Acetonitrile Accelerated Stereoselective C–H Bond Activation of the Cationic Ir(I) Complex Having the PN/CH_3 Heterochelate Hybrid Ligand

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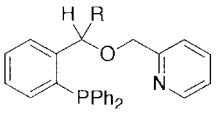
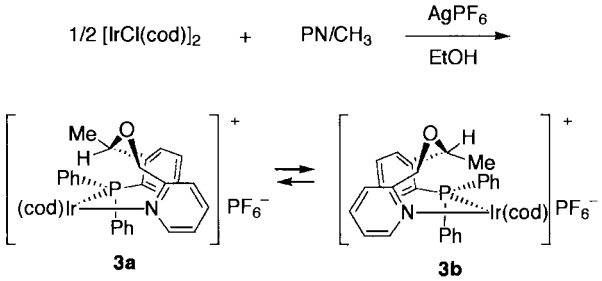
The cationic iridium(I) complex having a heterochelate ligand, [Ir(cod)(PN/CH_3)]PF_6 {PN/CH_3 = *o*-$Ph_2PC_6H_4CH(CH_3)$-$OCH_2(C_5H_4N$-2)} (**3**) was prepared and characterized. Complex **3** underwent stereoselective facile activation of the benzylic C–H bond in CH_3CN at 50 °C to produce the oxidative addition product, a hydrido alkyl complex *fac*-**4** after displacement of COD by 2 molecules of CH_3CN. The initially generated *fac*-**4** isomerized gradually to give the geometrical isomer selectively *mer*-**4** in CH_3CN.

Efficient and capable ligands for metal-mediated or -catalyzed stereoselective organic syntheses are considered to be able to coordinate strongly to a central metal supplying a rigid reaction environment.[1] If the ligand has too much flexibility in the coordination to the metal, the rigid environment collapsed and satisfactory stereoselectivity in the reaction could not be attained. Intentional introduction of flexibility to the metal complexes by using a hemilabile ligand, however, can lead to disclose new remarkable features.[2] We have recently paid much attention to flexibility of a ligand which could stabilize different types of coordination modes for its organometallic complexes. For example, we designed the hemilabile PN hybrid ligand (**1**) which was able to act as a P-N bidentate, a P-O-N tridentate or a P-C-N tridentate ligand[3] and showed that the flexibility of the PN ligand was an important factor for isolation of both Ir(I) and Ir(III) complexes before and after C–H bond activation.[4] Herein, we prepare another hemilabile ligand, a methyl-substituted PN ligand (PN/CH_3 ligand) (**2**),[5] and show interesting behavior, acetonitrile accelerated stereoselective C–H bond activation of its iridium complex.



PN Ligand : R = H (**1**)
PN/CH_3 Ligand : R = Me (**2**)

Reaction of $[IrCl(cod)]_2$ with two equiv of ligand **2** in the presence of excess $AgPF_6$ in ethanol gave the cationic complex [Ir(cod)(PN/CH_3)]PF_6 (**3**) as orange powders in 86% yield.[6] The ^{31}P NMR spectrum in CD_2Cl_2 showed that complex **3** was comprised of two diastereomers (major : minor = 67 : 33). Air-stable orange crystals of one diastereomer suitable for an X-ray analysis were obtained directly from the reaction mixture. An ORTEP drawing of complex **3a** having a S^*_c,S^*_{pl} configuration is shown in Figure 1.[7] Different from [Ir(cod)($PN_{n=1}$)]PF_6, previously reported by us,[4] no obvious interaction between the iridium and the oxygen atom [Ir···O = 4.152 Å] exists in a solid state. The crystals of complex **3a** used for the X-ray analysis gave again the same equilibrium mixture of the two diastereomers in CD_2Cl_2 (major : minor = 67 : 33). Complex **3** was stable in $CDCl_3$ or CD_2Cl_2 at room temperature or even at 50 °C for 18 h in $CDCl_3$, but after 69 h at 60 °C in $CDCl_3$ complex **3** decomposed completely to give a complex mixture.



Scheme 1.

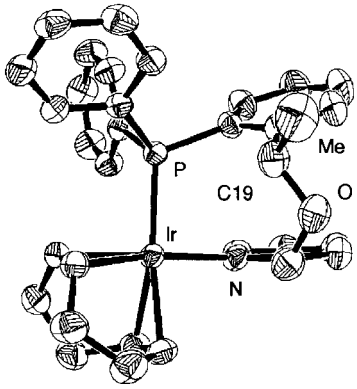
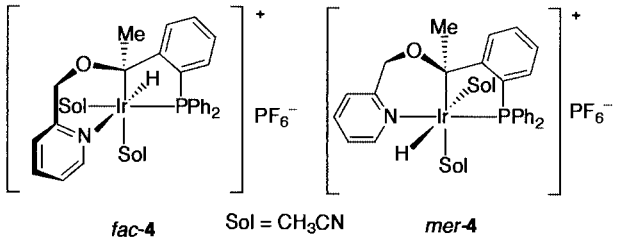


Figure 1. ORTEP drawing of the cationic part of **3a.**

The ^1H NMR of complex **3** in CD_3CN at 30 °C showed very broad signals different from that in CD_2Cl_2, though the spectrum at –20 °C showed sharp signals assignable to the two diastereomers of complex **3** (67 : 33), indicating that rapid interconversion between the two diastereomers was occurring without dissociation of COD at 30 °C (Scheme 1).[8] At 50 °C, the color of the CD_3CN solution of complex **3** gradually changed from orange to pale yellow. The reaction was monitored by ^1H NMR as well as ^{31}P NMR in CD_3CN. Sharp signals in the ^1H NMR assignable to the C–H bond activation product **4** and free COD appeared accompanying several signals for small amounts of unidentified products. After 1 day at 50 °C, complex **3** disappeared completely and the Ir(III) hydrido alkyl complex **4** was produced as a mixture of two geometrical isomers (major-**4** : minor-**4** = 94 : 6). The structure of the major isomer was fully characterized to be *fac*-**4** by elemental analysis as well as spectral data and was confirmed by an X-ray analysis (Figure 2).[9] The PN/CH_3 ligand acts as a P-C-N tridentate ligand and coordinates to the Ir center with a facial manner. The ^1H NMR signal of the proton at the 6-position of the pyridine ring in the PCN/CH_3 ligand[10] of *fac*-**4** showed a characteristic shape for that of the *cis*-coordinated PN ligand,[3] which is con-

sistent with the facial coordination of the PCN/CH_3 ligand. The ^{1}H and ^{31}P NMR indicated that *fac*-**4** was gradually converted further to minor-**4**, which can be tentatively assigned to a geometrical isomer *mer*-**4**.[11] After 17 days at 50 °C *mer*-**4** became the major isomer (*fac*-**4** : *mer*-**4** = 10 : 90). From the stereochemical consideration, *fac*-**4** and *mer*-**4** were exclusively derived from the isomer **3a.** We could not obtain the concrete evidence that the C–H bond activation of the diastereomer **3b** proceeded under these conditions.



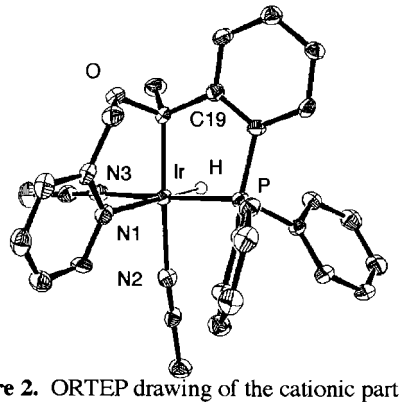


Figure 2. ORTEP drawing of the cationic part of *fac*-**4**.

The ^{1}H NMR of complex **3** in the presence of CH_3CN (ca. 1.7 equiv) in CD_2Cl_2 indicated a new signal at δ 1.99 due to the Ir-coordinated CH_3CN of an intermediate complex in addition to the signals of complex **3** and free CH_3CN (δ 1.98), but did not show any signals for free-COD. After 5 days at room temperature (ca. 20 °C), the C–H bond activation products **4** appeared (major-**3** : minor-**3** : *fac*-**4** : *mer*-**4** = 48 : 26 : 20 : 6). The C–H bond activation, however, did not proceed at all in the absence of CH_3CN under the same conditions. Complex **3** was stable in a mixed solvent of CD_2Cl_2 and CD_3OD and deuterium incorporation into complex **3** could not be detected; a plausible reversible C–H bond activation did not occur in these solvent systems. The hypothesis that dissociation of COD from complex **3** is the driving force for this C–H bond activation is inconsistent with the fact that the rate of the C–H bond activation in CD_3CN was not affected by the presence of excess COD. Coordination of CH_3CN renders the metal center more electron rich, which causes facile C–H bond activation in only complex **3a**.[12]

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References and Notes

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4 Y. Kataoka, Y. Imanishi, T. Yamagata, and K. Tani, *Organometallics*, **18**, 3563 (1999).
5 The PN/CH_3 ligand could be prepared by a similar method to that of the $PN_{n=1}$ ligand from 1-(*o*-diphenylphosphinophenyl)ethanol and 2-picolyl chloride. **2** (racemic compound): ^{1}H NMR ($CDCl_3$, 30 °C) δ 1.37 (d, *J* = 6.3 Hz, 3H), 4.35 (d, *J* = 13.2 Hz, 1H), 4.43 (d, *J* = 13.2 Hz, 1H), 5.36–5.50 (m, 1H), 6.86–6.98 (m, 1H), 7.10–7.46 (m, 14H), 7.58–7.72 (m, 2H), 8.46–8.56 (m, 1H). ^{31}P{^{1}H}NMR ($CDCl_3$, 30 °C) δ –17.0 (s). Anal. ($C_{26}H_{24}ONP$) C, H, N.
6 **3:** Mp 183.0 °C (dec.). Both **3**-major and **3**-minor showed very similar sets of ^{1}H NMR which can well explain structures **3a** or **3b**, respectively. Some representative NMR data: ^{1}H NMR (CD_2Cl_2, 30 °C) **3**-major δ 1.56 (d, *J* = 7.0 Hz, 3H, –CH*Me*O–), 5.02–5.20 (m, 1H, –*CH*Me–), 5.10 (d, *J* = 14.1 Hz, 1H, –OC*H*$_2$–py), 5.53 (d, *J* = 14.1 Hz, 1H, –OC*H*$_2$–py); **3**-minor 2.38 (d, *J* = 6.6 Hz, 3H, –CH*Me*O–), 5.02–5.20 (m, 1H, –*CH*Me–), 4.68 (d, *J* = 15.5 Hz, 1H, –OC*H*$_2$–py), 5.26 (d, *J* = 15.5 Hz, 1H, –OC*H*$_2$–py). ^{31}P{^{1}H}NMR (CD_2Cl_2, 30 °C) δ 5.37 (s, major), 7.46 (s, minor). Anal. Found: C, 48.12; H, 4.35; N, 1.75%. Calcd for $C_{34}H_{36}F_6IrNOP_2$: C, 48.45; H, 4.31; N, 1.66%.
7 Crystal data for **3a**: $C_{34}H_{36}F_6IrNOP_2$, fw = 842.78, Rigaku AFC7R, triclinic, *P*1 (No. 2), *a* = 11.259(8), *b* = 14.618(9), *c* = 9.926(10) Å, α = 95.39(7), β = 89.97(9), γ = 95.60(5) °, *V* = 1619(2) Å^3, *Z* = 2, *T* = 296(2) K, D_{calcd} = 1.729 Mg m^{-3}, λ = 0.71069 Å, *F*(000) = 832, μ = 4.287 mm^{-1}, T_{min} = 0.2789, T_{max} = 0.6057, 2θ(max) = 60 deg, 19598 measured reflections, 9417 unique reflections, R_{int} = 0.0302, solution method SIR97, refinement method SHELXL97, *R*(all data) = 0.0418, *wR*(all) = 0.0789, *R*(*I* > 2σ(*I*)) = 0.0279, *wR*(*I* > 2σ(*I*)) = 0.0737, GOF = 1.052, Δ/σ(max) = 0.001.
8 The ^{1}H NMR of complex **3** in the presence of additional free COD (ca. 10 equiv) in CD_3CN at 30 °C afforded the same broad signals besides the signals of the added free COD.
9 *fac*-**4**: mp 78.0 °C (dec.). ^{1}H NMR (CD_3CN, 30 °C) δ –20.72 (d, *J* = 22.7 Hz, 1H), 1.78–2.14 (br, 6H), 2.09 (s, 3H), 3.64 (d, *J* = 15.8 Hz, 1H), 4.09 (d, *J* = 15.8 Hz, 1H), 6.78–7.98 (m, 17H), 8.64 (d, *J* = 5.5 Hz, 1H). ^{31}P{^{1}H}NMR (CD_3CN, 30 °C) δ 27.4 (s), –143.2 (septet, *J* = 706 Hz, PF_6). MS (FAB) *m/z* 590 (M^+–PF_6–2CH_3CN). IR (nujol) 2280, 2178, 1606, 1111, 850, 838, 770, 750, 724 and 697 cm^{-1}. Anal. Found: C, 43.76; H, 3.44; N, 5.06%. Calcd for $C_{30}H_{30}F_6IrN_3OP_2$: C, 44.12; H, 3.70; N, 5.14%. Crystal data: $C_{30}H_{30}F_6IrN_3OP_2$, fw = 842.78, Rigaku RAXIS-RAPID, triclinic, *P*1 (No. 2), *a* = 11.7843(4), *b* = 14.5811(6), *c* = 9.4638(4) Å, α = 105.4882(14), β = 96.9441(15), γ = 97.2193(14) °, *V* = 1534.25(10) Å^3, *Z* = 2, *T* = 100(1) K, D_{calcd} = 1.768 Mg m^{-3}, λ = 0.71069 Å, *F*(000) = 800, μ = 4.521 mm^{-1}, T_{min} = 0.4592, T_{max} = 0.6958, 2θ(max) = 63 deg, 29369 measured reflections, 10149 unique reflections, R_{int} = 0.0745, solution method SIR97, refinement method SHELXL97, *R*(all data) = 0.0793, *wR*(all) = 0.0952, *R*(*I* > 2σ(*I*)) = 0.0488, *wR*(*I* > 2σ(*I*)) = 0.0871, GOF = 1.020, Δ/σ(max) = 0.000.
10 The PCN/CH_3 ligand represents the PN/CH_3 ligand acted as a P-C-N tridentate ligand.
11 Although isolation of pure *mer*-**4** has not been successful yet due to its instability, the structure of *mer*-**4** is determined by both the characteristic shape of the ^{1}H NMR signal for the proton at the 6-position of the pyridine ring[3] and the NOESY experiments. The proton at the 6-position of the pyridine ring in *mer*-**4** showed NOE only to the proton at the 5-position of the pyridine ring, while that in *fac*-**4** showed NOE to one of the aromatic protons except the pyridine protons, in addition to the proton at the 5-position of the pyridine ring. The relative positions of the hydrido ligand and the two CH_3CN ligands are also determined by NOESY experiments. The Ir-H in *mer*-**4** showed NOE to one of the α-methylene protons of the pyridine ring, but not to the methyl group of the PN/CH_3 ligand, while the Ir–H in *fac*-**4** showed NOE to the methyl group, but not to the α-methylene protons. ^{1}H NMR of *mer*-**4** (CD_3CN, 30 °C) δ –21.47 (d, *J* = 19.2 Hz, 1H), 1.10 (s, 3H), 1.78–2.14 (br, 6H), 4.66 (d, *J* = 20.6 Hz, 1H), 4.71 (d, *J* = 20.8 Hz, 1H), 6.92–8.12 (m, 17H), 9.08–9.18 (m, 1H). ^{31}P{^{1}H}NMR (CD_3CN, 30 °C) δ 21.4 (s), –143.2 (septet, *J* = 706 Hz, PF_6).
12 The accelerating effect by the coordination of CH_3CN to the metal center was also observed in the reaction of [Ir(cod)(PN)]PF_6. For example, C–H activation of [Ir(cod)(PN)]PF_6 in CH_3CN was almost completed at 50 °C for 3 h, while the C–H activation in $CDCl_3$ proceeded only ca. 20% under the same conditions.