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Enantioselective, High-Yielding Synthesis of Alcohol-Functionalized Diphosphanes Utilizing Asymmetric Control with a Chiral Auxiliary

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Enantiomerically pure, alcohol-functionalized diphosphane ligands carrying one phosphorus and three carbon stereogenic centers were generated from the Diels–Alder reactions of phosphane-functionalized terminal alkenols [3-(diphenylphosphanyl)but-3-en-1-ol and 2-(diphenylphosphanyl)prop-2-en-1-ol] with 3,4-dimethyl-1-phenyl-1*H*-phosphole. The reactions were promoted and controlled by the organoplatinum complex containing *ortho*-metalated (*R*)-[1-(dimethylamino)ethyl]naphthalene, and both cycloadditions showed excellent regio- and stereoselectivity under mild conditions with only one enantiomer being formed. The products were isolated in high yield and were characterized by single-crystal X-ray diffraction analysis. Their structures in solution were analyzed by 2D ^{1}H–^{1}H ROESY NMR spectroscopy. Subsequent decomplexation and repreparation of the products proved the optical purity of the alcohol-functionalized, chiral diphosphanes formed.

Introduction

Chiral bidentate phosphanes continue to be amongst the most important auxiliaries in enantioselective catalysis.[1] Although many effective chiral diphosphanes have been developed, it is important and necessary to continue the design and development of new chiral ligands with different functionalities and backbone structures in order to cater to the wide variety of highly diverse substrates in catalytic applications. In this context, chiral diphosphane ligands containing primary alcohols are interesting targets by virtue of the fact that besides the much-established potential of chiral diphosphanes, chiral primary alcohols themselves are emerging as exceedingly useful candidates for various applications in industry and also in studies of enzymatic mechanisms.[2] Furthermore, functionalized diphosphanes have also emerged as interesting drug candidates in chemotherapy, as shown by ongoing studies in our research group,[3] and therefore, an alcoholic functionality on similar motifs provide an opportunity for further functional variations targeted at structure–activity relationship studies.

Herein we report the highly enantioselective and high yield synthesis of two primary alcohol-functionalized diphosphanes containing one stereogenic phosphorus and three asymmetric carbon centers on a phosphanorbornene skeleton. This was achieved by utilizing a platinum(II) complex containing [1-(dimethylamino)ethyl]naphthalene as a chiral auxiliary for inducing asymmetric control during the course of the facile intramolecular cycloaddition reaction between unprotected terminal alkenols [3-(diphenylphosphanyl)but-3-en-1-ol and 2-(diphenylphosphanyl)prop-2-en-1-ol] and a cyclic phosphole (3,4-dimethyl-1-phenyl-1*H*-phosphole, DMPP). It is of interest to note that the phosphane-functionalized terminal alkenols used in this reaction were themselves prepared in a highly regioselective manner (Markovnikov addition) from the respective alkynols as part of a two-stage asymmetric hydrophosphination reported earlier by our group, which also showed an interesting Pd–O interaction that played a vital role in deciding the stereoselectivity observed.[4] This body of work is part of our ongoing efforts to synthesize chiral P systems of interest through facile asymmetric transformations by employing chiral cyclometalated amine complexes, with the aim to utilize them as catalyst precursors and templates for organic synthesis and also to further explore the factors affecting the stereoselectivity of such reactions.[5]

Results and Discussion

Platinum complex (R_C)-**1** was allowed to react in dichloromethane with the 3-(diphenylphosphanyl)but-3-en-1-ol ligand (**2**) obtained by the regioselective (Markovnikov) hydrophosphination of 3-butyn-1-ol to yield monophosphane complex (R_C)-**3** as a dark yellow solid in 69.9% yield (Scheme 1). Analysis of the $^{31}P\{^{1}H\}$ NMR spectrum of the complex (121 MHz, $CDCl_3$) showed a signal at δ = 22.14 (s, $^{1}J_{Pt,P}$ = 4182.8 Hz) ppm. The coordination shift and coupling constant was indicative of the formation of (R_C)-**3**. The chloride ligand of this complex was subsequently

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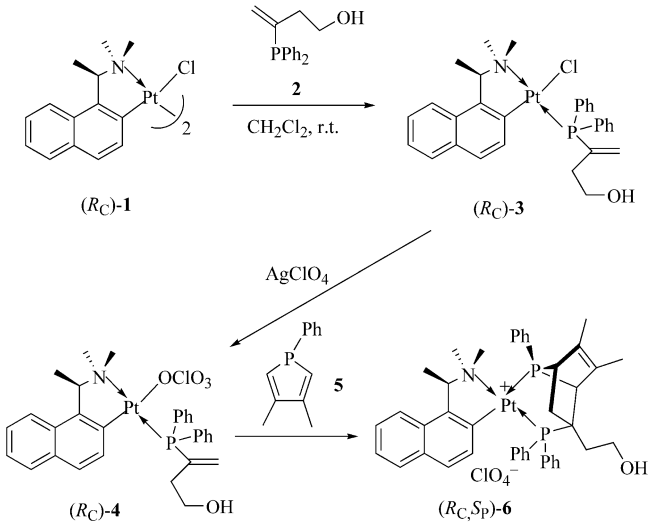
replaced by a ClO_4^- ligand through treatment of the chlorido complex with an excess amount of aqueous silver perchlorate in dichloromethane to thus generate a labile coordination site on the metal center, which thereby primed the metal complex for the subsequent intramolecular cycloaddition reaction.[6] Subsequently the perchlorato complex obtained, (R_C)-**4**, was treated with an equivalent of DMPP (**5**) at room temperature in dichloromethane for 8 h. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy and upon completion was found to be highly selective with only one diastereomer formed exclusively. The $^{31}P\{^1H\}$ NMR spectrum (121 MHz, $CDCl_3$) of the reaction product showed the following signals: δ = 39.62 (d, $^1J_{Pt,P}$ = 3567.4 Hz, $^3J_{P,P}$ = 22.8 Hz, 1 P), 115.45 (d, $^1J_{Pt,P}$ = 1580.4 Hz, $^3J_{P,P}$ = 22.8 Hz, 1 P). The low-field doublets are typical for bridgehead phosphorus adopting *exo–syn* stereochemistry.[5a] It is noteworthy that the Pt–P (bridgehead) coupling is significantly smaller (1580.4 Hz) than that observed for the nonbridgehead P atom in the cycloadduct (3567.4 Hz). This is typical of P donors located *trans* to a strong π-accepting aromatic carbon atom.[7] The reaction mixture was subsequently concentrated and layered with *n*-hexanes to yield yellow crystals in 79.7% yield.



Scheme 1.

The molecular structure and absolute configurations of recrystallized (R_C,S_P)-**6** were established by single-crystal X-ray crystallographic analysis (Figure 1). Structural analysis revealed that the bridgehead P atom in the cycloadduct is indeed substituted *trans* to the aromatic carbon of the naphthylamine chiral auxiliary. The cycloadduct is coordinated to the platinum(II) center as a bidentate chelate through its two P atoms. The analysis further confirmed that the absolute stereochemistry at the four newly generated chiral centers P2, C22, C19, and C18 was *S*, *S*, *S*, and *R*, respectively. Selected bond lengths and bond angles for (R_C,S_P)-**6** are given in Table 1. The coordination geometry is distorted square planar with angles at platinum ranging between 79.9(4)–100.4(3) and 175.9(3)–177.0(3), with the bite angles of both five-membered chelate rings being acute. The angle around the bridgehead phosphorus atom is 82.3(6) Å, which is typical for this class of phosphanorbornene ligands.[8] The Pt1–P1 and Pt1–P2 distances are not significantly different [2.252(3) and 2.279(3) Å, respectively].

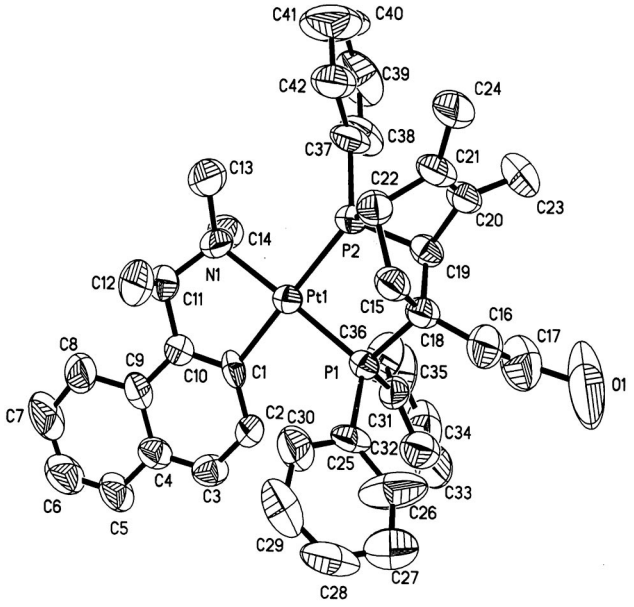


Figure 1. Molecular structure and absolute configuration of (R_C,S_P)-**6**.

Table 1. Selected bond lengths [Å] and angles [°] for (R_C,S_P)-**6**.

Pt1–C1	2.069(9)	Pt1–N1	2.125(9)
Pt1–P1	2.252(3)	Pt1–P2	2.279(3)
O1–C17	1.54(2)	C16–C17	1.54(2)
C16–C18	1.54(2)	C20–C21	1.30(2)
C1–Pt1–N1	79.9(4)	C1–Pt1–P1	96.9(3)
N1–Pt1–P1	175.9(3)	C1–Pt1–P2	177.0(3)
N1–Pt1–P2	100.4(3)	P1–Pt1–P2	82.67(9)
C18–P1–Pt1	106.2(3)	C19–P2–C22	82.3(6)
C19–P2–Pt1	109.1(3)	C22–P2–Pt1	119.2(4)
C22–C15–C18	107.0(9)	C19–C18–C15	102.8(8)
C19–C18–P1	105.3(7)	C15–C18–P1	106.5(7)

In order to confirm the structure of the cycloadduct in solution, a 500 MHz solution 2D ^1H–^1H ROESY NMR spectroscopic study of (R_C,S_P)-**6** was carried out in CD_2Cl_2. The resultant 2D ROESY NMR spectrum is shown in Figure 2. This figure also shows the numbering scheme adopted for the assignment. Strong NOE signals are observed for the interaction between H11 and all the three methyl groups viz. Me8, Me9, and Me10 (Figure 2, Signals F–H). These NOE interactions are consistent with the staggered orientation of these substituents when the (*R*)-naphthylamine ring adopts the δ conformation.[5a,8] Accordingly, Me10 shows interaction only with NMe(eq) (Figure 2, Signal C). The absence of a Me10–NMe(ax) NOE signal therefore indicates a δ conformation of the five-membered (*R*)-metalated naphthylamine ring. The interactions that provide the driving forces for Me10 to assume the axial position are also observed in the spectrum viz. H11–H19

and Me10–H19 (Figure 2, Signals I and N, respectively). The ROESY signals clearly reveal that, as evidenced in the solid state, the (*R*)-naphthylamine organometallic ring adopts the δ conformation in solution. It was also observed that as a result of the rigid skew ring conformation and the strict planarity of the naphthylamine ring, the H13 aromatic proton projects towards the space below the PPh_2 group of the cycloadduct and exhibits NOE signals at characteristically low chemical shifts, which are readily identified (Figure 2, Signals R and S). These signals also establish the regio- and stereochemistry of the cycloadduct. The absence of any NOE signal between H4 and PPh indicates that the P-phenyl group at the bridgehead adopts the *anti* position to the H4 group, which is consistent with the *S* absolute configuration at the bridgehead phosphorus center.

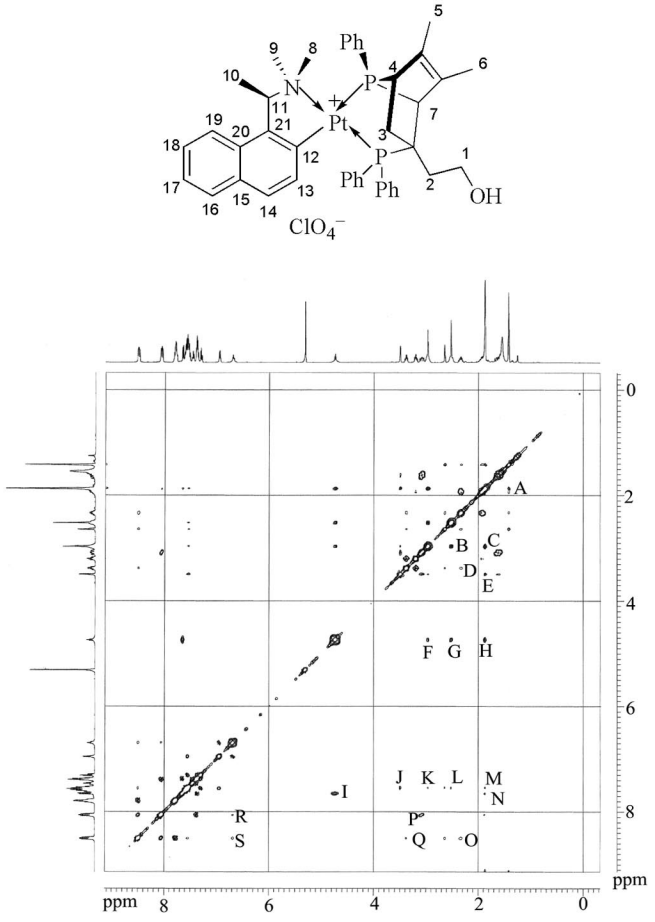
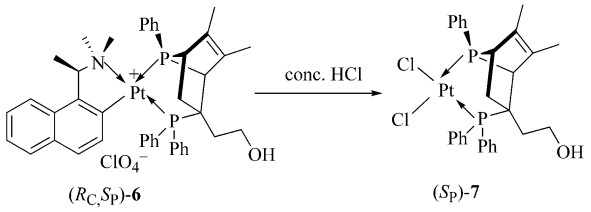


Figure 2. 500 MHz 2D ROESY spectrum of (R_C,S_P)-**6** in CD_2Cl_2. Selected NOE interactions: (A) Me5–Me6; (B) NMe(eq)–NMe(ax); (C) Me10–NMe(eq); (D) H3–H4; (E) Me6–H7; (F) NMe(ax)–H11; (G) NMe(eq)–H11; (H) Me10–H11; (I) H11–H19; (J) H7–PPh; (K) NMe(ax)–PPh; (L) NMe(eq)–PPh; (M) Me10–PPh; (N) Me10–H19; (O) H3–*o*-Ph; (P) H7–*o*-Ph; (Q) H7–*o*-Ph′; (R) H13–*o*-Ph; (S) H13–*o*-Ph′.

With the ultimate aim of obtaining the optically pure diphosphane, the chiral naphthylamine auxiliary in (R_C,S_P)-**6** was chemoselectively removed by stirring a dichloromethane solution of the complex with concentrated hydrochloric acid at room temperature (Scheme 2). Neutral dichlorido complex (S_P)-**7** precipitated as pale-yellow microcrystals from dichloromethane/*n*-hexanes in 89.5% yield. The $^{31}P\{^1H\}$ NMR spectrum of the complex in $CDCl_3$ showed the following signals: δ = 35.59 (d, $^1J_{Pt,P}$ = 3435.2 Hz, $J_{P,P}$ = 19.0 Hz, 1 P), 94.96 (d, $^1J_{Pt,P}$ = 3191.9 Hz, $J_{P,P}$ = 19.0 Hz, 1 P) ppm. In contrast to (R_C,S_P)-**6**, in (S_P)-**7** both nonequivalent phosphorus donor atoms are coordinated *trans* to the Cl ligands and therefore the two P,Pt couplings are similar in magnitude. The molecular structure and absolute configuration of complex (S_P)-**7** were established by single-crystal X-ray crystallographic analysis (Figure 3). Structural analysis revealed that the phosphanorbornene skeleton has not undergone any change during the removal of the chiral naphthylamine auxiliary. The geometry at the platinum metal center is distorted square planar with angles at platinum in the range between 83.11(5)–97.04(6) and 174.48(6)–179.17(6)°. The absolute configurations of the four stereogenic centers at P2, C1, C8, and C2 is *S*, *S*, *S*, and *R*, respectively. Selected bond lengths and angles are given in Table 2. Optically active diphosphane ligand (R_P)-**8** can be chemoselectively liberated from complex (S_P)-**7** by treatment of the dichlorido complex with aqueous potassium cyanide at room temperature (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of the free ligand in $CDCl_3$ exhibited two doublets at δ = 35.34 ($^3J_{P,P}$ = 26.5 Hz) and 98.46 ($^3J_{P,P}$ = 26.5 Hz) ppm. The low-field resonance confirms that the *exo–syn* stereochemistry is retained. It is to be noted that the apparent inversion of configuration that takes place at the phosphorus stereogenic center during the liberation process is merely a consequence of the Cahn–Ingold–Prelog (CIP) rules.[9] Owing to the extreme air sensitivity of the released ligand attributed to the noncoordinated phosphorus atom, liberated (R_P)-**8** cannot be stored in its pure form. Hence, the liberated ligand was re-coordinated to complex (R_C)-**1** (Scheme 4). This procedure also provides a means to confirm the optical purity of the released ligand. The re-coordination procedure was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. In $CDCl_3$, the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction product showed only the signals originally observed for the sole diastereomer generated from the original cycloaddition reaction. The absence of any other signals indicated that (R_P)-**8** is enantiomerically pure.



Scheme 2.

In order to further utilize the highly efficient methodology, which furthermore does not require any elaborate protection or deprotection for the alcoholic proton, the ligand 2-(diphenylphosphanyl)prop-2-en-1-ol (**9**; also obtained as part of our earlier hydrophosphination studies) in dichloro-

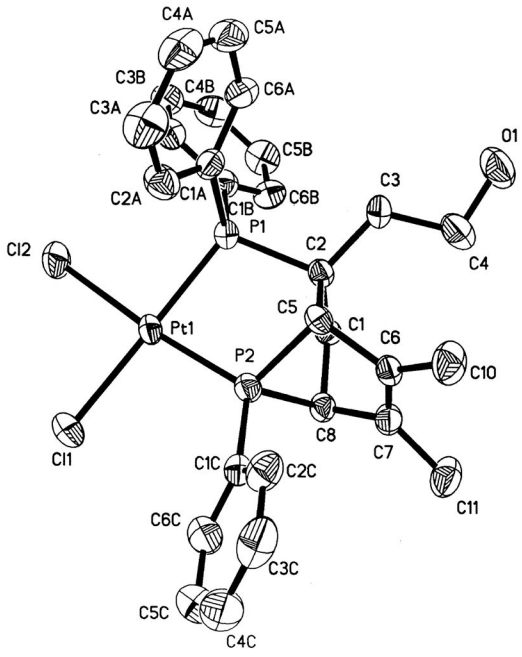
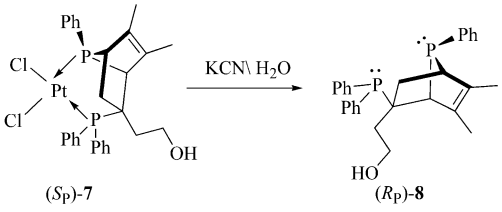


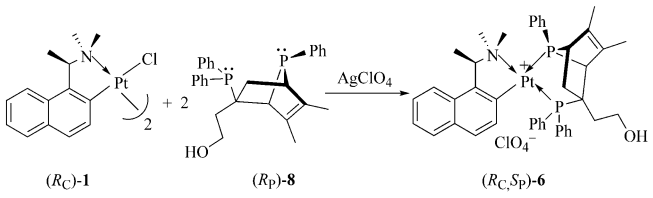
Figure 3. Molecular structure of (S_P)-**7**.

Table 2. Selected bond lengths [Å] and angles [°] of (S_P)-**7**.

Pt1–P2	2.213(1)	Pt1–P1	2.231(1)
Pt1–Cl2	2.350(1)	Pt1–Cl1	2.359(1)
P1–C2	1.876(5)	P2–C8	1.859(5)
P2–C5	1.847(5)		
P2–Pt1–P1	83.1(5)	P2–Pt1–Cl2	174.5(6)
P1–Pt1–Cl2	91.7(6)	P2–Pt1–Cl1	97.0(6)
P1–Pt1–Cl1	179.2(6)	Cl2–Pt1–Cl1	88.2(6)
C5–P2–C8	81.3(2)		

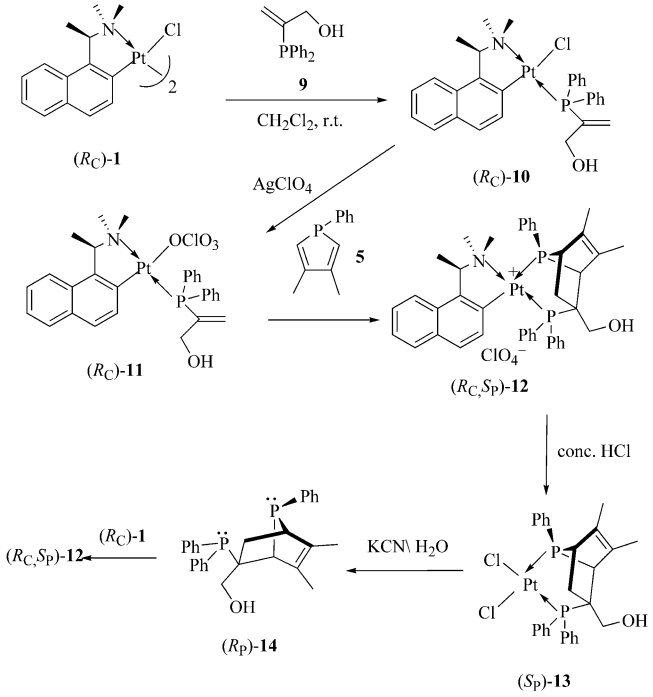


Scheme 3.



Scheme 4.

methane was added to a solution containing dimeric complex (R_C)-**1** to yield chlorido complex (R_C)-**10** in 73.9% yield (Scheme 5). The reaction mixture was concentrated and layered with *n*-hexanes to yield pale-yellow prisms of (R_C)-**10**. The single-crystal X-ray diffraction analysis data showed that ligand **9** was indeed coordinated *trans* to the NMe_2 group of the metal template (Figure 4). Selected bond lengths and bond angles are given in Table 3. Similar to the procedure adopted earlier, complex (R_C)-**10** was treated with aqueous silver perchlorate to yield complex (R_C)-**11**. A solution of (R_C)-**11** was then allowed to react with DMPP. The mixture was allowed to stir at room temperature for 8 h to yield a yellow solution of complex (R_C,S_P)-**12**. As in the case of the cycloaddition reaction involving 3-(diphenylphosphanyl)but-3-en-1-ol and DMPP, the $^{31}P\{^1H\}$ NMR spectrum was indicative of the formation of only one diastereomer. Upon crystallization, pale-yellow needle-like crystals were obtained by using a crystallizing solvent system consisting of acetonitrile/diethyl ether in 81.2% yield.



Scheme 5.

X-ray analysis of (R_C,S_P)-**12** reaffirmed that, as desired, an enantiomerically pure complex was formed (Figure 5). Selected bond lengths and bond angles are given in Table 4. Structural analysis confirmed the absolute stereochemistry at the newly generated four chiral centers P2, C21, C18, and C15 to be *S*, *S*, *S*, and *S*, respectively. The 2D ^1H ROESY NMR spectrum of (R_C,S_P)-**12** is shown in Figure 6. As in the case of (R_C,S_P)-**6**, strong NOE signals consistent with the staggered orientation of substituents when the (*R*)-naphthylamine ring adopts the δ conformation are observed for the interaction between H10 and all the three methyl groups viz. Me7, Me8, and Me9 (Figure 6, Signals H–J) consistent with the δ conformation of the (*R*)-naphthylamine ring. It was also observed that the H13 aromatic proton projects towards the space below the PPh_2 group of

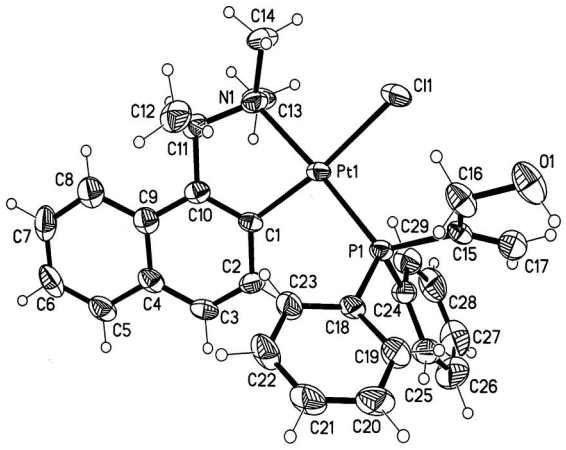


Figure 4. Molecular structure and absolute configuration of (R_C)-**10**.

Table 3. Selected bond lengths [Å] and angles [°] for complex (R_C)-**10**.

Pt1–C1	2.078(6)	Pt1–N1	2.181(5)
Pt1–P1	2.244(1)	Pt1–Cl1	2.423(1)
O1–C16	1.504(8)	C15–C17	1.311(8)
C15–C16	1.540(8)		
C1–Pt1–N1	74.00(1)	C1–Pt1–P1	102.1(2)
N1–Pt1–P1	175.6(1)	C1–Pt1–Cl1	171.2(1)
N1–Pt1–Cl1	98.0(1)	P1–Pt1–Cl1	86.1(5)

the cycloadduct and exhibits NOE signals at characteristically low chemical shifts (Figure 6, Signals T and U). These signals thus establish the regio- and stereochemistry of the cycloadduct in solution.

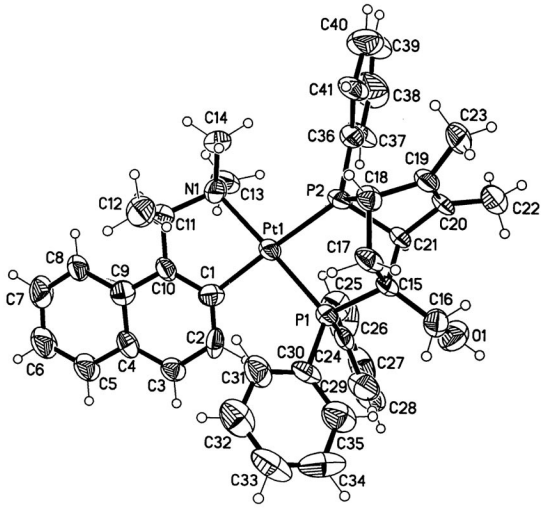
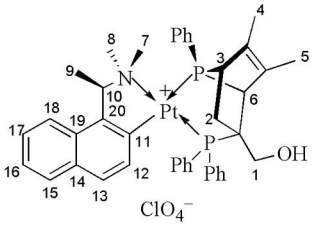


Figure 5. Molecular structure and absolute configuration of (R_C,S_P)-**12**.

The chiral naphthylamine auxiliary in (R_C,S_P)-**12** was chemoselectively removed by stirring a dichloromethane solution of the complex with concentrated hydrochloric acid at room temperature. Crystallization by using dichloromethane/*n*-hexanes yielded pale-yellow prisms of (S_P)-**13** in

Table 4. Selected bond lengths [Å] and angles [°] of (R_C,S_P)-**12**.

Pt1–C1	2.078(8)	Pt1–N1	2.157(6)
Pt1–P1	2.258(2)	Pt1–P2	2.285(2)
C15–C16	1.529(12)		
C1–Pt1–N1	80.9(3)	C1–Pt1–P1	95.8(2)
N1–Pt1–P1	175.1(2)	C1–Pt1–P2	174.9(2)
N1–Pt1–P2	100.5(2)	P1–Pt1–P2	82.5(7)
C21–P2–Pt1	109.1(2)	C18–P2–Pt1	119.8(3)
C17–C18–P2	99.7(5)	C15–C21–P2	96.0(5)
C17–C15–P1	106.4(5)	C16–C15–C17	112.0(7)
C15–P1–Pt1	106.4(3)		



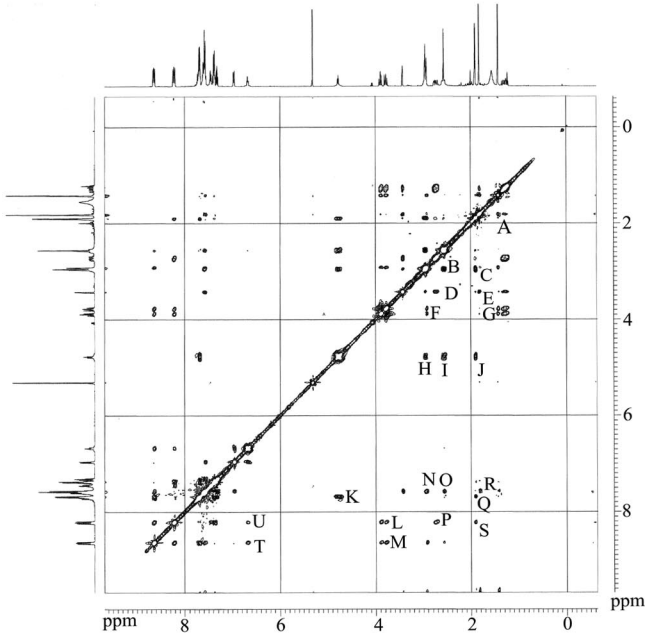


Figure 6. 500 MHz 2D ROESY spectrum of (R_C,S_P)-**12** in CD_2Cl_2. Selected NOE interactions: (A) Me4–Me5; (B) NMe(eq)–NMe(ax); (C) Me9–NMe(eq); (D) H2–H1; (E) Me5–H1; (F) Me(ax)–H3; (G) Me4–H3; (H) Me(ax)–H10; (I) Me(eq)–H10; (J) Me9–H10; (K) H10–H18; (L) H6–*o*-Ph; (M) H6–*o*-Ph′; (N) NMe(ax)–PPh; (O) NMe(eq)–PPh; (P) H2–*o*-Ph′; (Q) Me9–PPh; (R) Me5–PPh; (S) Me9–*o*-Ph′; (T) H12–*o*-Ph′; (U) H12–*o*-Ph.

91.5% yield. The molecular structure and the absolute stereochemistry of dichlorido complex (S_P)-**13** were determined by single-crystal X-ray structure analysis (Figure 7). Selected bond lengths and angles are listed in Table 5. The study revealed that the absolute configurations of (R_C,S_P)-**12** were retained. Treatment of a dichloromethane solution of (S_P)-**13** with saturated aqueous potassium cyanide liberated optically pure diphosphane (R_P)-**14** quantitatively as an air-sensitive oil. The $^{31}P\{^1H\}$ NMR spectrum of the free diphosphane in $CDCl_3$ exhibited a pair of doublets at δ =

19.21 and 108.89 ppm. The low-field ^{31}P resonance indicated that the *exo–syn* stereochemistry remained. The optical purity of (R_P)-**14** was also confirmed by the re-preparation of (R_C,S_P)-**12** from liberated ligand (R_P)-**14** and dimeric complex (R_C)-**1**.

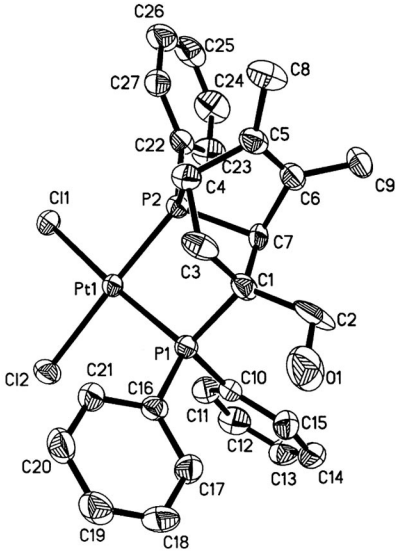


Figure 7. Molecular structure and absolute configuration of (S_P)-**13**.

Table 5. Selected bond lengths [Å] and angles [°] for (S_P)-**13**.

Pt1–P2	2.197(1)	Pt1–P1	2.248(1)
Pt1–Cl2	2.354(1)	Pt1–Cl1	2.367(1)
C1–C2	1.580(6)	O1–C2	1.378(6)
P2–Pt1–P1	84.0(4)	P2–Pt1–Cl2	176.7(4)
P1–Pt1–Cl2	93.0(4)	P2–Pt1–Cl1	93.2(4)
P1–Pt1–Cl1	173.9(4)	Cl2–Pt1–Cl1	89.9(4)
C1–P1–Pt1	104.9(1)	C7–P2–C4	81.9(2)
C7–C1–C3	104.6(3)	C3–C1–P1	104.9(3)
C4–C3–C1	106.2(3)	C5–C4–C3	107.2(4)
C5–C6–C7	111.2(4)	C6–C7–C1	109.7(3)

Conclusion

A naphthylamine complex promoted the asymmetric Diels–Alder reaction between DMPP and phosphane-functionalized terminal alkenols under mild conditions without the need for any protection on the hydroxy proton. The regio- and stereoselectivity was found to be good with only one isomer being formed exclusively. It should be noted that the cheaper palladium analogue of the chiral promoter was the initial choice for synthesizing the diphosphane ligands containing stereogenic phosphorus centers, but it was found to give poor selectivity. The formed alcohol-functionalized chiral diphosphanes have the potential of being employed in the synthesis of gold–phosphane drugs as well as in catalytic scenarios. Furthermore, the presence of the hydroxy functionality provides access to other derivatives, which can be used to study structure–activity relationships in future biological studies. Further studies involving other terminal and nonterminal phosphane-functionalized alcohols and other dienes such as cyclic arsines and cyclic silanes are currently in progress.

Experimental Section

General: All reactions and manipulations of air-sensitive compounds were carried out under a positive pressure of dry, oxygen-free nitrogen on a high-vacuum line or on a standard Schlenk line. Solvents were distilled, dried, and degassed by standard procedures where necessary. Column chromatography was performed by using silica gel 60 (0.040–0.063 mm, Merck). The 1D ^1H and $^{31}P\{^1H\}$ NMR spectra were measured at 25 °C with a Bruker ACF 300 spectrometer operating at 300.1 and 121.5 MHz, respectively. Multiplicities were given as follows: s (singlet), br. (broad), d (doublet), t (triplet), q (quartet), dd (doublets of doublets), m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H. Coupling constants are reported as *J* values in Hertz. Chemical shifts are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ = 0.0 ppm), relative to the signal of 85% H_3PO_4 (^{31}P NMR, 300 K). Phase-sensitive ROESY spectra were obtained with a Bruker AMX-500 spectrometer and were acquired into a 1024X512 matrix with a 250 ms spin lock time and a spin lock field strength such that $\gamma B_1/2\pi$ = 5000 Hz and then transformed into 1024 × 1024 points by using a sine bell weighting function in both dimensions. Optical rotations were measured with the specified solutions in a 1-cm cell at 25 °C by using a Perkin–Elmer model 341 polarimeter. Melting points were determined with an SRS-Optimelt MPA-100 apparatus and are uncorrected. The complex di-μ-chlorido{bis[(*R*)-1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*}-diplatinum(II) dichloromethane solvate [(R_C)-**1**],[10] 3,4-dimethyl-1-phenyl-1*H*-phosphole (**5**),[11] 3-(diphenylphosphanyl)but-3-en-1-ol (**2**) and 2-(diphenylphosphanyl)prop-2-en-1-ol (**9**)[4] were prepared as previously reported.

Caution! *All perchlorate salts should be handled as potentially explosive compounds.*[12]

Chlorido{(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C*,*N*}[3-(diphenylphosphanyl)but-3-en-1-ol] platinum(II) [(R_C)-3]: A solution of **2** (1.75 g, 0.007 mol) in dichloromethane was added dropwise with stirring to (R_C)-**1** (3.00 g, 0.003 mol) in dichloromethane. The reaction mixture was allowed to stir for 6 h at room temperature. A dark-yellow solid (3.35 g, 69.9%) was obtained upon removal of the solvents under reduced pressure. $[a]_D$ = +28.9 (c = 0.5, CH_2Cl_2). M.p. 223–226 °C. $C_{31}H_{35}Cl_3NOPPt$ (770.04): calcd. C 48.47, H 4.6, N 1.8; found C 48.7, H 4.7, N 1.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 22.14 (s, $^1J_{Pt,P}$ = 4182.8 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 1.97 (d, $^2J_{H,H}$ = 2.6 Hz, 3 H, CH*Me*), 2.91 (d, $^3J_{P,H}$ = 0.8 Hz, 3 H, N*Me*), 3.01 (d, $^3J_{P,H}$ = 1.3 Hz, 3 H, N*Me*), 4.00 (m, 2 H, CH_2CH_2OH), 4.48 (m, 2 H, CH_2CH_2OH), 4.6 (qn, $^3J_{H,H}$ = $^4J_{P,H}$ = 6.4 Hz, 1 H, C*H*Me), 5.19 (d, $^3J_{P,H}$ = 16.4 Hz, *cis*-PC=CH_2), 5.95 (d, $^3J_{P,H}$ = 33.7 Hz, *trans*-PC=CH_2), 6.49–8.14 (m, 16 H, *aromatics*) ppm.

{(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthyl-*C*,*N*}[(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphanyl)-7-phosphabicyclo(2.2.1)hept-5-en-2-ylethanol]platinum(II) perchlorate [(R_C,S_P)-6]: To a solution of (R_C)-**3** (3.00 g, 0.004 mol) in dichloromethane was added silver perchlorate (1.04 g, 0.005 mol) in water (3 mL), and the mixture was stirred vigorously for 30 min to ensure through mixing. The reaction mixture was then washed with water (3 × 10 mL) to remove the excess amount of perchlorate, and the extracted organic layer was dried with magnesium sulfate. Complex (R_C)-**4** (3.01 g, 91.1%) was obtained as a yellow solid upon removal of the solvents. A

solution of DMPP (**5**; 0.79 g, 0.004 mol) in dichloromethane was added dropwise to complex (R_C)-**4** (3.01 g, 0.004 mol) in dichloromethane, and the mixture was stirred at room temperature for 8 h. The reaction mixture was subsequently concentrated and layered with *n*-hexanes to yield yellow crystals (2.98 g, 79.7%). $[a]_D$ = –147.05 (*c* = 0.7, CH_2Cl_2). M.p. 236–238 °C. $C_{42}H_{46}ClNO_5P_2Pt$ (937.31): calcd. C 53.8, H 4.9, N 1.5; found C 53.6, H 4.9, N 1.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 39.62 (d, $^1J_{Pt,P}$ = 3567.4 Hz, $^3J_{P,P}$ = 22.8 Hz, 1 P), 115.45 (d, $^1J_{Pt,P}$ = 1580.4 Hz, $^3J_{P,P}$ = 22.8 Hz, 1 P) ppm. ^1H NMR (CD_2Cl_2): δ = 1.41 (s, 3 H, C=C*Me*), 1.86 (s, 3 H, C=C*Me*), 1.87 (d, $^2J_{H,H}$ = 6.0 Hz, 3 H, CH*Me*), 2.51 (s, 3 H, N*Me*), 2.65 (m, 2 H, Ph_2PCCH2), 2.95 (s, 3 H, N*Me*), 3.18 (m, 2 H,CH_2CH_2OH), 3.37 (m, 2 H, CH_2CH_2OH), 3.41 (m, 1 H, PhPC*H*), 3.47 (m, 1 H, PC*H*), 4.73 (qn, $^3J_{H,H}$ = $^4J_{P,H}$ = 6.0 Hz, 1 H, C*H*Me), 6.64–8.48 (m, 21 H, *aromatics*) ppm.

Dichlorido[(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphanyl)-7-phosphabicyclo(2.2.1)hept-5-en-2-ylethanol]platinum(II) [(S_P)-7]: A solution of (R_C,S_P)-**6** (2.53 g, 0.003 mol) in dichloromethane was stirred vigorously with concentrated hydrochloric acid (3 mL) for 8 h. The resultant mixture was then washed with water (3 × 20 mL), and the organic layer was dried with magnesium sulfate. Upon removal of the solvents a pale-yellow solid was obtained. Recrystallization from dichloromethane/*n*-hexanes yielded pale-yellow microcrystals (1.88 g, 89.5%). $[a]_D$ = –36.2 (*c* = 0.4, CH_2Cl_2). M.p. 288 °C (decomp.). $C_{28}H_{30}Cl_2OP_2Pt$ (710.48): calcd. C 47.4, H 4.3; found C 47.6, H 4.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 35.59 (d, $^1J_{Pt,P}$ = 3435.2 Hz, $J_{P,P}$ = 19.0 Hz, 1 P), 94.96 (d, $^1J_{Pt,P}$ = 3191.9 Hz, $J_{P,P}$ = 19.0 Hz, 1 P) ppm. ^1H NMR ($CDCl_3$): δ = 1.27 (s, 3 H, C=C*Me*), 1.71 (s, 3 H, C=C*Me*), 2.89 (m, 2 H, Ph_2PCCH_2), 3.13 (m, 2 H, CH_2CH_2OH), 3.19 (m, 2 H, CH_2OH) 3.44 (m, 1 H, PhPC*H*), 3.52 (m, 1 H, PhPC*H*), 7.47–8.26 (m, 15 H, *aromatics*) ppm.

Decomplexation of [(4*R*,7*S*)-5,6-Dimethyl-7-phenyl-2-(diphenylphosphanyl)-7-phosphabicyclo(2.2.1)hept-5-en-2-ylethanol] [(R_P)-8]: A solution of potassium cyanide (0.45 g, 7.00 mmol) in water (2 mL) was added to a solution of (S_P)-**7** (0.05 g, 0.07 mmol) in dichloromethane (20 mL), and the mixture was stirred vigorously to ensure through mixing. The reaction was complete in 4 h. The organic layer was washed with water (3 × 5 mL) and then dried with magnesium sulfate. A pale-yellow oil (0.018 g, 57.6%) was obtained upon complete removal of the solvents. $[a]_D$ = +38.5 (*c* = 0.1, CH_2Cl_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 35.34 (d, $^3J_{P,P}$ = 26.5 Hz), 98.46 (d, $^3J_{P,P}$ = 26.5 Hz) ppm.

A solution of the freshly released ligand in dichloromethane (0.007 g, 0.02 mmol) was added with stirring to a solution of complex (R_C)-**1** (0.007 g, 0.008 mmol) in dichloromethane and silver perchlorate (1.86 g, 0.009 mmol) in water (5 mL). The reaction mixture was stirred at room temperature for 30 min and then washed with water (3 × 5 mL) and dried with magnesium sulfate. The organic layer was dried to obtain a yellow solid. The $^{31}P\{^1H\}$ NMR spectrum was identical to that of (R_C,S_P)-**6**.

Chlorido{(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C*,*N*}[2-(diphenylphosphanyl)prop-2-en-1-ol]platinum(II) [(R_C)-10]: A solution of **9** (1.99 g, 0.008 mol) in dichloromethane (20 mL) was added dropwise with stirring to a solution of (R_C)-**1** (3.5 g, 0.004 mol) in dichloromethane. The reaction was allowed to stir for 6 h, after which the solvent was removed under reduced pressure to give the crude product as a yellow solid. The crude product was purified by silica-gel column chromatography (dichloromethane/*n*-hexanes, 3:1; then acetone/dichloromethane, 1:1). Crystallization from dichloromethane/diethyl ether afforded the pure product as yellow prisms (1.98 g, 73.9%). $[a]_D$ = +55.0 (*c* = 0.2, CH_2Cl_2). M.p. 240–241 °C. $C_{29}H_{31}ClNOPPt$ (671.08): calcd. C 51.9, H 4.6, N 2.1; found C 51.9, H 4.7, N 2.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 19.81 (s, $^1J_{Pt,P}$ = 4243.6 Hz, 1 P) ppm. ^1H NMR ($CDCl_3$): δ = 1.95 (d, $^2J_{H,H}$ = 6.4 Hz, 3 H, CH*Me*), 2.85 (d, $^3J_{P,H}$ = 0.8 Hz, 3 H, N*Me*), 3.18 (d, $^3J_{P,H}$ = 1.3 Hz, N*Me*), 4.09 (m, 2 H, CH_2OH), 4.61 (qn, $^3J_{H,H}$ = $^4J_{P,H}$ = 6.4 Hz, 1 H, C*H*Me), 5.19 (d, $^3J_{P,H}$ = 17.7 Hz, *cis*-PC=CH_2), 6.08 (d, $^3J_{P,H}$ = 36.1 Hz, *trans*-PC=CH_2), 6.68–8.26 (m, 16 H, *aromatics*) ppm.

{(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthyl-*C*,*N*}[(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphanyl)-7-phosphabicyclo(2.2.1)hept-5-en-2-ylmethanol]platinum(II) perchlorate [(R_C,S_P)-12]: To complex (R_C)-**10** (1.50 g, 0.002 mol) in dichloromethane was added silver perchlorate (0.62 g, 0.003 mol) in distilled water (2 mL), and the reaction mixture was stirred vigorously at room temperature for 30 min. The crude product was passed through Celite to remove the AgCl precipitate and subsequently washed with water (3 × 50 mL) and dried with magnesium sulfate. Removal of the solvents gave perchlorato (R_C)-**11** as a yellow solid (1.38 g, 93.8%). A solution of (R_C)-**11** (1.35 g, 0.002 mol) in dichloromethane was treated with DMPP (**5**; 0.37 g, 0.002 mol). The mixture was allowed to stir at room temperature for 8 h to yield a yellow solution. Crystallization from acetonitrile/diethyl ether afforded pale-yellow needle-like crystals (1.34 g, 81.2%). $[a]_D$ = +4.43 (*c* = 0.3, CH_2Cl_2). M.p. 253–245 °C. $C_{41}H_{44}ClNO_5P_2Pt$ (923.29): calcd. C 53.4, H 4.8, N 1.5; found C 52.9, H 4.6, N 1.7. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 42.04 (d, $^1J_{Pt,P}$ = 3591.9 ppm, $J_{P,P}$ = 22.8 Hz, 1 P), 117.82 (d, $^1J_{Pt,P}$ = 1586.1 Hz, $J_{P,P}$ = 19.0 Hz, 1 P) ppm. ^1H NMR ($CDCl_3$): δ = 1.42 (s, 3 H, C=C*Me*), 1.81 (s, 3 H, C=C*Me*), 1.94 (d, $^2J_{H,H}$ = 6.0 Hz, 3 H, CH*Me*), 2.55 (s, 3 H, N*Me*), 2.83 (m, 2 H, Ph_2PCCH_2), 3.03 (s, 3 H, N*Me*), 3.67 (m, 2 H, CH_2OH), 3.78 (m, 1 H, PC*H*), 3.95 (m, 1 H, PC*H*), 4.73 (qn, $^3J_{H,H}$ = $^4J_{P,H}$ = 6.4 Hz, 1 H, C*H*Me), 6.66–8.78 (m, 21 H, *aromatics*) ppm.

Dichlorido[(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphanyl)-7-phosphabicyclo(2.2.1)hept-5-en-2-ylmethanol]platinum(II) perchlorate [(S_P)-13]: A solution of (R_C,S_P)-**12** (1.02 g, 0.001 mol) in dichloromethane was treated with concentrated hydrochloric acid (5 mL), and the mixture was allowed to stir vigorously for 8 h at room temperature. The resultant solution was washed with water (3 × 20 mL), and the organic layer was dried with magnesium sulfate. Upon filtration and subsequent removal of the solvents a pale-yellow solid was obtained. Crystallization from dichloromethane/*n*-hexanes yielded pale-yellow prisms (0.7888 g, 91.5%). $[a]_D$ = –24.7 (*c* = 0.3, CH_2Cl_2). M.p. 230 °C (decomp.). $C_{27}H_{28}Cl_2OP_2Pt$ (696.46): calcd. C 46.6, H 4.0; found C 46.8, H 4.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 32.67 (d, $^1J_{Pt,P}$ = 3447.6 Hz, $J_{P,P}$ = 19.0 Hz, 1 P), 94.52 (d, $^1J_{Pt,P}$ = 3225.9 Hz, $J_{P,P}$ = 19.0 Hz, 1 P) ppm. ^1H NMR (CD_2Cl_2): δ = 1.51 (s, 3 H, C=C*Me*), 1.69 (s, 3 H, C=C*Me*), 2.91 (m, 2 H, Ph_2PCCH_2), 3.13 (d, 2 H, CH_2OH), 3.43 (m, 1 H, PhPC*H*), 3.89 (m, 1 H, PhPC*H*), 7.52–8.29 (m, 15 H, *aromatics*) ppm.

Decomplexation of [(4*R*,7*S*)-5,6-Dimethyl-7-phenyl-2-(diphenylphosphanyl)-7-phosphabicyclo(2.2.1)hept-5-en-2-yl methanol] [(R_P)-14]: A solution of (S_P)-**13** in dichloromethane (0.05 g, 0.075 mmol) in dichloromethane (10 mL) was thoroughly stirred for 3 h with an excess amount of potassium cyanide (0.24 g, 7.460 mmol) in water (1 mL). The organic layer was separated, washed with water (3 × 10 mL), and dried with magnesium sulfate. Removal of the solvent left (R_P)-**14** as a colorless air-sensitive oil (0.018 g, 56.2%). $[a]_D$ = –52.4 (*c* = 0.1, CH_2Cl_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 19.21 (d, $^3J_{P,P}$ = 113.9 Hz, 1 P), 108.89 (d, $^3J_{P,P}$ = 113.9 Hz, 1 P) ppm.

A solution of freshly released ligand (R_P)-**14** (0.005 g, 0.011 mmol) in dichloromethane was added to a solution of complex (R_C)-**1** (0.005 g, 0.006 mmol) in dichloromethane (10 mL) and silver per-

Table 6. Crystal data for compounds (R_C,S_P)-**6**, (S_P)-**7**, (R_C)-**10**, (R_C,S_P)-**12** and (S_P)-**13**.

	(R_C,S_P)-**6**	(S_P)-**7**	(R_C)-**10**	(R_C,S_P)-**12**	(S_P)-**13**
Formula	$C_{42}H_{46}ClNO_5P_2Pt$	$C_{28}H_{30}C_{l2}OP_2Pt$	$C_{29}H_{31}ClNOPPt$	$C_{43}H_{45}ClN_2O_5P_2Pt$	$C_{28}H_{30}Cl_4OP_2Pt$
Formula weight	937.28	710.45	671.06	962.29	781.35
Space group	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
a [Å]	9.3185(4)	11.1520(6)	12.3326(6)	9.419(2)	9.0762(10)
b [Å]	20.2115(9)	11.3003(5)	13.3464(7)	20.225(5)	17.7661(19)
c [Å]	21.4080(8)	21.2068(10)	16.1563(9)	21.293(6)	18.235(2)
V [Å^3]	4032.0(3)	2672.5(2)	2659.3(2)	4056.3(18)	2940.4(6)
Z	4	4	4	4	4
T [K]	223(2)	295(2)	223(2)	223(2)	223(2)
$\rho_{calcd.}$ [Mgm^{-3}]	1.544	1.766	1.676	1.576	1.765
Flack parameters	0.010(12)	–0.010(12)	0.006(7)	0.025(10)	0.004(5)
R_1 (obsd. data)[a]	0.0683	0.0355	0.0346	0.0529	0.0260
wR_2 (obsd. data)[b]	0.1477	0.0647	0.0670	0.1226	0.0576

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

chlorate (0.004 g, 0.022 mmol) in water (2 mL) with vigorous stirring. The reaction mixture was left to stir for 30 min and subsequently washed with water (3 × 10 mL), and the organic layer was dried with magnesium sulfate to yield the product as a yellow solid. The $^{31}P\{^1H\}$NMR ($CDCl_3$) spectrum was identical to the that of complex (R_C,S_P)-**12**.

X-ray Structure Determination: Crystal structure determination of complexes (R_C,S_P)-**6**, (S_P)-**7**, (R_C)-**10**, (R_C,S_P)-**12**, and (S_P)-**13** are given in Table 6. The structures were analyzed by using a Bruker X8 CCD diffractometer with graphic monochromated Mo-K_α radiation (λ = 0.71073 Å). The absorption corrections were applied with the aid of the SADABS program.[13] All non-hydrogen atoms were refined anisotropically by using the least-squares method on F^2 (Table 6). Hydrogen atoms were introduced at fixed distance from carbon atoms and were assigned fixed thermal parameters. The absolute configurations were determined unambiguously using the Flack parameter.[14] CCDC-717653 [for (R_C,S_P)-**6**], -717654 [for (S_P)-**7**], -717655 [for (R_C)-**10**], -717656 [for (R_C,S_P)-**11**], and -717657 [for (S_P)-**13**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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