Different Diastereoselectivities in the Stereoselective Oxidative Cyclization of Two Cyclopropenes at Palladium(0)

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The C_s-symmetrical cyclopropene **4a** provided the palladacycle *exo,exo*-**5** as the major product, accompanied by only small amounts of the *endo,exo*-**5** isomer. The stereochemical assignments were accomplished by crystal structure analyses of the corresponding bpy, bis(acetone), and bis(acetonitrile) complexes. The enantiomerically pure, C_1-symmetrical cyclopropene (*S*,*S*)-**7**, with two (*S*)-configured lactate units in the side-chain, delivered one dominant and three minor isomers. On the basis of one crystal structure analysis, the symmetry of the products, and the CD spectra, it was deduced that the (*S*)-lactate induced the (1*S*,2*S*,4*S*,6*S*) configuration in the palladacycle in the two major stereoisomers and the opposite configuration for the two minor diastereomers. For both configurational possibilities of the palladacycle, the *exo,exo* isomer was formed preferentially over the *endo,exo* isomer.

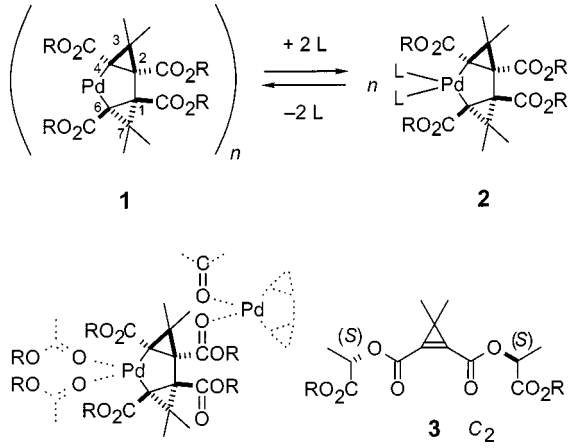
Introduction

In recent years we have been investigating enantiomerically pure metallacycloalkanes. Possible applications of these unique organometallic compounds are in stereoselective catalysis in the field of organic synthesis, self-assembly to larger and uncharged structures in the field of material science, and interaction with biomolecules in the field of life science.

A major challenge was the synthesis of such compounds. We had previously succeeded both in a resolution of racemic 5-pallada-*trans*-tricyclo[4.1.0.0^{2,4}]heptanes **1**[1] and in a highly diastereoselective synthesis of enantiomerically pure **1**.[2]

Very much like Maitlis' palladoles,[3] the neat compounds are coordination polymers in which the two free coordination sites at the palladium center (Pd^{II}, d^8) are occupied by the oxygen atoms of the carbonyl groups of neighboring molecules of **1**.[4] In the presence of stronger ligands L (both mono- and bidentate), this polymer is broken up into monomeric units and the complexes **2** are formed (Scheme 1).

For the diastereoselective synthesis of **1** mentioned above, we utilized lactic acid esters as chiral auxiliaries. In addition to the exclusive *trans* diastereoselectivity always observed,[5,6] these gave rise to the preferential formation of



Scheme 1. 5-Pallada-*trans*-tricyclo[4.1.0.0^{2,4}]heptanes and cyclopropenes

one diastereomer in a *dr* of 93:7 or better. Since the starting material − the cyclopropene **3** − is C_2-symmetrical, both π-faces of this strained olefin are homotopic. After coordination of the first cyclopropene unit to the palladium center, the resulting molecule is C_1-symmetrical and the two carbon atoms of the C=C double bond change from homotopic to diastereotopic. The diastereoselectivity now depends on the formation of the C−Pd bond and the C−C bond in the step of the reaction with the second cyclopropene unit to form **2**. The stereogenic center in the lactate efficiently controls the configuration of the four newly formed stereogenic centers in the palladacycles. This can be viewed as either a 1,4- or a 1,5-induction. It is easy to memorize that an (*S*) configuration in the lactate will induce a

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(1*S*,2*S*,4*S*,6*S*) configuration in the four newly formed stereogenic centers in the palladatricycle.

We have now investigated cyclopropenes that are still C_s-symmetrical, with facial selection as the point of interest in this case. We then tested cyclopropenes that also had diastereotopic π-faces, but which also bore chiral lactate esters and hence were C_1-symmetrical. This would permit attempts to combine both principles: the diastereoselectivity based on the substituents in the 3-position of the cyclopropene and that based on the lactate esters.

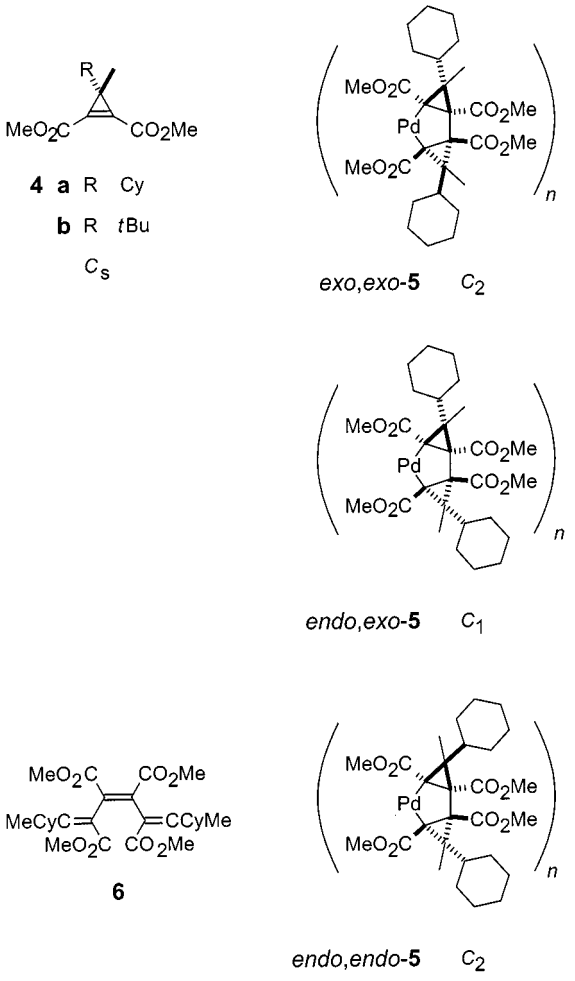
Results and Discussion

Diastereoselectivity Based on Two Different Substituents in the 3-Position of the Cyclopropene Unit

By use of a photochemical one-pot combination of Warkentin's[7] synthesis of diazoalkanes and Franck-Neumann's[8] synthesis of cyclopropenes, we prepared the C_s-symmetrical cyclopropenes **4a** and **4b**. Subjection of these to $Pd_2(dba)_3{\cdot}CHCl_3$ at room temperature in acetone only resulted in the formation of a palladatricycloheptane (PTH) in the case of **4a**.

In this case, only two of the three conceivable diastereomers − *exo*,*exo*-**5**, *endo*,*exo*-**5**, and *endo*,*endo*-**5** − were observed (Scheme 2). The minor diastereomer formed with **4a** (14% yield) could easily be identified as the C_1-symmetrical *endo*,*exo*-**5**, and this was confirmed by crystal structure analysis of the *endo*,*exo*-**5**·bpy complex.[9]

Diastereomer *endo*,*exo*-**5**·bpy has a molecular symmetry close to C_2, with the exception of the substituents at C7 and C19, which are reversed (Figure 1). The Pd atom has a strongly distorted square-planar coordination; the angle between the plane through atoms Pd, C1, and C4 and that through atoms Pd, N1, and N2 is 14.5°.[10] This deviation from planarity is due to steric interactions between the bipyridyl group and the carboxylate groups attached to C1 and C4. The observed H29···O2 contact distance of 2.28(2) Å and the H38···O8 distance of 2.33(2) Å each approach the van der Waals contact distance of 2.4 Å between O and H. A number of additional intramolecular O···H distances approach the van der Waals contact distance: O1···H21: 2.27(2) Å, O4···H9: 2.30(2) Å, O6···H20C: 2.25(2) Å, and O7···H8C: 2.29(2) Å. The angle between the planes of the two six-membered rings of the bipyridyl group is 8.4(1)°. The cyclohexyl groups have chair conformations. The C2−C7 and C3−C19 bonds have lengths of 1.571(2) and 1.570(2) Å and are slightly longer than the standard bond length of 1.54 Å for a single C−C bond. The C1−C7, C2−C3, and C4−C19 bonds, at 1.507(2), 1.508(2), and 1.501(2) Å, are rather short for single C−C bonds. The crystal structure contains two independent dichloromethane molecules; these solvent molecules are only involved in rather weak, electrostatic interactions (H···O contacts between 2.52 and 2.65 Å, Cl···H contacts between 3.07 and 3.11 Å) with the main molecules of *endo*,*exo*-**5**·bpy. The crystal packing shows a number of additional intermolecular O···H distances between 2.5 and 2.6 Å.



Scheme 2. Possible products from a C_s-symmetrical cyclopropene

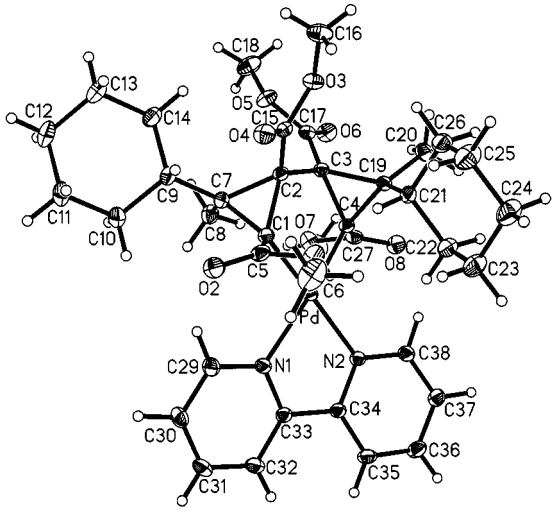


Figure 1. X-ray crystal structure of *endo*,*exo*-**5**·bpy (ORTEP plot)

The major diastereomer formed (84% yield) was C_2-symmetrical and could have been either *exo*,*exo*-**5** or *endo*,*endo*-**5**. Here, correct assignment really depended on X-ray crystal structure analysis. After fruitless efforts with the bpy

complexes, we finally succeeded in growing single crystals of both the bis(acetone) and the bis(acetonitrile) complexes, these unambiguously demonstrating that the major diastereomer was *exo*,*exo*-**5**.

The *exo*,*exo*-**5**·(acetone)$_2$ complex displays crystallographic C_2 symmetry, with the twofold rotation axis running through Pd1 and the bond between C2 and its symmetry equivalent (Figure 2).[9] The Pd atom has a square-planar coordination. The two Pd−C [2.030(1) Å] bonds and the two Pd−O [2.148(1) Å] bonds are equal, due to the symmetry of the molecule. The PdC_2O_2 subunit is not planar. The angle between the C1−Pd1−C1A plane and the O4−Pd1−O4A plane is 14.31(8)°. Two intramolecular (O21···H31 2.31 Å, O12A···H37A 2.38 Å) distances and one intermolecular (O11···H42B 2.35 Å) distance approach the van der Waals contact distance of 2.4 Å and may stabilize the molecular conformation through weak, electrostatic interactions. There are no solvent molecules in the crystal.

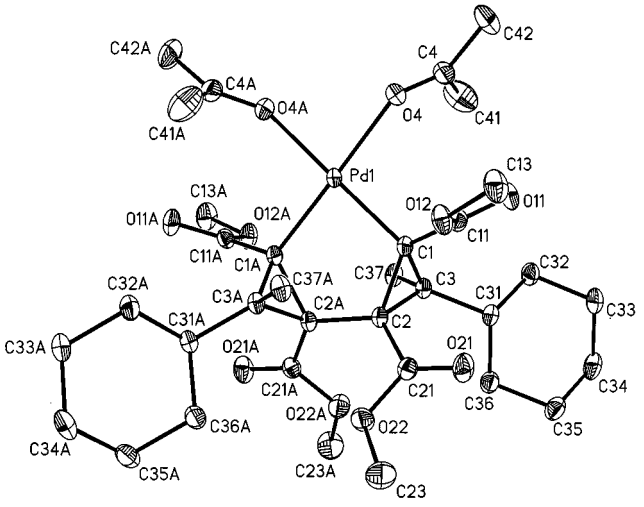


Figure 2. X-ray crystal structure of *exo*,*exo*-**5**·(acetone)$_2$ (ORTEP plot)

In *exo*,*exo*-**5**·(MeCN)$_2$, the Pd atom has the expected square-planar coordination, the angle between the C1−Pd−C4 plane and the N1−Pd−N2 plane being only 2.1° (Figure 3).[9] The two Pd−C bond lengths are 2.032(2) and 2.044(1) Å, the two Pd−N bond lengths are 2.083(2) and 2.099(2) Å. In the solid state the molecule shows only a small deviation from C_2 symmetry. The largest differences in torsion angles about related bonds are about 10°. Again, a number of intramolecular O···H distances approach the van der Waals contact distance of 2.4 Å and may stabilize the molecular conformation through weak, electrostatic interactions: O2···H20A 2.37 Å, O4···H9 2.29 Å, O6···H21 2.31 Å and O7···H8A 2.34 Å. Three chloroform molecules are attached through their C−H bonds to oxo groups of the title compound. The observed H···O distances of 2.1 to 2.2 Å are shorter than the van der Waals contact distance and these C−H···O interactions may thus be classified as weak hydrogen bonds. There are no other short intermolecular contact distances.

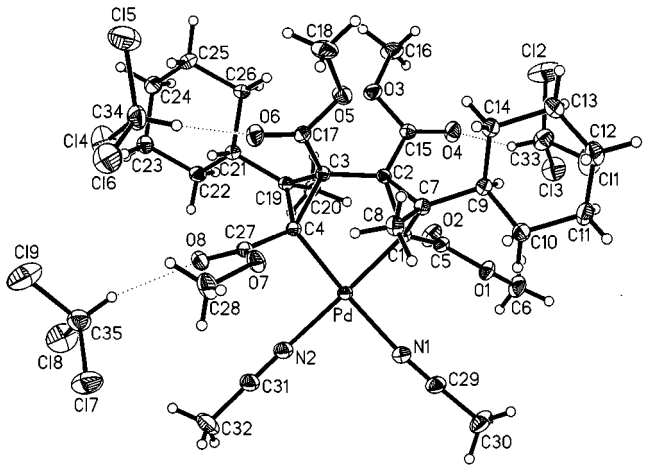


Figure 3. X-ray crystal structure of *exo*,*exo*-**5**·(MeCN)$_2$ (ORTEP plot)

It should be noted that all six carbon atoms of the PTH framework are now stereogenic centers.

Another product formed in this reaction is the hexatriene derivative **6**. It is diastereomerically pure, with either C_s or C_2 symmetry, but we do not know whether it is the (*Z*,*Z*,*Z*), the (*E*,*Z*,*E*), the (*Z*,*E*,*Z*), or the (*E*,*E*,*E*) derivative. Recent investigation[11,12] has suggested that the central double bond has a (*Z*) configuration, but both (*Z*,*Z*,*Z*) and (*E*,*Z*,*E*) are still possible.

The steric interactions of the C21−H21 bond of the *endo*-cyclohexyl substituent or the C8−H8C bond of the *endo*-methyl group in *endo*,*exo*-**5**·bpy should not differ (neither in *endo*,*exo*-**5** nor in the other conceivable isomers; see structure discussion above). Each is involved in an intramolecular C−H···O interaction with an H···O distance of about 2.28 Å and a C−H···O angle of 161−169°. The selectivity must thus originate from energy differences of intermediates or transition states rather than from product stability.

As can be seen in the crystal structures, three substituents − the two ester groups and the cyclohexyl group − end up on the same side of the cyclopropyl ring if the cyclohexyl group is in an *exo* position. The cyclohexyl groups can, however, still adopt a conformation that minimizes the interaction between these groups, for example in *exo*,*exo*-**5**·(MeCN)$_2$ by C9−H9 and C21−H21 pointing between the two ester groups (Figure 3), resulting in favorable H···O contact distances H9···O4 2.29 Å and H21···O6 2.31 Å. This is no longer possible when the cyclohexyl group is replaced by a *tert*-butyl group. Similar interactions in intermediates might be one reason for the failure of cyclopropene **4b** to provide palladacycles. On the other hand, this suggests that the metal should be able to coordinate to the side of the *tert*-butyl group of **4b**, since the ester group and the *tert*-butyl group are on different sides of the cyclopropane unit and the metal center should be shielded on one side by that *tert*-butyl group and on the other by the ester

groups. This principle indeed recently allowed us to obtain the very first crystal structure analysis of a stable nickel cyclopropene complex.[13]

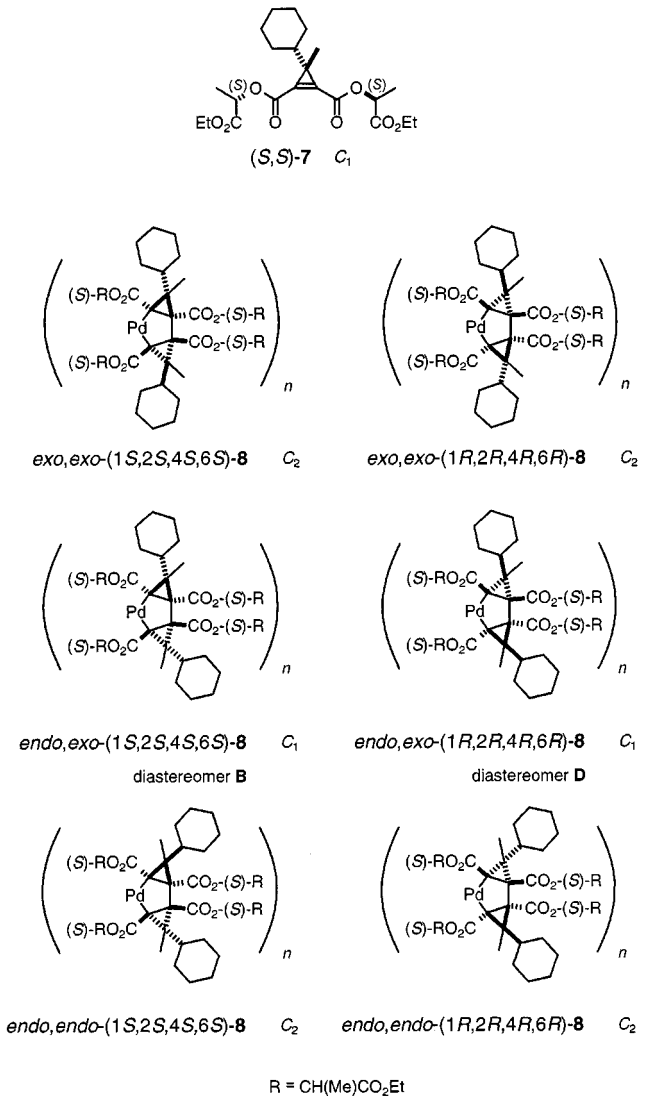
Diastereoselectivity Based on the Two Substituents in the 3-Position of the Cyclopropene Units and the Lactate

By the same methods as mentioned above, we prepared the enantiomerically pure cyclopropene (*S*,*S*)-**7**. Treatment of this with $Pd_2(dba)_3{\cdot}CHCl_3$ delivered four different diastereomers (**A**/**B**/**C**/**D** = 59:18:10:7% yield), which were separated by HPLC. The stereochemical assignment was now much more difficult: four out of the six conceivable stereoisomers are C_2-symmetrical [*exo*,*exo*-(1*S*,2*S*,4*S*,6*S*)-**8**, *exo*,*exo*-(1*R*,2*R*,4*R*,6*R*)-**8**, *endo*,*endo*-(1*S*,2*S*,4*S*,6*S*)-**8**, and *endo*,*endo*-(1*R*,2*R*,4*R*,6*R*)-**8**] and two are C_1-symmetrical [*endo*,*exo*-(1*S*,2*S*,4*S*,6*S*)-**8** and *endo*,*exo*-(1*R*,2*R*,4*R*,6*R*)-**8**] (Scheme 3). NMR studies proved that the diastereomers **A** and **C** were C_2-symmetrical, while **B** and **D** were C_1-symmetrical. At this point it could be asked whether the stereochemical analysis should not also consider PTHs with a *cis* arrangement of the three-membered rings. However, the CD spectra (see below) revealed that isomers **A**−**D** showed bands in regions typical for a palladium center in a helical chiral arrangement of the ligands,[14] ruling out a C_s-symmetrical *cis* arrangement of the cyclopropane rings. We again prepared the bpy complexes of all four diastereomers **A**−**D**, but only one of these − namely **B** − gave single crystals for a crystal structure analysis.

Diastereomer **B** was thus identified as the *endo*,*exo*-(1*S*,2*S*,4*S*,6*S*)-**8** isomer (Figure 4).[9] As in the other bpy complex mentioned above, the Pd atom has a distorted square-planar conformation, with the angle between the C1−Pd−C4 plane and the N1−Pd−N2 plane being 15.6°. The Pd−C distances are 2.053(1) and 2.055(1) Å, the Pd−N distances are 2.106(1) and 2.126(1) Å. Steric interactions of the C45−H45A and C54−H54A bonds with oxo groups prevent a planar coordination of the Pd atom. The observed H45A···O2 and H54A···O14 distances are 2.29 and 2.43 Å, respectively. The molecule shows ten additional intramolecular C−H···O interactions with H···O distances between 2.3 and 2.6 Å. These interactions mainly have a stabilizing effect on the conformation of the molecule. The angle between the planes of the two pyridyl groups is 7.0°. The C2−C11 and C3−C31 bonds have lengths of 1.572(2) and 1.560(2) Å, respectively, and are slightly longer than the value of 1.54 Å to be expected for a C−C single bond. The bulky cyclohexyl substituents at C11 and C31 may be responsible for this bond length elongation. The crystal packing shows four intermolecular C−H···O interactions with H···O distances between 2.4 and 2.6 Å. Three of these intermolecular contacts are donated by C−H bonds of the bipyridyl group.

As this diastereomer **B** was C_1-symmetrical, it was clear that the only other C_1-symmetrical stereoisomer **D** must be *endo*,*exo*-(1*R*,2*R*,4*R*,6*R*)-**8**.

Now, knowing the configurations of all six new stereogenic centers of **B** and **D**, we proceeded by taking CD spectra of the bpy complexes of the diastereomer identified



Scheme 3. Possible products from a C_1-symmetrical cyclopropene

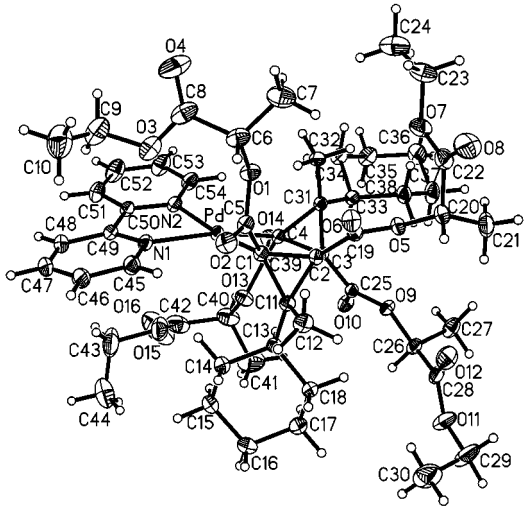


Figure 4. X-ray crystal structure of *endo*,*exo*-(1*S*,2*S*,4*S*,6*S*)-**8**·bpy (ORTEP plot)

by X-ray crystal structure analysis and of those of the yet unassigned diastereomers **A** and **C** (Figure 5). The helical distortion of the strong chromophores, the metal center and the aromatic bpy unit, overlaid all other effects of the other stereogenic centers next to the carbonyl groups of the esters. The spectra clearly showed that the helical distortion of **A** was in the same direction as that in **B**, while it had the opposite sign in **C**.[14]

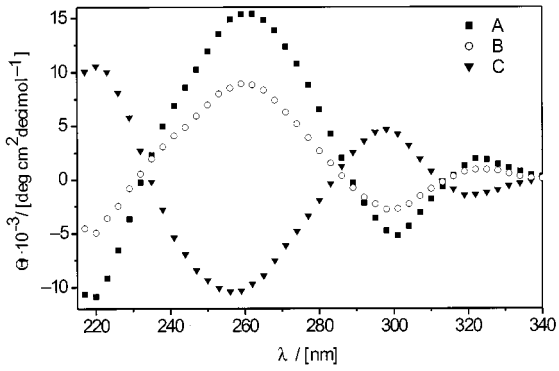


Figure 5. CD spectra of the bpy complexes of palladacycles **A**, **B**, and **C**

The crystal structures of the bpy complexes discussed above prove that a particular configuration of the stereogenic centers in the palladacycle induces a certain helical distortion of the bpy ligand. In combination with the fact that we did not observe any *endo*,*endo* diastereomers with **4a**, we assigned **A** as *exo*,*exo*-(1*S*,2*S*,4*S*,6*S*)-**8** (to have the same configuration as **B** and to be an *exo*,*exo* isomer) and **C** as *exo*,*exo*-(1*R*,2*R*,4*R*,6*R*)-**8** (to have the opposite configuration of **B** and also to be an *exo*,*exo* isomer).

Conclusion

The synthesis of PTHs from cyclopropenes bearing isopropyl-like substituents in the 3-position works well; on the other hand, the sterically more hindered *tert*-butyl-like substituents are not tolerated. With two substituents with different steric demand in the 3-position of the cyclopropene, a reasonable facial selectivity at the double bond of the cyclopropene was observed, the ratio of 5:1 for the oxidative cyclization of two cyclopropenes at a Pd^0 center corresponding to a ratio of 10:1 per cyclopropene, which is lower than the diastereoselectivity induced by the lactates reported earlier. The major diastereomer was the *exo*,*exo* product.

When the two principles − substituents with different steric demands in the 3-position of the cyclopropene and lactates − were combined, only a very moderate selectivity was achieved. However, the proportions of the diastereomers matched expectations, the major diastereomer being *exo*,*exo*-(1*S*,2*S*,4*S*,6*S*), followed by *endo*,*exo*-(1*S*,2*S*,4*S*,6*S*), *exo*,*exo*-(1*R*,2*R*,4*R*,6*R*), and *endo*,*exo*-(1*R*,2*R*,4*R*,6*R*).

It is therefore now also possible to vary the substituents in the 3- and 7-positions of the PTHs and to control the stereochemistry of the products.

Experimental Section

General Remarks: Preparative HPLC: Waters 590 programmable pump with Perfusor VI injector, 2150 peak separator, R 401 differential refractometer, 250 × 16 mm internal diameter column, Macherey−Nagel Nucleosil 50−10, flow 10 mL/min. $Pd_2(dba)_3$·$CHCl_3$ was prepared by a literature procedure.[15] Abbrevations: H: hexane, A: acetone, EA: ethyl acetate, AN: acetonitrile, MA: methyl acetate, IPR: 2-propanol, DCM: dichloromethane, dba: dibenzylideneacetone. The NMR signal assignments s (C_{quat}), d (CH), t (CH_2), and q (CH_3) for the ^{13}C NMR signals are based on DEPT 135 and DEPT 90 spectra.

Treatment of 4a with $Pd_2(dba)_3$·$CHCl_3$: A solution of **4a** (300 mg, 1.19 mmol) in acetone (3 mL) was added whilst stirring to a suspension of $Pd_2(dba)_3$·$CHCl_3$ (246 mg, 238 μmol) in acetone (30 mL). After this had stirred for 12 h at room temperature, **4a** (30.0 mg, 119 μmol) was added, followed after 3 h by a further 15.0 mg (59.5 μmol) and after another 3 h by a further 7.5 mg (30 μmol). A clear yellow solution was then obtained and no $Pd_2(dba)_3$ was detectable by TLC. The solvent was removed under reduced pressure, and the residue was purified by column chromatography. In this way, 104 mg (30% based on cyclopropene) of **6** could be isolated as a dark yellow oil. The larger part of the major diastereomer (*exo*,*exo*-**5**) could be separated by crystallization from acetone. The remaining mixture of *exo*,*exo*-**5** and *endo*,*exo*-**5** from the mother liquor could be separated by HPLC, to provide overall 244 mg (84%) of *exo*,*exo*-**5** and 40 mg (14%) of *endo*,*exo*-**5** [each based on $Pd_2(dba)_3$·$CHCl_3$] as yellow solids. The ratio of diastereomers was thus 6:1. Crystals suitable for crystal structure analysis of *exo*,*exo*-**5** could be obtained from both acetone [*exo*,*exo*-**5**·(acetone)$_2$] and acetonitrile/$CHCl_3$ [*exo*,*exo*-**5**·(acetonitrile)$_2$].

Diastereomer *exo*,*exo*-5: Column with H/A (10:1). R_f (H/A, 3:2) = 0.20. ^1H NMR ($CDCl_3$ and CD_3CN, 250 MHz): δ = 0.96 (m, 12 H), 1.43 (s, 6 H), 1.46 (m, 6 H), 1.76 (m, 2 H), 1.88 (m, 2 H), 3.29 (s, 6 H), 3.29 (s, 6 H). ^{13}C NMR ($CDCl_3$ and CD_3CN, 62.9 MHz): δ = 16.9 (q, 2 C), 26.3 (t, 2 C), 26.4 (t, 2 C), 26.7 (t, 2 C), 29.8 (t, 2 C), 30.8 (t, 2 C), 38.2 (d, 2 C), 42.3 (s, 2 C), 44.3 (s, 2 C), 48.1 (s, 2 C), 49.2 (q, 2 C), 49.7 (q, 2 C), 172.7 (s, 2 C), 173.7 (s, 2 C).

Diastereomer *endo*,*exo*-5: Column with H/A (10:1). R_f (H/A, 3:2) = 0.20. ^1H NMR ($CDCl_3$ and CD_3CN, 250 MHz): δ = 0.80−1.13 (m, 12 H), 1.19 (s, 3 H), 1.30−1.70 (m, 11 H), 2.40 (m, 2 H), 3.26 (s, 3 H), 3.27 (s, 3 H), 3.29 (s, 3 H), 3.33 (s, 3 H). ^{13}C NMR ($CDCl_3$ and CD_3CN, 62.9 MHz): δ = 12.2 (q), 17.7 (q), 25.6 (t), 26.0 (t), 26.4 (t), 26.7 (t, 2 C), 26.8 (t), 29.5 (t), 29.8 (t), 31.1 (t), 31.5 (t), 38.8 (d), 41.1 (d), 41.7 (s), 41.9 (s), 42.4 (s), 43.5 (s), 48.4 (s), 49.0 (q), 49.3 (q), 49.5 (q), 49.8 (s), 50.0 (q), 172.5 (s), 173.0 (s), 173.6 (s), 174.1 (s).

Compound 6: Column with H/A (10:1). R_f (H/A, 10:1) = 0.09. IR (film, NaCl): $\tilde{\nu}$ = 2926 cm^{-1}, 2853, 2361, 2343, 1723, 1617, 1283, 1252, 1208, 1117, 1059, 668. ^1H NMR ([D_6]acetone, 250 MHz): δ = 1.10−1.40 (m, 12 H), 1.45−1.82 (m, 14 H), 3.20 (m, 2 H), 3.57 (s, 6 H), 3.70 (s, 6 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.8 (q, 2 C), 25.9 (t, 2 C), 26.0 (t, 4 C), 30.6 (t, 4 C), 42.2 (d, 2 C), 51.2 (q, 2 C), 52.3 (q, 2 C), 121.3 (s, 2 C), 137.6 (s, 2 C), 161.8 (s, 2 C), 165.2 (s, 2 C), 167.3 (s, 2 C).

Synthesis of *exo*,*exo*-5·bpy: Solid bpy (5.70 mg, 36.5 μmol) was added to a solution of *exo*,*exo*-**5** (21.0 mg, 34.4 μmol) in a 1:1 mixture of CD_3CN/CD_2Cl_2 (0.5 mL), and the resulting mixture was left for 10 min at room temperature. The solvent was then evaporated and CH_3CN (0.5 mL) was added, and the precipitated solid was filtered off and washed with CH_3CN to afford 22.0 mg (80%) of *exo*,*exo*-**5**·bpy as yellow crystals. M.p. 270 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 2847, 1703, 1674, 1600, 1446, 1431, 1296, 1245, 1208, 1190, 1172, 1134, 1069, 1046. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.25−1.50 (bm, 12 H), 1.67−1.75 (bm, 10 H, including s, 1.71, 6 H), 1.79 (bm, 2 H), 2.15−2.32 (bm, 4 H), 3.43 (s, 6 H), 3.60 (s, 6 H), 7.49−7.55 (m, 2 H), 7.93−7.98 (m, 4 H), 9.13 (bd, $^3J_{H,H}$ = 5.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 18.2 (q, 2 C), 27.0 (t, 2 C), 27.1 (t, 2 C), 27.4 (t, 2 C), 30.5 (t, 2 C), 31.7 (t, 2 C), 38.4 (d, 2 C), 43.4 (s, 2 C), 45.2 (s, 2 C), 49.3 (s, 2 C), 50.4 (q, 2 C), 50.7 (q, 2 C), 121.2 (d, 2 C), 126.4 (d, 2 C), 137.8 (d, 2 C), 151.9 (d, 2 C), 155.0 (s, 2 C), 173.9 (s, 2 C), 175, 6 (s, 2 C). MS [FAB (+)]: *m*/*z* (%) = 766 (34) [(^{106}Pd) M^+], 261 (85), 157 (100). $C_{38}H_{48}N_2O_8Pd$ (767.2): calcd. C 59.49, H 6.31, N 3.65; found C 59.21, H 6.27, N 3.81.

Synthesis of *endo*,*exo*-5·bpy: A solution of bpy (5.40 mg, 34.6 μmol) in CH_2Cl_2 (1 mL) was added to a solution of *endo*,*exo*-**5** (21 mg, 34.4 μmol) in CH_2Cl_2 (5 mL), and the resulting mixture was stirred for 10 min at room temperature. The solvent was then evaporated, and the crude product was purified by column chromatography on SiO_2 to afford 19.0 mg (72%) *endo*,*exo*-**5**·bpy as yellow crystals. Column with hexane/ethyl acetate/dichloromethane (1:2:0.3). M.p. 280 °C. R_f (H/EA/DCM, 1:2:0.3) = 0.14. IR (film): $\tilde{\nu}$ = 2926 cm^{-1}, 2851, 1698, 1682, 1444, 1294, 1245, 1193, 1136, 1063. ^1H NMR (CD_2Cl_2, 250 MHz): δ = 1.00−1.59 (br. m, 23 H, including s at 1.26, 3 H, s at 1.58, 3 H), 1.70−1.82 (br. m, 1 H), 1.85−2.00 (br. m, 1 H), 2.11−2.24 (br. m, 1 H), 2.38−2.48 (br. m, 1 H), 2.50−2.65 (br. m, 1 H), 3.21 (s, 3 H), 3.36 (s, 3 H), 3.44 (s, 3 H), 3.46 (s, 3 H), 7.40−7.51 (m, 2 H), 7.85−7.95 (m, 4 H), 9.03 (bd, $^3J_{H,H}$ = 5.3 Hz, 1 H), 9.11 (bd, $^3J_{H,H}$ = 5.3 Hz, 1 H). ^{13}C NMR (CD_2Cl_2, 62.9 MHz): δ = 13.2 (q), 19.1 (q), 26.8 (t), 27.0 (t), 27.5 (t), 27.6 (t), 27.8 (t), 27.9 (t), 30.7 (t), 31.0 (t), 32.0 (t, 2 C), 39.5 (d), 41.6 (d), 42.9 (s), 43.0 (s), 43.3 (s), 43.9 (s), 50.0 (s), 50.3 (q), 50.4 (q), 50.6 (q), 51.0 (s), 51.1 (q), 121.9 (d), 122.2 (d), 126.5 (d), 126.9 (d), 138.7 (d, 2 C), 152.3 (d), 152.9 (d), 155.6 (s), 155.7 (s), 173.9 (s), 174.3 (s), 175.8 (s), 176.1 (s). $C_{38}H_{48}N_2O_8Pd$ (767.2): calcd. C 59.49, H 6.31, N 3.65; found C 57.74, H 6.26, N 3.47.

Treatment of (*S*,*S*)-7 with $Pd_2(dba)_3$·$CHCl_3$: Compound (*S*,*S*)-**7** (270 mg, 636 μmol) was added to a deep red suspension of $Pd_2(dba)_3$·$CHCl_3$ (158 mg, 153 μmol) in acetone (20 mL), and the resulting mixture was stirred at room temperature. After 20 h, TLC showed that all of the (*S*,*S*)-**7** had been consumed, so additional (*S*,*S*)-**7** (54.0 mg, 127 μmol) was added and the mixture was stirred for further 2 h to provide a clear yellow solution. The solvent was evaporated, the crude product was purified by column chromatography on SiO_2, and the diastereomers were separated by HPLC to deliver the diastereomers **A** (173 mg, 181 μmol, 59%), **B** (52.0 mg, 54 μmol, 18%), **C** (30.0 mg, 31 μmol, 10%), and **D** (20.0 mg, 21 μmol, 7%) as yellow solids.

Diastereomer A: Column with H/A (1:1), HPLC with H/AN/DC/MA (20:3:12:3.5), then H/IPR/AN (10:1:0.5). R_f (H/A, 1:1) = 0.50. ^1H NMR ([D_6]acetone, 250 MHz): δ = 1.01−1.50 (m, 38 H), 1.55−1.78 (bm, 6 H), 1.95−2.19 (br. s, 8 H), 4.01−4.19 (m, 8 H), 4.59−4.71 (m, 4 H). ^{13}C NMR ([D_6]acetone, 62.9 MHz): δ = 14.4 (q, 2 C), 17.4 (q, 6 C), 19.0 (q, 2 C), 27.6 (t, 2 C), 27.7 (t, 2 C), 27.9 (t, 2 C), 32.1 (t, 2 C), 32.3 (t, 2 C), 39.4 (d, 2 C), 41.5 (s, 2 C), 45.2 (s, 2 C), 47.7 (s, 2 C), 61.0 (t, 4 C), 68.7 (d, 2 C), 70.3 (d, 2 C), 171.6 (s, 4 C), 172.6 (s, 4 C).

Diastereomer B [*endo*,*exo*-(1*S*,2*S*,4*S*,6*S*)-8]: Column with H/A (1:1), HPLC H/AN/DCM/MA (20:3:12:3.5). R_f (H/A, 1:1) = 0.50. ^1H NMR ([D_6]acetone, 250 MHz): δ = 1.05−1.80 (bm, 44 H), 1.85−2.29 (bm, 6 H, partly hidden under acetone), 2.72−2.85 (bm, 1 H), 3.10−3.25 (bm, 1 H), 4.04−4.25 (m, 8 H), 4.57−4.60 (m, 1 H), 4.75−4.86 (m, 3 H). ^{13}C NMR ([D_6]acetone, 62.9 MHz): δ = 13.5 (q), 14.3 (q, 2 C), 14.4(q, 2 C), 17.2 (q), 17.4 (q), 17.6 (q), 17.8 (q), 19.7 (q), 26.5 (t), 26.9 (t), 27.5 (t), 27.7 (t), 28.0 (t), 29.7 (t), 31.3 (t), 32.2 (t), 32.4 (t), 33.5 (t), 39.3 (s), 39.5 (s), 40.4 (d), 42.9 (d), 44.2 (s), 44.7 (s), 48.1 (s), 50.1 (s), 60.9 (t, 2 C), 61.2 (t, 2 C), 68.7 (d), 68.9 (d), 69.7 (d), 70.4 (d), 171.3 (s, 2 C), 171.9 (s, 2 C), 172.3 (s, 2 C), 172.5 (s, 2 C).

Diastereomer C: Column with H/A (1:1), HPLC with H/AN/DCM/MA (20:3:12:3.5), then H/IPR/AN (10:1:0.5). R_f (H/A, 1:1) = 0.50. ^1H NMR ([D_6]acetone, 250 MHz): δ = 1.06−1.37 (m, 20 H), 1.39 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H), 1.51 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H), 1.53−1.78 (bm, 10 H), 1.92 (br. s, 6 H), 1.93−2.20 (bm, 4 H), 3.94−4.20 (m, 8 H), 4.77 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H), 4.92 (q, $^3J_{H,H}$ = 6.9 Hz, 2 H). ^{13}C NMR ([D_6]acetone, 62.9 MHz): δ = 14.3 (q, 2 C), 14.4 (q, 2 C), 17.2 (q, 2 C), 17.8 (q, 2 C), 18.6 (q, 2 C), 27.7 (t, 4 C), 28.1 (t, 2 C), 31.9 (t, 2 C), 32.6 (t, 2 C), 39.4 (d, 2 C), 39.9 (s, 2 C), 45.1 (s, 2 C), 47.5 (s, 2 C), 60.7 (t, 2 C), 61.3 (t, 2 C), 68.3 (d, 2 C), 70.1 (d, 2 C), 171.6 (s, 4 C), 172.1 (s, 2 C), 172.2 (s, 2 C).

Diastereomer D: Column with H/A (1:1), HPLC with H/AN/DCM/MA (20:3:12:3.5), then H/IPR/AN (10:1:0.5). R_f (H/A, 1:1) = 0.50. ^1H NMR ([D_6]acetone, 250 MHz): δ = 1.05−1.75 (m, 48 H), 4.03−4.23 (m, 8 H), 4.61−4.81 (m, 3 H), 4.89 (q, $^3J_{H,H}$ = 6.9 Hz, 1 H), signal of 4 H missing, covered by acetone signal.

Synthesis of A·bpy: A solution of bpy (8.80 mg, 56.4 μmol) in CH_2Cl_2 (5 mL) was added to a solution of **A** (53.6 mg, 56.1 μmol) in CH_2Cl_2 (20 mL), and the resulting mixture was stirred for 10 min at room temperature. The solvent was then evaporated and the crude product was purified by column chromatography on SiO_2 to afford 51.0 mg (82%) of **A**·bpy as a yellow solid. Column with H/EA/DCM (2:3:0.6). M.p. 97−100 °C. R_f (H/EA/DCM, 2:3:0.6) = 0.12. IR (film): $\tilde{\nu}$ = 2984 cm^{-1}, 2928, 2852, 1756, 1700, 1446, 1376, 1352, 1287, 1246, 1174, 1131, 1096. ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.77 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H), 1.00−1.45 (m, 30 H), 1.50−1.65 (m, 4 H), 1.68−1.80 (m, 2 H), 1.85 (s, 6 H), 1.93−2.08 (m, 2 H), 2.10−2.20 (m, 2 H), 3.41−3.71 (m, 4 H), 4.05 (q, $^3J_{H,H}$ = 7.1 Hz, 4 H), 4.58−4.68 (m, 4 H), 7.38−7.44 (m, 2 H), 7.74−7.93 (m, 4 H), 8.88−8.90 (br. d, $^3J_{H,H}$ = 5.2 Hz, 2 H). ^{13}C NMR (CD_2Cl_2, 62.9 MHz): δ = 14.0 (q, 2 C), 14.3 (q, 2 C), 16.8 (q, 2 C), 17.4 (q, 2 C), 19.2 (q, 2 C), 27.4 (t, 4 C), 27.9 (t, 2 C), 31.9 (t, 2 C), 32.0 (t, 2 C), 38.5 (d, 2 C), 45.7 (s, 2 C), 45.8 (s, 2 C), 48.9 (s, 2 C), 60.5 (t, 2 C), 61.1 (t, 2 C), 68.5 (d, 2 C), 70.2 (d, 2 C), 121.8 (d, 2 C), 126.7 (d, 2 C), 138.5 (d, 2 C), 152.4 (d, 2 C), 155.6 (s, 2 C), 171.7 (s, 2 C), 172.1 (s, 2 C), 173.3 (s, 2 C), 174.6 (s, 2 C). MS [FAB (+)]: *m*/*z* (%) = 1110 (15) [(^{106}Pd) M^+], 954 (75), 871 (15), 264 (49), 157.0 (100). $C_{54}H_{72}N_2O_{16}Pd$ (1111.6): calcd. C 58.35, H 6.53, N 2.52; found C 58.31, H 6.47, N 2.47. $[\alpha]_D^{20}$ = +70.4 (*c* = 0.17 g/100 mL, CH_2Cl_2)

Synthesis of B·bpy: A solution of bpy (8.50 mg, 54.4 μmol) in CH_3CN (3 mL) was added to a solution of **B** (52.0 mg, 54.4 μmol) in CH_3CN (15 mL), and the resulting mixture was stirred for 10 min at room temperature. The solvent was then evaporated, and the crude product was purified by column chromatography on SiO_2 to deliver 50.0 mg (83%) **B**·bpy as a yellow solid. Column with H/EA/DCM (2:3:0.6). M.p. 213 °C. R_f (H/EA/DCM, 2:3:0.6) = 0.20.

IR (film): $\tilde{\nu}$ = 2985 cm^{-1}, 2927, 2852, 1740, 1700, 1603, 1445, 1376, 1351, 1288, 1170, 1132, 1097, 1060, 1023. ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.70 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H), 0.80 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H), 1.00−1.65 (m, 38 H), 1.72−1.80 (m, 1 H), 1.82−1.87 (m, 1 H), 1.92 (s, 3 H), 2.20−2.30 (m, 1 H), 2.42−2.46 (m, 2 H), 3.33−3.50 (m, 2 H), 3.58−3.72 (m, 2 H), 3.95−4.21 (m, 4 H), 4.52 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H), 4.77 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H), 4.88 (q, $^3J_{H,H}$ = 6.7 Hz, 1 H), 5.05 (q, $^3J_{H,H}$ = 7.1 Hz, 1 H), 7.32−7.46 (m, 2 H), 7.81−7.95 (m, 4 H), 8.89−8.92 (m, 1 H), 9.04 (bd, $^3J_{H,H}$ = 5.2 Hz, 1 H). ^{13}C NMR (CD_2Cl_2, 62.9 MHz): δ = 13.2 (q), 13.9 (q), 14.1(q), 14.4 (q, 2 C), 16.7 (q), 17.3 (q), 17.6 (q), 17.8 (q), 19.7 (q), 26.0 (t), 26.3 (t), 27.1 (t), 27.2 (t), 27.4 (t), 27.8 (t), 30.8 (t), 31.9 (t, 2 C), 32.0 (t), 39.6 (d), 41.4 (d), 42.9 (s), 43.3 (s), 44.2 (s), 44.5 (s), 49.7 (s), 50.7 (s), 60.4 (t), 60.5 (t), 60.9 (t), 61.3 (t), 68.1 (d), 68.5 (d), 69.8 (d), 70.3 (d), 121.4 (d), 121.8 (d), 126.2 (d), 126.6 (d), 138.4 (d), 138.5 (d), 152.4 (d), 153.2 (d), 155.6 (s), 155.7 (s), 171.2 (s), 172.0 (s, 2 C), 172.2 (s), 172.6 (s), 172.8 (s), 174.4 (s), 174.8 (s). MS [FAB (+)]: *m/z* (%) = 1110 (14) [(^{106}Pd) M^+], 954 (71), 871 (13), 264 (49), 157.0 (100). $C_{54}H_{72}N_2O_{16}Pd$ (1111.6): calcd. C 58.35, H 6.53, N 2.52; found C 58.14, H 6.42, N 2.49. $[\alpha]_D^{20}$ = +10.9 (*c* = 0.14 g/100 mL, CH_2Cl_2).

Synthesis of C·bpy: A solution of bpy (4.90 mg, 31.4 μmol) in CH_3CN (3 mL) was added dropwise to a solution of **C** (30.0 mg, 31.4 μmol) in CH_3CN (15 mL), and the resulting mixture was stirred for 10 min at room temperature. The solvent was then evaporated, and the crude product was purified by column chromatography on SiO_2 to deliver 30 mg (86%) of **C** as a yellow solid. Column with H/EA/DCM (2:3:0.6). M.p. 99−102 °C. R_f (H/EA/DCM, 2:3:0.6) = 0.19. IR (film): $\tilde{\nu}$ = 2926 cm^{-1}, 2852, 1741, 1701, 1445, 1376, 1288, 1202, 1165, 1130, 1093. ^1H NMR (CD_2Cl_2, 250 MHz): δ = 1.00−1.87 (m, 48 H), 2.05−2.32 (m, 4 H), 3.80−4.25 (m, 8 H), 4.80 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H), 4.87 (q, $^3J_{H,H}$ = 6.9 Hz, 2 H), 7.47−7.54 (m, 2 H), 7.90−8.02 (m, 4 H), 9.14 (bd, $^3J_{H,H}$ = 5.2 Hz, 2 H). ^{13}C NMR (CD_2Cl_2, 62.9 MHz): δ = 14.2 (q, 2 C), 14.3 (q, 2 C), 17.2 (q, 2 C), 17.4 (q, 2 C), 18.9 (q, 2 C), 27.5 (t, 4 C), 27.9 (t, 2 C), 31.9 (t, 2 C), 32.3 (t, 2 C), 38.4 (d, 2 C), 45.7 (s, 2 C), 46.3 (s, 2 C), 49.0 (s, 2 C), 60.8 (t, 2 C), 60.9 (t, 2 C), 68.6 (d, 2 C), 70.1 (d, 2 C), 121.9 (d, 2 C), 126.8 (d, 2 C), 138.6 (d, 2 C), 153.1 (d, 2 C), 155.4 (s, 2 C), 171.6 (s, 4 C), 172.8 (s, 2 C), 173.7 (s, 2 C). MS [FAB (+)]: *m/z* (%) = 1110 (20) [(^{106}Pd) M^+], 954 (78), 871 (13), 264 (55), 157 (100). $C_{54}H_{72}N_2O_{16}Pd$ (1111.6): calcd. C 58.35, H 6.53, N 2.52; found C 58.06, H 6.57, N 2.35. $[\alpha]_D^{20}$ = −87.2 (*c* = 0.32 g/100 mL CH_2Cl_2).

Synthesis of D·bpy: A solution of bpy (3.30 mg, 21.1 μmol) in CH_3CN (2 mL) was added dropwise to a solution of **D** (20.0 mg, 20.9 μmol) in CH_3CN (10 mL), and the resulting mixture was stirred for 10 min at room temperature. The solvent was then evaporated, and the crude product was purified by column chromatography on SiO_2 to deliver 17.0 mg (73%) as a yellow solid. Column with H/EA/DCM (2:3:0.6). M.p. 97−100 °C. R_f (H/EA/DCM, 2:3:0.6) = 0.15. ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.84 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H), 1.03−2.30 (m, 49 H), 3.42−3.58 (m, 1 H), 3.62−3.75 (m, 1 H), 3.81−3.95 (m, 2 H), 4.05−4.22 (m, 4 H), 4.62−4.90 (m, 4 H), 7.45−7.55 (m, 2 H), 7.97−8.00 (m, 4 H), 8.91−8.94 (m, 1 H), 9.23 (bd, $^3J_{H,H}$ = 5.4 Hz, 1 H). ^{13}C NMR (CD_2Cl_2, 62.9 MHz): δ = 14.0 (q), 14.2(q, 2 C), 14.4 (q), 16.8 (q), 17.3 (q, 2 C), 17.5 (q), 19.1 (q), 19.4 (q), 27.4 (t, 3 C), 27.8 (t, 2 C), 30.1 (t), 31.6 (t), 32.0 (t, 2 C), 32.2 (t), 38.4 (d), 38.6 (d), 60.4 (t), 60.8 (t), 61.0 (t), 61.2 (t), 68.4 (d), 68.7 (d), 70.0 (d), 70.2 (d), 121.7 (d, 2 C), 126.7 (d), 126.8 (d), 138.4 (d, 2 C), 152.4 (d), 153.2 (d) (only the non-quaternary carbon atoms are listed, the others were invisible due to the low amount of material). MS [FAB (+)]: *m/z* (%) = 1110 (13) [(^{106}Pd) M^+], 954 (68), 871 (10), 264 (49), 157.0 (100). $[\alpha]_D^{20}$ = +27.2 (*c* = 0.14 g/100 mL CH_2Cl_2).

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[9] Crystal structure analysis of *endo*,*exo*-**5**·bpy: SIEMENS SMART diffractometer, empirical absorption correction by use of the SADABS program, structure was determined by direct methods by use of the SHELXS program. The H atoms were taken from a difference Fourier synthesis and were treated as riding atoms. The non-H atoms were refined with anisotropic thermal parameters. $C_{38}H_{48}N_2O_8Pd\cdot(CH_2Cl_2)_2$, M_r (incl. solvent) = 937.08, monoclinic, space group $P2_1/c$, *a* = 11.157(1) Å, *b* = 18.524(2) Å, *c* = 20.518(1) Å, β = 91.112(8)°, *V* = 4239.8(7) $Å^3$, *Z* = 4, $\rho_{calcd.}$ = 1.468 g cm^{-3}, μ = 0.742 mm^{-1}, min./max. transmission 0.488/0.552, crystal size 0.8 × 0.8 × 1.0 mm, Mo-K_α radiation, *T* = 152 K, scan range sphere, $2\theta_{max}$ = 66.7°, 56628 measured reflections, 14656 independent reflections; 503 parameters refined; final *R* indices [$I > 2\sigma(I)$]: *R*1 = 0.032, *wR*2 = 0.075, R indices all data *R*1 = 0.037, *wR*2 = 0.078, min./max. residual electron density −0.72/+1.16 e $Å^{-3}$. Crystal structure analysis of *exo*,*exo*-**5**·$(acetone)_2$: Absorption correction Empirical, SADABS (G. Sheldrick, **1996**), refinement method full-matrix, least squares on F^2, data/restraints/parameters 5127/0/207, goodness-of-fit on F^2 1.064, $C_{34}H_{52}O_{10}Pd$, M_r = 727.16, monoclinic, space group *C*2/*c*, *a* = 18.048(2) Å, *b* = 10.823(1) Å, *c* = 19.222(2) Å, β = 113.73(3)°, *V* = 3437.2(6) $Å^3$, *Z* = 4, $\rho_{calcd.}$ = 1.405 g cm^{-3}, μ = 0.594 mm^{-1}, max./min. transmission 0.842/0.797, crystal size 0.40 × 0.40 × 0.30 mm, λ = 0.71073 Å, *T* = 173(2) K, θ range for data collection 2.25−31.23°, 36160 measured reflections, 5127 independent reflections [*R*(int) = 0.0294], final *R* indices [$I > 2\sigma(I)$]: *R*1 = 0.0236, *wR*2 = 0.0565, *R* indices (all data) *R*1 = 0.0289, *wR*2 = 0.0584, largest diff. peak and hole 0.37 and −0.65 e$Å^{-3}$. Crystal structure analysis of *exo*,*exo*-**5**·$(MeCN)_2$: A single crystal was measured with a SIEMENS SMART diffractometer at 135 K. Repeatedly measured reflections remained stable. At room temperature in air the crystals deteriorated within minutes. An empirical absorption correction was made by use of the SADABS program. The cor-

rection factor ranged from 0.385 to 0.520. Equivalent reflections were averaged [$R(I)$internal = 0.022]. The structure was determined by direct methods by use of the SHELXS program. The H atoms were taken from difference Fourier syntheses and were treated as riding atoms. The non-H atoms were refined with anisotropic thermal parameters. The final difference density was between −0.87 and +1.04 e/Å^3. The maximum difference density is near the Cl atoms of the chloroform groups. $C_{32}H_{46}N_2O_8Pd\cdot(CHCl_3)_3$, M_r (incl. solvent) = 1051.27, crystal color yellow, transparent crystal, shape rod, crystal dimensions 0.66 × 0.66 × 1.7 mm, triclinic, space group $P\bar{1}$, a = 11.391(1) Å, b = 11.870(2), c = 17.541(2), α = 95.83(1)°, β = 100.14(1)°, = 101.883(7)°, V = 2261.2(6) Å^3, Z = 2, $\rho_{calcd.}$ = 1.544 g cm^{-3}, linear absorption coeff. 0.99 mm^{-1}, radiation Mo-K_α, scan range sphere, $(2\theta)_{max}$ = 64°, number of reflections measured 40229, number of independent reflections 13394, number of variables 505, final R indices [$I > 2\sigma(I)$]: $R1$ = 0.036, $wR2$ = 0.090; R indices (all data): $R1$ = 0.038, $wR2$ = 0.091. Crystal structure analysis of *endo*,*exo*-(1*S*,2*S*,4*S*,6*S*)-**8**: A single crystal (yellow, transparent block) was measured with a SIEMENS SMART diffractometer at a temperature of 141 K. Repeatedly measured reflections remained stable. Equivalent reflections were averaged. Friedel opposites were not averaged. The structure was determined by direct methods by use of the SHELXS program. The H atoms were geometrically positioned and were treated as riding atoms. The non-H atoms were refined with anisotropic thermal parameters. The structure was refined on F^2 values by use of the SHELXL-97 program. The absolute configuration of the structure was confirmed by the value of Flack's x parameter [x = −0.021(9)]. $C_{54}H_{72}N_2O_{16}Pd$, M_r = 1111.54, T = 141(2) K, λ = 0.71073 Å, orthorhombic, $P2_12_12_1$, a = 15.7978(13) Å, b = 16.4065(15) Å, c = 20.949(2) Å, V = 5429.8(9) Å^3, Z = 4, $\rho_{calcd.}$ = 1.360 Mg/m^3, μ = 0.411 mm^{-1}, crystal size 0.46 × 0.40 × 0.30 mm, θ range for data collection 1.79 to 34.26°, reflections collected/unique 118472/20739 [R(int) = 0.0327], absorption correction empirical (SADABS: G. Sheldrick, **2000**), max./min. transmission 0.884/0.846, refinement method full-matrix, least squares on F^2, data/restraints/parameters 20739/0/661, goodness-of-fit on F^2 = 1.002, final R indices [$I > 2\sigma(I)$] $R1$ = 0.030, $wR2$ = 0.061, R indices (all data) $R1$ = 0.038, $wR2$ = 0.064, largest diff. peak and hole 0.51 and −0.41 e·A^{-3}. CCDC-167167 (*endo*,*exo*-**5**·bpy), -167168 [*exo*,*exo*-**5**·(acetone)$_2$], -167169 [*exo*,*exo*-**5**·(MeCN)$_2$], and -167170 [*endo*,*exo*-(1*S*,2*S*,4*S*,6*S*)-**8**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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