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Synthesis, Structure, and Solvent-Induced Spontaneous Homochiral Assembly of Bidentate Bis(*N*,*N*′-diaryl-N-heterocyclic carbene)-Palladium Complexes

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A series of new bidentate bis(N-heterocyclic carbene)-palladium complexes **4a**–**e** and **6** with xanthene framework was synthesized. The X-ray analyses of the complexes revealed that the complexes have conformational chirality. Homochiral crystals of **4a** and **6** were obtained by recrystallization from THF or 1,4-dioxane as solvent. The energy barriers for racemization of the complexes were calculated from dynamic NMR spectroscopy.

Introduction

Chiral crystal packing of achiral compounds (one category of spontaneous resolution)[1] has attracted increasing attention in recent years[2] especially because the phenomenon includes a chiral amplification process during congregating of molecules in crystallization.[3] Such spontaneously resolved crystals have been applied to absolute asymmetric synthesis[4] and the construction of chiral architecture,[5] and the phenomenon has been translated into the origin of homochirality of life.[6] Although the mechanism of the chiral amplification process on crystallization is still unknown, it is probable that a chiral cluster (kinetic process) or chiral crystal packing (thermodynamic process)[7] would be more stable than the achiral (racemic) counterpart. The latter factor relies on the sum of the packing energy and the conformational energy of the molecule, which is sometimes influenced by solvent molecule in the crystal.[8] The formation of more than two types of crystals from a single compound without solvent molecule is defined as polymorphism,[9] and the formation of more than two types of crystal from a single compound with solvent molecule is defined as pseudopolymorphism.[10] In pseudopolymorphism, when the crystal without solvent molecule is achiral and that with solvent molecule is chiral, the solvent molecule acts as "chiral trigger", and in the opposite case, the solvent acts as "racemizing reagent". In both cases, the crystal solvents switch the optical activity of the crystals and such chirality control by crystal solvent provide powerful tool for design and development of various optical materials in the field of crystal engineering.[11]

Though metal complexes are attractive and potentially useful compounds in this field, the spontaneous resolution of the complexes[11,12] remains to be explored. Balavoine and co-workers demonstrated that the spontaneously resoluble bidentate phosphane-palladium complex could be utilized for the asymmetric catalysis.[13] On the other hand, few studies concerning the homochiral crystallization of achiral N-heterocyclic carbene (NHC)-metal complexes have been reported. It was reported that some NHC-metal complexes without any stereogenic element (chiral center, axis or face) gave crystals with a chiral space group.[14] However, these complexes were intrinsically achiral molecules which did not exist in enantiomerically stable conformation: the optical activity was caused only by the arrangement of the molecules in a chiral manner.

Recently we synthesized a series of bidentate NHC-palladium complexes with xanthene skeleton and the catalytic activity of the complexes for Mizoroki–Heck reaction and Suzuki–Miyaura reaction was examined.[15] In this communication, we report the first observation of spontaneous homochiral assembly of achiral bidentate NHC-palladium complexes with xanthene framework in crystalline state and the estimation of the energy barrier for the racemization of the complexes.

Results and Discussion

The bidentate NHC-palladium complexes **4a**–**e** were prepared by the reaction of 1-(4-iodoaryl)-3-aryl-4,5-dihydroimidazolinium salt (**1**)[16] and xanthenediboronic acid

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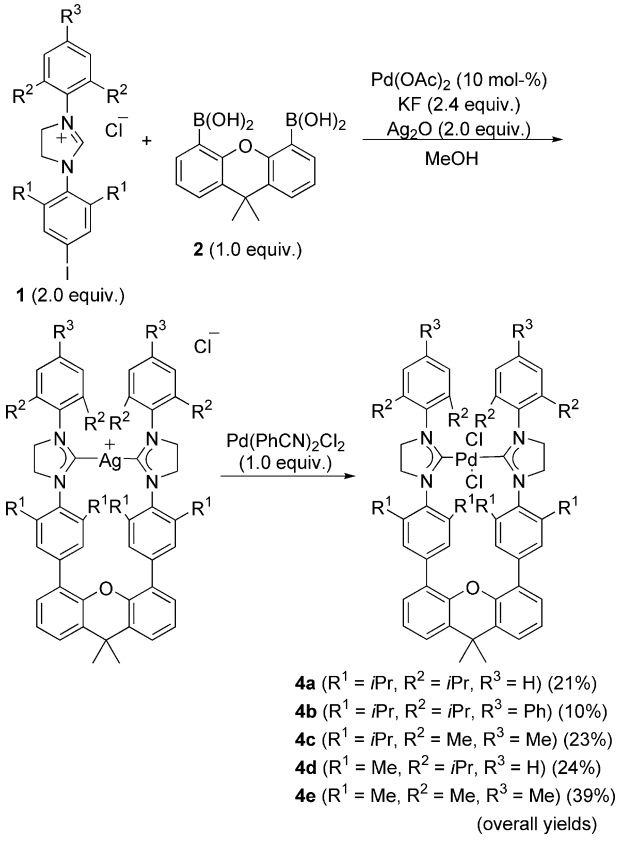
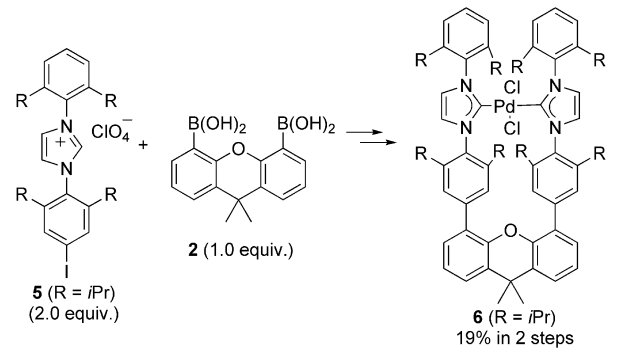
(**2**)[17] in the presence of $Pd(PPh_3)_4$ and Ag_2O followed by palladation[18] (Scheme 1). The bis(imidazolidene) derivative **6** was also synthesized in a similar way (Scheme 2).



Scheme 1. Synthesis of palladium complexes **4a**–**e**.



Scheme 2. Synthesis of palladium complex **6**.

Complexes **4a**–**e** and **6** could be isolated as single crystals and the X-ray analyses of the complexes were performed.[19] The results are summarized in Table 1.[20] All crystals of the complexes included solvent molecules in the crystalline lattice. Especially, complex **4a** afforded three types of crystals upon crystallization from various solvents (vide infra). Structural parameters showed that the C–Pd bond lengths of the complexes ($d_{C–Pd}$) increased compared to that of $Pd(IPr)_2Cl_2$ which was the palladium complex with *trans*-coordinating two NHCs.[21] The effect of the substituents at the aryl part (R^1, R^2, and R^3) on $d_{C–Pd}$ was small. It is also noteworthy that all complexes crystallized in twisted conformations (θ_1 and θ_2 on Table 1, Figure 1). We assume that the steric repulsion between the 2,6-disubstituted arenes is effectively reduced by adopting the twisted conformation. Consequently, the complexes have C_2 symmetry and could have a conformational chirality based on the twisted structure of the molecules.

Table 1. Selected structural parameters of **4a**–**e** and **6**.[a]

Complex	Included solvent	Space group	$d_{C–Pd}$ [Å][b]	θ_1 [°][c]	θ_2 [°][d]
4a (form A)	cyclohexane	$P\bar{4}$	2.048	31.05	28.90
4a (form B)	1,4-dioxane	$P4_12_12$	2.046	40.67	31.73
4a (form C)	THF	$P4_32_12$[e]	2.048	39.80	31.27
4b	THF	$P\bar{1}$	2.048	42.45	33.94
4c	CH_2Cl_2	$P2_1$	2.041	42.20	34.05
4d	THF	$P2_1/c$	2.037	42.61	34.07
4e	AcOEt	$P2_1/n$	2.028	40.23	40.83
6	THF	$P4_32_12$	2.039	34.97	32.34
$Pd(IPr)_2Cl_2$[f]	hexane	$P2_12_12_1$	2.019	39.82	–

[a] Parameters are the average of all molecules in an asymmetric unit. [b] Average bond length between $C_{carbene}$ and Pd. [c] Dihedral angle between N–C–N plane and N′–C′–N′ plane. [d] Torsion angle between $C_{4\text{-xan}}$–$C_{5\text{-xan}}$ and $C_{carbene}$–(Pd)–$C'_{carbene}$. [e] Enantiomeric crystal ($P4_12_12$) was also obtained (see Supporting Information). [f] See ref.[21]

X-ray analysis revealed that the complex **4a** exhibits pseudopolymorphism. The crystal of **4a** (form A), which was recrystallized from cyclohexane, was isolated as racemic crystals which contained both enantiomeric conformers. On the other hand, recrystallization of **4a** from 1,4-dioxane (form B) or THF (form C), respectively, afforded colorless prisms with chiral space group $P4_12_12$ or $P4_32_12$. The chirality of the crystals was derived from the assembly of single enantiomeric conformers of the complexes into the unit cell. The absolute configuration in each crystal was determined by the Flack parameter.[22] In the crystal of **4a** (form B), there are two 1,4-dioxane molecules between two neighboring molecules of **4a**. Weak interactions (CH–π and CH–O interaction)[23] were indicated between **4a** and 1,4-dioxane molecules (Figure 1, c). Thus, molecules of **4a** and the 1,4-dioxane molecules form a chiral helical network in the packing structure. Interestingly, homochiral crystals of **4a** (form C) was obtained with similar short contacts by using THF as the solvent for recrystallization.[20] Thus, the structural parameters of **4a** (form C) are very similar to those of **4a** (form B). In contrast, no intermolecular interaction was observed in the racemic crystal **4a** (form A) which was recrystallized from cyclohexane.[20] This result indicates that the interaction between the solvent molecule and the complex plays an important role for the homochiral crystallization and cyclic ether induced the homochirality of the crystals of **4a**. The crystal of **6** from THF also belongs to a chiral space group and the helical network in the packing structure was observed. However, the crystals of **4b**–**e** are racemic[24] and show no helical network structure although weak intermolecular interactions between complexes and solvent molecules exist.

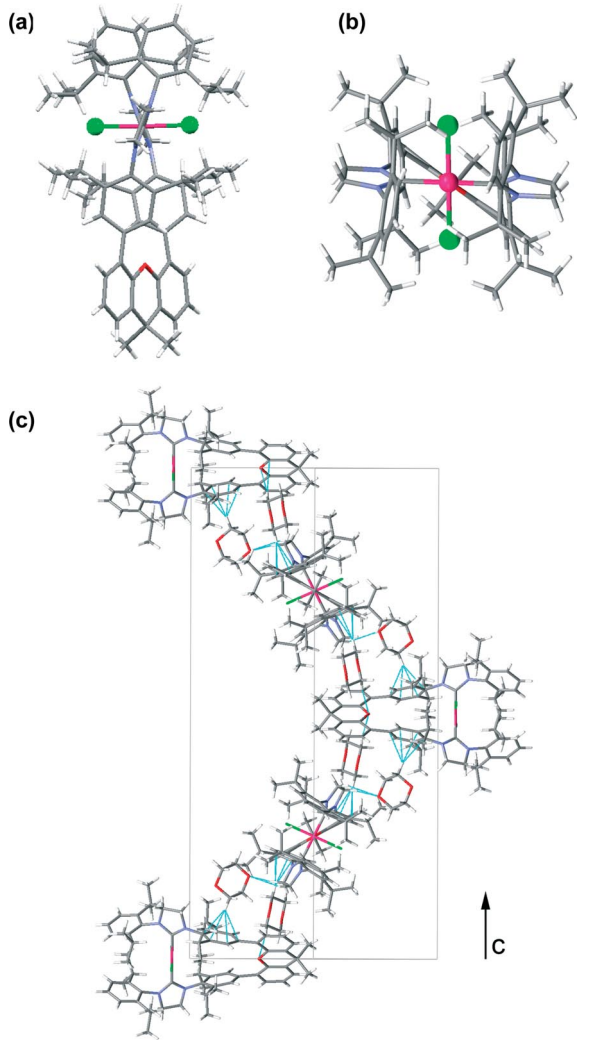


Figure 1. Crystal structure of **4a** (form B). Side view (a), top view (b) and packing structure (c). Short contacts with solvent molecules were shown as blue dotted lines.

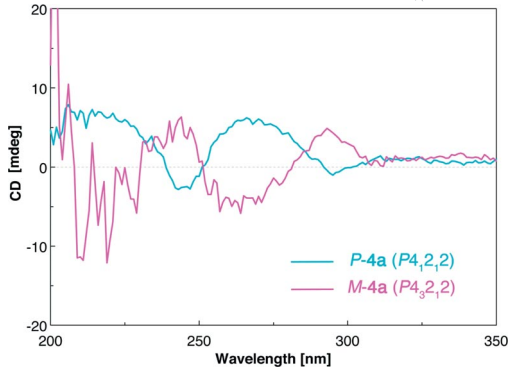
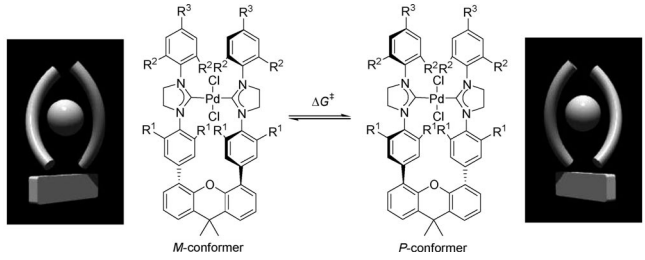


Figure 2. CD spectra of two enantiomeric crystals of **4a** (form C) in KBr.

Table 2. The energy barriers for the racemization of **4a**–**e** and **6** in CD_2Cl_2.



Complex	R^1	R^2	R^3	$\Delta G^{\ddagger}$ [kcal/mol] (T_c [K][a])
4a	*i*Pr	*i*Pr	H	10.4 (228),[b] 10.5 (208)[b]
4b	*i*Pr	*i*Pr	Ph	10.1 (218),[c] 9.9 (208)[c]
4c	*i*Pr	Me	Me	11.3 (248),[d] 11.2, 11.5 (248)[b]
4d	Me	*i*Pr	H	–[e]
4e	Me	Me	Me	–[f]
6	*i*Pr	*i*Pr	H	9.7 (213),[b] 9.8 (208)[b]

[a] An error range of $\Delta G^{\ddagger}$ is ±(0.2–0.3) kcal/mol. [b] Calculated from methyl protons of *i*Pr groups. [c] Calculated from CH protons of *i*Pr groups. [d] Calculated from 2-methyl protons of mesityl groups. [e] Broadening of NMR signals was observed at 183 K. [f] No separation or significant broadening of NMR signals was observed even at 183 K.

Solid-state CD spectra of the chiral crystals were measured in KBr matrix for *M*-**4a** (form C) and *P*-**4a** (form C). Mirror-image CD spectra were obtained for two chiral crystals (Figure 2). Crystals of **4a** exhibited marked Cotton effect below 300 nm and peaks around 245 nm, 260 nm, and 290 nm. The signs of the Cotton effect of the chiral complex **4a** were correlated to the absolute configuration determined from the Flack parameter in the X-ray analysis. The absolute configuration of the crystals with positive sign around 260 nm in the CD spectrum was *P*-**4a** and those with negative sign was *M*-**4a**.

Although each conformer is stable in the crystalline state at ambient temperature, fast racemization was observed in solution. The energy barriers for the racemization of **4a** and related complexes were calculated from dynamic NMR spectroscopy. The results are summarized in Table 2.

Since N–Ar bond rotation is restricted due to the steric repulsion,[25] four distinct methyl resonances of **4a** (Me^a, Me^b, Me^c and Me^d) were observed at ambient temperature (see Figures 3 and 4). NMR signals of Me^a and $Me^{a\prime}$, which were observed as identical sharp doublets at ambient temperature, were broadened by the reduced rate of the interconversion as the temperature decreased, and the complete signal separation was observed at low temperature. Similar changes were observed on other Me groups, and eight distinct resonances were observed below 193 K (Figure 3). The energy barrier for the racemization of **4a** was estimated to 10.35 ± 0.24 kcal/mol at T_c (228 ± 5 K, $\Delta\nu$ = 253 Hz) according to the ^{1}H NMR signals of one Me protons of *i*Pr group and 10.49 ± 0.22 kcal/mol at T_c (208 ± 5 K and $\Delta\nu$ = 18 Hz) according to the other Me protons of *i*Pr group (Table 2, Figure 3). The energy barriers of the other complexes are listed in Table 2. The analysis showed that the energy barriers depended on the size of substituent. When the methyl groups at R^1 were replaced by *i*Pr groups, the barrier to racemization significantly increased (complex **4c** in Table 2). The effect was not distinct when those at R^2 were replaced by *i*Pr groups (**4d**), because the distance

between the R^2 groups is longer than that between the R^1 groups. The introduction of *i*Pr groups on both of phenyl rings (**4a** or **4b**), however, reduced the energy barrier to racemization compared to **4c**. This would be because steric repulsion between the *i*Pr groups would significantly destabilize the ground state. Thus, these results suggest that the racemization rate can be controlled by the combination of the substituents.

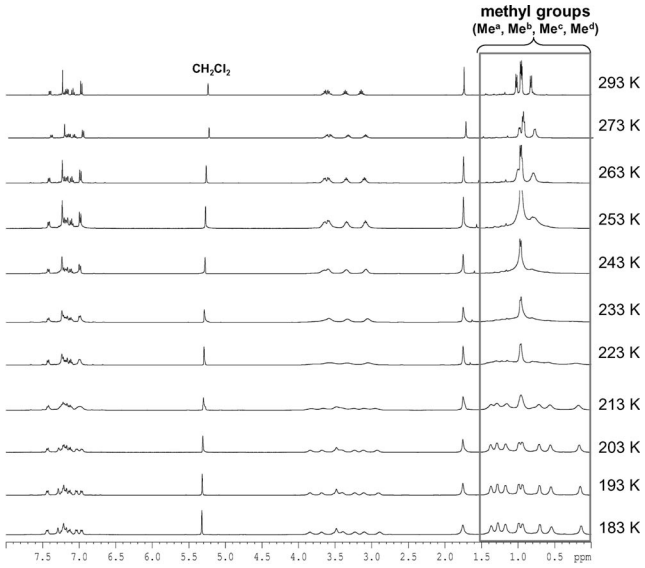


Figure 3. Dynamic NMR spectra of **4a** in CD_2Cl_2.

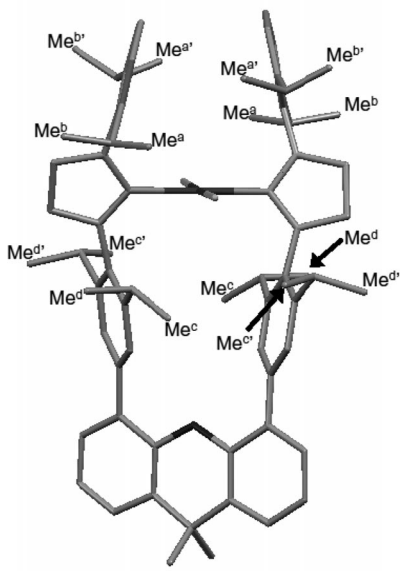


Figure 4. Numbering scheme for **4a**.

Conclusions

We disclosed a new class of spontaneously resolved palladium complexes which were composed of bidentate NHC ligands. The complex **4a** exhibited pseudopolymorphism, and some crystals of **4a** turned out to be homochiral. The chirality of the crystals was controlled by the solvent used for recrystallization, and the interaction between cyclic ether and the complexes might play a notable role for the formation of homochiral crystals. The absolute configuration of the complexes **4a** and **6** was determined by X-ray crystallographic analysis. Dynamic NMR studies revealed that the energy barrier for the racemization could be controlled by the choice of the substituent.

Experimental Section

Synthesis of Complex 4a: A mixture of **2** (1.49 g, 5 mmol), **1a** (4.55 g, 10 mmol), palladium acetate (112 mg, 0.5 mmol), potassium fluoride (696 mg, 12 mmol) and silver(I) oxide (2.32 g, 10 mmol) in methanol (50 mL) was stirred for 2 d at room temperature. CH_2Cl_2 (100 mL) was added, and the mixture was filtered through celite and concentrated. The residue and $Pd(PhCN)_2Cl_2$ (2.32 g, 10 mmol) was suspended in dioxane (80 mL), and the mixture was heated at 100 °C for 24 h. The resulting suspension was diluted with CH_2Cl_2 (100 mL), and the precipitate was removed by filtration through celite. The filtrate was concentrated and the product was purified by column chromatography [silica gel, Hex/AcOEt (25:1)] to afford Pd complex **4a** as pale yellow powder (2.44 g, 21%): m.p. >300 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 (dd, J = 7.8, 1.8 Hz, 2 H), 7.28 (s, 4 H), 7.26–7.23 (m, 4 H), 7.15 (t, J = 7.8 Hz, 2 H), 7.04 (d, J = 7.8 Hz, 4 H), 3.73–3.70 (m, 4 H), 3.66–3.63 (m, 4 H), 3.44 (septet, J = 6.6 Hz, 4 H), 3.25 (septet, J = 6.6 Hz, 4 H), 1.82 (s, 6 H) 1.10 (d, J = 7.8 Hz, 12 H), 1.04 (d, J = 7.2 Hz, 12 H), 1.02 (d, J = 7.2 Hz, 12 H), 0.91 (d, J = 7.2 Hz, 12 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 200.1, 147.6, 146.6, 146.5, 137.5, 136.5, 136.3, 130.3, 130.0, 129.4, 128.7, 125.53, 125.50, 124.2, 122.7, 54.2, 53.4, 34.4, 34.0, 28.4, 28.0, 26.6, 26.4, 24.2, 23.9 ppm. IR (KBr): $\tilde{\nu}$ = 2960, 2866, 1439, 1401, 1382, 1267, 1242 cm^{-1}. HR-MS (ESI-TOF): Calcd. for $C_{69}H_{86}Cl_2N_4OPdNa$ ($[M + Na]^+$). 1187.5114; found 1187.5095. $C_{69}H_{86}Cl_2N_4OPd$ (1164.77): calcd. C 71.15, H 7.44, N 4.81; found C 71.26, H 7.28, N 4.80.

Supporting Information (see also the footnote on the first page of this article): Detailed procedure for the synthesis of complexes **4a**–**e** and **6**, and spectroscopic data of new compounds. Details of X-ray crystallographic data of complexes **4a**–**e** and **6**. The results of dynamic NMR of the complexes **4a**–**c** and **6**.

[1] In this article, "racemic compound" means an equimolecular mixture of stable enantiomers or isolable enantiomeric conformers at ambient temperature in solution and an "achiral compound" means a compound which is interconverting between enantiomeric conformations swiftly at ambient temperature in solution, unless otherwise noted.

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[19] Crystal structures were solved and refined by program package Bruker SHELXTL (G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122).

[20] CCDC-685660 [for **4a** (form A)], -685661 [for **4a** (form B)], -685662 [for *M*-**4a** (form C)], -685663 [for *P*-**4a** (form C)], -685664 (for **4b**), -685665 (for **4c**), -685666 (for **4d**), -685667 (for **4e**) and -685668 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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