Acetonitrile Accelerated Stereoselective C–H Bond Activation of the Cationic Ir(I) Complex Having the PN/CH₃ Heterochelate Hybrid Ligand

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(Received January 15, 2001; CL-010034)

The cationic iridium(I) complex having a heterochelate ligand, $[Ir(cod)(PN/CH_3)]PF_6$ {PN/CH₃ = *o*-Ph₂PC₆H₄CH(CH₃)-OCH₂(C₅H₄N-2)} (**3**) was prepared and characterized. Complex **3** underwent stereoselective facile activation of the benzylic C–H bond in CH₃CN at 50 °C to produce the oxidative addition product, a hydrido alkyl complex *fac*-4 after displacement of COD by 2 molecules of CH₃CN. The initially generated *fac*-4 isomerized gradually to give the geometrical isomer selectively *mer*-4 in CH₃CN.

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 ligand³ 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.



Reaction of $[IrCl(cod)]_2$ with two equiv of ligand **2** in the presence of excess AgPF₆ in ethanol gave the cationic complex $[Ir(cod)(PN/CH_3)]PF_6$ (**3**) as orange powders in 86% yield.⁶ The ³¹P NMR spectrum in CD₂Cl₂ 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^*_{cr}, 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 CD₂Cl₂ (major : minor = 67 : 33). Complex **3** was stable in CDCl₃ or CD₂Cl₂ at room temperature or even at 50 °C for 18 h in CDCl₃,

but after 69 h at 60 °C in $CDCl_3$ complex 3 decomposed completely to give a complex mixture.



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

The ¹H NMR of complex **3** in CD₂CN at 30 °C showed very broad signals different from that in CD₂Cl₂, 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 CD₃CN solution of complex 3 gradually changed from orange to pale yellow. The reaction was monitored by ¹H NMR as well as ³¹P NMR in CD₃CN. 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/CH₃ 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/CH₃ ligand¹⁰ 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/CH₃ ligand. The ¹H and ³¹P 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 ¹H NMR of complex **3** in the presence of CH₃CN (ca. 1.7 equiv) in CD₂Cl₂ indicated a new signal at δ 1.99 due to the Ircoordinated CH3CN of an intermediate complex in addition to the signals of complex **3** and free CH₃CN (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 CH₃CN under the same conditions. Complex 3 was stable in a mixed solvent of CD₂Cl₂ and CD₃OD 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 CD₃CN was not affected by the presence of excess COD. Coordination of CH₃CN renders the metal center more electron rich, which causes facile C-H bond activation in only complex 3a.¹²

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan.

References and Notes

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- 5 The PN/CH₃ ligand could be prepared by a similar method to that of the In a 14 Graphian Band from 1-(*o*-diphenylphosphinophenyl)ethanol and 2-picolyl chloride. **2** (racemic compound): ¹H NMR (CDCl₃, 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). ³¹P{¹H}NMR (CDCl₃, 30 °C) δ –17.0 (s).
- (m, 2h), 8.40–8.50 (m, m). The transformation of the set of the s 6
- In the equation of the state $\Delta/\sigma(\max) = 0.001$.
- The ¹H NMR of complex **3** in the presence of additional free COD (ca. 8 10 equiv) in CD₃CN at 30 °C afforded the same broad signals besides
- To equiv) in CD₃CP at 50°C another the tank CTLL 4.9 in the signals of the added free COD. fac-4: mp 78.0 °C (dec.). ¹H NMR (CD₃CN, 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, 100 (m 17H) 8.64 (d, J = 5.5 Hz, 100 (m 17H) 8.64 (d, J = 5.5 Hz, 100 (m 17H) 8.64 (d, J = 5.5 Hz, 100 (m 17H) 8.64 (d, J = 5.5 Hz, 100 (m 17H) 8.64 (d, J = 5.6 Hz, 100 (m 17H) 8.64 (d, J Hz, PF₆). MS (FAB) m/z 590 (M⁺–PF₆–2CH₃CN). IR (nujol) 2280, 2178, 1606, 1111, 850, 838, 770, 750, 724 and 697 cm⁻¹. Anal. Found: 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) Å³, *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, 20(max) = 63 deg, 29369 measured reflections, 10149 unique reflections, *R*₋₁ = 0.0745, solution method SIR97. refinement method reflections, $R_{int} = 0.0745$, solution method SIR97, refinement method SIR1XL97, R(all data) = 0.0793, wR(all) = 0.0952, $R(I > 2\sigma(I)) = 0.0488$, $wR(I > 2\sigma(I)) = 0.0871$, GOF = 1.020, $\Delta/\sigma(max) = 0.000$.
- The PCN/CH3 ligand represents the PN/CH3 ligand acted as a P-C-N tridentate ligand.
- 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 ¹H NMR signal for the proton at the 6-position of the pyridine ring3 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 CH₃CN 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/CH₃ ligand, while the Ir–H in *fac*-4 showed NOE to the methyl group, but not to the α -methylene protons. ¹H NMR of *mer*-4 (CD₃CN, 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 21.4° (d, 5 = 20.6 Hz, 1H), 4.71 (d, J = 20.8 Hz, 1H), 6.92–8.12 (m, 17H), 9.08–9.18 (m, 1H). $^{31}P\{^{1}H\}NMR$ (CD₃CN, 30 °C) δ 21.4 (s), -143.2 (septet, J = 706 Hz, PF₆).
- The accelerating effect by the coordination of CH₃CN to the metal cen-12 ter was also observed in the reaction of [Ir(cod)(PN)]PF₆. For example, C-H activation of [Ir(cod)(PN)]PF6 in CH3CN was almost completed at 50 °C for 3 h, while the C-H activation in CDCl₃ proceeded only ca. 20% under the same conditions.