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Steric effects on the control of *endo*/*exo*-selectivity in the asymmetric cycloaddition reaction of 3,4-dimethyl-1-phenylarsole†

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The asymmetric cycloaddition reactions of 3,4-dimethyl-1-phenylarsole and (*Z*/*E*)-diphenyl-1-propenylphosphine/diphenyl-1-styrylphosphine promoted by a chiral organopalladium(II) complex derived from (*S*)-[1-(dimethylamino)ethyl]naphthalene proceeded stereoselectively to generate different *exo*/*endo*-products. The reactions involving the (*Z*/*E*)-methyl substituted phosphines gave the individual optically pure *exo*- and *endo*-cycloadducts in very high stereoselectivity (33 : 1). However, when the methyl group was replaced by a Ph moiety both (*Z*/*E*)-phenyl substituted phosphines produced the same *endo*-cycloadduct in a stereoselectivity of 15 : 1. Every reaction produced five new chiral centers (four of them are sterically independent) in a single step and all three optically pure As–P heterobidentate ligands were obtained in high yields. The mechanism involved in the conversion of *exo*- to *endo*-product was investigated *via* density functional theory calculations. Computational results were consistent with the experimentally observed *endo*/*exo*-selectivity.

Introduction

Chiral compounds are widely distributed in nature and play a vital role in the metabolism of all living organisms. They have a wide variety of successful applications in many fields such as pharmaceuticals, insecticides, herbicides, and biological systems. In studies concerning the syntheses and stereochemistry of chelating arsine ligands with resolved chiral donor atoms, several types of As–As, As–S, As–N, and As–P bidentate ligands have been resolved *via* the metal complexation techniques.[1] When monodentates or other resolving agents are involved, however, the resolution process could become rather tedious and inefficient. Furthermore, separation of diastereomers is a prerequisite when the target ligand contains more than one stereogenic centre. For instance, in the case of the ligand 1-(methylphenylarsino)-2-(methylphenylphosphino)bezene, this involved the somewhat difficult separation of the (*R**,*R**) and (*R**,*S**) diastereoisomers prior to the individual resolution of the two pairs of racemic diastereoisomers.[2] Therefore the development of a more efficient asymmetric synthetic technique for generation of these arsenic-based bidentate ligand systems deserves attention.

The asymmetric Diels–Alder reaction is one of the best known reactions with high efficiency for the construction of chiral six-membered rings. The ability of this reaction in which the formation of two carbon–carbon bonds lead to the creation of up to four stereogenic centres in a single step from the achiral dienophiles and dienes makes it one of the most fascinating and elegant methods in asymmetric organic synthesis.[3] Diels–Alder cycloadditions are sensitive to steric factors: sterically bulky substituents on either the diene or dienophile generally suppress the reaction and affect the stereoselectivity. For example, the Diels–Alder reactions of a series of silyloxydienes and silylated dienes with acyclic α, β-unsaturated ketones and *N*-acyloxazolidinones have been reported quite recently.[4] The authors found that the *endo*/*exo* stereochemical outcome is strongly influenced by the substitution pattern of the reactants. High *exo* selectivity was observed when the termini of the diene and the dienophile involved in the shorter of the forming bonds were both substituted, while the normal *endo* preference was found otherwise.

Compared to the relatively well investigated chemistry of phospholes,[5] less attention has been concentrated on the arsoles due to their inherent instability.[6] This has led to relatively few reports on the preparation and characterization of the arsenic analogs of phosphines of synthetic value and precluded the large scale investigation of such compounds as medical agents and catalysts. However, arsenic chemistry often offered unexpected and interesting results which were different from those of phosphorus compounds. In this paper, we investigate the steric effect associated with the methyl and phenyl groups in (*Z*/*E*)-diphenyl-1-propenylphosphine and (*Z*/*E*)-diphenyl-1-styrylphosphine for the controllable preparation of three new enantiomerically pure As–P heterobidentate ligands *via* asymmetric Diels–Alder reactions and their mechanism *via* density functional theory (DFT) calculations.

Results and discussion

Asymmetric cycloaddition reactions between DMPA and (*Z*/*E*)-diphenyl-1-propenylphosphine

The asymmetric cycloaddition reactions between complex (+)-**1** and (*Z*/*E*)-diphenyl-1-propenylphosphine in dichloromethane

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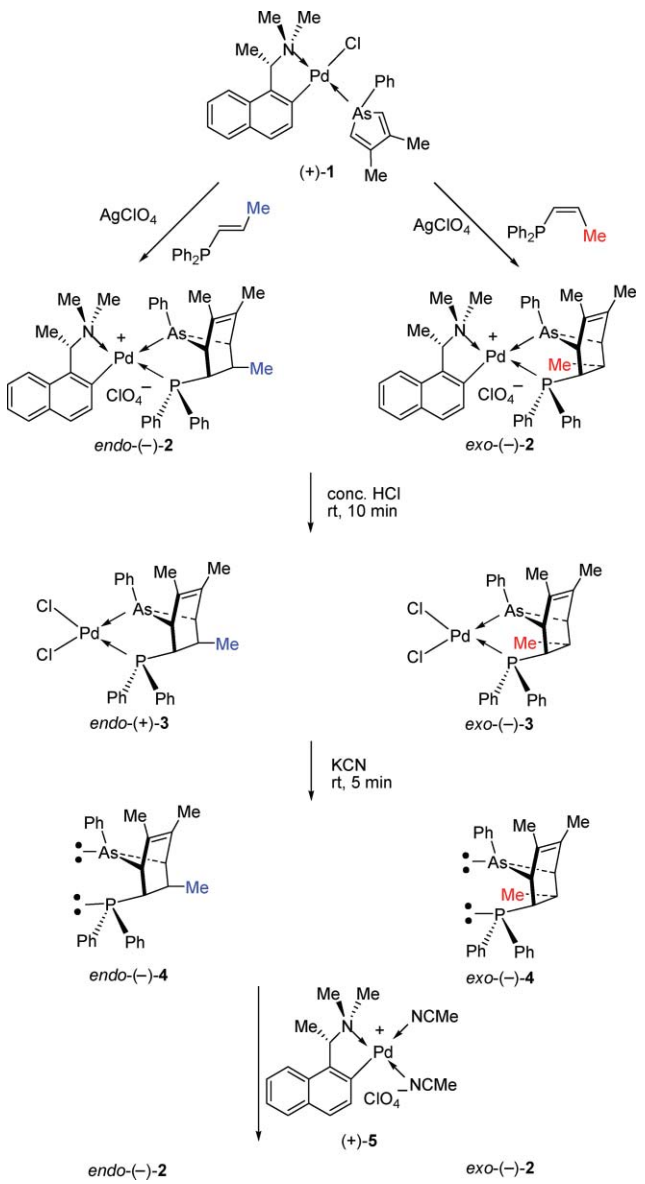
† Electronic supplementary information (ESI) available: Cartesian coordinates, energies and thermal corrections for all of the optimized reactants, products and transition structures, and comparisons of selected geometric parameters between crystal data and *ab initio* calculations for *endo*-(–)-**7**. CCDC reference numbers 734386 (*endo*-(+)-**6**), 734387 (*exo*-(+)-**6**) and 734388 (*endo*-(–)-**7**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b924613d

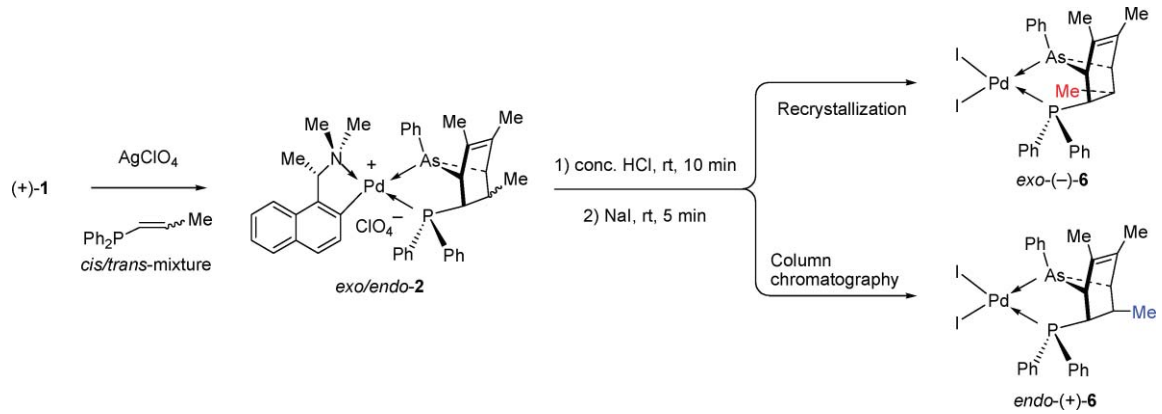
proceeded to completion in 3 days at 40 °C after the chloro ligand was replaced with the non-coordinating perchlorate (Scheme 1). Finally, two isomers were observed in the ratio of 33 : 1 in each reaction as indicated by the $^{31}P\{^{1}H\}$ NMR spectrum in $CDCl_3$. Upon completion of the reaction, the major diastereomers *endo*/*exo*-(−)-**2** were isolated by column chromatography in 61% and 60% yields respectively. The complex *endo*-(−)-**2** has a similar $^{31}P\{^{1}H\}$ NMR chemical shift for the 5-phosphino phosphorus atom as in the analogous diphosphine complex (δ 50.7 ppm)[7] and in its ^{1}H NMR spectrum the proton resonance ($CHCH_3$, δ 4.52 ppm) near the chiral carbon of the naphthylamine auxiliary is a quintet, not a quartet which is a further indication of the arsenic being coordinated *cis* to the NMe_2 group. The minor isomer in the present cycloaddition showed relatively close $^{31}P\{^{1}H\}$ NMR chemical shifts (δ 49.7 and 46.5 ppm, respectively), however, the similar diphosphine complexes have significantly different $^{31}P\{^{1}H\}$ NMR chemical shifts with a magnitude greater than 20 ppm for the 5-phosphino phosphorus (δ 50.7 and 26.8 ppm, respectively).[7] So unlike the two isomers of the corresponding diphosphine complex which are related as regio-isomers, these two isomers obtained from the reaction between (*E*)-diphenyl-1-propenylphosphine and DMPA should be diastereomers based on the comparison with the corresponding analogous diphosphine complexes. The similar phenomenon was also observed for the cycloadduct *exo*-(−)-**2**.



Scheme 1

The chiral naphthylamine in *endo*/*exo*-(−)-**2** could be removed from the palladium template chemoselectively by treatment with concentrated HCl in dichloromethane for 10 min at room temperature. The chiral auxiliary can be recovered quantitatively from the mother liquor after treatment with base. The neutral dichloro complexes *endo*-(+)-**3**/*exo*-(−)-**3** were obtained as pale yellow crystals in 85% and 81% yield. The enantiomerically pure As–P bidentate ligands *endo*/*exo*-(−)-**4** were liberated from *endo*-(+)-**3**/*exo*-(−)-**3** by treatment with KCN for 5 min at room temperature. The liberated ligands were obtained as air-sensitive white solids in quantitative yield. The $^{31}P\{^{1}H\}$ NMR spectra of the free ligands in $CDCl_3$ exhibited singlets at δ −11.3 and −9.0 ppm respectively. It is noteworthy that the apparent inversion of configuration that takes place at the bridgehead arsenic stereogenic centre (*R* to *S*) when the As–P bidentate ligand is liberated from the metal is merely a consequence of the Cahn–Ingold–Prelog (CIP) sequence rules.[8] The optically active *endo*/*exo*-(−)-**4** could not be stored because of their inherent instability. Therefore it is necessary to re-coordinate the liberated ligands to metal centres immediately upon liberation. Accordingly the liberated ligands were re-coordinated to the bis(acetonitrile) complex (+)-**5**. The re-coordination processes were monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy. The $^{31}P\{^{1}H\}$ NMR spectrum of the crude products showed only one signal at δ 49.7 and 42.3 ppm respectively which was identical to that recorded for the original cycloaddition reaction. No other $^{31}P\{^{1}H\}$ NMR signal could be detected, thus confirming that the liberated *endo*/*exo*-(−)-**4** were optically pure.

In addition to the above method, there is a more efficient route to prepare and separate the above *exo*- and *endo*-arsanorbornene ligands. The perchlorate complex of (+)-**1** was reacted with the mixture of (*Z*/*E*)-diphenyl-1-propenylphosphine ligands (Scheme 2). The cycloadduct mixtures were then treated with concentrated HCl for 10 min at room temperature, however, the resultant neutral dichloro complexes could not be separated into their enantiopure counterparts *via* recrysallization or column chromatography. Therefore NaI was added to the crude mixed dichloro complexes and allowed to react for another 5 min. The diiodo complexes *endo*-(+)-**6** and *exo*-(−)-**6** obtained were readily separated. First the *exo*-(−)-**6** was crystallized from the crude reactive mixture in dichloromethane–diethyl ether as red microcrystals in 75% yield, $[\alpha]_D$ −149.5 (*c* 0.2, CH_2Cl_2). Subsequently the mother liquid was further purified by column chromatography on a silica column with dichloromethane to give *endo*-(+)-**6** as a solid which was subsequently recrystallized from chloroform–diethyl ether–n-hexane in the form of red crystals. Most importantly, the *exo*/*endo*-occupancy of the methyl group at C6 position in cycloadducts *exo*-(−)-**6** and *endo*-(+)-**6** are consistent with its *Z*/*E*-geometrical relationship with the PPh_2 group in (*Z*/*E*)-diphenyl-1-propenylphosphine (Fig. 1 and 2). They were treated individually with KCN to liberate the corresponding optically pure *exo*/*endo*-(−)-**4**.



Scheme 2

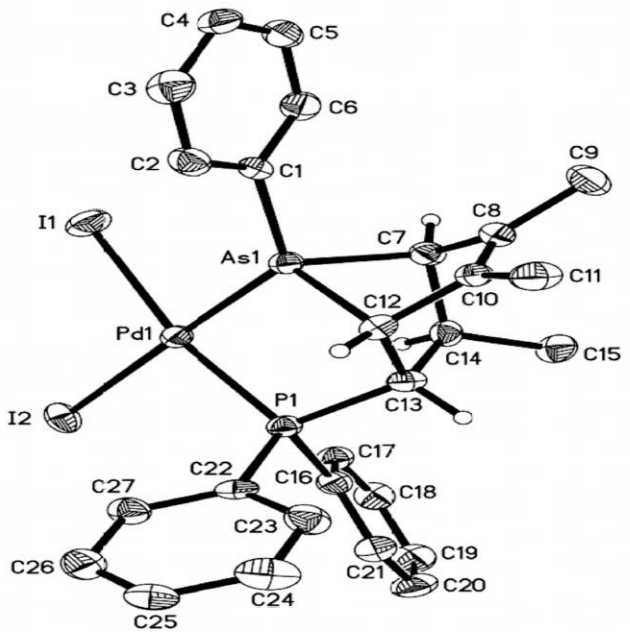


Fig. 1 Molecular structure of *endo*-(+)-**6**. Selected bond lengths (Å) and angles (deg): Pd1–P1 = 2.288(1), Pd1–As1 = 2.353(1), Pd1–I1 = 2.636(1), Pd1–I2 = 2.647(1), As1–C7 = 1.968(6), As1–C12 = 1.985(5); P1–Pd1–As1 = 83.4(1), P1–Pd1–I1 = 168.8(1), As1–Pd1–I1 = 87.4(1), P1–Pd1–I2 = 95.0(1), As1–Pd1–I2 = 178.2(1), I2–Pd1–I1 = 94.41, C12–As1–C7 = 77.0(2).

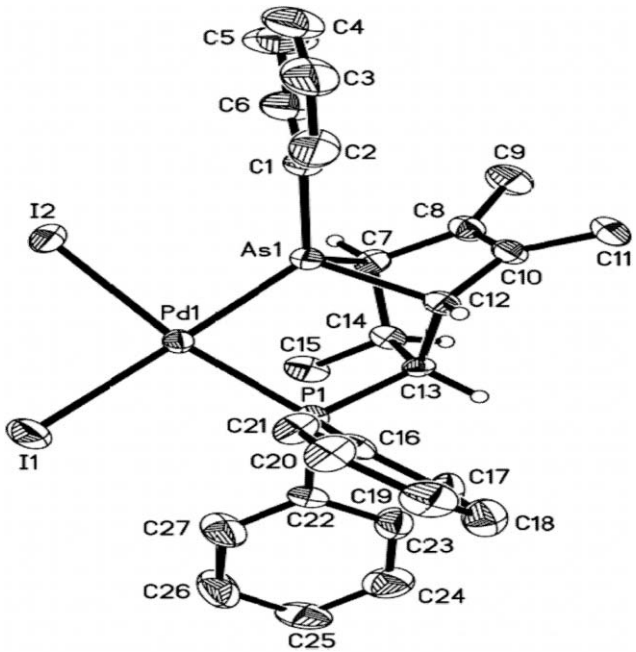
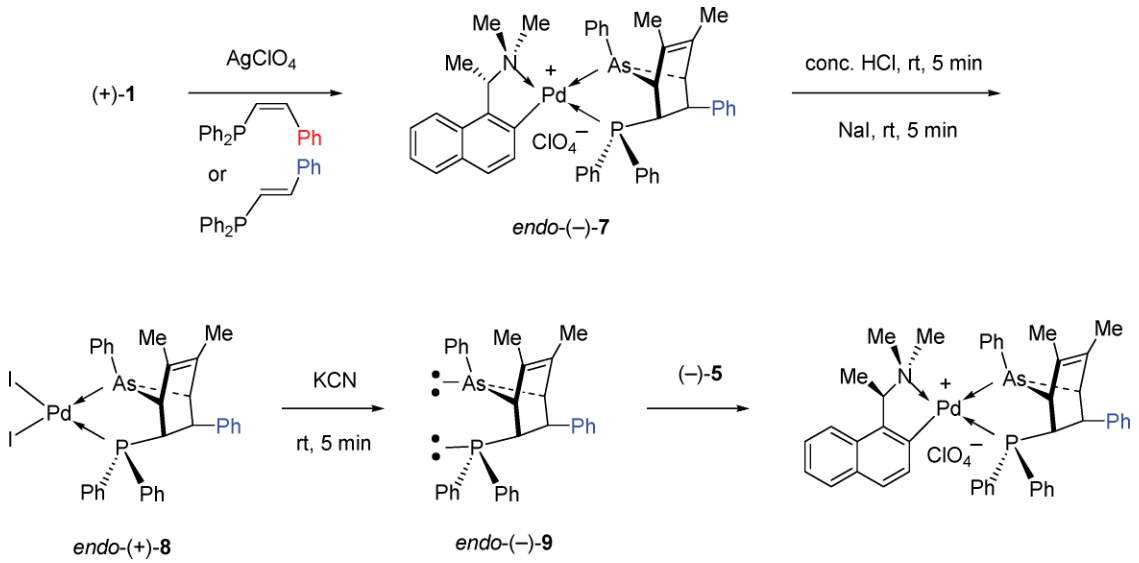


Fig. 2 Molecular structure of *exo*-(–)-**6**. Selected bond lengths (Å) and angles (deg): Pd1–P1 = 2.299(2), Pd1–As1 = 2.346(1), Pd1–I1 = 2.649(1), Pd1–I2 = 2.640(1), As1–C7 = 1.997(7), As1–C12 = 1.997(7); P1–Pd1–As1 = 82.2(1), P1–Pd1–I2 = 168.1(1), As1–Pd1–I2 = 87.5(1), P1–Pd1–I1= 98.7(1), As1–Pd1–I1 = 170.9(1), I2–Pd1–I1 = 92.5(1), C12–As1–C7 = 76.1(3).

Asymmetric cycloaddition reactions between DMPA and (*Z*/*E*)-diphenyl-1-styrylphosphine: steric effect

In order to provide further evidence as to whether the steric interactions between the axial methyl substituent and the methyl group on the chiral centre of the (*S*)-naphthylamine auxiliary are the determining factors for the selectivity and the rate of the reaction, a more bulky phenyl group was introduced onto the terminal position of the diphenylvinylphosphine. The reaction between (+)-**1** and (*E*)-diphenyl-1-styrylphosphine was completed in 45 h at room temperature to give the major product *endo*-(–)-**7** as colorless crystals in 70% yield, $[\alpha]_D$ –98.6 (*c* 0.7, CH_2Cl_2) (Scheme 3). It should be noted that, prior to purification, the $^{31}P\{^1H\}$ NMR spectrum of the crude cycloadducts in $CDCl_3$ exhibits only two sharp singlets at δ 51.0 and 49.0 ppm in the ratio of 15 : 1. More surprisingly the reaction between (+)-**1** and (*Z*)-diphenyl-1-styrylphosphine also produced the same cycloadduct *endo*-(–)-**7** in the same selectivity (15 : 1). The X-ray analysis of *endo*-(–)-**7** (Fig. 3) showed that the *endo*-occupancy of the phenyl group at the terminal position of (*Z*)-diphenyl-1-styrylphosphine is not consistent with its *Z*-geometrical relationship with the PPh_2 group in the dienophile precursor. This reaction could be completed in 41 h at 40 °C, however, when it was performed at room temperature there were many unknown peaks other than those for the cycloadducts recorded in the crude $^{31}P\{^1H\}$ NMR spectrum and it required a longer time to complete.



Scheme 3

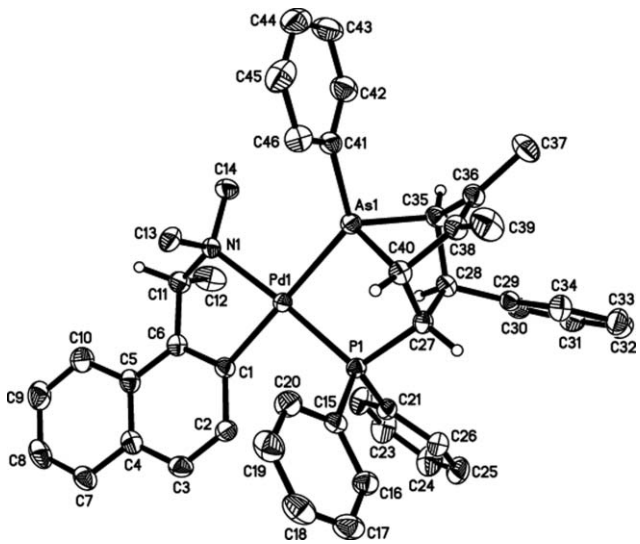


Fig. 3 Molecular structure of *endo*-(–)-**7**. Selected bond lengths (Å) and angles (deg): Pd1–C1 = 2.042(2), Pd1–N1 = 2.114(2), Pd1–P1 = 2.253(1), Pd1–As1 = 2.472(1), As1–C35 = 1.986(2), As1–C40 = 1.978(2); C1–Pd1–N1 = 81.6(1), C1–Pd1–P1 = 94.6(1), N1–Pd1–P1 = 175.9(1), C1–Pd1–As1 = 172.2(1), N1–Pd1–As1 = 99.9(1), P1–Pd1–As1 = 83.6(1), C40–As1–C35 = 76.6(1).

Due to the difficulty in isolation of the corresponding dichloro complex, it was converted into the analogous diiodo complex *endo*-(+)-**8**. The *endo*-(+)-**8** was readily isolated by column chromatography on a silica column with dichloromethane as eluting solvent. It was obtained as yellow solid in 97% yield, $[\alpha]_D$ +7.1 (*c* 0.4, CH_2Cl_2). Similar to its dichloro analogue, *endo*-(+)-**8** was also unstable in solution and decomposed after being kept for 2 days in $CDCl_3$. Treatment of *endo*-(+)-**8** with KCN for 5 min at room temperature liberated the optically active ligand *endo*-(–)-**9** as a solid in quantitative yield, $[\alpha]_D$ –240.0 (*c* 0.3, CH_2Cl_2). Significantly the $^{31}P\{^1H\}$ NMR spectrum of *endo*-(–)-**9** in $CDCl_3$ exhibited a sharp singlet at δ –7.3 ppm. When it was re-coordinated to (–)-**5**, there was only one peak at δ 30.0 ppm in its $^{31}P\{^1H\}$ NMR spectrum which confirmed that the liberated *endo*-(–)-**9** was optically pure.

To gain more insight into the reaction mechanism of (+)-**1** with (*Z*/*E*)-diphenyl-1-propenylphosphine and (*Z*/*E*)-diphenyl-1-styrylphosphine, we investigated the above reaction pathways by DFT calculations using the B3LYP functional. For the basis set, the Pd atom was represented by LANL2DZ (Los Alamos effective core potential plus double-ζ), while the other atoms were represented by 6-31G*. The cycloaddition reaction from (+)-**1** to *endo*/*exo*-(–)-**2** should proceed in a stepwise manner. First, the chloro ligand in (+)-**1** was replaced with perchlorate by treatment with $AgClO_4$. The resultant perchlorate complex (+)-**10** was obtained in essentially quantitative yield and the similar phosphorus analogue has been characterized by X-ray crystallography,[9] hence this highly reactive species was not isolated. It was treated directly with a stoichiometric amount of (*Z*/*E*)-diphenyl-1-propenylphosphine. Subsequently the incoming dienophile, (*Z*/*E*)-diphenyl-1-propenylphosphine, could coordinate instantly onto the palladium centre to produce the corresponding intermediate *cis*/*trans*-Me-1 as the Pd–O bond in (+)-**10** is very labile and the (*Z*/*E*)-diphenyl-1-propenylphosphine is a stronger coordinating ligand than perchlorate. Because of the distinct electronic-directing effects originating from the σ-donating nitrogen and the π-accepting aromatic carbon of the orthometalated naphthylamine ring, it has been well-established that the position *trans* to the NMe_2 group invariably takes up the softest donor atom available because of the antisymbiotic effect.[10] Therefore a ligand redistribution subsequently occurred to give another intermediate *cis*/*trans*-Me-2 which we deem is closest to the final cycloadduct. The reactions of the (*Z*/*E*)-phenyl substituted analogue proceeded similarly.

DFT calculations

We first computationally examined cycloaddition reactions between (+)-**1** and (*Z*/*E*)-diphenyl-1-propenylphosphine (Fig. 4). Due to the fact that the molecules investigated are relatively larger than the small organic compounds, including all the

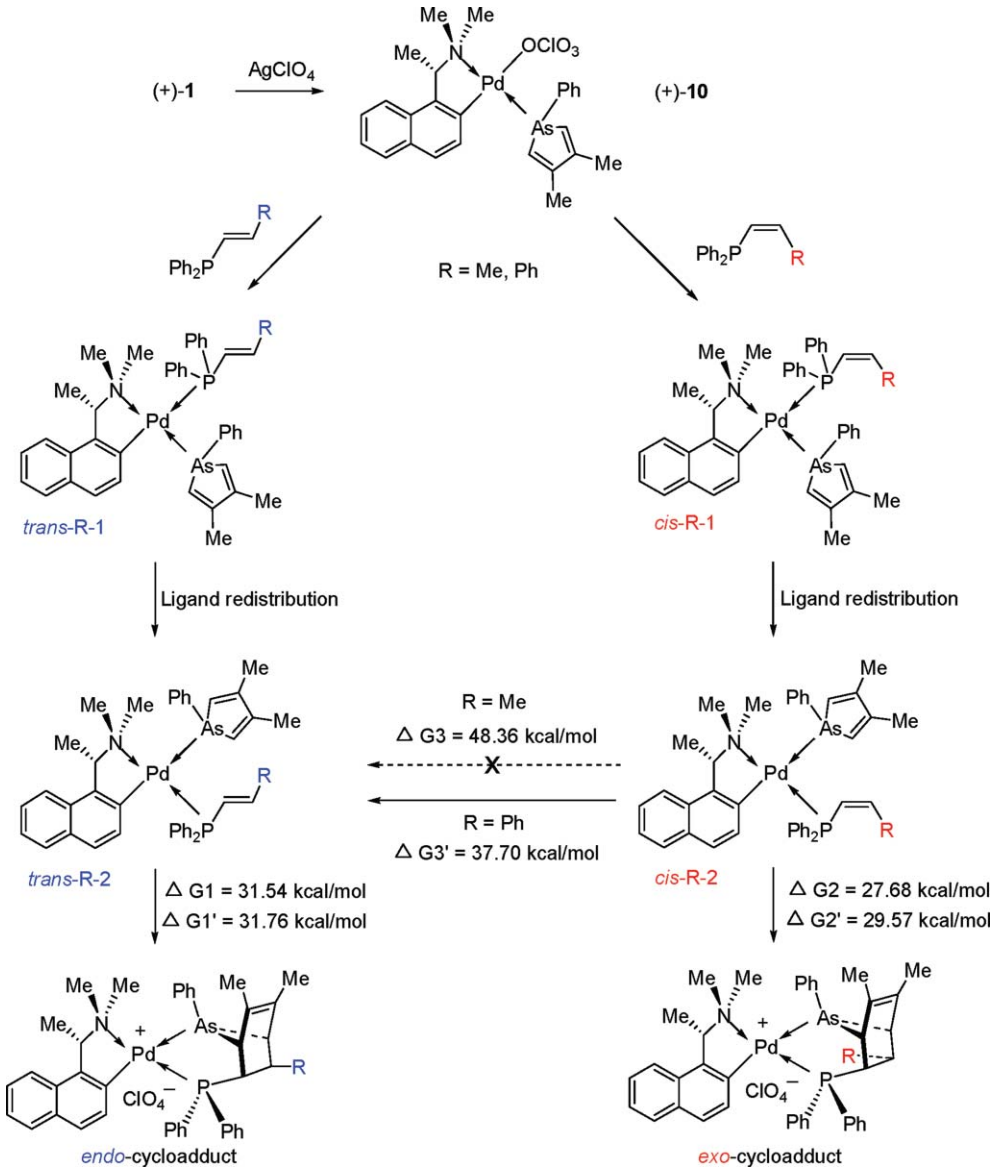
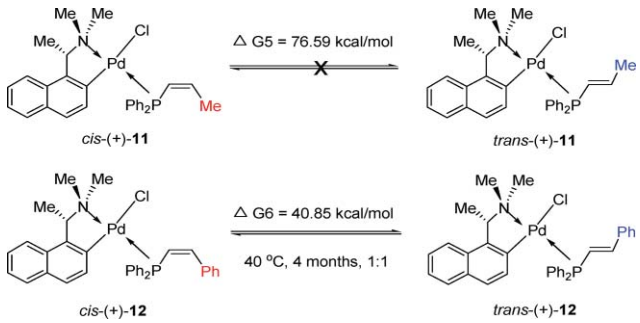


Fig. 4 ΔG1, ΔG2 and ΔG3 are for the methyl group; ΔG1′, ΔG2′ and ΔG3′ are for the phenyl group.

geometry optimizations needed exhaustive calculations, so we started calculations from some crucial intermediates (*cis*/*trans*-R-2 in Fig. 4). The reference points of all the following energy profiles are the Gibbs free energies for the *cis*-complexes, which are set equal to 0.0 kcal mol^{-1}.

As shown in Fig. 5, the activation barrier from *cis*-Me-2 to *trans*-Me-2 (ΔG3) is significantly higher by 20.68 kcal mol^{-1} (ΔG4) than that of *cis*-Me-2 to *exo*-(−)-**2** (ΔG2) which clearly explained the reason why the *Z*-Me-substituted phosphine starting material cannot generate the *endo*-product (*endo*-(−)-**2**) because it needed a high activation energy. However, the activation energy of the similar process from *cis*-Ph-2 to *trans*-Ph-2 is only slightly higher (ΔG4′ = 8.13 kcal mol^{-1}, Fig. 6) than that of *cis*-Ph-2 to *exo*-(−)-**7**. This agrees with the experimental observation: at room temperature (low energy) with (*Z*)-diphenyl-1-styrylphosphine it was very difficult to produce the *endo*-product (*endo*-(−)-**7**); on the other hand, when the reaction temperature was increased to 40 °C which produced a relative higher energy to overcome the activation barrier of interconversion (ΔG3′), the same reaction was completed very much faster. This was caused by two factors: comparing *cis*-Me-2 to *trans*-Me-2 (ΔG3 = 48.36 kcal mol^{-1}), the activation energy of *cis*-Ph-2 to *trans*-Ph-2 decreased to 37.70 kcal mol^{-1} (ΔG3′), whereas the activation energy of *cis*-Ph-2 to *exo*-(−)-**7** increased from 27.68 to 29.57 kcal mol^{-1} (ΔG2 *vs.* ΔG2′) in comparison with that of *cis*-Me-2 to *exo*-(−)-**2**. These energy gaps mean that *cis*-Ph-2 could be converted into *trans*-Ph-2 relatively easier than *cis*-Me-2 to *trans*-Me-2. This key step of the reaction from *cis*-R-2 to *trans*-R-2 (R = Me, Ph) is further elucidated by the following experiments: when the DMPA ligand in the above four intermediates was displaced by Cl (Scheme 4), we found that under the same reaction conditions (40 °C in CH_2Cl_2), phenyl-substituted *cis*-(+)-**12** could be slowly converted into *trans*-(+)-**12**, but the interconversion between methyl-substituted *cis*-(+)-**11** and *trans*-(+)-**11** cannot be observed even after a prolonged



Scheme 4

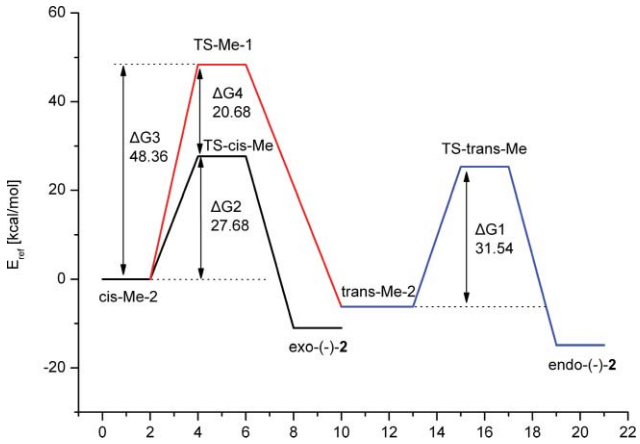


Fig. 5 Energy diagrams for the asymmetric cycloaddition reaction between DMPA and (*Z*/*E*)-diphenyl-1-propenylphosphine.

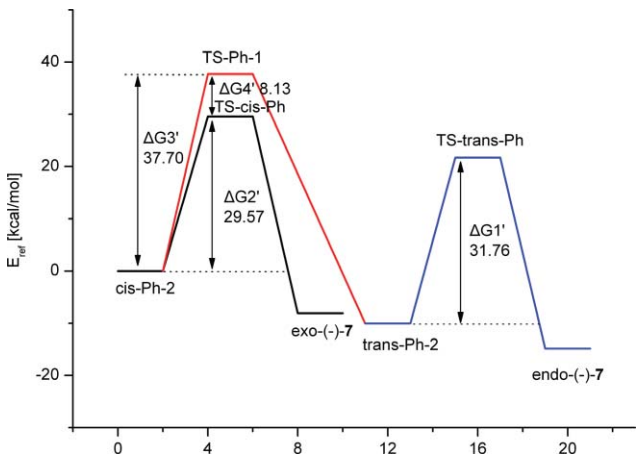


Fig. 6 Energy diagrams for the asymmetric cycloaddition reaction between DMPA and (*Z*/*E*)-diphenyl-1-styrylphosphine.

reaction time. The DFT calculations clearly showed that a very high activation energy for the conversion of *cis*-(+)-**11** to *trans*-(+)-**11** was required (ΔG5 = 76.59 kcal mol^{-1}, Fig. 7), however, *cis*-(+)-**12** was readily converted into *trans*-(+)-**12** due to it only needing 40.85 kcal mol^{-1} (ΔG6) which is a little higher than the activation energy of *cis*-Ph-2 to *trans*-Ph-2 (ΔG3′).

From the above experiments, the *exo*-oriented methyl group in *exo*-(−)-**2** is stable. However, the analogous complex *exo*-(−)-**7** could not be formed when the methyl group was replaced by a phenyl moiety. We believe that the conversion of the

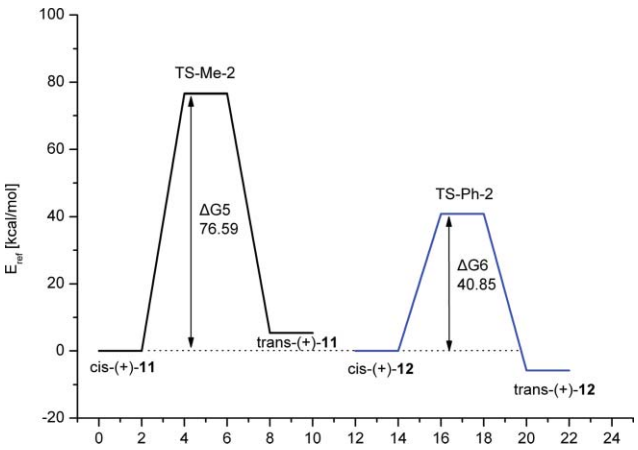


Fig. 7 Energy diagram for the conversion of *cis*-(+)-**11** to *trans*-(+)-**11** and *cis*-(+)-**12** to *trans*-(+)-**12**.

Ph group from the *exo* to the *endo* position was due to the steric hinderance between the terminal phenyl group on the (*Z*)-diphenyl-1-styrylphosphine and the methyl group on the chiral center of the (*S*)-naphthylamine auxiliary (which lies on the same side of the palladium coordination plane). Furthermore, the phenyl group is sterically significantly bigger than the methyl group which results in another huge repulsion between the terminal phenyl group and one neighboring phenyl group on the PPh_2. This intra ligand repulsion forces the terminal phenyl group from the *exo*-position to the *endo*-position during the course of the Diels–Alder reaction when both diene and dienophile are simultaneously coordinated on the palladium.

Conclusions

A series of substituent-dependent *endo*/*exo*-selective asymmetric cycloaddition reactions involving arsenic cyclic diene and methyl/phenyl substituted diphenylvinylphosphines have been investigated experimentally and computationally. All reactions could produce one arsenic and four new carbon chiral centers in a single step with high stereoselectivity and appreciable yield. The terminal substituent of phosphine ligand has a considerable effect on the *endo*/*exo*-selectivity of cycloaddition reactions. When the terminal substituent is a methyl group, as expected, asymmetric Diels–Alder reactions between (+)-**1** and (*Z*/*E*)-diphenyl-1-propenylphosphine give the corresponding *exo*/*endo*-cycloadducts [*exo*-(−)-**2** and *endo*-(−)-**2**] respectively. However, the reaction is totally different when the terminal methyl group was replaced by a phenyl moiety, only the *endo*-cycloadduct [*endo*-(−)-**7**] was obtained. DFT calculations on the reaction mechanism provide a reasonable explanation for the above observations. Currently the application of the synthesized ligand systems as catalyst for organic transformations is being investigated.

Experimental

General procedures

Reactions involving air-sensitive compounds were performed under an inert atmosphere of argon using standard Schlenk techniques. Solvents were dried and freshly distilled according

to standard procedures and degassed prior to use when necessary. NMR spectra were recorded at 25 °C on Bruker Avance 300, 400, and 500 spectrometers. Optical rotations were measured on the specified solution in a 0.1 dm cell at 20 °C with a Perkin-Elmer 341 polarimeter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry at Nanyang Technological University. Melting points were measured on a Stanford Research Systems OptiMelt MPA 100 instrument and are uncorrected.

(*Z*/*E*)-Diphenyl-1-propenylphosphine,[11] (*Z*/*E*)-diphenyl-1-styrylphosphine,[12] (+)-**1**,[13] (±)-**5**,[14] *trans*/*cis*-(+)-**11**,[7] and *trans*/*cis*-(+)-**12**[15] were prepared following the literature procedures. All other chemicals were obtained from commercial suppliers and used as received.

Caution!

Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.

Preparation of *endo*-(−)-2. A solution of (+)-**1** (0.81 g, 1.42 mmol) in CH_2Cl_2 (60 mL) was stirred for 2 h in the presence of a solution of silver perchlorate (0.4 g) in H_2O (1 mL). The organic layer, after the removal of AgCl, was then washed with H_2O (3 × 60 mL), dried ($MgSO_4$), and subsequently treated with (*Z*)-diphenyl-1-propenylphosphine (0.32 g, 1.42 mmol) at 40 °C for 3 d. Removal of the solvent gave *endo*-(−)-**2** as a solid, which was then recrystallized from $CHCl_3$–Et_2O to give the complex as pale yellow needles (0.75 g, 61%). $[\alpha]_D = -65.0°$ (*c* 0.6, CH_2Cl_2). Mp: 172–173 °C. Anal. calc. for $C_{41}H_{44}AsClNO_4PPd$: C, 57.1; H, 5.1; N, 1.6; found: C, 57.2; H, 5.4; N, 1.7%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 49.7. ^1H NMR (CD_2Cl_2): δ 0.75 (d, $^3J_{HH} = 6.8$ Hz, 3H, PCC*CH*$_3$); 1.47 (s, 3H, =C*CH*$_3$); 1.69 (d, $^5J_{PH} = 1.0$ Hz, 3H, =C*CH*$_3$); 2.02 (d, $^3J_{HH} = 6.3$ Hz, 3H, CH*CH*$_3$); 2.63 (dt, $^3J_{HH} = 2.3$, $^2J_{PH} = 8.9$ Hz, 1H, P*CH*); 2.79 (s, 1H, As*CH*); 2.82 (d, $^4J_{PH} = 1.5$ Hz, 3H, N*CH*$_3$); 2.87 (d, $^4J_{PH} = 3.8$ Hz, 3H, N*CH*$_3$); 3.07 (m, 1H, PCH*CH*); 3.46 (d,$^3J_{HH} = 2.4$ Hz, 1H, As*CH*); 4.52 (qn, $^3J_{HH} = {}^4J_{PH} = 6.3$ Hz, 1H, *CH*CH$_3$); 6.71–8.28 (m, 21H, aromatics).

Synthesis of the dichloro complex *endo*-(+)-3. The complex *endo*-(−)-**2** (0.45 g, 0.52 mmol) was dissolved in CH_2Cl_2 (50 mL) and treated with excess concentrated HCl (3 mL) for 10 min at room temperature. The mixture was then washed with H_2O (3 × 50 mL), dried ($MgSO_4$), and subsequently recrystallized from $CHCl_3$–Et_2O as pale yellow crystals *endo*-(+)-**3** (0.28 g, 85%). $[\alpha]_D = +32.6°$ (*c* 0.5, CH_2Cl_2). Mp: 131–132 °C. Anal. calc. for $C_{27}H_{28}AsCl_2PPd$: C, 51.0; H, 4.4; found: C, 50.7; H, 4.5%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.2. ^1H NMR ($CDCl_3$): δ 0.68 (d, $^3J_{HH} = 6.8$ Hz, 3H, PCC*CH*$_3$); 1.57 (s, 3H, =C*CH*$_3$); 1.66 (s, 3H, =C*CH*$_3$); 2.47 (d, $^2J_{PH} = 6.5$ Hz, 1H, P*CH*); 3.04 (m, 1H, PCH*CH*); 3.16 (s, 1H, As*CH*); 3.49 (d,$^3J_{HH} = 2.4$ Hz, 1H, As*CH*); 7.37–8.30 (m, 15H, aromatics).

Liberation of the As–P ligand *endo*-(−)-4. A solution of diiodo complex *endo*-(+)-**3** (0.10 g, 0.16 mmol) in CH_2Cl_2 (20 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1.0 g) for 5 min at room temperature. The organic layer was separated, then washed with water (3 × 20 mL), and dried ($MgSO_4$). Upon removal of the solvent, the free ligand *endo*-(−)-**4** was obtained as an air-sensitive white solid in quantitative yield. $[\alpha]_D = -80.0°$ (*c* 0.8, CH_2Cl_2).$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −11.3.

Preparation of *exo*-(−)-2. The cycloaddition reaction was performed similarly from (+)-**1** (0.63 g, 1.10 mmol) and (*E*)-diphenyl-1-propenylphosphine (0.25 g, 1.10 mmol). Yield: 0.57 g, 60%. $[\alpha]_D = -43.3°$ (*c* 0.3, CH_2Cl_2). Mp: 195–196 °C. Anal. calc. for $C_{41}H_{44}AsClNO_4PPd$: C, 57.1; H, 5.1; N, 1.6; found: C, 56.9; H, 5.3; N, 1.7%.$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 42.3. ^1H NMR (CD_2Cl_2): δ 1.39 (d, $^3J_{HH} = 2.3$ Hz, 3H, PCC*CH*$_3$); 1.41 (s, 3H, =C*CH*$_3$); 1.70 (s, 3H, =C*CH*$_3$); 2.04 (d, $^3J_{HH} = 6.2$ Hz, 3H, CH*CH*$_3$); 2.56 (m, 1H, PCH*CH*); 2.75 (s, 1H, As*CH*); 2.76 (s, 3H, N*CH*$_3$); 2.88 (d, $^4J_{PH} = 3.7$ Hz, 3H, N*CH*$_3$); 3.10 (s, 1H, As*CH*); 3.43 (dt,$^3J_{HH} = 2.0$, $^2J_{PH} = 9.6$ Hz, 1H, P*CH*); 4.51 (qn, $^3J_{HH} = {}^4J_{PH} = 6.2$ Hz, 1H, *CH*CH$_3$); 6.83–8.34 (m, 21H, aromatics).

Synthesis of the dichloro complex *exo*-(−)-3. The chiral auxiliary was removed similarly from *exo*-(−)-**2** (0.48 g, 0.56 mmol) using concentrated HCl. Yield: 0.29 g, 81%. $[\alpha]_D = -90.9°$ (*c* 0.1, CH_2Cl_2). Mp: 139–140 °C. Anal. calc. for $C_{27}H_{28}AsCl_2PPd{\cdot}CH_2Cl_2$: C, 46.7; H, 4.2; found: C, 46.7; H, 4.5%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 20.5. ^1H NMR (CD_2Cl_2): δ 1.50 (s, 3H, =C*CH*$_3$); 1.56 (d, $^3J_{HH} = 7.4$ Hz, 3H, PCC*CH*$_3$); 1.63 (d, $^5J_{PH} = 1.0$ Hz, 3H, =C*CH*$_3$); 2.57 (m, 1H, PCH*CH*); 2.96 (s, 1H, As*CH*); 3.08 (s, 1H, As*CH*); 3.36 (dt, $^3J_{HH} = 2.4$, $^2J_{PH} = 7.6$ Hz, 1H, P*CH*); 7.43–8.41 (m, 15H, aromatics).

Liberation of the As–P ligand *exo*-(−)-4. The free ligand *exo*-(−)-**4** was liberated similarly from *exo*-(−)-**3** (0.21 g, 0.33 mmol) by treatment with aqueous potassium cyanide as an air-sensitive white solid in quantitative yield. $[\alpha]_D = -40.0°$ (*c* 0.1, CH_2Cl_2).$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −9.0.

Synthesis of the diiodo complex *endo*-(+)-6 and *exo*-(−)-6. A solution of (+)-**1** (0.50 g, 0.88 mmol) in CH_2Cl_2 (60 mL) was stirred for 2 h in the presence of a solution of silver perchlorate (1.0 g) in water (1 mL). The organic layer, after the removal of AgCl, was then washed with water (3 × 60 mL), dried ($MgSO_4$), and subsequently treated with (*Z*/*E*)-diphenyl-1-propenylphosphine (0.20 g, 0.88 mmol) for 3 days at 40 °C. The mixture was treated with excess concentrated hydrochloric acid (2 mL) for 10 min at room temperature. The solution was then washed with water (2 × 60 mL). The solutions of crude dichloro complexes were mixed with sodium iodide (0.7 g) in water (80 mL) and stirred vigorously for 5 min. The solvents were removed and the residue was extracted with dichloromethane. Removal of the solvent gave the product as a solid, which was then recrystallized from dichloromethane–diethyl ether to give *exo*-(−)-**6** as red microcrystals (0.27 g, 75%). $[\alpha]_D = -149.5°$ (*c* 0.2, CH_2Cl_2). Mp: 130–131 °C. Anal. calc. for $C_{27}H_{28}AsI_2PPd$: C, 39.6; H, 3.5; found: C, 39.2; H, 3.5%.$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.1. ^1H NMR (CD_2Cl_2): δ 1.40 (s, 3H, =C*CH*$_3$); 1.62 (s, 3H, =C*CH*$_3$); 1.64 (s, 3H, PCC*CH*$_3$); 2.56 (m, 1H, PCH*CH*); 2.77 (s, 1H, As*CH*); 3.10 (s, 1H, As*CH*); 3.13 (dd, $^3J_{HH} = 2.5$, $^2J_{PH} = 8.4$ Hz, 1H, P*CH*); 7.43–8.41 (m, 15H, aromatics).

The remainder was purified by column chromatography on a silica column with dichloromethane to give *endo*-(+)-**6** as a solid, which was recrystallized from chloroform–diethyl ether–n-hexane in the form of red crystals (0.26 g, 72%). $[\alpha]_D = +106.3°$ (*c* 0.2, CH_2Cl_2). Mp: 144–145 °C. Anal. calc. for $C_{27}H_{28}AsI_2PPd$: C, 39.6; H, 3.5; found: C, 39.5; H, 3.5%.$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.4. ^1H NMR ($CDCl_3$): δ 0.66 (d, $^3J_{HH} = 6.8$ Hz, 3H, PCC*CH*$_3$); 1.57 (s, 3H, =C*CH*$_3$); 1.64 (s, 3H, =C*CH*$_3$); 2.31 (dt, $^3J_{HH} = 2.2$,

Table 1 Crystallographic data for complexes *exo*-(−)-**6**, *endo*-(+)-**6** and *endo*-(−)-**7**

	exo-(−)-**6**	*endo*-(+)-**6**	*endo*-(−)-**7**
Empirical formula	$C_{27}H_{28}AsI_2PPd$	$C_{27}H_{28}AsI_2PPd$	$C_{49}H_{52}AsCl_7NO_4PPd$
Formula weight	818.58	818.58	1179.36
Space group	*P*1	$P2_12_12_1$	$P2_12_12_1$
Crystal system	Triclinic	Orthorhombic	Orthorhombic
a/Å	9.0804(5)	10.3021(4)	12.6237(3)
b/Å	9.1106(9)	14.7810(7)	17.1807(4)
c/Å	9.3713(5)	18.3942(8)	23.4194(5)
α (°)	100.727(4)	90	90
β (°)	110.589(3)	90	90
γ (°)	98.244(4)	90	90
V/Å^3	694.44(9)	2801.0(2)	5079.3(2)
Z	1	4	4
T/K	173(2)	173(2)	173(2)
D_c/g cm^{-3}	1.957	1.941	1.542
λ/Å	0.71073	0.71073	0.71073
μ/mm^{-1}	4.144	4.110	1.455
F(000)	390	1560	2392
R_1 (obs data)[a]	0.0416	0.0363	0.0278
wR_2 (obs data)[b]	0.1011	0.0917	0.0678
Flack parameter	0.022(15)	0.027(14)	0.002(5)

[a] $R1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; [b] $wR2 = \sqrt{\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}}$, $w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP$.

$^2J_{PH}$ = 7.0 Hz, 1H, PC*H*); 3.08 (s, 1H, AsC*H*); 3.14 (m, 1H, PCHC*H*); 3.41 (d,$^3J_{HH}$ = 2.8 Hz, 1H, AsC*H*); 7.38–8.31 (m, 15H, aromatics).

Preparation of *endo*-(−)-7. A solution of (+)-**1** (0.85 g, 1.49 mmol) in CH_2Cl_2 (80 mL) was stirred for 2 h in the presence of a solution of silver perchlorate (0.4 g) in water (1 mL). The organic layer, after the removal of AgCl, was then washed with H_2O (3 × 50 mL), dried ($MgSO_4$), and subsequently treated with (*Z*)-diphenyl-1-styrylphosphine (0.43 g, 1.49 mmol) for 41 h at 40 °C. Removal of the solvent gave *endo*-(−)-**7** as a solid, which was then recrystallized from CH_2Cl_2 to give the complex as colourless crystals (0.97 g, 70%). $[\alpha]_D$ = −98.6° (*c* 0.7, CH_2Cl_2). Mp: 176–177 °C. Anal. calc. for $C_{46}H_{46}AsClNO_4PPd$: C, 59.8; H, 5.0; N, 1.5; found: C, 59.4; H, 5.2; N, 1.7%.$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 51.0. ^1H NMR (CD_2Cl_2): δ 1.12 (d, $^5J_{HH}$ = 0.8 Hz, 3H, =CC*H*$_3$); 1.57 (s, 3H, =CC*H*$_3$); 2.08 (d, $^3J_{HH}$ = 6.3 Hz, 3H, CHC*H*$_3$); 2.84 (d, $^4J_{PH}$ = 1.2 Hz, 3H, NC*H*$_3$); 2.94 (d, $^4J_{PH}$ = 3.8 Hz, 3H, NC*H*$_3$); 3.08 (s, 1H, AsC*H*); 3.49 (dt,$^3J_{HH}$ = 2.6, $^2J_{PH}$ = 9.5 Hz, 1H, PC*H*); 3.75 (d, $^3J_{HH}$ = 2.1 Hz, 1H, AsC*H*); 4.09 (dt,$^3J_{HH}$ = 3.0, $^3J_{PH}$ = 28.0 Hz, 1H, PhC*H*); 4.54 (qn, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, 1H, C*H*CH$_3$); 6.70–8.24 (m, 26H, aromatics). ^{13}C NMR (CD_2Cl_2): δ 14.88 (s, =CC*H*$_3$); 16.19 (s, =CC*H*$_3$); 25.09 (s, CHC*H*$_3$); 42.83 (d, $^1J_{PC}$ = 125.0 Hz, PC*H*); 49.27 (d, $^2J_{PC}$ = 30.6 Hz, PhC*H*); 52.35 (s, NC*H*$_3$); 52.73 (d,$^3J_{PC}$ = 8.9 Hz, NC*H*$_3$); 56.23 (d,$^2J_{PC}$ = 43.6 Hz, AsC*H*); 59.89 (s, AsC*H*); 74.82 (d,$^4J_{PC}$ = 10.9 Hz, C*H*CH$_3$); 123.90; 124.14, 124.63; 125.29; 125.41; 125.47; 126.21; 126.39; 126.64; 127.06; 127.67; 128.38; 128.60; 128.74; 128.85; 129.36; 129.82; 129.89; 129.93; 130.51; 130.99; 132.03; 132.23; 132.26; 132.66; 132.74; 132.89; 132.96; 132.99; 133.26; 134.64; 134.65; 134.73; 134.86; 135.37; 135.45; 135.48; 135.57; 140.61; 140.68; 151.82; 151.84; 154.37; 154.43 (aromatics).

Synthesis of the diiodo complex *endo*-(+)-8. The *endo*-(−)-**7** (0.37 g, 0.40 mmol) was dissolved in CH_2Cl_2 (50 mL) and treated with excess concentrated HCl (3 mL) for 5 min at room temperature. The solution was then washed with H_2O (3 × 50 mL). The crude dichloro complex was mixed with sodium iodide (0.5 g) in H_2O (50 mL) and stirred vigorously for 5 min. The solution was washed with H_2O (3 × 50 mL), dried ($MgSO_4$). Removal of the solvent gave *endo*-(+)-**8** as a solid, which was then isolated by column chromatography on a silica column with dichloromethane–diethyl ether (0.34 g, 97%). $[\alpha]_D$ = +7.1° (*c* 0.4, CH_2Cl_2). Mp: 143–144 °C. Anal. calc. for $C_{32}H_{30}AsI_2PPd$: C, 43.6; H, 3.4; found: C, 43.3; H, 3.5%.$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.4. ^1H NMR ($CDCl_3$): δ 1.10 (d, $^5J_{HH}$ = 1.0 Hz, 3H, =CC*H*$_3$); 1.64 (s, 3H, =CC*H*$_3$); 3.11 (d, $^3J_{HH}$ = 1.3 Hz, 1H, AsC*H*); 3.22 (dt,$^3J_{HH}$ = 2.5, $^2J_{PH}$ = 7.6 Hz, 1H, PC*H*); 3.63 (d, $^3J_{HH}$ = 2.8 Hz, 1H, AsC*H*); 4.30 (dt,$^3J_{HH}$ = 2.8, $^3J_{PH}$ = 25.0 Hz, 1H, PhC*H*); 6.81–8.22 (m, 20H, aromatics).

Liberation of the As–P ligand *endo*-(−)-9. A solution of *endo*-(+)-**8** (0.16 g, 0.18 mmol) in CH_2Cl_2 (20 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1.0 g) for 5 min. The organic layer was separated, then washed with water (3 × 20 mL), and dried ($MgSO_4$). Upon removal of the solvent, the free ligand *endo*-(−)-**9** was obtained as an air-sensitive solid in quantitative yield. $[\alpha]_D$ = −240.0° (*c* 0.3, CH_2Cl_2).$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −7.3.

X-ray crystal structure determination

Crystallographic data for complexes *endo*-(+)-**6**, *exo*-(+)-**6** and *endo*-(−)-**7** were given in Table 1. Diffraction data were collected on a Bruker X8 CCD diffractometer with Mo-Kα radiation (graphite monochromator). SADABS absorption corrections were applied. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. The absolute configuration of the chiral complex was determined unambiguously by using the Flack parameter. contained in the supplementary crystallographic data for this paper.

Computational methods

All calculations were performed using the Gaussian 03 program.[16] Unrestricted spin DFT calculations were performed in the flavor of B3LYP. The standard basis set 6-31G* was used for C, H, N, Cl, As and P atoms, while the LANL2DZ basis set and pseudopotential were adopted for the Pd atom. Geometry optimizations were carried out without any geometrical constraints, and all of the energy minima and transition states were subjected to frequency analysis: The number of imaginary frequencies confirmed the intermediates ($N_{\mathrm{Imag}} = 0$) and transition state structures ($N_{\mathrm{Imag}} = 1$), the connection between the starting and final minima geometries has also been checked by the intrinsic reaction coordinate calculations. The energies presented throughout the paper correspond to Gibbs free energy values computed at 298.15 K and 1 atm. The geometries calculated from DFT calculations were in good agreement with X-ray analyses for *endo*-(–)-**7** which effectively verified our computational methodology.

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