Synthesis of β-Cyclodextrin-Functionalized (2*S*,4*S*)-(−)-4-(Diphenylphosphino)-2-(diphenylphosphinomethyl)pyrroli Ligands and Their Rhodium and Platinum Complexes

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Treatment of mono(6-*O*-trifluoromethanesulfonyl)-permethylated-β-cyclodextrin with (2*S*,4*S*)-(−)-4-(diphenylphosphino)-2-(diphenylphosphinomethyl)pyrrolidine (PPM) produced mono-[6-deoxy-6-*N*-(4′-(diphenylphosphino)-2′-(diphenylphosphinomethyl)pyrrolidinyl)]-permethylated-β-cyclodextrin (CDPPM). Reaction of mono(6-*o*-$BrCH_2C_6H_4CH_2O$)-permethylated-β-cyclodextrin with PPM produced mono[6-*O*-(4′-(diphenylphosphino)-2′-(diphenylphosphinomethyl)pyrrolidinylmethyl-*o*-benzyl)]-permethylated-β-cyclodextrin (CDPhPPM). Reactions of $[Rh(COD)_2]BF_4$ with CDPPM and CDPhPPM produced $[Rh(COD)(CDPPM)]BF_4$ and $[Rh(COD)(CDPhPPM)]BF_4$, respectively. Treatment of $PtCl_2(COD)$ with CDPPM and CDPhPPM gave $PtCl_2$(CDPPM) and $PtCl_2$(CDPhPPM), respectively.

Introduction

Cyclodextrins (CDs) are bucket-shaped cyclic glucose oligomers with hollow hydrophobic cavities. One of the most interesting properties of cyclodextrins and their derivatives is that they have molecular recognition ability and can form inclusion complexes with selected organic and organometallic guest molecules.[1,2] Because of this unique property, metal complexes of functionalized cyclodextrins have attracted considerable attention, for they could be used as chiral receptors and enzymatic models.[3] Until now, most of the reported metal complexes of functionalized cyclodextrins are those with nitrogen and/or oxygen donor ligands.[3,4] In contrast, only a few metal complexes with cyclodextrin-functionalized phosphine ligands have been reported,[5] despite of the fact that phosphines are excellent ligands to form a variety of metal complexes[6] and that there has been considerable interest in the uses of phosphine ligands made from sugars in coordination chemistry and catalysis.[7] Metal complexes with phosphine ligands attached to cyclodextrins are especially attractive for catalysis, because phosphine complexes have been used widely in homogeneous catalysis and presence of the cyclodextrin moiety could improve the regioselectivity, stereoselectivity, and substrate selectivity in catalytic reactions (due to the possibility of additional substrate interaction with the cyclodextrin functionalilty). Ligands that can interact with substrates through secondary

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interaction have found increasing applications in asymmetric catalysis in recent years.[8,9] Thus it is desirable to synthesize new phosphine ligands linked to cyclodextrins as well as their complexes.

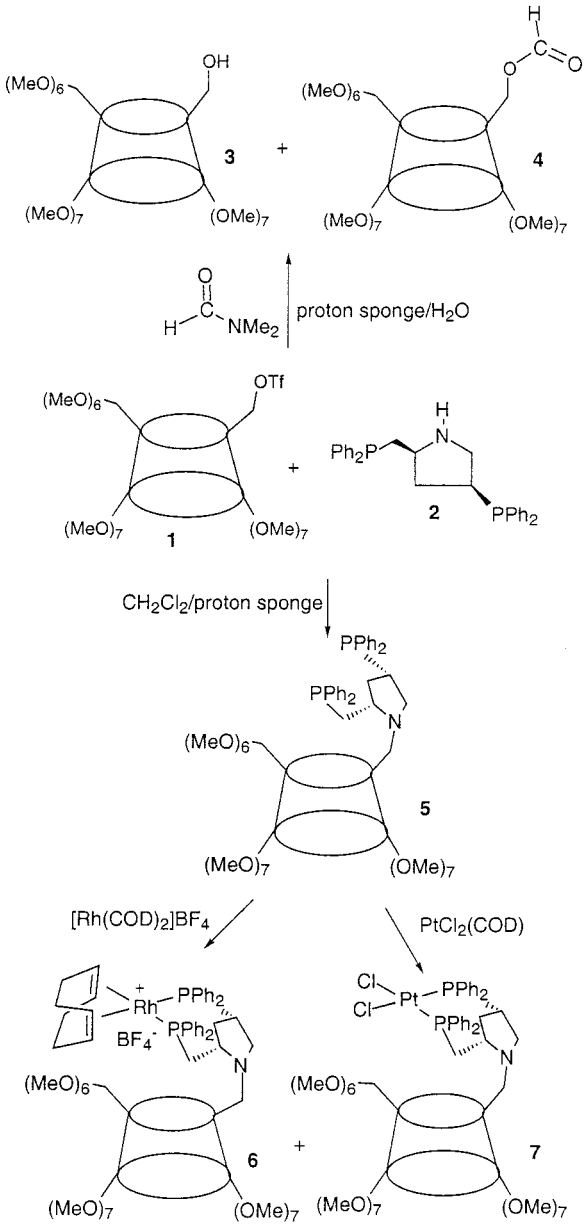
In our approach to combine molecular recognition and homogeneous catalysis, we have tried to attach *β*-cyclodextrin to phosphine ligands that have demonstrated good catalytic properties. The purpose of this paper is to report the synthesis and characterization of two *β*-cyclodextrin-functionalized PPM ligands [PPM = (2*S*,4*S*)-(−)-4-(diphenylphosphino)-2-(diphenylphosphinomethyl)pyrrolidine[10] (**2**); see Scheme 1 for its structure] and their rhodium and platinum complexes. Derivatives of PPM such as BPPM (with a CO_2Bu^t group at the nitrogen), PPPM (with a $COBu^t$ group at the nitrogen), and polymer-supported PPM systems have been widely exploited for asymmetric catalysis.[11,12]

Results and Discussion

Synthesis of Ligands. In our initial attempts to attach PPM to *β*-cyclodextrin, we have reacted PPM (**2**) with mono[6-*O*-(*p*-tolylsulfonyl)]-*β*-cyclodextrin,[13] mono-[6-*O*-(*p*-tolylsulfonyl)]-permethylated-*β*-cyclodextrin[14] and mono(6-*O*-methanesulfonyl)-permethylated-*β*-cyclodextrin.[15] However, the expected ligands could not be obtained from the reactions, because of the low reactivity of the reagents. To overcome this problem, we have investigated the reaction of PPM with the recently reported mono(6-*O*-trifluoromethanesulfonyl)-permethylated-*β*-cyclodextrin (**1**).[16] Since triflate is a much better leaving group than tosylate and mesylate,[17] it is expected that **1** should be more reactive toward PPM. In fact, it has been demonstrated that the triflate group in **1** can be readily replaced with RHN groups on treatment of **1** in DMF with RNH_2.[16] When **1** in DMF was treated with PPM in the presence of proton sponge (1,8-bis(dimethylamino)naphthalene), a mixture of products were obtained. The major products were identified to be mono(6-hydroxy)-permethylated-*β*-cyclodextrin (**3**)[14,18] and mono(6-formyl)-permethylated-*β*-cyclodextrin (**4**), which can be isolated in pure form by chromatography (see Scheme 1). The expected ligand CDPPM (**5**) could only be obtained as a minor product. The products **3** and **4** can be readily characterized by FAB-MS and multinuclear (^1H, and ^{13}C) NMR spectroscopy. For example, compound **4** in $CDCl_3$ displayed characteristic ^1H and $^{13}C\{^1H\}$ signals of O_2CH at 8.12 and 161.2 ppm, respectively. It is not clear to us how compounds **3** and **4** were produced under the reaction condition. Our attempts to eliminate the side reaction products **3** and **4** in DMF failed.

To avoid the formation of **4**, which is related to the solvent DMF, we have carried out the reaction of PPM with **1** in other solvents. It was subsequently found that **1** reacted smoothly with PPM in CH_2Cl_2 in the presence

Scheme 1



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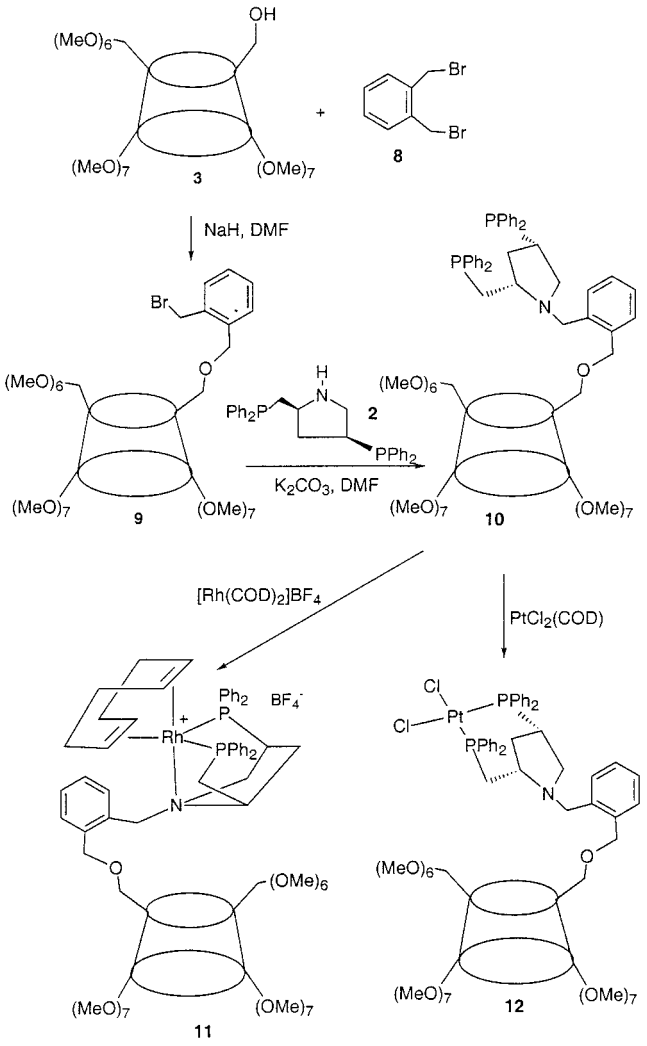
Scheme 2



of proton sponge to give the β-cyclodextrin-functionalized phosphine ligand CDPPM (**5**) (Scheme 1). An analytically pure sample of **5** can be obtained in 74% yield by column chromatography of the crude product on silica gel using $CHCl_3$/MeOH (30:1) as the eluent. Since PPM could not be separated easily from **5** by column chromatography, PPM has to be used as the limiting reagent in the reaction in order to facilitate the purification of **5**.

Ligand **5** is soluble in organic solvents such as methanol, ether, benzene, and dichloromethane and has been characterized by multinuclear NMR, MS, and elemental analysis. In particular, the FAB-MS showed the expected molecular ion peak at *m*/*z* 1851. The $^{31}P\{^1H\}$ NMR spectrum (in $CDCl_3$) showed two singlet resonances at −5.7 and −21.2 ppm. CDPPM represents a rare example of chiral bidentate phosphine ligands linked to a β-cyclodextrin unit.

For future comparative studies, it is desirable to have ligand systems that can hold active metal centers at variable distances from the cavity of β-cyclodextrin. To this end, we have tried to link PPM ligand to the cyclodextrin functionality through the spacer group *o*-$CH_2C_6H_4CH_2$. The synthetic route to the new ligand is outlined in Scheme 2. Treatment of mono(6-hydroxy)-permethylated-β-cyclodextrin (**3**)[18] with α,α'-dibromo-*o*-xylene (**8**) in DMF produced **9**. The ligand CDPhPPM (**10**) was then obtained from the reaction of **9** with PPM in the presence of K_2CO_3. Ligand **10** can be readily identified by MS and multinuclear NMR spectroscopy. In particular, the FAB-MS showed the expected molecular ion peak at *m*/*z* 1971. The $^{31}P\{^1H\}$ NMR spectrum (in $CDCl_3$) showed two singlet resonances at −4.3 and −21.9 ppm.

Synthesis of Metal Complexes. Since rhodium and platinum complexes of derivatives of PPM such as BPPM, PPPM, and polymer-supported PPM systems are catalytically active for a multitude of reactions,[10−12] we have synthesized rhodium and platinum complexes with ligands **5** and **10**.

Reaction of $[Rh(COD)_2]BF_4$ with 1 equiv of ligand **5** in dichloromethane produced the orange compound [Rh(COD)(CDPPM)]BF_4 (**6**; see Scheme 1). Formulation of **6** is supported by FAB-MS, which displayed the expected ion peak of $[Rh(COD)(CDPPM)]^+$ at *m*/*z* 2061. It is noted that PPM and related ligands can bind to a metal center as either a tridentate ligand or a bidentate ligand, depending on whether the nitrogen atom is coordinated or not. For example, $[Rh(COD)(PPM)]^+$ is a five-coordinated complex in which the nitrogen and the two phosphorus atoms of PPM are bound to rhodium;[19] $[Rh(COD)(BPPM)]^+$ and $[Rh(COD)(PPPM)]^+$ are four-coordinated complexes in which only the two phosphorus atoms of BPPM and PPPM are linked to rhodium.[11f,20] The two coordination modes of PPM-based ligands on rhodium can be easily distinguished by their $^{31}P\{^1H\}$ NMR data. For example, $[Rh(COD)(PPM)]^+$, in which the PPM ligand is a tridentate ligand, shows two closely spaced $^{31}P\{^1H\}$ signals at 29.5 (J(RhP) = 109 Hz) and 38.9 (J(RhP) = 114 Hz) ppm; $[Rh(COD)(PPPM)]^+$, in which the PPPM ligand is a bidentate ligand, shows two $^{31}P\{^1H\}$ signals at 12.1 (J(RhP) = 139 Hz) and 43.1 (J(RhP) = 146 Hz) ppm.[11f,20] Complex **6** in $CDCl_3$ displayed two $^{31}P\{^1H\}$ signals at 18.6 (J(RhP) = 132.5 Hz) and 41.4 (J(RhP) = 140.5 Hz) ppm. Since the chemical shifts of the $^{31}P\{^1H\}$ signals as well as the J(RhP) coupling constants of $[Rh(COD)(CDPPM)]^+$ are close to that of [Rh(COD)(PPPM)]BF_4,[11f,20] it can be safely concluded that the coordination sphere of $[Rh(COD)(CDPPM)]^+$ is similar to that of $[Rh(COD)(BPPM)]^+$ and that only the two phosphorus atoms of CDPPM are coordinated to the rhodium, to give a four-coordinated complex. As CDPPM is electronically similar to PPM, one might expect that the coordination sphere of $[Rh(COD)(CDPPM)]^+$ should be similar to that of $[Rh(COD)(PPM)]^+$, which is a five-coordinated complex. The fact that $[Rh(COD)(CDPPM)]^+$ adopts a four-coordinate geometry around rhodium is likely related to the bulkiness of the cyclodextrin functionality.

The platinum complex $PtCl_2$(CDPPM) (**7**) can be prepared by stirring a mixture of CDPPM and $PtCl_2$(COD) in CH_2Cl_2 for 24 h. Compound **7** has been characterized by NMR, MS, and elemental analysis. In particular, the FAB-MS showed the expected molecular ion peak at *m*/*z* = 2117. The $^{31}P\{^1H\}$ NMR in $CDCl_3$ exhibited the CH_2PPh_2 signal at 31.2 ppm and the $CHPPh_2$ signal at 3.2 ppm. As the $^{31}P\{^1H\}$ data are very similar to those of $PtCl_2$(BPPM),[12] it is reasonable to

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assume that complexes **7** and $PtCl_2$(BPPM) have similar coordination spheres.

As shown in Scheme 2, the rhodium and platinum complexes **11** and **12** can also be prepared starting from **10**. The $^{31}P\{^1H\}$ NMR data of platinum complex **12** is very similar to those of the analogous complex **7**, indicating that the coordination sphere of **12** is the same as that of **7**. However, the $^{31}P\{^1H\}$ NMR data of the rhodium complex **11** is quite different from those of complex **6**, implying that they have different coordination spheres. In CD_2Cl_2, complex **11** displayed two $^{31}P\{^1H\}$ signals at 34.7 ppm (J(Rh−P) = 123.5 Hz) and 28.6 ppm (J(RhP) = 126.9 Hz). The difference in the chemical shifts of the two ^{31}P signals is significantly smaller than those of the four-coordinated complexes [Rh(COD)(PPPM)]$^+$ and **6**, but it is close to that of the five-coordinated complex [Rh(COD)(PPM)]$^+$. Thus, we tentatively assign complex **11** as a five-coordinated complex in which the nitrogen atom is also coordinated to rhodium. Consistent with the formulation, the J(RhP) coupling constants of **11** are smaller than those of the four-coordinated complexes [Rh(COD)(PPPM)]$^+$ and **6**. It is probably not surprising that both complexes [Rh(COD)(PPM)]$^+$ and **11** adopt a five-coordinated geometry around rhodium, as PPM and CDPhPPM are electronically similar. As mentioned previously, complex **6** adopts a four-coordinated geometry around rhodium. The difference in the geometry of complexes **6** and **11** could be related to the fact that the rhodium center in complex **11** is further away from the cyclodextrin moiety. Thus, the steric effect caused by the cyclodextrin moiety in **11** is not as significant as that in complex **6**.

Summary

In summary, we have successfully prepared two novel cyclodextrin-modified PPM ligands and their rhodium and platinum complexes. In the future, we will explore the catalytic properties and molecular-recognition ability of complexes with these interesting ligands.

Experimental Section

Unless otherwise stated, all manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium−benzophenone (ether, THF, benzene) or calcium hydride (CH_2Cl_2, DMF). The starting materials mono(6-*O*-trifluoromethanesulfonyl)-permethylated-β-cyclodextrin,[16] mono(6-hydroxyl)-permethylated-β-cyclodextrin,[18] and [Rh(COD)$_2$]BF$_4$[21] were prepared according to literature methods. All other reagents were used as purchased from Aldrich Chemical Co. or Strem.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were collected on a Bruker ARX-300 or a JEOL EX-400 spectrometer. ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. Mass spectra were recorded on a Finnigan TSQ7000 spectrometer. Microanalyses were performed by M−H−W Laboratories (Phoenix, AZ).

Reaction of Mono(6-*O*-trifluoromethanesulfonyl)-permethylated-β-cyclodextrin with PPM in DMF. A mixture of mono(6-*O*-trifluoromethanesulfonyl)-permethylated-β-cyclodextrin (0.78 g, 0.50 mmol), (2*S*,4*S*)-(−)-4-(diphenylphosphino)-2-(diphenylphosphinomethyl)pyrrolidine (PPM) (96 mg, 0.21 mmol), and proton sponge (1,8-bis(dimethylamino)naphthalene, 108 mg, 0.50 mmol) in DMF (10 mL) was stirred at room temperature for 3 h. The solvent was removed completely under vacuum. The residue was redissolved in ether (30 mL) and the solution was washed with brine (3 × 20 mL). The organic layer was then dried over $MgSO_4$ and then filtered to give a clear yellow solution. The ether was then removed to afford a yellow solid (0.79 g). Three pure compounds can be separated from the crude product by column chromatography (silica gel, $CHCl_3$/CH_3OH: 80/1): mono(6-hydroxyl)-permethylated-β-cyclodextrin (**3**, 220 mg), mono(6-formyl)-permethylated-β-cyclodextrin (**4**, 100 mg), and CDPPM (**5**, 52 mg). In addition to compounds **3**−**5**, another unidentified phosphorus-containing species, which appears to be unrelated to the cyclodextrin moiety, was also produced as a minor product. As indicated by the FAB-MS, the species is likely (4-PPh_2-2-$PPh_2CH_2C_4H_6N)_2CHOH$. However, the compound could not be fully characterized because we have failed to get pure sample of the species. Characterization data for **4** are as follows. FAB-MS: m/z = 1443 (M^+). ^1H NMR (300.13 MHz, $CDCl_3$): δ 8.12 (s, 1 H, O_2CH), 5.23−5.09 (m, 7 H, H-1), 4.65 (br d, J(HH) = 11.4 Hz, 1 H, H-6′), 4.36 (dd, J(HH) = 11.4, 4.5 Hz, 1 H, H-6′), 3.99−3.17 (m, 101 H, OMe, H-2, H-3, H-4, H-5 and H-6). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 161.2 (s, O_2CH), 100.3−99.4 (m, C-1), 83.0−79.1 (m, C-2,3,4), 72.4−69.7 (m, C-5,6), 63.9 (s, C-6′), 62.3−58.8 (m, OCH_3). Anal. Calcd for $C_{63}H_{110}O_{36}$: C, 52.42; H, 7.68. Found: C, 52.48; H, 7.57.

CDPPM (5). A mixture of mono(6-*O*-trifluoromethanesulfonyl)-permethylated-β-cyclodextrin (**1**) (0.50 g, 0.32 mmol), (2*S*,4*S*)-(−)-4-(diphenylphosphino)-2-(diphenylphosphinomethyl)pyrrolidine (73 mg, 0.16 mmol), and proton sponge (40 mg, 0.19 mmol) in dichloromethane (10 mL) was stirred at room temperature for 2 days. The reaction mixture was then washed with brine (2 × 15 mL). The solvent of the organic layer was removed under vacuum. The residue was redissolved in ether. The solution was filtered to get rid of a white solid insoluble in ether. The ether was removed to afford a white crystalline solid. The crude product, which was contaminated with **1**, can be used in the preparation of metal complexes without further purification. An analytically pure specimen of **5** can be obtained by column chromatography (silica gel, $CHCl_3$/CH_3OH: 30/1). Yield: 0.22 g, 74%. $[\alpha]^{25}_D$ = 103.7° (*c*, 1.5, $CHCl_3$). FAB-MS: m/z = 1851 (M^+). ^1H NMR (400 MHz, $CDCl_3$): δ 7.67−7.24 (m, 20 H, PPh_2), 5.06−4.86 (m, 7 H, H-1), 3.81−1.8 (m, 109 H, OMe, H-2, H-3, H-4, H-5 and H-6; CH_2 and CH of PPM), 1.55 (m, 1 H, CHCH_2CH of PPM). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$): δ 139.2−128.2 (m, PPh_2), 98.9−97.5 (m, C-1), 82.3−79.1 (m, C-2,3,4), 72.6−70.6 (m, C-5,6), 63.2 (d, J(PC) = 17.5 Hz, NCH of PPM), 61.5−58.3 (m, OCH_3), 53.7 (CH_2N of CD), 58.2 (br, NCH_2 of PPM), 36.0 (m, CH_2 of PPM), 34.1 (d, J(PC) = 8.3 Hz, CHPPh_2), 33.1 (d, J(PC) = 15.0 Hz, CH_2PPh_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ −5.7 (s), −21.2 (s). Anal. Calcd for $C_{91}H_{137}NO_{34}P_2$: C, 59.05; H, 7.46; N, 0.76; P. 3.35. Found: C, 59.92; H, 7.70; N, 0.68; P. 3.19.

[Rh(COD)(CDPPM)]BF4 (6). A solution of CDPPM (0.30 g, 0.16 mmol) in dichloromethane (5 mL) was added dropwisely to a deep red-brown solution of [Rh(COD)$_2$]BF$_4$ (0.063 g, 0.16 mmol) in dichloromethane (5 mL). After the mixture was stirred for 0.5 h, the solvent was removed under vacuum to give an orange solid, which was washed with ether and dried under vacuum. Yield: 0.20 g, 60%. FAB-MS: m/z = 2061 ([Rh(COD)(CDPPM)]$^+$), 1953 ([Rh(CDPPM)]$^+$), 1851 ([CDPPM]$^+$). ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.76−7.30 (20 H, PPh_2), 5.13−4.74 (m, 7 H, H-1), 4.41 (br, 2 H, olefinic H of COD), 4.21 (br, 2 H, olefinic H of COD), 3.83−2.09 (m, 117 H, OMe, H-2, H-3, H-4, H-5 and H-6; CH_2 and CH of PPM; CH_2 of COD), 1.22 (m, 1 H, CHCH_2CH of PPM). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 41.4 (dd, J(RhP) = 140.5 Hz, J(PP) = 18.4 Hz), 18.6 (br d, J(RhP) = 132.5 Hz). Anal. Calcd for $C_{99}H_{149}BF_4NO_{34}P_2$Rh: C, 55.34; H, 6.99; N, 0.65; P, 2.88. Found: C, 54.92; H, 7.26; N, 0.65; P, 2.51.

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$PtCl_2$(CDPPM) (7). A solution of CDPPM (200 mg, 0.108 mmol) in dichloromethane (5 mL) was added dropwisely to a solution of $PtCl_2$(COD) (40.4 mg, 0.108 mmol) in dichloromethane (5 mL). After the mixture was stirred at room temperature for 24 h, the solvent was removed under vacuum to give a pale yellow solid, which was collected by filtration, washed with 1:1 hexane/diethyl ether mixture, and dried under vacuum. Yield: 200 mg, 87.5%. FAB-MS: m/z = 2117 ([$PtCl_2$(CDPPM)]$^+$), 2081 ([PtCl(CDPPM)]$^+$). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.31−7.57 (m, 20 H, PPh_2), 5.30−5.08 (m, 7 H, H-1), 3.29−2.19 (m, 109 H, OMe, H-2, H-3, H-4, H-5 and H-6; CH_2 and CH of PPM), 1.43 (m, 1 H, CHCH_2CH of PPM). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 31.2 (d with Pt satellites, J(PP) = 15.2 Hz, J(PtP) = 3603 Hz), 3.2 (d with Pt satellites, J(PP) = 15.2 Hz, J(PtP) = 3587 Hz). Anal. Calcd for $C_{91}H_{137}Cl_2NO_{34}P_2Pt$: C, 51.63; H, 6.52; N, 0.66; P, 2.93; Cl, 3.35. Found: C, 51.78; H, 6.59; N, 0.63; P. 2.79; Cl, 3.16.

Mono(6-*o*-BrCH_2-C$_6H_4$-CH_2O)-permethylated-β-cyclodextrin (9). Mono(6-hydroxy)-permethylated-β-cyclodextrin (**3**) (3.0 g, 2.1 mmol) was added to a suspension of NaH (0.33 g, 14 mmol) in DMF (6 mL). After the mixture was stirred for 1 h, α,α′-dibromo-*o*-xylene (2.8 g, 11 mmol) was introduced. The mixture was stirred at room temperature for 3 days. The solvent was then removed under vacuum. The residue was redissolved in dichloromethane (20 mL) and then washed with brine (2 × 15 mL). The combined organic layer was dried over $MgSO_4$. The dichloromethane was removed under vacuum to afford a light-yellow solid, which was purified by column chromatography (silica gel, $CHCl_3$/CH_3OH: 30/1) to give a white crystalline solid (2.1 g, 62%). $[\alpha]^{25}_D$ = 135.2° (*c*, 1.5, $CHCl_3$). FAB-MS: m/z = 1622 ([M + Na]$^+$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.20 (m, 4 H, C_6H_4), 5.07−5.03 (m, 7 H, H-1), 4.69−4.51 (m, 4 H, O$CH_2C_6H_4$, CH_2Br), 3.97−3.07 (m, 102 H, OMe, H-2, 3, 4, 5, 6). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$): δ 136.8, 135.6, 130.3, 129.0, 128.6, 128.0 (C_6H_4), 98.9−98.8 (m, C-1), 82.0−80.0 (m, C-2,3,4), 71.3−70.8 (m, C-5,6), 69.6 (CH_2-$OCH_2C_6H_4$), 61.6−58.3 (m, OCH_3), 70.6 (O$CH_2C_6H_4$), 31.1 (CH_2-Br). Anal. Calcd for $C_{70}H_{117}BrO_{35}$: C, 52.60; H, 7.38. Found: C, 52.78; H, 7.20.

CDPhPPM (10). A mixture of **9** (0.530 g, 0.33 mmol), (2*S*,4*S*)-(−)-4-(diphenylphosphino)-2-(diphenylphosphinomethyl)pyrrolidine (0.109 g, 0.24 mmol) and K_2CO_3 (0.22 g, 1.5 mmol) in DMF (6 mL) was stirred at room temperature for 3 days. DMF was then pumped away under vacuum. The residue was redissolved in dichloromethane and the K_2CO_3 was removed by filtration. The solution was washed with brine (2 × 15 mL) and dried over $MgSO_4$. The dichloromethane was removed to afford a white solid (0.50 g). The crude product, which was contaminated with **9**, can be used in the preparation of metal complexes without further purification. Pure **10** can be obtained by column chromatography (silica gel, $CHCl_3$/CH_3OH: 80/1). $[\alpha]^{25}_D$ = 72.8° (*c*, 1.6, $CHCl_3$). FAB-MS: m/z = 1971 (M$^+$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69−7.16 (m, 24 H, C_6H_4, PPh_2), 5.13−5.04 (m, 7 H, H-1), 4.75−4.54 (m, 4 H, O$CH_2C_6H_4$, $C_6H_4CH_2$N), 4.03−1.98 (m, 109 H, OMe, H-2, 3, 4, 5, 6; CH_2 and CH of PPM), 1.53 (m, 1 H, CHCH_2CH of PPM). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$): δ 138.8−126.4 (m, C_6H_4, PPh_2), 98.9−98.6 (C-1), 82.1−80.0 (C-2,3,4), 71.5−71.0 (C-5,6), 69.2 ($CH_2OCH_2C_6H_4$), 61.5−58.4 (m, OCH_3), 70.7 (O$CH_2C_6H_4$), 55.0 ($C_6H_4CH_2$N), 63.0 (d, J(PC) = 19.9 Hz, NCH), 57.3 (d, J(PC) = 19 Hz, NCH_2), 37.5 (br, CH_2), 33.2 (br, $CHPPh_2$), 32.7 (br, CH_2PPh_2). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): −4.3 (s), −21.9 (s). Anal. Calcd for $C_{99}H_{145}NO_{35}P_2$: C, 60.32; H, 7.42; N, 0.71. Found: C, 60.30; H, 7.32; N, 0.69.

[Rh(COD)(CDPhPPM)]BF_4 (11). A solution of **10** (0.63 g, 0.32 mmol) in dichloromethane (5 mL) was added dropwise to a deep red-brown solution of [Rh(COD)$_2$]BF_4 (0.12 g, 0.30 mmol) in dichloromethane (5 mL). After the mixture was stirred for 1 h, the solvent was removed under vacuum to give a red-brown solid, which was collected by filtration, washed with ether, and dried under vacuum. Yield: 0.47 g, 70%. FAB-MS: m/z = 2182 ([Rh(COD)(CDPhPPM)]$^+$), 2074 ([Rh(CDPhPPM)]$^+$). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 7.74−6.95 (m, 24 H, C_6H_4, PPh_2), 5.10−5.00 (m, br, 7 H of H-1 and 1 H of the olefinic H of COD), 4.60−1.58 (m, other proton signals). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 34.7 (dd, J(RhP) = 123.5 Hz, J(PP) = 19.8 Hz), 28.6 (dd, br, J(RhP) = 126.9 Hz, J(PP) = 19.4 Hz). Anal. Calcd for $C_{107}H_{157}BF_4NO_{35}P_2Rh$: C, 56.64; H, 6.97; N, 0.62; Found: C, 56.64; H, 7.07; N, 0.75.

$PtCl_2$(CDPhPPM) (12). A mixture of **10** (210 mg, 0.107 mmol) and $PtCl_2$(COD) (38 mg, 0.10 mmol) in dichloromethane (5 mL) was stirred at room temperature for 24 h. The solvent was removed under vacuum. The resulting pale-yellow solid was washed with ether and then dried under vacuum. Yield: 160 mg, 70%. FAB-MS: m/z = 2237 ([$PtCl_2$(CDPhPPM)]$^+$), 2201 ([PtCl(CDPhPPM)]$^+$). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 8.05−7.16 (m, 20 H, PPh_2), 5.39−5.06 (m, 7 H, H-1), 4.75−4.64 (m, 4 H, O$CH_2C_6H_4$, $C_6H_4CH_2$N), 4.07−2.01 (m, 109 H, OMe, H-2, H-3, H-4, H-5 and H-6; CH_2 and CH of PPM), 1.5 (m, 1 H, CHCH_2CH of PPM). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 29.4 (d with Pt satellites, J(PP) = 16.3 Hz, J(PtP) = 3621 Hz), 3.9 (d with Pt satellites, J(PP) = 16.4 Hz, J(PtP) = 3587 Hz). Anal. Calcd for $C_{99}H_{145}Cl_2NO_{35}P_2Pt$: C, 53.15, H, 6.53, N, 0.63. Found: C, 52.91, H, 6.27, N, 0.73.

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