doi:10.1246/cl.2010.643

Axially Chiral Anilido–Aldimine Aluminum Complexes with a Pseudobinaphthyl Skeleton

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Axially chiral anilido–aldimine aluminum complexes with a pseudobinaphthyl skeleton **3a** and **3b** have been prepared. X-ray analysis indicates that complex **3b** adopts a conformation similar to that of 1,1′-binaphthyls. The racemization barrier of **3a** was determined to be 23.0 kcal mol^{-1}, which was higher by ca. 4 kcal mol^{-1} than the corresponding diarylamine precursor with an N–H–N hydrogen bond.

Chiral binaphthyls have been extensively used in asymmetric synthesis. In particular, metal complexes of 2,2′-disubstituted-1,1′-binaphthyls **1** have been shown to be extremely effective catalysts for a variety of asymmetric transformations (Figure 1).[1–3] While the catalytically active metal center (M) in **1** is located far from the chiral axis (C(1)–C(1′)) by three bonds, it is quite effective for asymmetric induction in many cases. The ultimate structure to minimize the distance between the catalytically active metal center and the chiral axis is shown as **2**, where the central metal is directly connected to the chiral C(1′)–X axis. Here we report the first example of the preparation and structural elucidation of such organometallic complexes as exemplified by anilido–aldimine aluminum complexes **3**.

Crucial questions about **2** and **3** are whether (1) they adopt the conformation like that of 1,1′-binaphthyls, (2) enantiomers of **2** and **3** with axial chirality could exist without rapid racemization at ambient temperature. We have investigated possible precursors for **2**, and found that axially chiral diarylamines with an intramolecular N–H–N hydrogen bond are tolerant against racemization at ambient temperature. For example, the racemization barrier of **4** was found to be 28.2 kcal mol^{-1}, which corresponds to a half-life of racemization of 24 months at 20 °C (Figure 2). The diarylamine **5** was shown to adopt quite similar conformation to that of 1,1′-binaphthyls by X-ray structural analysis.[4] Here we describe the structure and racemization barrier of anilido–aldimine aluminum complexes **3**.

Preparation of anilido–aldimine aluminum complexes **3a** and **3b** is shown in Scheme 1. Aldehyde **6** was prepared via Buchwald cross coupling reaction[5] between 2-methylnaphthalene-1-amine and aryl bromide as reported previously.[4] Condensation of **6** with isopropylamine gave **7a** in 83% yield. Anilido–aldimine aluminum complex **3a** was obtained by treatment of **7a** with 1.0 equiv of trimethylaluminum in dry toluene at 0 °C to room temperature in quantitative yield. Disappearance of the N*H* signal of **7a** (11.47 ppm) and appearance of the resonance of $AlMe_2$ protons at high field (−0.48 and −0.52 ppm) in the ^{1}H NMR in benzene-d_6 indicates the formation of the aluminum complex **3a**. The formation of **3a** was further confirmed by the observation of a molecular ion peak of **3a** in the mass spectrum (m/z 343). The observation of the CH imine proton at 8.24 ppm in the ^{1}H NMR in benzene-d_6 shifted to higher field at 7.66 ppm as well as the observation that the resonance of imine carbon at 162.1 ppm in ^{13}C NMR shifted to lower field at 167.7 ppm are consistent with the reported formation of anilido–aldimine aluminum complexes from the corresponding anilido–aldimine ligands.[6a] Anilido–aldimine aluminum complex **3b** was also prepared from **6** via condensation with 3,5-di-*tert*-butylaniline followed by treatment with trimethylaluminum in dry toluene in 54% overall yield. Formation of **3b** was confirmed by ^{1}H NMR, ^{13}C NMR, MS, elemental analysis, and X-ray structural analysis.[7,8]

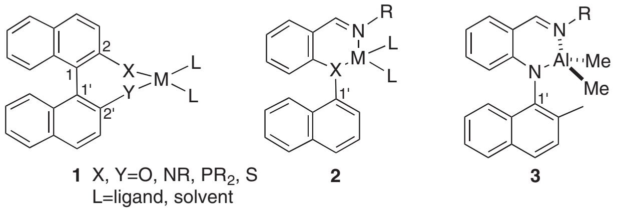


Figure 1. Metal complexes of 1,1′-binaphthyls **1** and organometallic complexes with a pseudobinaphthyl skeleton **2** and **3**.

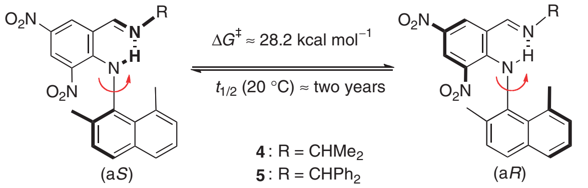
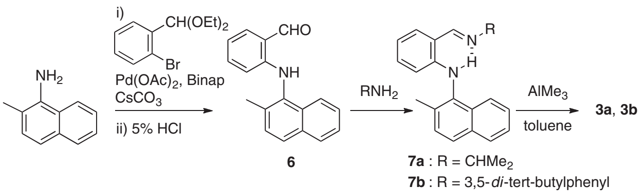


Figure 2. Axially chiral binaphthyl surrogates with long half-lives of racemization.



Scheme 1. Preparation of anilido–aldimine aluminum complexes **3a** and **3b**.

A single crystal of **3b** for X-ray analysis was obtained by recrystallization of **3b** from hexane at −30 °C. The crystal structure of **3b** is shown in Figure 3 along with selected bond lengths and angles.[8] Anilido–aldimine aluminum complex **3b** adopts a distorted tetrahedral geometry around the aluminum center chelated by the imine and amido nitrogen atoms. The Al–N (imine) distance (1.958 Å) and Al–N (amido) distance (1.893 Å) are similar to the reported bond lengths of the related anilido–aldimine aluminum complexes.[6,9] In complex **3b**, the six-membered chelate ring is nearly planar with the aluminum atom lying 0.114 Å out of the plane,[10] and is almost coplanar with the adjacent phenyl ring (side view). Thus, the ring

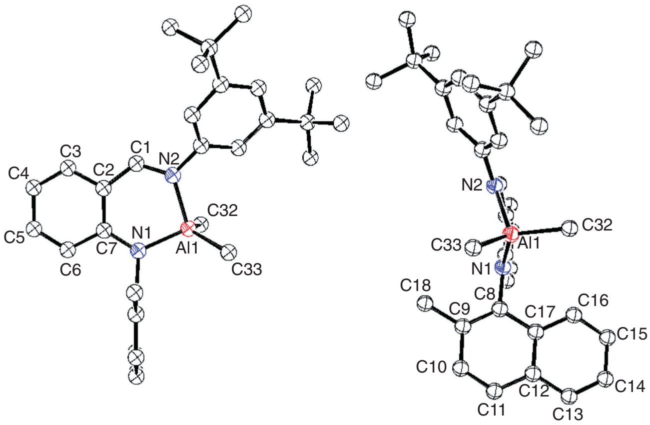


Figure 3. ORTEP drawings of top view (left) and side view (right) of Al-complex **3b** with thermal ellipsoid plots (50% probability). H-atoms and the minor disorder component observed in the *t*-butyl group were omitted for clarity. Selected bond lengths [Å] and angles [°] of **3b**: Al(1)–N(1) 1.893(3), Al(1)–N(2) 1.958(3), Al(1)–C(32) 1.968(3), Al(1)–C(33) 1.959(4), N(1)–C(7) 1.369(4), N(2)–C(1) 1.315(4), C(1)–C(2) 1.430(4), C(2)–C(7) 1.426(4), N(1)–Al(1)–N(2) 94.26(11), N(1)–Al(1)–C(32) 111.35(14), N(1)–Al(1)–C(33) 112.77(14), N(2)–Al(1)–C(32) 106.80(13), N(2)–Al(1)–C(33) 112.16(15), C(33)–Al(1)–C(32) 117.04(16), Al(1)–N(2)–C(1) 120.3(2), C(7)–N(1)–Al(1) 125.3(2), N(2)–C(1)–C(2) 127.1(3), C(1)–C(2)–C(7) 124.2(3), C(2)–C(7)–N(1) 121.1(3), Al(1)–N(1)–C(8)–C(17) −82.9(3), C(7)–N(1)–C(8)–C(17) 88.1(3).

consisting of ten atoms of N(1)–Al(1)–N(2)–C(1)–C(2)–C(3)–C(4)–C(5)–C(6)–C(7) adopts the conformation like a naphthalene skeleton. The dihedral angle between the six-membered chelate ring and the naphthalene ring is 88.1°. This observation indicates that the anilido–aldimine aluminum complex **3b** adopts a conformation similar to that of 1,1′-binaphthyls.

We then investigated the racemization barrier of **3a**. Two methyl peaks of the isopropyl group of **3a** appeared separately at 20 °C, indicating the diastereotopic environment due to the restricted bond rotation along the C(1′)–N axis (Figure 4a). The rotational barrier of **3a** was determined to be 23.0 kcal mol^{-1} at 142.5 °C by variable NMR measurement in *o*-dichlorobenzene-d_4 ($\Delta\nu_{AB} = 3.15$ Hz, $T_{coales} = 415.5$ K, Figure 4b), which corresponds to the half-life of racemization of ca. 2 h at 20 °C based on the assumption that $\Delta S^{\neq}$ of the restricted bond rotation is nearly zero (Figure 5). Comparing the rotational barrier of **3a** with the reported rotational barrier of **7a** (19.3 kcal mol^{-1} at 92 °C),[4] introduction of a dimethyl aluminum group was found to result in an increase in the racemization barrier by ca. 4 kcal mol^{-1}. Although the configurational stability of **3a** is far from required for practical use as asymmetric catalysts, organometallic complexes derived from **4** are expected to have configurational stability suitable for this purpose.[11] Preparation of organometallic complexes from the diarylamine precursors with high configurational stability is currently under investigation in our laboratory.

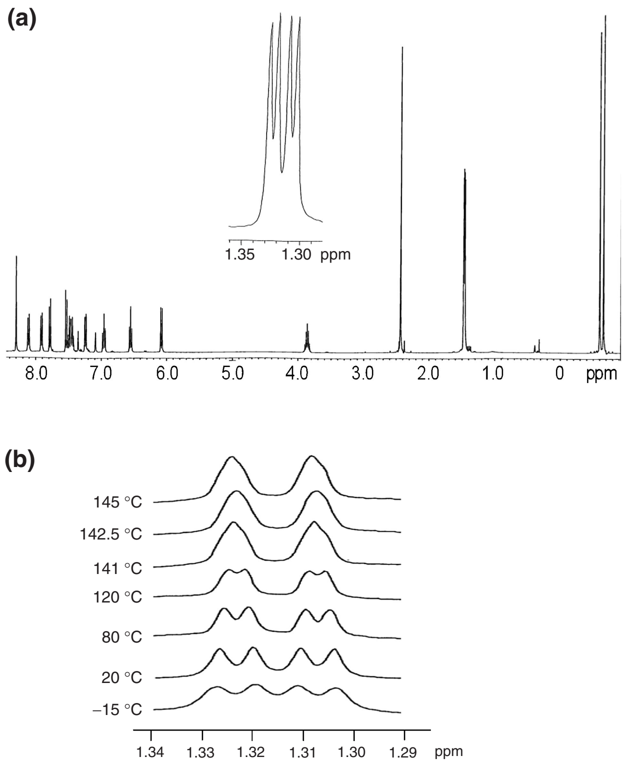


Figure 4. (a) ^{1}H NMR spectrum of **3a** in *o*-dichlorobenzene-d_4 at 20 °C and (b) temperature dependence of the signals of the isopropyl group of **3a**.

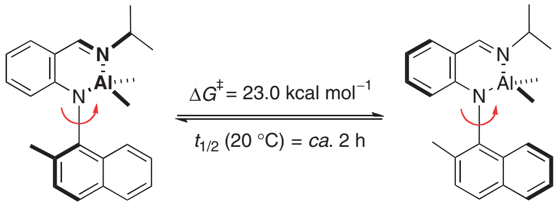


Figure 5. Axially chiral anilido–aldimine aluminum complex with a pseudobinaphthyl skeleton **3a**.

We are grateful to Mrs. Kyoko Ohmine, Institute for Chemical Research, Kyoto University, for the measurement of variable temperature NMR. This work was supported by a Grant-in-Aid for Exploratory Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by Grant-in-Aid for JSPS Fellows to K. H.

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7 A solution of **7b** (216 mg, 0.48 mmol) in 9.0 mL of dry toluene was slowly added to a solution of $AlMe_3$ (1.0 M in

hexane, 0.48 mL) at 0 °C. After stirring the mixture at 0 °C for 30 min, stirring was continued at room temperature for additional 2 h. The solvent was removed in vacuo to give the crude product. Pure **3b** (165 mg, 68%) was obtained as orange crystals by recrystallization from hexane at −30 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.91 (d, $J = 8.3$ Hz, 1H), 7.84 (d, $J = 7.3$ Hz, 1H), 7.71 (d, $J = 8.2$ Hz, 1H), 7.45 (d, $J = 8.3$ Hz, 1H), 7.42–7.33 (m, 5H), 7.19 (s, 1H), 7.18 (s, 1H), 7.02 (td, $J = 7.8$, 1.8 Hz, 1H), 6.52 (t, $J = 6.9$ Hz, 1H), 5.99 (d, $J = 8.7$ Hz, 1H), 2.33 (s, 3H), 1.36 (s, 18H), −0.92 (s, 3H), −0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 156.7, 152.5, 147.0, 139.2, 137.1, 136.5, 133.6, 132.5, 131.5, 129.6, 127.9, 125.7, 125.6, 125.1, 124.7, 121.3, 117.0, 116.8, 115.8, 114.5, 35.1, 31.5, 18.6, −7.8, −9.1; IR ($CHCl_3$): 2963, 1612, 1573, 1529, 1437 cm^{-1}; MS (FAB) m/z (rel intensity): 527 (MNa^+, 1), 505 (MH^+, 11), 489 ($(M - Me)^+$, 100); HRMS (FAB^+) m/z: calcd for $C_{34}H_{42}AlN_2$ (MH^+): 505.3163, found 505.3172. Anal. Calcd for $C_{34}H_{41}AlN_2$: C, 80.91; H, 8.19; N, 5.55%. Found: C, 80.96; H, 8.26; N, 5.58%.

8 See Supporting Information for crystallographic data of **3 b**, which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett. The crystallographic data have been deposited with Cambridge Crystallographic Data Centre as a supplementary publication No. CCDC-771984. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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10 The sum of the internal angles of the six-membered chelate ring is 712°, which is comparable with 720° for the completely planar six-membered ring.

11 Attempted formation of anilido–aldimine aluminum complexes from **4** or the related diarylamines with high configurational stability under the conditions similar to those for **7** was not successful so far.