Chiral tether-mediated stabilization and helix-sense control of complementary metallo-double helices†

Miki Horie,a Naoki Ousaka,b Daisuke Taura and Eiji Yashima*a

A series of novel PtII-linked double helices were prepared by inter- or intrastrand ligand-exchange reactions of the complementary duplexes composed of chiral or achiral amidine dimer and achiral carboxylic acid dimer strands joined by trans-PtII-acetylide complexes with PPh3 ligands using chiral and achiral chelating diphosphines. The structure and stability of the PtII-linked double helices were highly dependent on the diphosphine structures. An interstrand ligand exchange took place with chiral and achiral 1,3-diphosphine-based ligands, resulting in trans-PtII-bridged double helices, whose helical structures were quite stable even in dimethyl sulfoxide (DMSO) due to the interstrand cross-link, whereas a 1,2-diphosphine-based ligand produced non-cross-linked cis-PtII-linked duplexes, resulting from an intrastrand ligand-exchange that readily dissociated into single strands in DMSO. When enantiopure 1,3-diphosphine-based ligands were used, the resulting trans-PtII-bridged double helices adopted a preferred-handed helical sense biased by the chirality of the bridged diphosphines. Interestingly, the interstrand ligand exchange with racemic 1,3-diphosphine toward an optically-active PtII-linked duplex, composed of chiral amidine and achiral carboxylic acid strands, was found to proceed in a diastereoselective manner, thus forming complete homochiral trans-PtII-bridged double helices via a unique chiral self-sorting.

Introduction

Biological helices, such as double-helical DNA and α-helical peptides, have prompted a number of chemists to construct artificial single- and double-stranded helical polymers1 and oligomers (foldamers)2 not only due to their unique structures, but also to their sophisticated functions. Currently, a wide variety of single-stranded helices have been synthesized,1,2 which enable us to rationally design a single-helical structure from its primary sequence, although it remains a great challenge to create a new structural motif for double-helical structures.3 However, DNA analogues (peptide nucleic acids, PNAs)4 and double-stranded helicenes are known to intertwine to form double helices assisted by hydrogen bonds and metal-directed coordination, respectively.5a,c,d,5f A new class of double-stranded helices has recently been developed by Lehn, Huc and co-workers5k–j that mainly rely on multiple hydrogen bonds between the strands and/or interstrand aromatic-aromatic interactions,6,7 the stability of which strongly depends on the type of solvent (polar or non-polar)6a and sequence,6b except for the hydrophobic-driven double helices in water.8

It is well-known that intramolecular cross-linking stabilizes a helical conformation of single-stranded helical polymers,9ae,b foldamers,k–m and oligopeptides,b thus leading to the development of smart chiral materials and biologically active materials. The interstrand cross-linking of DNA that reinforces its double-helical structure was also reported to have applications for clinical use.12 However, to the best of our knowledge, there is at least one precedent of a synthetic double helix whose helical conformation was significantly stabilized as a result of interstrand cross-linking.12

Recently, we have developed a versatile method to construct a series of complementary double helices by utilizing amidinium–carboxylate salt bridges that possess high stability and well-defined directionality along their N+-H...O- lines, thereby enabling the intertwining of the two complementary molecular strands composed of crescent-shaped rigid m-terphenyl backbones.1c,d,f,g,h,i,j This structural feature has a great advantage such that various types of linker units, such as diacetylene,14ac,k p-diethylbenzene14f,k and trans-PtII-acetylide linkages,12g,14c,k can be introduced while maintaining the double-helical structures. In addition, the helical sense and handedness of the double helices are readily controlled by the chiral substituents introduced on the amidine groups,14 or by using chiral
monodentate phosphine ligands, such as (R)- or (S)-2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl (MOP), coordinated to the PtII atom in the linkage (Scheme 1A).15

We found that an optically-active double helix composed of two complementary strands bearing achiral amidine or carboxylic acid residues, linked through the PtII-acetylide complexes with (R)- or (S)-MOP or achiral triphenylphosphine (PPh3) ligands, exhibited an inversion of the helicity in different solvents at low temperatures,12 suggesting the dynamic nature of the PtII-linked double helix.15 The chiral and achiral monodentate phosphine ligands on the PtII atoms could be quantitatively replaced by an achiral diphosphine ligand, such as bis(diphenylphosphino)methane (DPPM), through the interstrand ligand-exchange reaction, resulting in the bridged double helix (right in Scheme 1A).12 Interestingly, the bridged double helix, which no longer possessed any chiral components, except for helicity, maintained its preferred-handed helical conformation induced by the chiral MOP ligand for a long time period (over 100 days at 298 K). This enantiomerically-enriched double helix further catalyzed the asymmetric cyclopropanation of styrene with a high enantioselectivity (up to 85% enantiomeric excess) when complexed with CuI ions, thus providing the first asymmetric catalyst based on a unique bridged double-helical structure.12

It has been reported that the trans-PtII-acetylide complexes with PPh3 ligands can be readily transformed into the cis-PtII-acetylide in the presence of chelating diphosphine ligands, such as cis-[bis(diphenylphosphino)ethylene, cyclic diphosphines, and substituted diphosphinoethanes, by an intrastrand ligand exchange, whereas achiral 1,3-diphenylphosphinopropane (DPPPr) and chiral 2,4-bis(diphenylphosphino)pentane (DPPPe) produced dimeric trans-PtII-acetylide complexes bridged by the diphosphine ligands through the interstrand ligand exchange.16,17

Based on these results, together with our previous findings,12 we anticipated that both the stability and helical handedness of the PtII-linked double helices could be enhanced and controlled using chiral chelating diphosphine ligands as cross-linkers.

Scheme 1 Structures of the PtII-acetylide-linked amidine and carboxylic acid dimers (A and B), and their complementary duplexes before and after reactions with chiral (B) and achiral (A and B) diphosphines.
during the ligand-exchange reactions. Although a variety of single-stranded helical polymers and foldamers have been developed, a “chiral cross-linking” approach has not yet been employed to control the helicity, except for a few examples. To this end, we synthesized a series of PtII-linked dimer strands composed of chiral or achiral amidine (1a–1c) and achiral carboxylic acid dimer strands (2), and investigated the effects of chiral diphosphine ligands, such as (S,S)- or (R,R)-DPPPe and

![Fig. 1](image)

**Fig. 1** Partial $^1$H NMR (500 MHz, 2.0 mM) spectra of (A) (S,S)-3a, (B) (S,S)-3b, (C) (S,S)-3c (D) (R,R)-3c, and (E) 3d in CDCl$_3$ at 25 °C.

![Fig. 2](image)

**Fig. 2** (A) Schematic representation of the helix inversion of the duplex 3d. The “outer” and “inner” N–H protons (Hc’ and Hc”) in the salt bridges become non-equivalent due to the interconvertible right- and left-handed double-helical structures under slow-exchange conditions. (B) Variable-temperature (from −60 to 25 °C) $^1$H NMR (500 MHz, 2.0 mM) spectra of 3d in CDCl$_3$ (the temperatures from −69 to −44 °C, used to estimate $T_c$, are also shown in Fig. S3†).
(S,S)- or (R,R)-2,3-bis(diphenylphosphino)butane (CHIRAPHOS), and substituents on the amidine residues. These included the effect of chirality on the structures, stabilities, and chiroptical properties of the double helices (3-4) resulting from the ligand-exchange reactions on the PtII atoms (Scheme 1B), measured using absorption, circular dichroism (CD), and 1H and 31P NMR spectroscopies. We also found that the ligand-exchange reaction on the PtII atoms with racemic DPPPe proceeded in a diastereoselective manner, producing the non-racemic bridged double helix, when a PtII-linked chiral amidine dimer (1c) and 2 were used as a precursor duplex.

Results and discussion

Synthesis and the ligand-exchange reaction

The achiral (1a)12 and chiral ((R)-1c)14 amidine dimers and the achiral carboxylic acid dimer (2)12 connected through the PtII-acetylide complex with two PPh3 ligands, and their corresponding duplexes (1a-2,12 and 1c-2)14 were prepared according to previously reported methods (Scheme 1B). A novel achiral amidine dimer (1b) and its complementary duplex (1b-2) were also synthesized in a similar way.

The ligand-exchange reactions on the PtII atoms of the trans-PtII duplexes 1a-c-2 were carried out using 2 equiv. of the chiral diphosphines, (S,S)- or (R,R)-DPPPe and (S,S)- or (R,R)-CHIRAPHOS, and achiral DPPPr. The resulting double helices were purified by size-exclusion chromatography (SEC) and characterized and identified using 1H and 31P NMR spectroscopies, and elemental analyses or cold-spray ionization mass spectrometry (CSI-MS) measurements (Fig. S1 and S2, and ESI†).

Effect of the chiral and achiral diphosphines on the duplex structures

The ligand-exchange reaction of the trans-PtII duplexes 1a-c-2 with a chiral diphosphine, (S,S)- or (R,R)-DPPPe (2 equiv.), gave the optically-active bridged double helices, (S,S)- and (R,R)-3a-c, respectively, while maintaining the trans geometry around the PtII center (Scheme 1B), as confirmed by the 1H and 31P NMR spectra (Fig. 1 and S1†).18 The analogous achiral diphosphine, DPPPr, also produced the trans-PtII-bridged double helix (3d) (Scheme 1B), as supported by its 31P NMR spectra (Fig. S1†).18 These results indicated that the ligand exchange of 1a-c-2 with 1,3-diphosphine-based ligands (DPPPe and DPPPr) takes place via an interstrand fashion, thus producing the bridged double

Scheme 2 Synthesis of the cis-PtII-acetylide-linked amidine (5a-c) and carboxylic acid (6) dimers with (S,S)- or (R,R)-CHIRAPHOS ligand.
helices. However, treating the duplexes 1a–c with 2 equiv. of (S,S)- or (R,R)-CHIRAPHOS led to the formation of the non-cross-linked duplexes 4a–c whose 31P NMR spectra were different from those of 3a–d (Fig. S1†; see below for more details) (Scheme 1B).

As previously reported,19 the related complementary double helices, composed of chiral amidine and achiral carboxylic acid dimeric strands connected by various types of linkers including PtII–acetylide linkages, possess an excess of either a right- or left-handed double-helical structure. Therefore, the salt-bridged N–H protons (Hc0 and Hc00) exhibited in their 1H NMR spectra two sets of non-equivalent signals around 12–14 ppm due to “outer” and “inner” N–H protons, as observed for the present optically-active 3a–c (Fig. 1A–D), most likely derived from the preferred-handed double-helical structures as depicted in Fig. 2A.14

In contrast, the bridged duplex 3d displayed a single set of sharp peaks including the salt-bridged N–H proton resonances that appeared as the equivalent doublet peak at 12.37 ppm in CDCl3 at 25°C (Fig. 1E). The bridged duplex 3d was optically inactive, but existed as a racemic mixture of interconvertible right- and left-handed double helices; the rate of helix inversion that accompanied the C–C bond rotation between the amidine and m-terphenyl groups (Fig. 2A) may have been too fast on the present NMR time scale to detect the non-equivalent N–H protons at this temperature.14 We then measured the variable-temperature 1H NMR spectra of 3d in CDCl3 to estimate its helix inversion barrier and also to evaluate the effect of the interstrand cross-linking on the thermodynamic stability of the duplex (Fig. 2B).

Upon cooling to lower temperatures, the N–H proton signals of 3d gradually broadened and subsequently split into two sets of non-equivalent signals at –60°C (Fig. 2B) via the coalescence temperature (Tc = –46°C) (Fig. S3†). We noted that an analogous PtII–acetylide-linked double helix bearing the triethylphosphine (PET3) ligands instead of DPPPr did not show such nonequivalent signal splitting, even at –80°C in CD2Cl2,14 indicating the significant enhancement of the stability of the duplex by the interstrand cross-link. The obtained Tc, along with the chemical shift difference between the split signals (Δδ = 313 Hz), enables us to estimate that the free energy of activation for the helix inversion (ΔG‡) of the duplex 3d is 42.7 kJ

Fig. 4 (A) Interstrand ligand exchange of 1c–2 with 4 equiv. of rac-DPPPe. (B) Time-dependent 1H NMR spectral changes of 1c–2 (TMS region) before and after the addition of 4 equiv. of rac-DPPPe in CDCl3 at 25°C; [1c–2]0 = 0.5 mM, [rac-DPPPe]0 = 2.0 mM. The 29Si satellite peaks are marked with asterisks. (C) Plots of the yields and diastereomeric excess (de) of the resulting duplexes 3c versus time. The yields were estimated using an internal standard (1,3,5-trioxane).
mol⁻¹ at 25 °C, which corresponds to the lifetime of the one-handed helical state (τ) of 4.98 × 10⁻⁶ s. The ΔG² value obtained for 3d appears to be much higher than that for the PtII-linked duplex bearing the PtII ligands,¹⁴ but lower than that of the bridged double helix by the DPPM ligands (Scheme 1A), because the enantiomERICally-enriched DPPM-bridged double helix retains its optical activity for a long time.¹⁵

These results clearly indicated that the helix-inversion barrier, in other words, the stability of the bridged double-helical conformations, significantly depends on the structure of the chelating diphosphines, in particular, the length between the phosphorous atoms and the flexibility of the diphosphines, which determines the distance between the two PtII atoms on each complementary strand after the ligand exchange. In fact, the energy-minimized double-helical structure of 3d (determined using the PM6 method in MOPAC2012 (ref. 21)) revealed that the Pt–Pt distance (5.4 Å) is much longer than that of the DPPM-linked double helix (3.1 Å) in the crystalline state¹² (Fig. S4A†).

In contrast to 3d, the amidinium N–H proton resonances in the ¹H NMR spectra of (S,S)-3a and -3b in CDCl₃, at 25 °C showed two sets of non-equivalent signals, even though the amine groups are achiral (Fig. 1A and B), suggesting that these double helices probably adopt a preferred-handed double-helical structure induced by the chiral cross-linkers. The enantiomERICally enriched dimeric duplex bearing the chiral amine groups with an (R)-configuration, whose helical structure was determined to be right-handed by the single-crystal X-ray analysis.¹⁴ In the ¹H NMR spectrum of (S,S)-3c showed a series of sharp signals, including two sets of sharp doublet peaks assigned to the non-equivalent salt-bridged N–H protons at 14.00 and 12.29 ppm (Fig. 1C), while most of the proton signals, in particular, the N–H protons, of (R,R)-3c became considerably broadened (Fig. 1D).

The energy difference (ΔE) between the right- and left-handed double helices of (S,S)-3a and (R,R)-3c was then estimated using semi-empirical molecular orbital (MO) calculations (using the PM6 method in MOPAC2012 (ref. 21)), which revealed that the right-handed double-helical structure is 34.2 kJ mol⁻¹ more stable than the other (Fig. S4B†), which is consistent with the preferred-handed helix sense predicted by its CD pattern.

Interestingly, the diastereomeric (S,S) and (R,R)-3c duplexes with the same (R)-configuration at the amidine residues also exhibited mirror image-like CD spectra (Fig. 3C), suggesting that the helix sense of 3c is predominantly governed by the chirality of the cross-linkers rather than the chirality of the amidine groups.¹⁵ However, the CD and absorption intensities between the diastereomers of 3c around 375 nm are significantly different from each other, probably due to the difference in the conformational flexibility around the PtII-phenylacetylide moieties, the absorption bands of which (metal-to-ligand charge transfer: MLCT) appear in this region.²⁴ In fact, the ¹H NMR spectrum of (S,S)-3c showed a series of sharp signals, including two sets of sharp doublet peaks assigned to the non-equivalent salt-bridged N–H protons at 14.00 and 12.29 ppm (Fig. 1C), while most of the proton signals, in particular, the N–H protons, of (R,R)-3c became considerably broadened (Fig. 1D).

The energy-minimized structures of the left-handed (R,R)-3c and right-handed (S,S)-3c duplexes suggest that the molecular motion of the (R,R)-3c duplex is highly restricted compared to the other due to the steric repulsion between the m-terphenyl groups and the bridged diphosphine ligands (Fig. 3C). The temperature-dependent CD and absorption spectral changes further support this speculation; the CD and absorption spectra of the (R,R)-3c hardly changed in the temperature range –10 to...
50 °C, while the CD intensity of the (S,S)-3c increased with decreasing temperature (Fig. S6†).

It is noteworthy that all the bridged duplexes with chiral DPPPe ligands (3a–c) showed intense CD signals in CHCl3 and even in dimethyl sulfoxide (DMSO) (Fig. S7†). In DMSO, the salt-bridge formation is strongly hampered,44 and therefore, the non-cross-linked 1c-2 duplex readily dissociates into each strand in DMSO, thus showing a very weak CD spectrum identical to that of the 1c strand (Fig. S7†) and indicating that the interstrand cross-linking remarkably stabilizes the complementary double helices.

The interstrand ligand-exchange reaction

In contrast to the interstrand ligand-exchange reactions discussed above, the duplexes 1a-2, 1b-2, and 1c-2 were found to undergo ligand exchange via an intrastrand mechanism when 2 equiv. of (S,S)- or (R,R)-CHIRAPHOS were used as a chiral chelating diphosphine, leading to the formation of the non-cross-linked 4a-c through the isomerization of the trans- to cis-PtII-acetylide moieties.19 The structures were confirmed by 31P NMR measurements, in which the $^1$$J_{P-Pt}$ coupling constants of 4a-c were in the range of 2198-2249 Hz, that are consistent with the reported values for the cis-PtII-acetylide complexes with the phosphine ligands (Scheme 1B and Fig. S1†).

In order to further support the structural assignments, a series of model dimers, cis-PtII-acetylide-linked amide (5a-c) and carboxylic acid (6) dimers with (S,S)- or (R,R)-CHIRAPHOS ligands, were prepared (Scheme 2) starting from 1a-c and 2.19,25,36 The $^1$H NMR, CD, and absorption spectra of the model duplexes (S,S)-5a-6, (S,S)-5b-6, (S,S)-5c-6, and (R,R)-5c-6 are almost identical to those of the (S,S)-4a, (S,S)-4b, (S,S)-4c, and (R,R)-4c duplexes, respectively (Fig. S8–S11†).

Unlike in the case of the bridged 3a-c duplexes, 4a-c and their model duplexes (5-6) almost completely dissociated into corresponding single strands in DMSO, based on their CD spectra in DMSO (Fig. S12†),48 and most of the $^1$H NMR signals of 4a-c measured in CDCl3 at 25 °C were highly broadened (Fig. S8A–S11A†) as anticipated because of their non-cross-linked structures. The amidinium N–H proton resonances of (S,S)-4a and -4b (Fig. S8A and S9A†) displayed an equivalent broad singlet peak (12.02 ppm), despite the N–H signals of (S,S)-3a and -3b showing non-equivalency (Fig. 1A and B). It seems likely that (S,S)-4a and -4b are in equilibrium between the single strands and the duplex, or adopt a double-helical structure without a helix-sense bias. Therefore, their CD intensities were much lower than those of the bridged duplexes 3a and 3b (Fig. 3 and S13†). This is probably due to conformational flexibility around the chiral phosphine moieties of 4a and 4b, resulting in an inefficient stereochemical communication between the chiral phosphine groups and the main chain. Unexpectedly, the N–H proton resonances of (R,R)-4c showed multiple N–H signals in CDCl3 (Fig. S11A†), whereas those of (S,S)-4c exhibited two sets of non-equivalent signals (Fig. S10A†). The reason for this is not clear at present, but is considered to be due to the presence of two conformers that may slowly interconvert on the present NMR time scale via dissociation and association of the salt bridges for (R,R)-4c.29

The diastereoselective interstrand ligand-exchange reaction

The optically-active PtII-linked (R)-1c-2 possesses an excess one-handed double-helical structure induced by the chiral amide residues, and exhibited intense CD signals in the m-terphenyl chromophore region as well as in the PtII-acetylide complex region (ca. 330-400 nm) (Fig. 3C).14,15,16,17 Therefore, we anticipated that the interstrand ligand-exchange reaction on the PtII atoms of the optically active 1c-2 using racemic DPPPe (rac-DPPPe) could diastereoselectively proceed, assisted by the one-handed double-helical structure of 1c-2, thus selectively producing either the right- or left-handed bridged duplex 3c (Fig. 4A). To this end, the optically-active 1c-2 was allowed to react with excess rac-DPPPe (4 equiv.) in CDCl3 at 25 °C, and the reaction progress was monitored by $^1$H NMR spectroscopy.

The $^1$H NMR spectra (TMS region, Fig. 4B) of the mixtures after 1 h showed two distinct sets of signals derived from the amide and carboxylic acid strands, namely the bridged duplexes (S,S)-3c (blue triangles) and (R,R)-3c (red squares) in addition to unknown signals (green circles), which gradually decreased with time and almost disappeared within 30 h (Fig. 4C).27 We assigned this unknown product to the low-symmetric, heterochiral bridged duplex ((S,S)-3c) bearing both the (S,S)- and (R,R)-DPPPe ligands, that may be formed during the ligand-exchange reaction under kinetic control and which should be labile. This assignment was supported by the following facts: (1) the unknown signals remained even after 24 h when 2 equiv. of rac-DPPPe was added to a solution of 1c-2, so that no further ligand exchange took place between the homochiral duplexes (S,S)- and (R,R)-3c once the DPPPe ligands were consumed (Fig. S14 and S15†); (2) a similar trend was observed for a mixture of (S,S)- and (R,R)-3c that is inert to the ligand-exchange reaction even in the presence of an excess amount of free ligands with the opposite configuration (2 equiv.) (Fig. S16†), leading to the conclusion that there is no ligand exchange among the three homo- and heterochiral bridged duplexes 3c once formed under the present conditions (Fig. 5, 1st step).

The initial stage of the diastereoselective ligand-exchange reaction resulted in the formation of an excess of (S,S)-3c over (R,R)-3c in 14% diastereomeric excess (de) ([S,S]-rich) (Fig. 4B and C). Interestingly, as the reaction progressed, (R,R)-3c was preferentially formed, accompanied by a gradual decrease in the amount of (S,R)-3c with time, leading to reversed diastereoselectivity up to 19% de ([R,R]-rich) after 30 h (Fig. 4C).28 This change in the diastereoselectivity could be explained as follows: the initial rate of formation of (S,S)-3c from the reaction of 1c-2 with enantiopure (S,S)-DPPPe is higher than that of (R,R)-3c from the reaction of 1c-2 with enantiopure (R,R)-DPPPe (Fig. S17†). As described above, the two homochiral double helices, (S,S)- and (R,R)-3c, are inert once formed by the ligand-exchange reaction, whereas the heterochiral (S,R)-3c is optically active and labile, thus, it is converted into either homochiral (S,S)- or (R,R)-3c in the presence of free DPPPe ligands. The
formation of (R,R)-3c is preferred to that of (S,S)-3c (Fig. 5, 2nd step). Thus, the complete diastereoselective homochiral sorting eventually takes place under total kinetic control. The diastereoselectivity of rac-DPPPe was initially determined by a preferred-handed double helix assisted by the chiral amidine residues under kinetic control, while the overall diastereoselectivity was governed by the kinetically-formed (S,R)-3c.

Conclusions

In summary, we have successfully synthesized a series of novel PtII-linked double helices through inter- or intrastrand ligand-exchange reactions of the corresponding complementary duplexes using chiral and achiral 1,3-diphosphine-based ligands. The diphosphine structures significantly influenced the duplex structures; chiral and achiral 1,3-diphosphine-based ligands produced the trans-PtII-bridged double helices via an interstrand ligand exchange reaction, whereas a 1,2-diphosphine-based ligand gave non-cross-linked cis-PtII-linked duplexes through an intrastrand ligand exchange reaction. The former duplexes were quite stable even in DMSO due to the interstrand cross-link, while the latter duplexes readily dissociated into each strand in DMSO. When enantiomerically-pure 1,3-diphosphine-based ligands were used, optically-active trans-PtII-bridged double helices could be obtained; the helix sense was controlled by the chirality of the bridged diphosphines. Interestingly, the interstrand ligand exchange with racem 1,3-diphosphine toward an optically-active PtII-linked duplex composed of a chiral amidine strand diastereoselectively proceeded, finally producing totally homochiral trans-PtII-bridged double helices via complete homochiral self-sorting. The present findings will provide a versatile means for the rational design of functional double helix-based chiral materials for chiral recognition and also asymmetric catalysis with high stability and selectivity. Further work along this line is currently ongoing in our laboratory.

Acknowledgements

This work was supported in part by Grant-in-Aid for Scientific Research (S) from the Japan Society for the Promotion of Science and by the Nanotechnology Platform Program (Molecule and Material Synthesis) of the Ministry of Education, Culture, Sports, Science and Technology, Japan. M. H. expresses her thanks for a JSPS Research Fellowship for Young Scientists (no. 10192).

Notes and references


18 The $J_{\text{Fe-Pt}}$ coupling constants of the bridged double helices in the range 2545–2663 Hz are consistent with the reported values for the trans-PtII-acetylide complexes with phosphine ligands.$^{14b}$

19 Tykwinski and coworkers reported that the trans-PtII–alkenyl complexes with PPh3 ligands could be smoothly transformed into the corresponding cis-form via a ligand-exchange reaction with CHIRAPHOS or cis-bis(diphenylphosphino)ethylen.$^{14b,17c,b}$


22 The CD and absorption intensities of 3a around 375 nm are smaller than those of 3b, which may be attributed to a conformational flexibility arising from the less bulky amidine substituents of 3a, compared to 3b.

23 The right- and left-handed double-helical structures of (S,$S$)-3c and (R,$R$)-3c are 53.8 and 18.5 kJ mol$^{-1}$ more stable than the corresponding opposite-handed duplexes, respectively, estimated by semi-empirical MO calculations (using the PM6 method$^{29}$ in MOPAC2012 [ref. 21]) (Fig. S4C and D$^\dagger$).


25 It should be noted that the absorption band around 375 nm observed in 3a–c with the trans-PtII geometry completely disappeared in the non-cross-linked cis-PtII–4a–c and their model duplexes 5a–c–6 (Fig. S8–S11$^\dagger$).$^{14b}$

26 The rate of chain exchange between the dimeric strands in the related PtII-linked duplexes was reported to be much slower than the NMR time scale.$^{14b}$

27 The relatively lower yields of 3c during the initial stage of the ligand-exchange reaction may be due to imperfect bridging by DPPPe, resulting in complicated intermediates, such as duplexes bearing non-bridged DPPPe and PPh3 ligands with different molar ratios, the signals of which would be highly broad. In fact, the TMS signals due to the 1c-2 (0.25 and 0.23 ppm) completely disappeared within 1 h (Fig. 4B).

28 A similar diastereoselectivity switching has been observed in the template synthesis of complementary double helices through the formation of dynamic-covalent imine bonds.$^{19}$

29 The diastereoselective ligand exchange of heterochiral (S,$R$)-3c toward (S,$S$)- and (R,$R$)-DPPPe was investigated as follows (Fig. S18$^\dagger$); first 1c-2 was allowed to react with 2 equiv. of rac-DPPPe to form unreactive homochiral (S,$S$)- and (R,$R$)-3c ((S,$S$) rich) as well as reactive (S,$R$)-3c. Upon the further addition of 2 equiv. of rac-DPPPe, the (S,$R$)-3c preferentially reacted with (R,$R$)-DPPPe over the antipode (S,$S$)-DPPPe, thus producing totally homochiral 3c slightly rich in the (R,$R$)-3c duplex, which clearly revealed the (R,$R$)-selectivity of the heterochiral (S,$R$)-3c, although its diastereoselectivity was not high.