Diastereoselective Formation of Metallaphosphacyclo Iridium(III) Complexes from Phosphoranido Iridium(III) Complex

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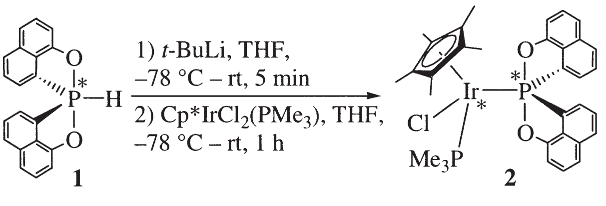
(Received January 7, 2003; CL-030022)

A phosphoranido iridium(III) complex is prepared by the reaction of $Cp^*IrCl_2(PMe_3)$ with lithium phosphoranide generated from a P–H spirophosphorane bearing two 8-oxy-1-naphthyl groups. The complex is thermally converted into metallaphosphacyclo complexes with diastereoselectivity.

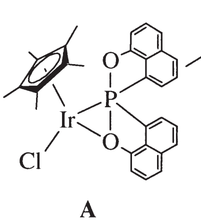
The phosphorus–carbon bond cleavage of phosphine complexes have been well researched.[1] In the case of phosphoranido complexes, metalated phosphoranes, bearing several P–C bonds it can be expected that the cleavage of the P–C bond will be more facile, when the bond locates in an apical site.[2] Although a large number of phosphoranido complexes have been reported so far,[3,4] there were only a few reports on the transformation of phosphoranido iron adducts into phosphane iron complexes through 1,2-shift of aryl or allyl groups on phosphorus to iron.[4] However, the iron adducts could be only confirmed by ^{31}P NMR analyses in the reaction mixtures, and the aryl or allyl groups were monodentate ligands. Here we report the diastereoselective formations of a metallaphosphacyclo complex **3** and a cationic metallaphosphacyclo complex **4** by heating the solutions of a phosphoranido iridium complex **2** in xylene and EtOH, respectively, through 1,2-shift of the carbon of an 8-oxy-1-naphthyl group as bidentate ligand on phosphorus to iridium.

The reaction of $Cp^*IrCl_2(PMe_3)$ with a lithium phosphoranide generated from a P–H spirophosphorane **1**[3e] in THF gave a diastereomeric mixture of the phosphoranido iridium(III) complex **2** in 73% yield (Scheme 1).[5] ^{31}P NMR spectrum showed four doublets for phosphoranide and PMe_3 due to two-bond phosphorus-phosphorus couplings. Additionally, in the ^{1}H NMR spectrum the resonance of the Cp* methyl proton appeared as doublets of doublets with small coupling constants.

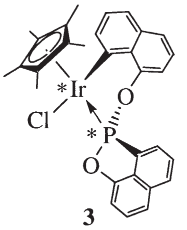
The diastereomeric mixture of **2** was used for thermal conversion in various solvents[6] since the isomerization between the diastereomers seemed to be very fast. The complex **2** was very stable in refluxing $CHCl_3$, THF or CH_3CN for 3 days. Thermolysis of **2** completed in xylene at 150 °C for 8 h to give a new compound *u*-**3**[7,8] [δ_P ($CDCl_3$) = 117.9] as a single diastereomer (Table 1, Entry 1). ^{1}H NMR analysis of *u*-**3** indicated the loss of PMe_3, and the existence of Cp* and two naphthyl groups. Therefore we expected that the structure of *u*-**3** should be a η^2 structure **A** as shown in a Martin phosphoranido rhodium complex.[3d] However, the ^{31}P chemical shift of *u*-**3** did not significantly vary with the solvents or by the addition of PMe_3 or TsOH in THF.



Scheme 1.



A



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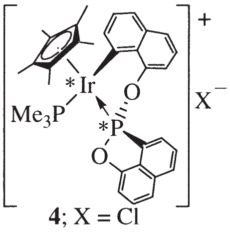


4; X = Cl
5; X = OTf

Table 1. Thermal conversion of the complex **2** into metallacyclo complexes

Entry	Solvent	Temp./°C	Time/h	Yield/% (*l*:*u*) **3**	Yield/% (*l*:*u*) **4**
1	xylene	150	8	97 (<1:>99)	no
2	EtOH	80	3	no	60 (84:16)
3	PhCN	190	3	41 (<1:>99)	36 (50:50)

Finally the structure of the compound *u*-**3** could be elucidated by the X-ray structural analysis (Figure 1).[9] The iridium atom has a piano-stool geometry coordinated by a Cp* ligand, a Cl ligand, and a *P*,*C*-chelate ligand. The relative stereochemistry at iridium and phosphorus atoms was found to be *RS(SR)*. The P1–Ir1 bond length of 2.164(1) Å is shorter than those (2.273–2.332 Å) of reported phosphane Ir(III) complexes bearing a Cp* group[10] probably due to a rigid naphthyl group constituted a six-membered metallacycle.

On the other hand, the complex **2** in refluxing EtOH for 3 h

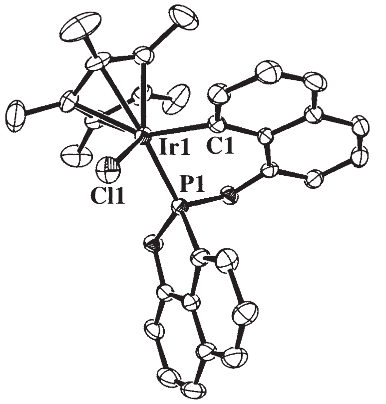


Figure 1. The ORTEP drawing of *u*-**3**·benzene showing the thermal ellipsoids at the 30% probability level. All hydrogens and a benzene molecule are omitted for clarify. Selected bond distances (Å): Ir1–P1, 2.164(1); Ir1–C11, 2.406(2); Ir1–C1, 2.098(5). Selected bond angles (degree): P1–Ir1–C11, 93.45(6); C11–Ir1–C1, 90.4(2); C1–Ir1–P1, 80.3(2).

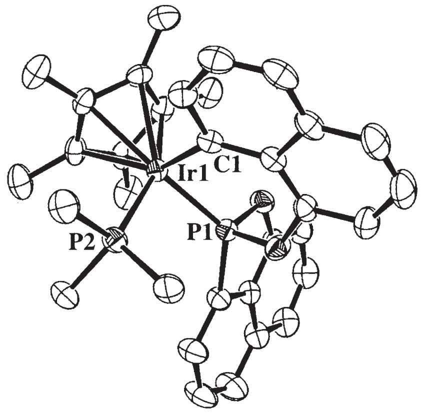
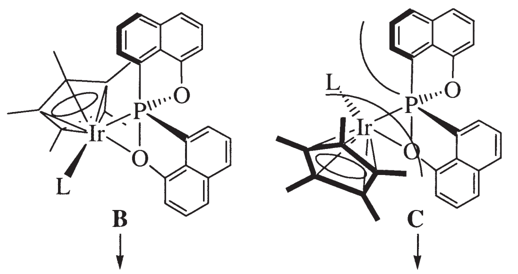


Figure 2. The ORTEP drawing of *l*-**5**·1/2hexane showing the thermal ellipsoids at the 30% probability level. All hydrogens, $CF_3SO_3^-$ counterion and 1/2 hexane molecule are omitted for clarify. Selected bond distances (Å): Ir1–P1, 2.187(1); Ir1–P2, 2.307(1); Ir1–C1, 2.104(4). Selected bond angles (degree): P1–Ir1–P2, 93.54(4); P2–Ir1–C1, 84.2(1); C1–Ir1–P1, 90.0(1).

afforded cationic metallacyclo complex **4** [*l*-**4**: δ_P ($CDCl_3$) = 108.5, −40.5, J_{PP} = 17.1 Hz; *u*-**4**: δ_P ($CDCl_3$) = 114.0, −34.9, J_{PP} = 34.2 Hz] (Table 1, Entry 2). The exchange of counter anions was achieved by the treatment of the diastereomeric mixture of **4** with AgOTf in THF to give a complex **5** (*l*-**5**:*u*-**5** = 85:15) quantitatively.[11] It is significant that the d.e. value, ^{31}P chemical shifts, and two-bond P–P coupling constants of **5** [*l*-**5**: δ_P ($CDCl_3$) = 108.9, −40.7, J_{PP} = 17.1 Hz; *u*-**5**: δ_P ($CDCl_3$) = 114.3, −35.0, J_{PP} = 34.2 Hz] is almost same as those of **4**. These infers no structural transformation of the cation moiety during the exchange of the counter anions. Recrystallization of the diastereomeric mixture of **5** from hexane–$CHCl_3$ gave single crystals of *l*-**5** as yellow prisms and the crystal structure of *l*-**5** was determined by the X-ray structural analysis (Figure 2).[12] It appears that *l*-**5** is the cationic metallacyclo complex with piano-stool geometry and the relative stereochemistry is *RR(SS)*. Similarly to the complex *u*-**3**, the Ir1–P1 distance of 2.187(1) is shorter than those of the reported complexes[10] and the Ir1–P2 distance of 2.307(1).

The migration of the naphthyl group from phosphorus to iridium would be explained by the 1,2-sigmatropic shift.[4d] Key intermediates may be O-C apical[13] phosphoranido adducts **B** and **C** in which a broken P–C bond is an apical bond[2] and the conformation around P–Ir bond is restrained (Figure 3). These intermediates can be generated from **2** through the dissociation equilibrium of PMe_3 or Cl^-, and the permutation processses by Berry pseudorotation.[14] The leaving ligand might be dependent on the reaction temperature and the polarity of the solvents (Table 1, Entry 3).[15] In migration of the apical naphthyl carbon on phosphorus to give the three-membered transition state, it is expected that Cp* ligand interacts more with the naphthalene ring than L. Diastereoselectivity would be dependent on the size of L and the reaction temperature.



u-**3**; L = Cl
l-**4**; L = PMe_3

l-**3**; L = Cl
u-**4**; L = PMe_3

Figure 3. Leaving ligands and the symbols of electronic charge are omitted.

This paper demonstrate the first example of diastereoselective and irreversible 1,2-shift of the carbon of an 8-oxy-1-naphthyl group as bidentate ligand on phosphorus to metal in phosphoranido complex chemistry. This tactics should be a novel synthetic method of metallacyclo complex.

References and Notes

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2 An apical bond is called hypervalent bond, three-center four-electron (3c-4e) bond. See: a) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969). b) K.-y. Akiba in "Chemistry of Hypervalent Compounds," ed. by K.-y. Akiba, Wiley-VCH, New York (1998), Chap. 1.

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5 Purification on silica gel column chromatography (CH_2Cl_2-hexane-MeOH = 10:10:1) afforded **2** (**isomer-a/b** = 1.5) as yellow powder. Anal. calcd for $C_{33}H_{36}ClIrO_2P_2$: C, 52.55; H, 4.81%. Found: C, 52.23; H, 4.91%. **2-a**: ^1H NMR ($CDCl_3$) δ 7.82 (dd, J = 9.8, 7.3 Hz, 2H), 7.63 (dd, J = 8.1, 2.9 Hz, 2H), 7.39–7.28 (m, 4H), 7.03–6.97 (m, 2H), 6.47 (d, J = 7.3 Hz, 2H), 1.77 (d, J_{HP} = 11.0 Hz, 9H), 1.54 (dd, J_{HP} = 3.4, 2.2 Hz, 15H); ^{31}P NMR ($CDCl_3$) δ −32.1 (d, J_{PP} = 53.7 Hz, phosphine), −46.2 (d, J_{PP} = 53.7 Hz, phosphoranide). **2-b**: ^1H NMR ($CDCl_3$) δ 8.02 (dd, J = 10.3, 7.8 Hz, 2H), 7.58 (dd, J = 8.3, 2.7 Hz, 2H), 7.39–7.28 (m, 4H), 6.99–6.93 (m, 2H), 6.60 (d, J = 7.3 Hz, 2H), 1.56 (d, J_{HP} = 9.5 Hz, 9H), 1.47 (dd, J_{HP} = 3.2, 2.4 Hz, 15H); ^{31}P NMR ($CDCl_3$) δ −32.7 (d, J_{PP} = 51.3 Hz, phosphine), −45.5 (d, J_{PP} = 51.3 Hz, phosphoranide).

6 The diastereomeric mixture of **2** (50 mg) was dissolved in freshly distilled solvents (100 mL). The reaction mixture was purified with silica gel chromatography (CH_2Cl_2-hexane = 20:1).

7 *u*-**3**: ^1H NMR ($CDCl_3$) δ 8.02 (d, J = 6.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.54–7.48 (m, 4H), 7.40–7.33 (m, 2H), 7.22–7.17 (m, 2H), 7.10 (t, J = 6.8 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 1.67 (d, J_{HP} = 2.9 Hz, 15H).

8 We applied symbols *u* (*unlike*) and *l* (*like*) in order to describe the relative configuration of the complexes **3**–**5**. See: D. Seebach and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **21**, 654 (1982).

9 Recrystallization of **3** from benzene gave single crystals as yellow plates. Crystal data for *u*-**3**·benzene: $C_{36}H_{33}ClIrO_2P$; $FW = 756.30$; monoclinic, $P2_1$, $Z = 2$; $a = 9.415(3)$ Å, $b = 8.437(2)$ Å, $c = 19.302(2)$ Å, $\beta = 93.85(1)°$; $V = 1529.8(6)$ Å^3, $Dc = 1.642$ g cm^{-3}; 8894 unique reflections used, 404 parameters to $R = 0.032$, $Rw = 0.080$; Goodness of fit $S = 1.01$.

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11 *l*-**5**: ^1H NMR ($CDCl_3$) δ 8.20 (d, J = 8.1 Hz, 1H), 7.92–7.87 (m, 1H), 7.80 (t, J = 7.8 Hz, 1H), 7.70–7.62 (m, 4H), 7.43 (d, J = 7.8 Hz, 1H), 7.30–7.20 (m, 2H), 7.14 (d, J = 7.3 Hz, 1H), 6.82 (d, J = 7.1 Hz, 1H), 1.751 (dd, J_{HP} = 2.2, 1.0 Hz, 15H), 1.749 (d, J_{HP} = 10.7 Hz, 9H); *u*-**5**: ^1H NMR ($CDCl_3$) δ 8.21–6.82 (m, 12H), 1.77–1.75 (m, 24H).

12 Crystal data for *l*-**5**·1/2hexane: $C_{37}H_{43}F_3IrO_5P_2S$; $FW = 910.97$; triclinic, $P\bar{1}$, $Z = 2$; $a = 12.933(2)$ Å, $b = 13.846(2)$ Å, $c = 11.434(1)$ Å, $\alpha = 92.20(1)°$, $\beta = 95.51(1)°$, $\gamma = 68.025(8)°$; $V = 1889.9(4)$ Å^3, $Dc = 1.601$ g cm^{-3}; 8657 unique reflections used, 485 parameters to $R = 0.030$, $Rw = 0.074$; Goodness of fit $S = 1.05$.

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14 R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

15 Isomerization of **4** did not occur under same condition.