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Metal Template Synthesis and Coordination Chemistry of Functionalized P-Chiral Phosphanorbornenes

Pak-Hing Leung,[a,*] Guosen He,[a] Huifang Lang,[a] Anming Liu,[a] Soh-Kheang Loh,[a] S. Selvaratnam,[a] K. F. Mok,[a] Andrew J. P. White[b] and David J. Williams[b]

[a]*Department of Chemistry, National University of Singapore, Kent Ridge 119260, Singapore*
[b]*Department of Chemistry, Imperial College, London SW7 2AY, UK*

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Abstract—The organopalladium complex containing the (*S*)-form of *ortho*-palladated (1-(dimethylamino)ethyl)-naphthylalene has been used successfully as the chiral template to promote the asymmetric cycloaddition reactions between coordinated 3,4-dimethyl-1-phenylphosphole and two dienophiles: *N*,*N*-dimethylacrylamide and styrene. The mechanism, the rate and the stereoselectivity of these chiral template promoted reactions are affected by the number of coordination sites available on the palladium template and the coordination potential of the dienophiles. At room temperature, the intramolecular cycloaddition reaction with *N*,*N*-dimethylacrylamide gave the corresponding P-chiral (−)-(S_p)-*exo*-amidophosphanorbornene stereospecifically in 3 d. Under similar conditions, the corresponding intermolecular process gave a pair of separable diastereomeric *endo*-substituted amidophosphanorbornene complexes in 32 d. With styrene, the intermolecular cycloaddition reaction at 80°C gave a pair of diastereomeric *endo*-substituted phenylphosphanorbornene complexes in 3 d. No *exo*-cycloaddition reaction occurred when styrene was used as the dienophile. The first optically active and stable amido-O bonded platinum complex (R_p,R_p)-[Pt(*exo*-amidophosphanorbornene-*P*,*O*)$_2$](ClO$_4$)$_2$ and its palladium analogue have been isolated and characterized by ^{31}P NMR spectroscopy and X-ray crystallography.

Introduction

Recently we have been interested in the chiral organopalladium complex-promoted asymmetric Diels–Alder reaction between 3,4-dimethyl-1-phenylphosphole (DMPP) and various dienophiles.[1] This asymmetric synthetic route was chosen because it is the most elegant and efficient approach to the important class of functionalized ligands containing chiratopic phosphorus donor atoms.[2] In cases where substituted vinylphosphines were used as dienophiles, new phosphorus stereogenic centres have been generated stereospecifically outside the rigid phosphanorbornene skeletons.[3] Furthermore, we are able to select either the *exo* or the *endo* cycloaddition reaction pathways in these asymmetric syntheses simply by controlling the number of coordination sites on the *ortho*-palladated naphthylamine template (Scheme 1).[4,5]

In the *endo*-cycloaddition pathway, the kinetically stable[6] chloro ligand in (S_c)-**1a** remains coordinated to the neutral template throughout the course of the inter-molecular cycloaddition reaction and hence the reacting dienophile cannot be involved in any form of metal complexation. In the *exo*-cycloaddition pathway, however, the kinetically labile perchlorato ligand on the palladium template (S_c)-**1b** is displaced by the reacting dienophile to form a cationic intermediate such that both DMPP and the reacting dienophile are coordinated simultaneously onto the chiral template during the course of cycloaddition reaction. Due to these interesting mechanistic and electronic features, the *exo*-cycloaddition reactions are usually found to proceed with much higher stereoselectivities but at significantly slower rates than that observed for their analogous *endo*-cycloaddition processes. In order to explore further the role of metal complexation in this class of chiral organopalladium template promoted Diels–Alder reaction, we herein report the asymmetric cycloaddition reactions of coordinated DMPP with *N*,*N*-dimethylacrylamide and styrene. The former dienophile contains a potential N–O ambidentate function[7] and the latter is able to form alkene–metal bonds.[8] The ligating properties of the resulting cycloadducts will also be discussed.

Result and Discussion

Amido-substituted phosphanorbornenes

As illustrated in Scheme 2, the intermolecular *endo*-cycloaddition reaction between (S_c)-**1a** and *N*,*N*-dimethylacrylamide was carried out at room temperature in dichloromethane in the presence of twofold excess of the dienophile. The reaction was monitored by ^{31}P NMR

* Corresponding author. Tel.: +65-772-2682; fax: +65-779-1691; e-mail: chmlph@nus.sg

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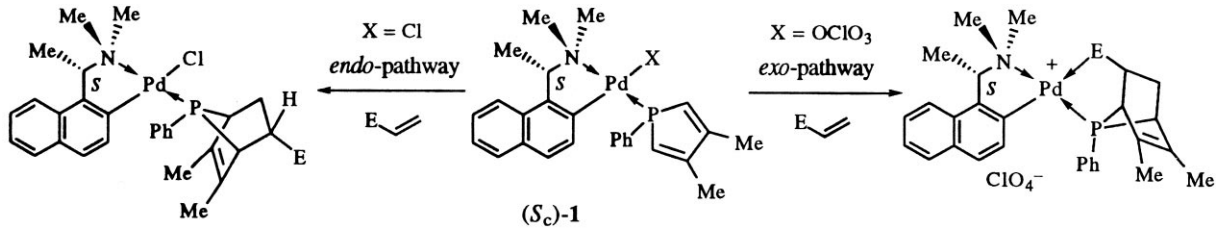
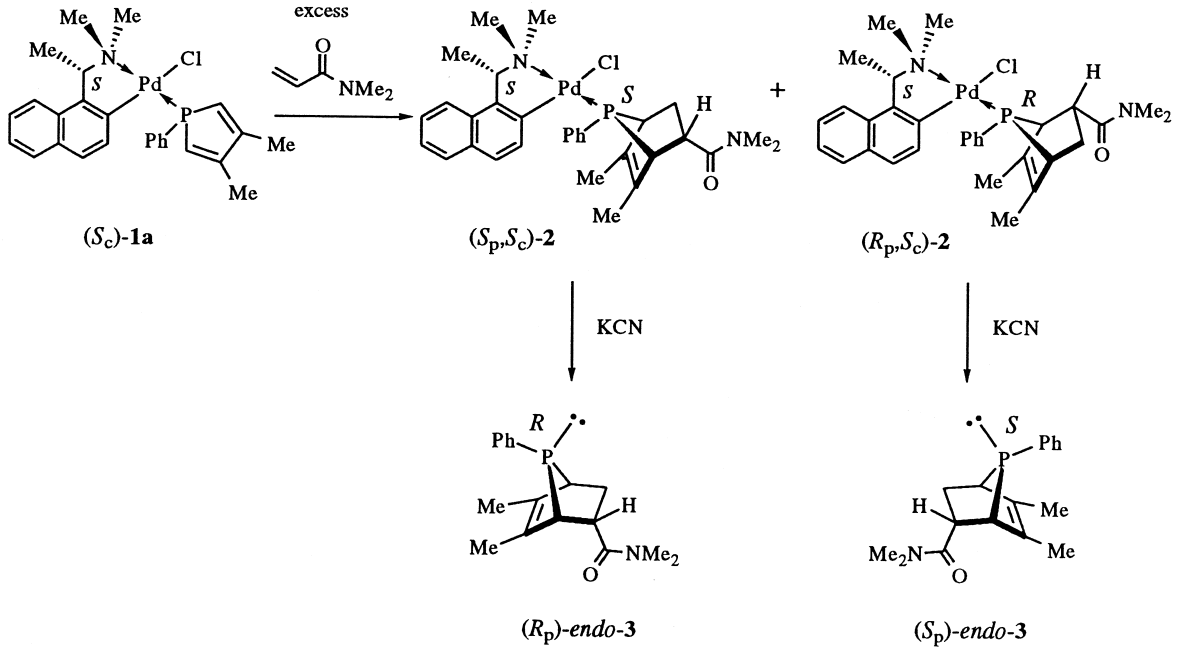


Scheme 1. (S_c)-**1a** X=Cl, (S_c)-**1b** X=$OClO_3$.



Scheme 2.

spectroscopy and was found to be complete in 32 d. Prior to purification, the ^{31}P NMR spectrum of the crude reaction product in $CDCl_3$ exhibited two sharp singlets at δ 121.2 and 123.2 in the ratio of 2:1. No other ^{31}P NMR signals were detected in the 202 MHz spectrum, thus confirming that only two diastereomeric complexes were formed in the cycloaddition reaction.

The diastereomeric cycloadducts were separated by fractional crystallization. Interestingly, the minor isomer was found to be less soluble than the major product in all the solvent systems employed and could be crystallized efficiently from dichloromethane–diethyl ether as pale yellow prisms in 25.6% isolated yield, $[\alpha]_D$=+60.7 (c=0.5, CH_2Cl_2). In $CDCl_3$, the ^{31}P NMR spectrum of the less soluble isomer exhibited, as desired, only one sharp singlet at δ 123.2. Following the isolation of the minor product, repeated crystallization of the residue complex from the same solvent system eventually gave the more soluble major isomer as yellow blocks in 26.5% isolated yield, $[\alpha]_D$=+26.7 (c=0.5, CH_2Cl_2). The molecular structure and absolute stereochemistry of both diastereomers were determined by X-ray structural analyses (Figs. 1 and 2, respectively). Studies revealed that the chloro ligand in both molecules remains coordinated to the original site of the palladium template and the *endo*-cycloadducts function exclusively as monodentates via their bridgehead phosphorus donor atoms. Fig. 1 shows the highly crystalline isomer (R_p,S_c)-**2**; The absolute configurations of the four newly generated stereogenic centres at P(13), C(14), C(17) and C(19) are *R*, *S*, *R* and *S*, respectively, with the amide functional group orientated in the *endo* position at C(19). On the other hand, the amide group in the more soluble major cycloadduct (S_p,S_c)-**2** orientated in the *endo*

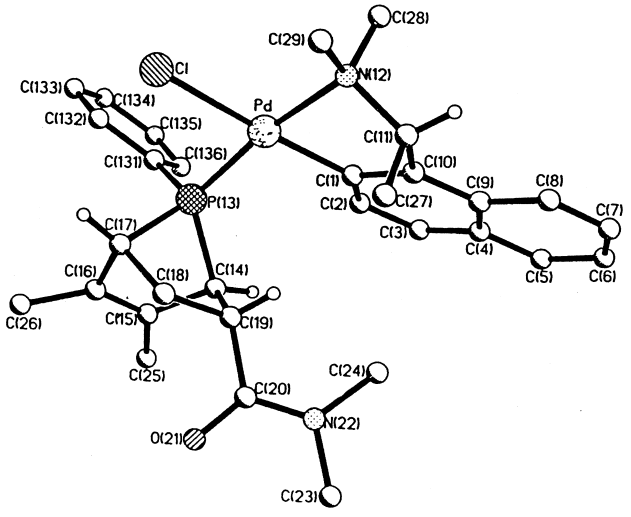


Figure 1. Molecular structure of (R_p,S_c)-**2**.

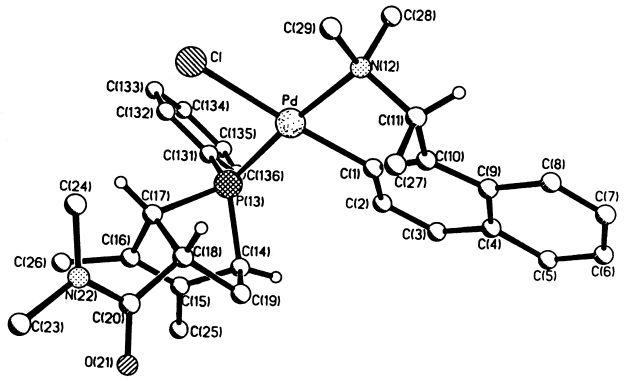


Figure 2. Molecular structure of (S_p,S_c)-**2**.

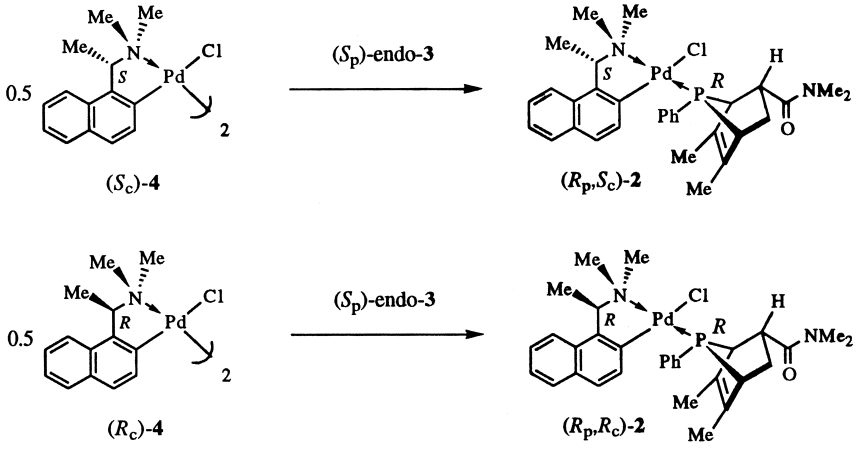
position at C(18) with the absolute configurations at P(13), C(14), C(17) and C(18) stereogenic centres being *S*, *S*, *R* and *R*, respectively (Fig. 2). Selected bond distances and bond angles of both diastereomers are given in Table 1.

Treatment of (R_p,S_c)-**2** in dichloromethane with aqueous potassium cyanide for 2 h dissociated the template complex efficiently. The organic layer which contains the naphthylamine auxiliary and the optically active phosphinoamide was first extracted with dilute sulphuric acid to remove the naphthylamine moiety. Pure (S_p)-*endo*-**3** was isolated as an air-sensitive colourless oil in 63% yield, $[\alpha]_{365}=+5.9$ ($c=2.8$, CH_2Cl_2). The ^{31}P NMR spectrum of the liberated phosphinoamide in $CDCl_3$ exhibited a sharp singlet at δ 104.7. It is noteworthy that the apparent inversion of configuration that takes place at the bridgehead phosphorus stereogenic centre during the liberation process is merely a consequence of the CIP sequence rules.[9] Stereospecific displacement of the optically active phosphinoamide from the template complex was confirmed by the quantitative repreparation of (R_p,S_c)-**2** from the liberated (S_p)-*endo*-**2** and dimeric complex (S_c)-**4**[10] (Scheme 3). The 202 MHz ^{31}P NMR spectrum of the crude product indicated diastereomer (R_p,S_c)-**2** only. In a further test of optical purity, the more soluble diastereomer (R_p,R_c)-**2** was prepared from (S_p)-*endo*-**3** and (R_c)-**4**: only a sharp singlet was detected at δ 121.2. As expected, optically pure (R_p)-*endo*-**3** was liberated similarly from (S_p,S_c)-**2**, $[\alpha]_{365}=-5.7$ ($c=2.5$, CH_2Cl_2).

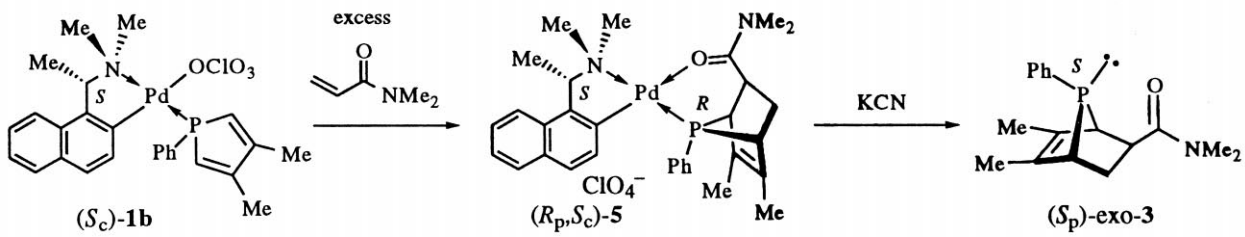
The analogous intra-molecular *exo*-cycloaddition reaction between (S_c)-**1b** and *N*,*N*-dimethylacrylamide was carried out under similar reaction conditions (Scheme 4). Interestingly, the ^{31}P NMR studies indicated that the reaction was complete in only 3 d. Furthermore, the reaction is highly stereospecific giving the *exo*-cycloadduct (R_p,S_c)-**5** as the sole reaction product in essentially quantitative yield. In a recent preliminary communication,[11] we reported the X-ray structure of the template complex (R_p,S_c)-**5** and the isolation of (−)-(S_p)-*exo*-**3**. In $CDCl_3$, the ^{31}P NMR spectra of

Table 1. Selected bond distances (Å) and angles (°) of (R_p,S_c)- and (S_p,S_c)-**2**

	(R_p,S_c)-**2**	(S_p,S_c)-**2**		(R_p,S_c)-**2**	(S_p,S_c)-**2**
Pd–C(1)	2.004(4)	2.001(5)	C(1)–Pd–N(12)	80.5(2)	80.3(2)
Pd–N(12)	2.153(4)	2.152(5)	C(14)–P(13)–C(17)	80.9(2)	80.2(3)
Pd–Cl	2.392(2)	2.400(2)	C(14)–C(15)–C(16)	110.7(4)	110.2(6)
Pd–P(13)	2.218(1)	2.226(2)	C(15)–C(16)–C(17)	110.8(4)	109.9(6)
P(13)–C(14)	1.856(4)	1.840(7)	C(16)–C(17)–C(18)	106.9(4)	108.3(5)
P(13)–C(17)	1.836(4)	1.848(6)	C(17)–C(18)–C(19)	106.3(4)	105.7(5)
C(14)–C(15)	1.516(6)	1.491(9)	C(19)–C(18)–C(14)	105.4(3)	105.1(5)
C(15)–C(16)	1.323(6)	1.348(9)	C(14)–C(15)–C(25)	120.4(4)	121.8(6)
C(16)–C(17)	1.514(6)	1.506(9)	C(16)–C(15)–C(25)	129.0(4)	128.0(6)
C(17)–C(18)	1.551(6)	1.561(9)	C(15)–C(16)–C(26)	128.7(5)	129.3(6)
C(18)–C(19)	1.534(6)	1.546(9)	C(18/19)–C(20)–O(21)	119.8(4)	121.9(6)
C(18/19)–C(20)	1.532(6)	1.509(9)	C(18/19)–C(20)–N(22)	117.7(4)	118.3(6)
C(20)–O(21)	1.220(5)	1.237(8)	O(21)–C(20)–N(22)	122.5(4)	119.8(6)
C(20)–N(22)	1.335(6)	1.353(9)	C(23)–N(22)–C(24)	114.9(4)	115.3(6)



Scheme 3.



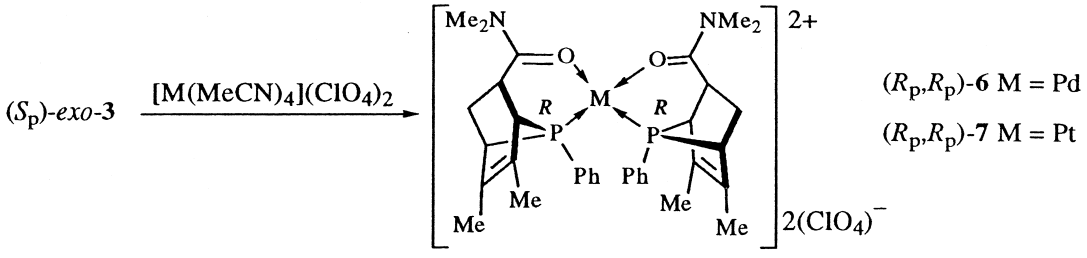
Scheme 4.

(R_p,S_c)-**5** and (−)-(S_p)-*exo*-**3** each exhibited a sharp singlet at δ 109.2 and 98.0, respectively.

It is noteworthy that in this class of *exo*/*endo*-stereochemically controlled Diels–Alder reaction, the *endo*-cycloaddition process usually proceeds at notably faster rates. For example, the *endo*-cycloaddition reaction between (S_c)-**1a** and ethyl vinyl ketone at room temperature requires only 6 d to give a pair of diastereomeric *endo*-cycloadducts.[4] Under similar reaction conditions, however, the *exo*-cycloaddition reaction between (S_c)-**1b** and ethyl vinyl ketone required 9 d for completion.[4] As outlined in the Introduction, the intermolecular *endo*-cycloaddition reaction involves a neutral transition state but the corresponding intramolecular *exo*-cycloaddition involves a cationic intermediate. Therefore the slower reaction rate in the *exo*-process has been ascribed to the lower degree of electronic activation offered by the metal template to the cyclic diene. On the other hand, the prolonged reaction time (31 d) observed in the present *endo*-cycloaddition reaction between (S_c)-**1a** and *N*,*N*-dimethylacrylamide can be attributed to the classic electron resonance features within the amido function group. Accordingly, the olefin moiety in *N*,*N*-dimethylacrylamide is indeed expected to be less reactive than its counterpart in ethyl vinyl ketone. Considering these electronic-reactivity factors, it was rather intriguing to observe the relatively fast reaction rate (3 d) for the *exo*-cycloaddition reaction between (S_c)-**1b** and *N*,*N*-dimethylacrylamide. Clearly, some unusual driving forces must be at work in this intra-molecular process. We believe that there is a strong coordination between the amido-oxygen atom and the electronically deficient template site which is *trans* to the strong π accepting *ortho*-metallated carbon atom. Formation of this strong O→Pd bond in the transition state dramatically enhances the polarization of the vinylic group in the dienophile. Consequently, the electronic density at the α-olefinic carbon is reduced and the vinyl group is more potent for the Diels–Alder reaction. Furthermore, the supplementary electronic density offered by the hard amido oxygen donor to the cationic template facilitates the activation of the coordinated cyclic diene. These synchronized electronic effects accelerate the intramolecular *exo*-cycloaddition reaction between the otherwise unreactive diene and dienophile. On the other hand, due to the absence of any resonance stabilization, the keto-oxygen atom in ethyl vinyl ketone is a markedly poorer electronic donor than its counterpart in *N*,*N*-dimethylacrylamide. Hence, a slower reaction rate was observed in the *exo*-cycloaddition between (S_c)-**1b** and the theoretically more reactive dienophile.

The *exo*-cycloadduct (S_p)-*exo*-**3** is a sterically rigid ligand that contains a typically soft phosphorus and classic hard oxygen donors. This hetero-donor bidentate is capable of forming stable P–O chelates with platinum metal ions, regardless of the strong electronically directing naphthylamine auxiliary present. For example, when (S_p)-*exo*-**3** was treated with $[M(MeCN)_4](ClO_4)_2$ (M=Pd, Pt) in acetonitrile, the corresponding bisbidentate palladium(II) and platinum(II) complexes were obtained efficiently (Scheme 5). It is noteworthy that amido O-bonded platinum complexes are rare as it has been reported that platinum prefers to coordinate to amides via their nitrogen donors.[7,12]

The palladium complex (R_p,R_p)-**6** was crystallized as yellow prisms from acetone–diethyl ether in 77% yield, $[\alpha]_D$=+370 (c=0.5, CH_2Cl_2). The ^{31}P NMR spectrum of the palladium complex in $CDCl_3$ exhibited the usual low field resonance signal as a sharp singlet at δ 101.4. Similarly, the platinum complex (R_p,R_p)-**7** was obtained as pale yellow prisms in 62% yield, $[\alpha]_D$=+175 (c=0.5, CH_2Cl_2). In contrast to (R_p,R_p)-**6** and all reported transition metal complexes containing this class of *exo*-*syn*-substituted phosphanorbornene ligand, the ^{31}P NMR spectrum of (R_p,R_p)-**7** in $CDCl_3$ did not exhibit the expected low field resonance signal. Instead, a comparatively higher field sharp singlet was recorded at δ 69.0 ($^1J_{Pt-P}$=3607.0 Hz). A literature search revealed that this is the highest field resonance so far recorded for platinum(II) complexes containing *exo*-*syn*-substituted 7-phosphanorbornenes. Although there



Scheme 5.

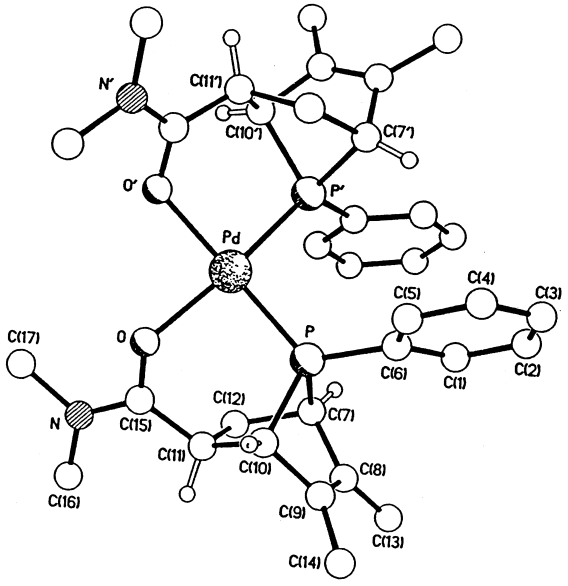


Figure 3. Molecular structure of (R_p,R_p)-**6**.

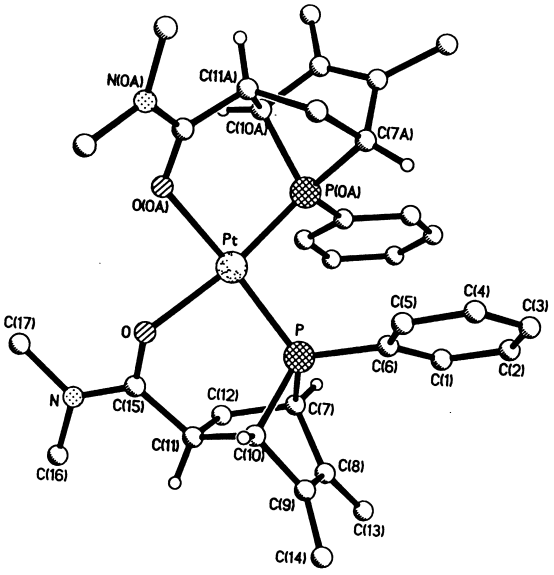


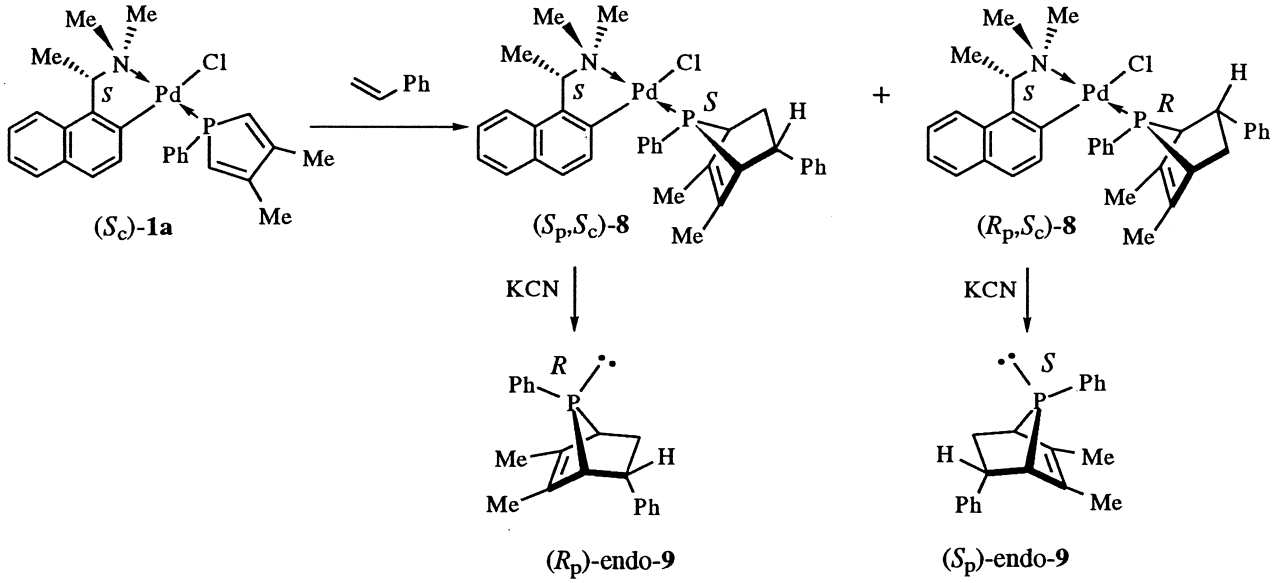
Figure 4. Molecular structure of (R_p,R_p)-**7**.

were no reported examples of *trans* P–Pt–O complexes with 7-phosphanorbornene ligands, all reported *trans* P–M-halide (M=Pd, Pt) complexes exhibit ^{31}PNMR signals within the range of δ 96–126.[13] In order to ensure that the unusual amido-O coordination is indeed adopted in (R_p,R_p)-**7** and to examine any major differences between the two bisbidentate complexes, both compounds were examined by single crystal X-ray crystallography. Figs. 3 and 4 show the cations in these complexes. Selected bond distances and bond angles of both complexes are given in Table 2.

The structural analyses revealed that the two cationic complexes are isostructural and there are no striking differences in their molecular architectures. The bidentate ligand adopts the P–O chelation mode in both complexes. Both cations have crystallographic C_2 symmetry about the axes passing through the central metal atom, and bisecting the O–M–O′ and P–Pd–P′ angles. Interestingly, the structural analyses clearly illustrated that the amido functional group is rather sensitive to metal complexation. For instance, the amido C=O bond distance in the P–O chelating palladium complex (R_p,R_p)-**6** [1.259(6) Å] is markedly longer than those observed in the analogous non-chelating palladium complexes (R_p,S_c)- and (S_p,S_c)-**2** [1.220(5) and 1.237(8) Å, respectively]. Similar lengthening of the C=O distance is also observed in the template complex (R_p,S_c)-**5** [1.252(7) Å].[11] Evidently, the C=O double bond character is weakened when the amido-oxygen is coordinated to palladium.[7] Furthermore, a dramatic lengthening of the C=O bond [1.277(9) Å] is observed in the platinum complex (R_p,R_p)-**7**. This C=O bond is longer than the only other reported structure containing an acetamide O-coordinated to a platinum centre [Pt(Me$_5$diene){O–MeC(O)NH$_2$}]$^{2+}$ [1.262(7) Å]—in which oxygen is coordinated *trans* to a nitrogen atom.[12] From an electronic standpoint, the marked lengthening of the C=O bond in (R_p,R_p)-**7** may be attributed to the electronic directing effects originating from both platinum and the *trans*-coordinating phosphorus. We believe that the unusually high field shift observed in the ^{31}P NMR spectrum of (R_p,R_p)-**7** is indeed due to this strong intramolecular C=O–Pt–P electronic interaction. It should be noted that, in contrast to all proposed O-bonded platinum complexes, (R_p,R_p)-**7** is indefinitely stable in solution and the Pt–O bonds cannot be displaced by water.

Table 2. Selected bond distances (Å) and angles (°) of (R_p,R_p)-**6** and (R_p,R_p)-**7**

	(R_p,R_p)-**6**	(R_p,R_p)-**7**		(R_p,R_p)-**6**	(R_p,R_p)-**7**
M–P	2.199(1)	2.188(2)	P–M–O	92.0(1)	91.8(2)
M–O	2.108(4)	2.102(5)	P–M–O′	169.0(1)	168.8(2)
O–C(15)	1.259(6)	1.275(9)	P–M–P′	92.9(1)	95.2(1)
N–C(15)	1.310(8)	1.308(11)	O–M–O′	84.9(2)	82.7(3)
C(11)–C(15)	1.504(8)	1.498(11)	O–M–P′	169.0(1)	168.8(2)
P–C(6)	1.802(3)	1.807(8)	M–O–C(15)	124.0(3)	122.2(5)
P–C(7)	1.840(6)	1.842(7)	C(15)–N–C(16)	124.6(5)	124.0(7)
P–C(10)	1.843(5)	1.824(7)	C(15)–N–C(17)	118.7(5)	119.4(7)
C(7)–C(8)	1.524(7)	1.523(11)	C(16)–N–C(17)	116.5(5)	116.3(8)
C(8)–C(9)	1.339(9)	1.327(13)	N–C(15)–C(11)	120.2(5)	121.0(7)
C(9)–C(10)	1.501(8)	1.510(11)	C(7)–P–C(10)	82.4(2)	82.2(4)
C(10)–C(11)	1.553(8)	1.559(12)	C(7)–C(8)–C(9)	110.8(5)	111.2(7)
C(11)–C(12)	1.575(8)	1.577(12)	C(8)–C(9)–C(10)	111.2(5)	110.6(7)
C(12)–C(7)	1.544(8)	1.533(11)	C(8)–C(9)–C(14)	128.2(7)	128.8(9)



Scheme 6.

Phenyl-substituted phosphanorbornenes

Styrene does not bear an electron withdrawing group in the vinylic position and is generally regarded as a poor dienophile. Furthermore, unlike *N,N*-dimethylacrylamide, styrene does not bear a potential donor atom and thus cannot be activated by Lewis acids or metal templates. Consequently, styrene is rarely used as a dienophile in classic Diels–Alder reactions.[14] Indeed, no cycloaddition reaction was observed when a mixture of styrene and free DMPP was heated at 100°C in a sealed tube for 2 months. Similarly, the treatment of styrene with (S_c)-**1a** and (S_c)-**1b**, respectively, at room temperature failed to give any cycloadduct. However, we found that the Diels–Alder reaction could be achieved when a chlorobenzene solution containing (S_c)-**1a** and excess styrene was heated at 80°C for 3 d (Scheme 6). The intermolecular cycloaddition reaction generated a 1:1.5 diastereomeric pair of the expected *endo*-cycloadducts, (S_p,S_c)-**8** and (R_p,S_c)-**8**, respectively. Prior to crystallization, the ^{31}P NMR spectrum of the crude product in $CDCl_3$ exhibited two sharp singlets at δ 122.5 (minor) and 124.5 (major). No signals due to the starting material and other side products were detected in the 202 MHz ^{31}P NMR spectrum. The two diastereomers were separated by fractional crystallization from dichloromethane–hexane. The less soluble diastereomer (S_p,S_c)-**8** was obtained as pale yellow prisms in 30% isolated yield, $[\alpha]_D$=+22.0 (c=0.5, CH_2Cl_2). The more soluble *endo*-cycloadduct (R_p,S_c)-**8** was subsequently obtained in its optically pure form from the concentrated mother liquor as pale yellow blocks in 33% yield, $[\alpha]_D$=+34.0 (c=0.5, CH_2Cl_2). The molecular structure and absolute stereochemistry of both diastereomers were determined by X-ray structural analyses (Figs. 5 and 6). Selected bond distances and bond angles of both diastereomers are given in Table 3.

Treatment of (R_p,S_c)-**8** in dichloromethane with aqueous potassium cyanide for 2 h liberated (S_p)-*endo*-**9** as an air-sensitive colourless oil in 85% yield with $[\alpha]_D$=+102 (c=0.5, CH_2Cl_2). The ^{31}P NMR spectrum of the liberated phosphine in $CDCl_3$ exhibited a sharp singlet at δ 107.9.

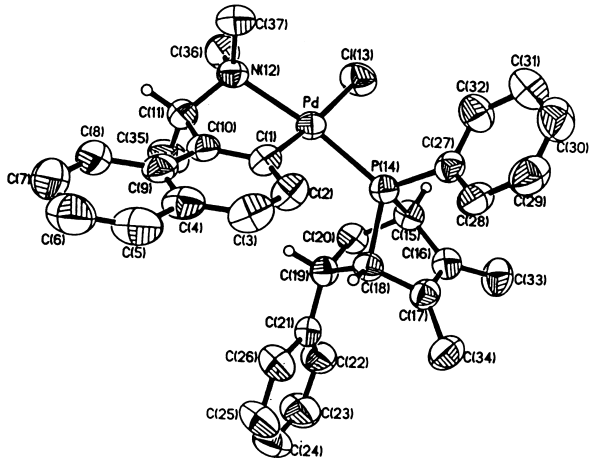


Figure 5. Molecular structure of (R_p,S_c)-**8**.

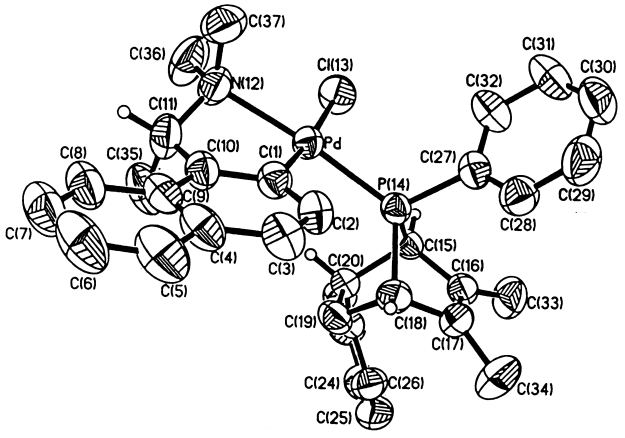


Figure 6. Molecular structure of (S_p,S_c)-**8**.

Table 3. Selected bond distances (Å) and angles (°) of (R_p,S_c)- and (S_p,S_c)-**8**

	(R_p,S_c)-**8**	(S_p,S_c)-**8**		(R_p,S_c)-**8**	(S_p,S_c)-**8**
Pd–C(1)	2.004(3)	2.003(3)	C(15)–C(20)	1.563(4)	1.577(4)
Pd–N(12)	2.137(2)	2.158(3)	C(19/20)–C(21)	1.504(4)	1.519(5)
Pd–Cl(13)	2.390(1)	2.397(1)	C(1)–Pd–N(12)	80.9(1)	80.3(1)
Pd–P(14)	2.219(1)	2.222(1)	C(15)–P(14)–C(18)	81.0(1)	80.9(1)
P(14)–C(15)	1.842(3)	1.848(3)	C(15)–C(16)–C(17)	110.9(3)	109.9(3)
P(14)– C(27)	1.814(3)	1.807(3)	C(16)–C(17)–C(18)	110.2(3)	110.9(3)
C(15)–C(16)	1.510(4)	1.514(4)	C(17)–C(18)–C(19)	107.8(2)	107.5(3)
C(16)–C(17)	1.329(4)	1.338(5)	C(18)–C(19)–C(20)	104.6(2)	106.9(2)
C(17)–C(18)	1.516(4)	1.520(5)	C(19)–C(20)–C(15)	106.3(2)	104.4(2)
C(18)–C(19)	1.571(4)	1.547(5)	C(20)–C(15)–C(16)	107.0(3)	107.7(2)
C(19)–C(20)	1.559(4)	1.555(5)	C(20)–C(15)–P(14)	98.4(2)	99.7(2)

Similarly, optically pure (R_p)-*endo*-**9** was obtained from (S_p,S_c)-**8** $[\alpha]_D=-102$ (c=0.5, CH_2Cl_2). The optical purity of both enantiomers has been confirmed by means of our standard metal complexation technique that involves the dimeric complexes (R_c)- and (S_c)-**4** (see Scheme 3).

It is important to note that no Diels–Alder reaction was observed between styrene and (S_c)-**1b**, despite the fact that similar and even stronger reaction conditions were utilized. Neither the *endo* nor the *exo*-cycloadducts were generated in these attempts. From a mechanistic standpoint, the olefinic group in styrene may function as a π-bonded ligand to the readily available template site. However, model studies revealed that this mode of π-coordination would not permit an appropriate orientation for the intra-molecular [4+2] cycloaddition reaction. Furthermore, even if the styrene is capable of displacing the perchlorato ligand in (S_c)-**1b**, the new electroneutral metal–alkene bond in the resulting cationic species would not provide sufficient activation to the coordinating DMPP for the strict inter-molecular *endo*-cycloaddition reaction. Compared to the π-bonded styrene ligand, the anionic chloro ligand in (S_c)-**1a** is clearly a better reaction activator for the coordinated DMPP. Further exploration of the Diels–Alder reaction of DMPP is in progress in our laboratories.

Experimental

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. Proton NMR spectra were recorded at 500.14 MHz and ^{31}P spectra at 202.46 MHz on a Bruker AMX500 NMR spectrometer. Optical rotations were measured on specified solutions in a 1-dm cell at 25°C with a Perkin–Elmer model 341 polarimeter. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry at the National University of Singapore.

The chiral templates (S_c)-**1a**[1] and (S_c)-**1b**[1] and the dimeric complexes (R_c)- and (S_c)-**4**,[10] were prepared according to literature methods. The *exo*-amidophosphine template complex (R_p,S_c)-**5** and free (−)-(S_p)-*exo*-**3** were obtained as previously described.[11]

Synthesis and isolation of *endo*-amidophosphine complexes (R_p,S_c)-2 and (S_p,S_c)-2. A solution of the chloro complex (S_c)-**1a** (3.00 g, 5.68 mmol) in dichloromethane (20 mL) was stirred with *N*,*N*-dimethylacrylamide (0.9 mL, 8.52 mmol) at room temperature for 32 d. Removal of solvent left a yellow oil. The ^{31}P{^{1}H} NMR of the crude product prior to crystallization indicated a 2:1 mixture of the diastereomeric products at δ 121.2 and 123.2. Both compounds could be isolated by fractional crystallization in dichloromethane–diethyl ether. The less soluble, minor diastereomer (R_p, S_c)-**2** crystallized as yellow prisms: 0.91 g (25.6%); mp 218°C (dec); $[\alpha]_D$+60.7 (c=0.4, CH_2Cl_2); IR (KBr, cm^{-1}) 1644 (C=O); ^{1}H NMR ($CDCl_3$) δ 1.54 (s, 3H, C=C*Me*), 1.64 (s, 3H, C=C*Me*), 1.91 (d, 3H, $^3J_{HH}$=6.2 Hz, CH*Me*), 2.16–2.25 (m, 1H, H_{6endo}), 2.32 (br s, 3H, N*Me*$_{amide}$), 2.55 (s, 3H, N*Me*$_{ax}$), 2.73 (s, 1H, N*Me*$_{amide}$), 2.87 (d, 3H, $^4J_{PH}$=2.9 Hz, N*Me*$_{eq}$), 3.01–3.05 (m, 1H, H_{6exo}), 3.28 (s, 1H, H_4), 3.54 (s, 1H, H_1), 3.87 (br m, 1H, H_5), 4.27 (qn, 1H, $^3J_{HH}$=$^4J_{PH}$=6.1 Hz, C*H*Me), 7.27–7.87 (m, 11H, aromatics); ^{1}H NMR (CD_2Cl_2) δ 1.53 (s, 3H, C=C*Me*), 1.61 (s, 3H, C=C*Me*), 1.91 (d, 3H, $^3J_{HH}$=6.4 Hz, CH*Me*), 2.15 (ddd, 1H, $^3J_{PH6endo}$=33.4 Hz, $^2J_{H6endoH6exo}$=11.7 Hz, $^3J_{H5H6endo}$=4.4 Hz, H_{6endo}), 2.28 (br s, 3H, N*Me*$_{amide}$), 2.53 (d, 3H, $^4J_{PH}$=1.2 Hz, N*Me*$_{ax}$), 2.68 (s, 1H, N*Me*$_{amide}$), 2.83 (d, 3H, $^4J_{PH}$=3.1 Hz, N*Me*$_{eq}$), 2.96–3.00 (m, 1H, H_{6exo}), 3.30 (s, 1H, H_4), 3.48 (d, 1H, $^2J_{PH}$=1.3 Hz, H_1), 3.82 (br m, 1H, H_5), 4.29 (qn, 1H, $^3J_{HH}$=$^4J_{PH}$=6.0 Hz, C*H*Me), 7.27–7.90 (m, 11H, aromatics); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 123.2 (s). Anal. Calcd for $C_{31}H_{38}ClN_2OPPd$: C, 59.3; H, 6.1; Cl, 5.7; N, 4.5; P, 4.9. Found: C, 59.2; H, 6.1; Cl, 5.6; N, 4.2; P, 5.0. The more soluble, major diastereomer (S_p,S_c)-**2** crystallized as yellow blocks: 0.94 g (26.7%); mp 221–222 °C (dec); $[\alpha]_D$=+26.7 (c=0.2, CH_2Cl_2); IR (KBr, cm^{-1}) 1644 (C=O); ^{1}H-NMR ($CDCl_3$) δ 1.33 (s, 3H, C=C*Me*), 1.82 (s, 3H, C=C*Me*), 1.92 (d, 3H, $^3J_{HH}$=6.4 Hz, CH*Me*), 2.21 (dddd, 1H, $^3J_{PH6endo}$=33.8 Hz, $^2J_{H6endoH6exo}$=12.2 Hz, $^3J_{H5H6endo}$=4.7 Hz, $^3J_{H1H6endo}$=1.5 Hz, H_{6endo}), 2.27–2.31 (m, 1H, H_{6exo}), 2.56 (s, 3H, N*Me*$_{ax}$), 2.87 (d, 3H, $^4J_{PH}$=3.0 Hz, N*Me*$_{eq}$), 2.90 (s, 3H, N*Me*$_{amide}$), 3.03 (d, 1H, $^2J_{PH}$=1.7 Hz, H_4), 3.37 (s, 3H, N*Me*$_{amide}$), 3.71 (s, 1H, H_1), 4.27 (qn, 1H, $^3J_{HH}$=$^4J_{PH}$=6.1 Hz, C*H*Me), 4.52–4.55 (m, 1H, H_5), 7.07–7.95 (m, 11H, aromatics); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 121.1 (s). Anal. Calcd for $C_{31}H_{38}ClN_2OPPd$: C, 59.3; H, 6.1; Cl, 5.7; N, 4.5; P, 4.9. Found: C, 59.4; H, 6.1; Cl, 5.9; N, 4.4; P, 5.3.

Synthesis of the bisbidentate palladium(II) complex (R_p,R_p)-6. A freshly prepared sample of (S_p)-*endo*-**3** (0.17 g, 0.58 mmol) in degassed acetonitrile (10 mL) was stirred with a freshly prepared solution of $[Pd(CH_3CN)_4](ClO_4)_2$ (0.14 g, 0.29 mmol) in acetonitrile (20 mL) for 2 h. Removal of solvent left a greyish yellow

Table 4. Crystallographic data for complexes (R_p,S_c)-**2**, (S_p,S_c)-**2**, (R_p,R_p)-**6**, (R_p, R_p)-**7**, (R_p, S_c)-**8** and (S_p, S_c)-**8**

	(R_p,S_c)-**2**	(S_p,S_c)-**2**	(R_p,R_p)-**6**	(R_p,R_p)-**7**	(R_p,S_c)-**8**	(S_p,S_c)-**8**
Formula	$C_{31}H_{38}ClN_2OPPd$	$C_{31}H_{38}ClN_2OPPd$	$[C_{34}H_{44}N_2O_2P_2Pd][ClO_4]_2$	$[C_{34}H_{44}N_2O_2P_2Pt][ClO_4]_2$	$C_{34}H_{37}ClNPPd$	$C_{34}H_{37}ClNPPd{\cdot}0.5\ Et_2O$
M	627.50	627.50	879.95	968.64	632.47	699.53
Crystal system	Orthorhombic	Orthorhombic	Trigonal	Trigonal	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P3_221$	$P3_221$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	11.835(2)	10.865(3)	10.522(1)	10.514(2)	11.146(2)	11.721(1)
b (Å)	14.090(3)	11.303(2)	10.522(1)	10.514(2)	13.037(2)	14.554(1)
c (Å)	18.162(4)	24.707(5)	29.944(1)	30.061(6)	21.470(5)	22.177(1)
γ (°)	–	–	120	120	–	–
V (Å^3)	3028(1)	3034(1)	2871(1)	2878(1)	3120(1)	3783(1)
Z	4	4	3	3	4	4
T (K)	298	298	293	293	293	293
D_c (g cm^2)	1.376	1.374	1.527	1.677	1.346	1.175
λ (Å)	0.71073	0.71073	1.54178	0.71073	0.71073	0.71073
μ (cm^{-1})	7.79	7.78	64.69	39.36	7.54	6.26
R_1(obs)[a]	3.24	4.32	3.44	3.37	3.07	3.21
wR_2(obs)[b]	3.62	4.47	9.25	8.14	7.43	9.76

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[b] $wR_2 = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

glass. Crystallization of the crude product in acetone–diethyl ether yielded pale yellow prisms: 0.20 g (77%); mp 278–279 °C (dec); $[\alpha]_D$=+370 (c=0.5, CH_2Cl_2); IR (KBr, cm^{-1}) 1589 (C=O), 1086 (ClO_4); ^{1}H NMR (CD_2Cl_2) δ 1.36 (s, 6H, C=C*Me*), 1.58 (s, 6H, C=C*Me*), 2.24 (dddd, 2H, $^3J_{PH6endo}$=36.4 Hz, $^2J_{H6endoH6exo}$=13.7 Hz, $^3J_{H5H6endo}$=10.5 Hz, $^3J_{H1H6endo}$=1.6 Hz, H_{6endo}), 2.71 (m, 2H, H_4), 2.93–2.97 (m, 2H, H_{6exo}), 3.16–3.28 (m, 2H, H_5), 3.23 (s, 6H, N*Me*$_{amide}$), 3.24 (s, 6H, N*Me*$_{amide}$), 3.31 (m, 2H, H_1), 7.01–7.64 (m, 10H, aromatics); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 101.4 (s); Λ_M 207.0 cm^2 Ω^{-1} mol^{-1} (acetone) (2:1). Anal. Calcd for $C_{34}H_{44}Cl_2N_2O_{10}P_2Pd$: C, 46.4; H, 5.0; Cl, 8.1; N, 3.2. Found: C, 46.4; H, 4.9; Cl, 8.4; N, 3.3.

Synthesis of the bisbidentate platinum(II) complex (R_p,R_p)-7. A freshly prepared sample of (S_p)-*endo*-3 (0.17 g, 0.58 mmol) in degassed acetonitrile (10 mL) was treated with a fresh solution of $[Pt(CH_3CN)_4](ClO_4)_2$ (0.16 g, 0.29 mmol) in acetonitrile (20 mL) for 2 h. The greyish pale yellow residue obtained was extracted with chloroform. Upon removal of solvent, a crystalline pale yellow solid (90%) was obtained. Recrystallization of the crude product in acetone–diethyl ether yielded pale yellow prisms: 0.17 g (62%); mp >300°C; $[\alpha]_D$=+175 (c=0.5, CH_2Cl_2); IR (KBr, cm^{-1}) 1584 (C=O), 1086 (ClO_4); ^{1}H-NMR ($CDCl_3$) δ 1.38 (s, 6H, C=C*Me*), 1.63 (s, 6H, C=C*Me*), 2.09–2.28 (m, 2H, H_{6endo}), 2.79 (m, 2H, H_4), 2.98–3.03 (m, 2H, H_{6exo}), 3.21–3.26 (m, 2H, H_5), 3.30 (s, 6H, N*Me*$_{amide}$), 3.33 (m, 2H, H_1), 3.35 (s, 6H, N*Me*$_{amide}$), 6.98–7.60 (m, 10H, aromatics); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 69.0 (s, 2P, $^1J_{PtP}$=3607 Hz, *cis*-isomer); ^{195}Pt{^{1}H} NMR (CD_3CN) δ −4293.7 (s, 1Pt, $^1J_{PtP}$=3607 Hz, *cis*-isomer); Λ_M 206.0 cm^2 Ω^{-1} mol^{-1} (acetone) (2:1). Anal. Calcd for $C_{34}H_{44}Cl_2N_2O_{10}P_2Pt$: C, 42.2; H, 4.6; Cl, 7.3; N, 2.9. Found: C, 42.2; H, 4.7; Cl, 7.4; N, 2.9.

Synthesis and isolation of *endo*-phenylphosphine complexes (R_p,S_c)-8 and (S_p,S_c)-8. A solution of the chloro complex (S_c)-**1a** (6.00 g, 10.98 mmol) in chlorobenzene (80 mL) was stirred with styrene (30 mL) at 80°C for 30 d. Removal of solvent and excess styrene under reduced pressure gave a dark brown residue. The ^{31}P{^{1}H} NMR of the crude product prior to crystallization indicated a 1:1.5 mixture of the diastereomeric products at δ 122.5 and 124.5. Both compounds could be isolated by fractional crystallization in dichloromethane–hexane. The less soluble, minor diastereomer (S_p,S_c)-**8** crystallized as yellow prisms: 2.1 g (30%); mp 220–223°C (dec); $[\alpha]_D$=+22.0 (c=0.5, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 3H, C=C*Me*), 1.56 (s, 3H, C=C*Me*), 1.74–1.92 (m, 1H, H_{6endo}), 1.90 (d, 3H, $^3J_{HH}$=6.3 Hz, CH*Me*), 2.58 (s, 3H, N*Me*$_{ax}$), 2.60–2.65 (m, 1H, H_{6exo}), 2.93 (d, 3H, $^4J_{PH}$=2.9 Hz, N*Me*$_{eq}$), 3.14 (s, 1H, H_4), 3.67 (s, 1H, H_1), 4.28 (qn, 1H, $^3J_{HH}$=$^4J_{PH}$=6.1 Hz, C*H*Me), 4.90–5.05 (br m, 1H, H_5), 7.21–7.94 (m, 16H, aromatics); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 122.5 (s). Anal. Calcd for $C_{34}H_{37}ClNPPd$: C, 64.6; H, 5.9; N, 2.2. Found: C, 64.8; H, 5.7; N, 2.1. The more soluble, major diastereomer (R_p,S_c)-**8** crystallized as yellow blocks from the concentrated mother liquor: 2.2 g (33%); mp 121–122°C (dec); $[\alpha]_D$=+34.0 (c=0.5, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 3H, C=C*Me*), 1.62 (s, 3H, C=C*Me*), 1.90–2.10 (m, 1H, H_{6endo}), 1.96 (d, 3H, $^3J_{HH}$=6.3 Hz, CH*Me*), 2.58 (s, 3H, N*Me*$_{ax}$), 2.93 (d, 3H, $^4J_{PH}$=3.0 Hz, N*Me*$_{eq}$), 3.17 (s, 1H, H_4), 3.32–3.45 (m, 1H, H_{6exo}), 3.65 (s, 1H, H_1), 4.11–4.22 (br m, 1H, H_5), 4.31 (qn, 1H, $^3J_{HH}$=$^4J_{PH}$=6.1 Hz, C*H*Me), 6.74–7.92 (m, 16H, aromatics); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 124.5 (s). Anal. Calcd for $C_{34}H_{37}ClNPPd$: C, 64.6; H, 5.9; N, 2.2. Found: C, 64.7; H, 5.7; N, 2.3.

Liberation of (+)-(S_p)-*endo*-3. A solution of (R_p,S_c)-**2** (0.40 g, 0.64 mmol) in dichloromethane (10 mL) was treated with excess potassium cyanide (2.0 g, 50 equiv.) in water (2 mL) for 3 h under vigorous stirring. The organic layer was separated, washed thoroughly with water (4×20 mL), extracted with dilute H_2SO_4 (0.5 M), washed with water (2×20 mL) and dried over anhydrous $MgSO_4$. Removal of solvent under partial pressure left a colourless viscous oil, (S_p)-*endo*-3: 0.12 g (63%); $[\alpha]_{365}$=+5.9° (*c* 2.8, CH_2Cl_2); $[\alpha]_D$=+1.0 (c=2.8, CH_2Cl_2); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 104.7 (s). The enantiomer, (−)-(R_p)-*endo*-**3** was liberated similarly from (S_p,S_c)-**2**, $[\alpha]_{365}$=−5.7° (c=2.5, CH_2Cl_2); $[\alpha]_D$=−1.0 (c=2.5, CH_2Cl_2); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 104.7 (s). It is noteworthy that *syn*-phosphanorbornenes are air-sensitive and configurationally unstable.[15] When in contact with polar solvents, the *syn* isomers rapidly transform into the corresponding more

stable *anti* structures.[15] Thus, after the aqueous potassium cyanide treatment, the liberated ligands must be re-complexed to selected metal ions within ca. 30 min. The configurational instabilities of (R_p)- and (S_p)-*endo*-**3** therefore precluded the ligands from further purification and elemental characterization.

Liberation of (−)-(R_p)-*endo*-9. The monodentate (−)-(R_p)-*endo*-**9** was liberated in a similar manner from (S_p,S_c)-**8**, 85%, $[\alpha]_D$=−102 (c=0.5, CH_2Cl_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 107.9 (s). The enantiomer, (+)-(S_p)-*endo*-**9** was obtained from (R_p,S_c)-**8**, 88%, $[\alpha]_D$=+102 (c=0.5, CH_2Cl_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 107.9 (s).

Crystal structure determination of complexes (R_p,S_c)-2, (S_p,S_c)-2, (R_p,R_p)-6, (R_p,R_p)-7, (R_p,S_c)-8 and (S_p,S_c)-8. Crystal data for all six complexes and a summary of the crystallographic analyses are given in Table 4. The bis-bidentate palladium complex (R_p,R_p)-**6** was analysed at Imperial College using a Siemens P4/PC diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. The other five structures were analysed at the National University of Singapore using a Siemens R3m/V four-circle diffractometer with graphite monochromated Mo-Kα radiation. For all six complexes, semiempirical absorption corrections were applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distance from carbon atoms and were assigned fixed thermal parameters. The absolute configurations of all complexes were determined unambiguously by use of the Flack parameter and by internal reference to the known naphthylamine centre.

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