6 and 18.9 ($^2J_{PP}$ = 463 Hz), assignable to

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phosphaalkene and phosphine units, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, a doublet due to the vinylic carbon appeared at δ 73.1 ($^1J_{PC}$ = 64 Hz). The vinylic proton signal was observed at δ 3.89 as a virtual triplet (J_{app} = 4.0 Hz) in the ^{1}H NMR spectrum. Furthermore, three signals due to the dearomatized pyridine ring protons appeared at δ 6.13, 6.03, and 5.93, respectively.[14]

Complex **3** reacted with CO (1 atm) at room temperature to form [Ir(CO)(PPEP*)] (**4**), which exhibited a ν_{CO} band at 1958 cm^{-1} in the IR spectrum. This wavenumber is clearly higher than that of [Ir(CO)(PNP*)] (ν_{CO} = 1932 cm^{-1}) and comparable to that of $[Ir(CO)(PNP)]^+$ as a cationic species (ν_{CO} = 1962 cm^{-1}).[7d] Hence, the electron-deficient nature of iridium was suggested.

The structures of [K(18-crown-6)][**3**] and **4** with a dearomatized pyridine ring were confirmed by X-ray diffraction analysis (Figure 1; see Figure S1 for **4**). Complex **3** adopts a square planar geometry around iridium. The iridium center is coordinated with PPEP* and Cl ligands, and the Cl ligand is further associated with a [K(18-crown-6)] ion. The Ir–Cl length (2.351(2) Å) is typical of dative bonding (2.313(1) Å for **1**).[10d] On the other hand, the Cl and K atoms are significantly distant from each other (2.930(3) Å), showing an electrostatic interaction between these atoms. Accordingly, the four-coordinate iridium complex **3** may be described as an anionic species.

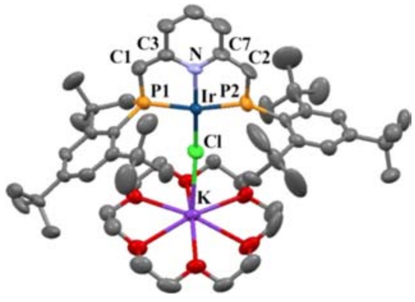


Figure 1. Molecular structure of [K(18-crown-6)][**3**] with 50% probability ellipsoids. Hydrogen atoms and disordered carbon atoms (^{t}Bu) are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir–P1 2.260(2), Ir–P2 2.206(2), Ir–N 2.056(5), Ir–Cl 2.351(2), Cl–K 2.930(3), P1–Ir–P2 164.38(9), N–Ir–Cl 173.88(18); see also Table 1.

Table 1 lists selected bond distances for **3** and **4**. For both complexes, the P1–C1 bond is significantly shorter than typical P–C single bonds, and the C1–C3 bond distance is between those expected for a single and double bond. These bond variations are characteristic of dearomatized pincer ligands.[14] On the other hand, the P2–C2 bond of the phosphaalkene unit in **3** is longer than that in **4**, whereas the C2–C7 bond is shorter in **3** than **4**. In this case, the P2–C2 and C2–C7 bonds in **3** are lengthened and shortened, respectively, whereas those in **4** are average for phosphaalkene complexes (1.668(4) and 1.445(5) Å for **1**).[10d]

Table 1. Selected Bond Distances (Å) for 3 and 4

complex	3	4
P1–C1	1.744(9)	1.764(7)
C1–C3	1.391(13)	1.389(9)
P2–C2	1.701(12)	1.674(7)
C2–C7	1.389(17)	1.432(9)

Figure 2 shows schematic diagrams of the frontier orbitals of PPEP*. The LUMO contains an antibonding interaction between the P2 and C2 atoms and a bonding interaction between the C2 and C7 atoms. Thus, it is reasonable that the bond alteration in **3** is caused by π-back-donation from the iridium center to this orbital. On the other hand, the C1 atom has a large distribution of the HOMO and, therefore, functions as a base site.

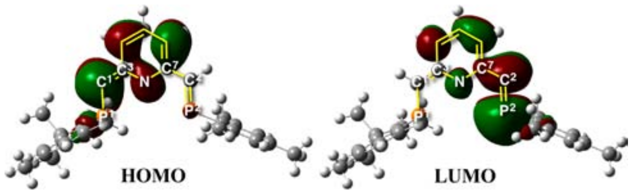
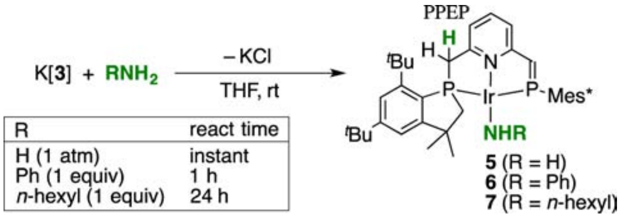


Figure 2. Frontier orbitals of PPEP*.

Complex **3** readily reacted with ammonia and amines to afford amido complexes **5**–**7** in quantitative yields as confirmed by NMR spectroscopy (Scheme 3). The reaction with ammonia (1 atm) was completed instantly at room temperature and within 2 h at 0 °C. The reactions with aniline and *n*-hexylamine also proceeded at room temperature. Complexes **5**–**7** were isolated as crystalline solids and identified by X-ray diffraction studies (see Figures S2–S4). In the ^{1}H NMR spectrum of **5**, the signals assignable to the parent amido ligand and the benzylic protons of the aromatized PPEP ligand appeared at δ 3.82 (br) and 4.12 (d, $^2J_{PH}$ = 10.4 Hz), respectively. The reaction of **3** with ND_3 formed a deuterated complex **5**-*d*, for which the amido proton signal disappeared and the benzylic proton signal reduced its intensity approximately in half.

Scheme 3. N–H Bond Cleavage by Dearomatized Complex 3 with a Phosphaalkene Unit



R	react time
H (1 atm)	instant
Ph (1 equiv)	1 h
n-hexyl (1 equiv)	24 h

The reaction with ammonia was examined by DFT calculations using the anionic part **3** as a computational model. Figure 3 presents an energy diagram obtained for the whole reaction: see the Supporting Information for details of the computation. The reaction involves three reaction steps: (i) coordination of NH_3 to the apical site of **3**; (ii) cooperative cleavage of the N–H bond by Ir and the vinylic carbon; (iii) elimination of Cl^- to afford **5**. The energy change (ΔE) and activation energy (E_a) for the NH_3 coordination to **3** (step i) were calculated to be +6.8 and 9.5 kcal/mol, respectively. The N–H bond cleavage in step ii proceeds in an exothermic manner (ΔE = −2.2 kcal/mol) with moderate activation energy (E_a = 12.8 kcal/mol). In step iii, elongation of the Ir–Cl bond in **9** induces the migration of the NH_2 ligand from the apical site to the equatorial site. This step is the most exothermic (ΔE = −11.6 kcal/mol) and requires an activation energy of 11.0 kcal/mol. The activation energy for the overall process (19.6

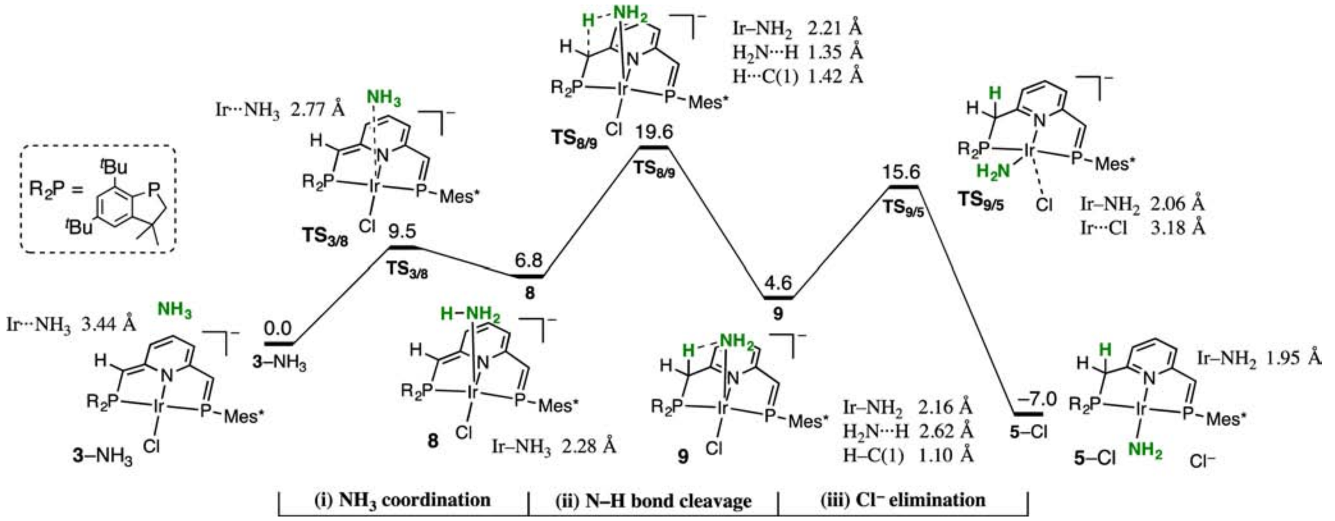


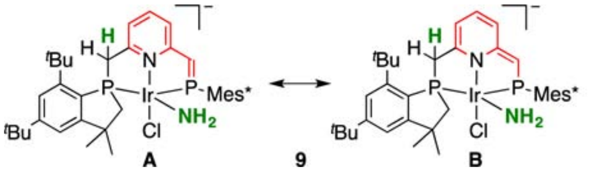
Figure 3. Schematic geometrical changes and energy changes (ΔE, kcal/mol) in the reaction of **3** with NH_3 in THF evaluated by DFT calculations using the B3LYP-D method.

kcal/mol) is consistent with the facile N−H bond cleavage of ammonia at room temperature.

Table 2 summarizes the changes in the Mayer bond order of the pincer ligand during the N−H bond cleavage process. The atomic numbering scheme follows that in Figure 1. As expected, the bond orders of P1−C1 and C1−C3 are reduced by the proton shift from the NH_3 ligand to the vinylic carbon (C1). On the other hand, the bond order of P2−C2 decreases whereas that of C2−C7 increases to a considerable extent during the reaction. As already discussed for **3**, these bond alterations in P2−C2 and C2−C7 must be caused by π-back-donation from iridium to the phosphaalkene unit; i.e., the electron density of iridium should be enhanced by the conversion of neutral NH_3 into the anionic NH_2 ligand. As a result, a large contribution of the canonical structure **B** in eq 1 will appear in amido complex **9**. This remarkable π-conjugation induced by the strong π-accepting ability of the phosphaalkene unit may effectively reduce the instability arising from a notable increase in the electron density, thereby facilitating the N−H bond cleavage of ammonia.

Table 2. Changes in the Mayer Bond Order of the Pincer Ligand in the N−H Bond Cleavage of Ammonia

complex	3	8	$TS_{8/9}$	9
P1−C1	1.08	1.08	0.96	0.89
C1−C3	1.46	1.31	1.08	1.01
P2−C2	1.45	1.19	1.12	1.06
C2−C7	1.19	1.30	1.39	1.46



(1)

In conclusion, we have succeeded for the first time in the preparation of a PNP-pincer type phosphaalkene complex (**3**) that exhibits noninnocent behavior. Complex **3** possesses extremely high reactivity toward N−H bond cleavage of ammonia via metal−ligand cooperation to afford parent amido complex **5** in quantitative yield. The notable bond variations in X-ray structures and calculated structures have indicated the occurrence of effective π-back-donation to the phosphaalkene unit. We consider that this particular ligand property, in conjunction with noninnocent behavior of the dearomatized pincer system, leads to the extremely high reactivity of **3** toward N−H bond cleavage of ammonia.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details including DFT calculations; CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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