Palladium and Platinum Complexes with a β-Cyclodextrin-Functionalized Phosphine Ligand

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Treatment of *o*-$Ph_2PC_6H_4CHO$ with 6-$H_2NCH_2CH_2NH$-β-CD (CD = cyclodextrin) produced 6-(*o*-$Ph_2PC_6H_4CH{=}NCH_2CH_2NH$)-$\beta$-CD (CDNNP), which reacted with MCl_2(COD) (M = Pd, Pt) and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ to give [MCl(CDNNP)]Cl and $[PdCl(\eta^1\text{-}C_3H_5)$(CDNNP)]Cl, respectively.

Introduction

Cyclodextrins (CDs) are bucket-shaped cyclic glucose oligomers with hollow hydrophobic cavities.[1] One of the most interesting properties of cyclodextrins is that they can form inclusion complexes with selected organic/inorganic guest molecules. Because of this unique property, cyclodextrins and their derivatives have been widely studied as models for enzymatic reactions.[2] A common approach to develop artificial enzymes based on cyclodextrins is to functionalize cyclodextrins with proper coenzyme factors. As many transition-metal complexes are catalytically active for various reactions, it would be interesting to attach them to cyclodextrins and to study the catalytic properties of the resulting complexes. Until now, reported metal complexes attached to cyclodextrins have been mainly those with nitrogen and/or oxygen donor ligands.[3,4]

As phosphines are excellent ligands to stabilize a variety of metal complexes and have been used widely in homogeneous catalysis,[5] it is desirable to functionalize cyclodextrins with phosphine ligands. In principle, cyclodextrin-functionalized phosphine ligands can support the active metal centers through the phosphine functionalities and, in the meantime, can interact with substrates by means of secondary interaction through cyclodextrins' hydrophobic cavities and/or groups on the outer surface of the torus, which may improve regio- and stereoselectivity in catalytic reactions. The design, synthesis, and characterization of new ligands that can interact with substrates through secondary interaction have received considerable attention in recent years.[6,7] In addition, as cyclodextrins are water-soluble, it may be possible to carry out catalytic reactions with these systems in water or biphasic medium.[8] Despite the potentials, reported cyclodextrin-functionalized phosphine ligands and their metal complexes are still very limited.[9−12] The purpose of this paper is to report the

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synthesis and characterization of a potentially tridentate β-cyclodextrin-functionalized NNP mixed donor ligand and its palladium and platinum complexes. Phosphorus–nitrogen mixed donor ligands either bidentate or polydentate in nature are very useful ligands in organometallic chemistry and catalysis.[13–18]

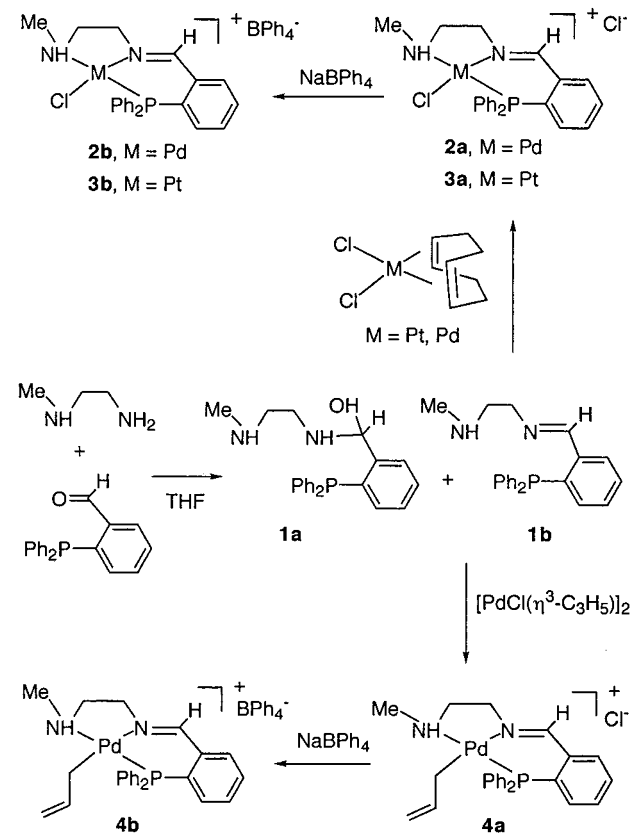
Results and Discussion

Reaction of *o*-$Ph_2PC_6H_4CHO$ with $H_2NCH_2CH_2NHCH_3$. Reactions of *o*-$Ph_2PC_6H_4CHO$ with appropriate amines R–NH_2 have been successfully employed previously to prepare potentially bidentate or polydentate iminophosphine ligands.[13–15] It is therefore expected that the novel phosphine ligand 6-(*o*-$Ph_2PC_6H_4CH$=NCH_2CH_2NH)-β-CD (CDNNP) may also be obtained from the reaction of *o*-$Ph_2PC_6H_4CHO$ with the easily accessible amine-modified β-cyclodextrin 6-$NH_2CH_2CH_2$-NH-β-CD.[19] The closely related ligand *o*-$Ph_2PC_6H_4CH$=NCH_2CH_2-2-pyridine has been previously prepared from the reaction of *o*-$Ph_2PC_6H_4CHO$ with 2-(2-aminoethyl)-pyridine.[13]

As 6-$NH_2CH_2CH_2NH$-β-CD is only soluble in polar solvents such as DMSO, methanol, and DMF, one might expect that the phosphine ligand CDNNP as well as its metal complexes may also have low solubility. The low solubility together with high molecular weights would make characterization of the compounds by NMR a more difficult task. To facilitate the characterization of the cyclodextrin-modified phosphine ligand and its metal complexes and to make future comparative study on the catalytic properties of systems with and without the CD substituent, we initially attempted to prepare the analogous ligand $Ph_2PC_6H_4CH$=NCH_2CH_2NHMe (NNP) from the reaction of *o*-$Ph_2PC_6H_4CHO$ with $H_2NCH_2CH_2NHCH_3$. It should be easy to fully characterize the ligand $Ph_2PC_6H_4CH$=NCH_2CH_2NHMe and its metal complexes.

Treatment of *o*-$Ph_2PC_6H_4CHO$ with $H_2NCH_2CH_2NHCH_3$ in THF at room temperature for 3 h led to the formation of a mixture of the carbinolamine phosphine *o*-$Ph_2PC_6H_4CH(OH)NHCH_2CH_2NHCH_3$ (**1a**) and the iminophosphine *o*-$Ph_2PC_6H_4CH$=$NCH_2CH_2NHCH_3$ (NNP; **1b**) in about a 3:1 ratio (Scheme 1). Apparently, dehydration of **1a** to give **1b** is not complete under the reaction conditions. Although not very common, there are reported examples of isolation of carbinolamines from the reactions of amines with ketones or aldehydes.[20] Our attempts to complete the dehydration of

Scheme 1



1a to give **1b** by carrying out the reaction for longer reaction times or under refluxing were not successful. For example, the relative amount of **1a** only decreased slightly after a mixture of $H_2NCH_2CH_2NHCH_3$ and *o*-$Ph_2PC_6H_4CHO$ in THF was allowed to stand at room temperature for 6 days. Fortunately, it was subsequently found that **1a** undergoes spontaneous dehydration to give **1b** upon complexation to Pd and Pt. Thus, there is no need to use pure samples of **1b** to make NNP complexes, as a mixture of **1a** and **1b** can be employed conveniently.

Compounds **1a** and **1b** were characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. In particular **1a** and **1b** (in CD_2Cl_2) displayed singlet $^{31}P\{^1H\}$ signals (in CD_2Cl_2) at −18.6 and −13.3 ppm, respectively. In the ^{1}H NMR spectrum (in CD_2Cl_2), the characteristic C*H*(OH) proton signal of **1a** was observed at 4.58 ppm, and the characteristic CH=N proton signal of **1b** was observed at 8.79 ppm.

Synthesis of Pd and Pt Complexes with NNP. A ligand of the type *o*-$Ph_2PC_6H_4CH$=NCH_2CH_2NHR could bind to a metal in either a bidentate or a tridentate mode. To facilitate the characterization of analogous Pt and Pd complexes with CDNNP (see discussion below), the reactions of ligand **1** with $MCl_2(COD)$ (M = Pd, Pt) and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ were investigated.

Reactions of ligand **1** with $PdCl_2(COD)$ or $PdCl_2(PhCN)_2$ in dichloromethane produced [PdCl(NNP)]Cl (**2a**) (Scheme 1). Thus, **1a** has undergone dehydration during the reaction. The presence of CH=N in **2a** is indicated by the appearances of the ^{1}H and ^{13}C NMR (in $CDCl_3$) signals of CH=N at 9.56 and 166.3 ppm, respectively. The tridentate nature of the NNP ligand is supported by the NMR spectroscopic data. In par-

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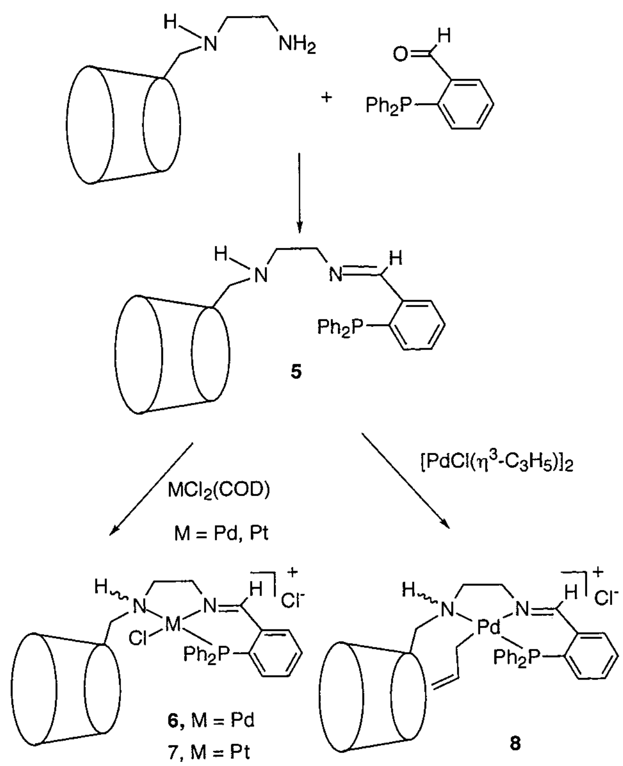
ticular, the $^{31}P\{^1H\}$ NMR spectrum (in $CDCl_3$) showed a singlet at 30.1 ppm; the ^1H NMR spectrum (in $CDCl_3$) showed the coordinated NH signal at 5.84 ppm. For comparison, the NH signals for $[PdCl(H_2N(CH_2)_3NH(CH_2)_3NH_2)]^+$ and $[PdCl(H_2N(CH_2)_3NH(CH_2)_4NH_2)]^+$ were observed at 5.43 and 6.74 ppm, respectively.[21] When the NH of the NNP ligand is coordinated to Pd, the nitrogen center becomes stereogenic and the two protons of the CH_2 attached to the NH group in **2a** should be inequivalent. In the ^1H NMR spectrum, the two ^1H signals were observed at 3.34 and 2.57 ppm. Formation of chiral N centers for complexes of amine ligands with nitrogen bearing three different substituents have previously been proposed or implied.[16] Formulation of compound **2a** as a monocationic complex with one of the chlorides as the counteranion is supported by the fact that **2a** undergoes a metathesis reaction with $NaBPh_4$ to give $[PdCl(NNP)]BPh_4$ (**2b**), which has ^{31}P, ^1H, and ^{13}C NMR data (except the additional signals due to BPh_4) similar to those of **2a**.

Similarly, **1** reacted with $PtCl_2(COD)$ to give [PtCl(NNP)]Cl (**3a**). The presence of CH=N in **3a** has been confirmed by the observation of the ^1H and ^{13}C NMR (in $CDCl_3$) signals of CH=N at 9.77 and 166.6 ppm, respectively. Consistent with the structure, **3a** undergoes a metathesis reaction with $NaBPh_4$ to give $[PtCl(NNP)]BPh_4$ (**3b**), which has ^{31}P, ^1H and ^{13}C NMR data (except the additional signals due to BPh_4) similar to those of **3a**.

Treatment of ligand **1** with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ in dichloromethane produced the allyl complex $[Pd(\eta^1\text{-}C_3H_5)(NNP)]Cl$ (**4a**). In the ^1H NMR spectrum (in CD_2Cl_2), the CH=N signal was observed at 8.80 ppm; the allyl signals were observed at 5.86 (CH=), 4.47 (CH_2=), and 2.02 (CH_2Pd) ppm. In the ^{13}C NMR spectrum (in CD_2Cl_2), the CH=N signal was observed at 164.3 ppm; the allyl signals were observed at 110.1 (=CH_2), 141.4 (CH=), and 25.4 (CH_2Pd) ppm. The NMR data of the allyl ligand are inconsistent with those reported for $Pd(\eta^3\text{-}C_3H_5)$[14,22] but are in agreement with those reported for $Pd(\eta^1\text{-}C_3H_5)$.[23] The chloride in **4a** is not coordinated to Pd, as **4a** readily reacted with $NaBPh_4$ to give $[Pd(\eta^1\text{-}C_3H_5)(NNP)]BPh_4$ (**4b**), which has ^{31}P, ^1H, and ^{13}C NMR data (except the additional signals of BPh_4) similar to those of **4a.** Very few allyl complexes with potentially tridentate ligands have been reported.[13,24] Closely related examples of such complexes include $[Pd(\eta^1\text{-}C_3H_5)(o\text{-}Ph_2PC_6H_4CH{=}NCH_2CH_2\text{-}2\text{-pyridine})]^+$ [13] and $[Pd(C_3H_5)(2,2',6',6''\text{-terpyridine})]^+$.[24a] Interestingly, η^1-allyl and η^3-allyl forms are present both in solution and in the solid state for the latter complex.

Synthesis of 6-(o-$Ph_2PC_6H_4CH{=}NCH_2CH_2NH$)-$\beta$-CD (CDNNP). Stirring a mixture of o-$Ph_2PC_6H_4CHO$ and 6-$H_2NCH_2CH_2NH$-β-CD in methanol at room temperature for 24 h produced a yellow solution from which

Scheme 2



CDNNP (**5**) can be isolated as a pale yellow solid (Scheme 2). Compound **5** has been characterized by ^{31}P, ^1H, and ^{13}C NMR as well as MS spectroscopy. In particular, compound **5** (in DMSO) exhibited a singlet $^{31}P\{^1H\}$ signal at −14.1 ppm. The ^{31}P chemical shift is very close to that of the analogous iminophoshine ligand **1b**. The FAB mass spectrum showed the molecular ion peak at m/z 1449. In the ^1H and ^{13}C NMR spectra, the signals of CH=N were observed at 8.84 and 159.8 ppm, respectively. As indicated by the $^{31}P\{^1H\}$ NMR spectra, samples of **5** thus obtained were usually contaminated with a small amount (<5%) of phosphorus-containing species having a singlet $^{31}P\{^1H\}$ signal at −20.6 ppm (in DMSO). It can be shown that the species does not interfere with the preparation of Pd and Pt complexes. We tentatively attribute the phosphorus-containing species to 6-(o-$Ph_2PC_6H_4CH(OH)NHCH_2CH_2NH$)-$\beta$-CD, because the ^{31}P chemical shift of −20.6 ppm is close to that (−18.6 ppm) of o-$Ph_2PC_6H_4CH(OH)NHCH_2CH_2NHCH_3$.

Synthesis of Pt and Pd Complexes with CDNNP. Reactions of ligand **5** with $PdCl_2(NCPh)_2$ in methanol produced [PdCl(CDNNP)]Cl (**6**) (Scheme 2). The compound is only slightly soluble in polar solvents such as MeOH, DMSO, and DMF but is insoluble in organic solvents such as acetone, dichloromethane, and benzene. The compound has been characterized by mass spectroscopy and ^{31}P, ^1H, and ^{13}C NMR spectroscopy. The FAB mass spectrum displayed a $[PdCl(CDNNP)]^+$ ion peak at m/z 1589. The ^1H and ^{13}C NMR spectra exhibited the ^1H and ^{13}C signals of CH=N at 9.26 and 162.5 ppm, respectively. The $^{31}P\{^1H\}$ NMR spectrum in CD_3OD showed two closely spaced ^{31}P signals at 31.4 and 31.3 ppm. The chemical shifts are very close to those of the analogous complex [PdCl(NNP)]Cl, confirming that the two complexes have similar coordination spheres.

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The observation of two ^{31}P signals for **6** is not surprising. When the NH of CDNNP is coordinated to Pd, the nitrogen becomes stereogenic. Because the CD functionality is chiral, two diasteroisomers are therefore expected for **6**. However, the difference in the ^{1}H and ^{13}C chemical shifts of CH═N in the two isomers must be very small, as only one set of ^{1}H and ^{13}C data were observed for **6**.

The analogous Pt complex [PtCl(CDNNP)]Cl (**7**) was produced from the reaction of ligand **5** with $PtCl_2$(COD) in methanol. Like complex **6**, complex **7** in methanol also showed two closely spaced ^{31}P{^{1}H} signals at 4.59 and 4.52 ppm. Because the chemical shifts are very similar to those of **3a**, it is reasonable to assume that the complexes **3a** and **7** have similar coordination spheres. Consistent with the structure, the FAB mass spectrum of **7** displayed a $[PtCl(CDNNP)]^+$ ion peak at m/z 1643; the ^{1}H NMR spectrum of **7** showed the CH═N signal at 9.29 ppm.

Treatment of ligand **5** with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ in methanol produced the allyl complex $[Pd(\eta^1\text{-}C_3H_5)$(CDNNP]-Cl (**8**). Complex **8** also exists as two isomers, as the ^{31}P{^{1}H} NMR spectrum (in CD_3OD) displayed two ^{31}P signals at 31.6 and 31.5 ppm. The similarity in the ^{31}P chemical shifts of complexes **4** and **8** suggests that the coordination sphere of **8** is similar to that of **4**. The assumption is supported by the mass and ^{1}H and ^{13}C NMR spectroscopy. For example, the FAB mass spectrum displayed the $[Pd(\eta^1\text{-}C_3H_5)(CDNNP)]^+$ ion peak at m/z 1631; the ^{1}H NMR spectrum (in DMF-d_7) showed a CH═N signal at 9.12 ppm and allyl signals at 5.67 (CH═), 4.22 (CH_2═), and 3.10 (CH_2Pd) ppm.

In summary, we have prepared the novel cyclodextrin-functionalized iminophosphine ligand CDNNP and its Pd and Pt complexes. In the future, we shall study catalytic reactions using metal complexes with the phosphine ligand in order to investigate the effects of the CD substituent on the regio- and stereochemistry of catalytic reactions.

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). The starting material 6-$NH_2CH_2CH_2NH$-β-CD was prepared according to a literature method.[19] All other reagents were used as purchased from Aldrich Chemical Co. or Strem.

^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were collected on a Bruker ARX-300 or a JEOL EX-400 spectrometer. ^{1}H 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). Since cyclodextrin derivatives have a high affinity for water or other solvent molecules, it is usually difficult to get satisfactory analytical data for them. In fact, analytical data for cyclodextrin derivatives are often either not reported or have to be fitted with variable amounts of water or other solvent molecules in the literature. In our case, it is also necessary to add some water molecules, as usual, to the formula in order to match the experimental values.

***o*-$Ph_2PC_6H_4$-CH(OH)$NHCH_2CH_2NHCH_3$ (1a) and *o*-Ph_2-PC_6H_4-CH═$NCH_2CH_2NHCH_3$ (NNP, 1b).** A mixture of *N*-methylethylenediamine (2.3 mL, 26.2 mmol) and *o*-$Ph_2PC_6H_4$-CHO (2.4 g, 8.3 mmol) in THF (15 mL) was stirred at room temperature for 3 h to give a red-brown solution. The solvent was then removed completely under vacuum to give a red-brown oil. Addition of acetonitrile (30 mL) to the residue afforded a pale yellow solid, which was collected by filtration, washed with acetonitrile, and dried under vacuum. Yield: 2.1 g. NMR data indicate that the solid is a mixture of *o*-$Ph_2PC_6H_4$-CH(OH)$NHCH_2CH_2NHCH_3$ (**1a**) and *o*-$Ph_2PC_6H_4$-CH═NCH_2-CH_2NHCH_3 (NNP; **1b**) in about a 3:1 ratio. Selected characterization data for **1a** are as follows. EI-MS: m/z 361 ($[M - 3]^+$). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ -18.6 (s). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 7.68 (m, 1 H, C_6H_4), 6.93 (m, 1 H, C_6H_4), 7.36−7.18 (m, other aromatic signals mixed with **1b**), 4.58 (d, J(HH) = 5.3 Hz, 1 H, CH(OH)), 3.26−3.17 (m, 1 H of CH_2NHCH(OH) and 1 H of CH_2NHCH_3), 2.98 (m, 1 H, CH_2-NHCH_3), 2.33 (m, 1 H, CH_2NHCH(OH)), 1.87 (s, 3 H, CH_3); the OH and NH signals are merged with that of water at 1.87 ppm. ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 146.2−128.4 (m, aromatic signals mixed with **1b**), 82.2 (d, J(PC) = 19.9 Hz, *C*H(OH)), 55.9 (s, *C*H_2NHCH(OH)), 45.7 (s, *C*H_2NHCH_3), 38.9 (s, CH_3). Selected characterization data for **1b** are as follows. EI-MS: m/z 347 ($[M + 1]^+$). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2-Cl_2): δ −13.3 (s). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 8.79 (d, J(PH) = 4.3 Hz, 1 H, CH═N), 7.87 (m, 1 H, C_6H_4), 6.87 (m, 1 H, C_6H_4), 7.36−7.18 (m, other aromatic signals mixed with **1a**), 3.56 (t, J(HH) = 5.5 Hz, 2 H, CH_2N═), 2.62 (t, J(HH) = 5.5 Hz, 2 H, CH_2NH), 2.22 (s, 3 H, CH_3). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 161.3 (d, J(PC) = 16.8 Hz, CH═N), 146.2−128.4 (m, aromatic signals mixed with **1a**), 61.3 (s, CH_2N═), 52.7 (s, CH_2NH), 36.6 (s, CH_3).

[PdCl(NNP)]Cl (2a). Method 1. A solution of **1** (200 mg, ca. 0.56 mmol) in dichloromethane (10 mL) was added dropwise to a dichloromethane solution (10 mL) of $PdCl_2$(COD) (165 mg, 0.58 mmol) to give a yellow solution. The reaction mixture was stirred for 1 h at room temperature. The volume of the reaction mixture was then reduced to ca. 2 mL under vacuum. Addition of ether (20 mL) to the reaction mixture afforded a light brown solid. After the mixture was stirred for an additional 2 h, the solid was collected by filtration, washed with ether, and dried under vacuum. Yield: 0.27 g, 93%.

Method 2. A solution of **1** (250 mg, 0.69 mmol) in 10 mL of dichloromethane was added to a solution of $PdCl_2(PhCN)_2$ (290 mg, 0.74 mmol) in 15 mL of dichloromethane. The mixture was stirred for 1 h at room temperature. Then the solvent was removed under vacuum to afford a light brown solid. The solid was washed with ether and then dried under vacuum. Yield: 0.31 g, 88%. CI-MS: m/z 487 ($[PdCl(NNP)]^+$), 452 ($[Pd(NNP)]^+$). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 30.1 (s). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 9.56 (br, 1 H, CH═N), 8.40 (m, 1 H, C_6H_4), 7.77 (m, 1 H, C_6H_4), 7.64−7.42 (m, 11 H, 1 H of C_6H_4 and 10 H of PPh_2), 7.23 (m, 1 H, C_6H_4), 5.84 (s, br, 1 H, NH, disappeared in the presence of D_2O), 4.53 (s, br, 2 H, CH_2N═), 3.34 (s, br, 1 H, CH_2NH), 2.70 (t, J(HH) = J(PH) = 5.0 Hz, 3 H, CH_3), 2.57 (s, br, 1 H, CH_2NH). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 166.3 (d, J(PC) = 6.7 Hz CH═N), 140.1−127.4 (m, PPh_2, C_6H_4), 67.3 (s, CH_2N═), 53.0 (s, CH_2NH), 39.5 (s, CH_3).

[PdCl(NNP)]BPh_4 (2b). A solution of $NaBPh_4$ (0.12 g, 0.35 mmol) in methanol (10 mL) was added to a solution of [PdCl-(NNP)]Cl (150 mg, 0.29 mmol) in methanol (10 mL) to give a gray precipitate. The solid was collected by filtration, washed with methanol and water, and dried under vacuum. Yield: 0.17 g, 78%. FAB-MS: m/z 487 ($[PdCl(NNP)]^+$), 452 ($[Pd(NNP)]^+$). Anal. Calcd for $C_{46}H_{43}BClN_2PPd\cdot H_2O$: C, 66.93; H, 5.50; N, 3.39. Found: C, 66.65; H, 5.53; N, 3.14. ^{31}P{^{1}H} NMR (121.5 MHz, DMSO-d_6): δ 29.4 (s). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ 9.00 (br, 1 H, CH═N), 8.17 (m, 1 H, C_6H_4), 8.03 (m, 1 H, C_6H_4), 7.94 (m, 1 H, C_6H_4), 7.79−7.64 (m, 10 H, PPh_2), 7.49 (m, 1 H, C_6H_4), 7.30−6.88 (m, 20 H, BPh_4), 6.15 (m, 1 H, NH), 4.34 (m, 1 H, CH_2N═), 4.08 (m, 1 H, CH_2N═), 3.45 (br, water), 3.10 (m, 1 H, CH_2NH), 2.76 (t, J(HH) = J(PH) = 5.3 Hz, 3 H, CH_3), 2.71 (m, 1 H, CH_2NH). ^{13}C{^{1}H} NMR (75.5 MHz, DMSO-d_6): δ 165.0 (d, J(PC) = 6.7 Hz, CH=N), 163.3 (1:1:1:1 quartet, J(BC) = 49.2 Hz, ipso BPh_4), 138.4−118.8 (m, C_6H_4, PPh_2, BPh_4), 66.4 (s, CH_2N=), 51.0 (s, CH_2NH), 37.6 (d, J(PC) = 3.0 Hz, CH_3).

[PtCl(NNP)]Cl (3a). A solution of **1** (170 mg, 0.47 mmol) in 10 mL of dichloromethane was added to a dichloromethane solution (10 mL) of $PtCl_2$(COD) (184 mg, 0.49 mmol) to give a greenish yellow solution. The mixture was stirred for 1 h at room temperature. The volume of the reaction mixture was then reduced to ca. 5 mL under vacuum. Addition of ether (40 mL) to the reaction flask afforded a yellow solid. After the mixture was stirred for another 2 h, the solid was collected by filtration, washed with ether and dried under vacuum. Yield: 0.25 g, 86%. CI-MS: m/z 575 ([PtCl(NNP)]$^+$), 541 ([Pt(NNP)]$^+$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 4.1 (s with Pt satellites, J(PtP) = 3344 Hz). ^1H NMR (300.13 MHz, $CDCl_3$): δ 9.77 (br, 1 H, CH=N), 8.42−7.33 (m, 14 H, C_6H_4, PPh_2), 6.96 (s, br, 1 H, NH), 4.50 (br, 2 H, CH_2N=), 3.28 (br, 1 H, CH_2NH), 2.82 (t, J(HH) = 4.5 Hz, 3 H, CH_3), 2.56 (m, br, 1 H, CH_2NH). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 163.6 (d, J(PC) = 7.6 Hz, CH=N), 139.4−127.4 (m, C_6H_4, PPh_2), 68.4 (s, CH_2N=), 53.8 (s, CH_2NH), 39.5 (s, CH_3).

[PtCl(NNP)]BPh$_4$ (3b). A solution of $NaBPh_4$ (0.10 g, 0.29 mmol) in methanol (10 mL) was added to a solution of [PtCl(NNP)]Cl (150 mg, 0.26 mmol) in methanol (10 mL) to give a yellow precipitate. The solid was collected by filtration, washed with methanol and water, and then dried under vacuum. Yield: 0.17 g, 76%. FAB-MS: m/z 575 ([PtCl(NNP)]$^+$), 541 ([Pt(NNP)]$^+$). Anal. Calcd for $C_{46}H_{43}BClN_2PPt$: C, 61.65; H, 4.84; N, 3.13. Found: C, 61.49; H, 4.86; N, 2.94. $^{31}P\{^1H\}$ (121.5 MHz, DMSO-d_6): δ 3.9 (s with Pt satellites, J(PtP) = 3306 Hz). ^1H NMR (300.13 MHz, DMSO-d_6): δ 9.29 (br, 1 H, CH=N), 8.23−7.46 (m, 14 H, C_6H_4, PPh_2), 7.30−6.86 (m, 20 H, BPh_4), 4.47 (m, 1 H, CH_2N=), 4.21 (m, 1 H, CH_2N=), 3.06 (m, 1 H, CH_2N), 2.76 (t, J(HH) = 5.3 Hz, 3 H, CH_3), 2.71 (m, 1 H, CH_2NH), the NH signal is merged with that of water at 3.46 ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, DMSO-d_6): δ 165.0 (d, J(PC) = 6.7 Hz, CH=N), 163.3 (1:1:1:1 quartet, J(BC) = 49.2 Hz, ipso-BPh_4), 138.4−121.5 (m, C_6H_4, PPh_2, BPh_4), 67.5 (s, CH_2N=), 51.8 (s, CH_2NH), 37.9 (s, CH_3).

[Pd(η^1-C_3H_5)(NNP)]Cl (4a). A solution of **1** (180 mg, 0.50 mmol) in 10 mL of dichloromethane was added to a solution of [PdCl(η^3-C_3H_5)]$_2$ (95 mg, 0.26 mmol of Pd) in 10 mL of dichloromethane to give a greenish yellow solution. The mixture was stirred for 1 h at room temperature, and then the solvent was removed under vacuum to afford a yellow solid. The residue was washed with ether and dried under vacuum. Yield: 0.17 g, 94%. FAB-MS: m/z 493 ([Pd(C_3H_5)(NNP)]$^+$), 452 ([Pd(NNP]$^+$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 34.7 (s). ^1H NMR (300.13 MHz, CD_2Cl_2): δ 8.80 (br, 1 H, CH=N), 7.86 (m, 1 H, C_6H_4), 7.66 (m, 2 H, C_6H_4), 7.55−7.37 (m, 12 H, C_6H_4, PPh_2), 6.00 (s, br, 1 H, NH), 5.86 (m, 1 H, CH_2=CH), 4.47 (m, 2 H, CH_2=CH), 4.09 (br, 2 H, CH_2N=), 2.97 (br, 2 H, CH_2NH), 2.69 (m, 3 H, CH_3), 2.02 (m, 2 H, CH_2Pd). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 164.3 (d, J(PC) = 3.8 Hz, CH=N), 141.4 (s, HC=CH_2), 138.7−128.6 (m, C_6H_4, PPh_2), 110.1 (s, HC=CH$_2$), 62.9 (s, CH_2N=), 53.8 (s, CH_2NH), 38.3 (s, CH_3), 25.4 (s, CH_2Pd).

[Pd(η^1-C_3H_5)(NNP)]BPh$_4$ (4b). A solution of $NaBPh_4$ (80 mg, 0.23 mmol) in methanol (10 mL) was added to a solution of [Pd(η^1-C_3H_5)(NNP)]Cl (100 mg, 0.19 mmol) in methanol (10 mL) to give a yellow precipitate. The solid was then collected by filtration, washed with methanol and water, and dried under vacuum. Yield: 0.14 g, 94%. Anal. Calcd for $C_{49}H_{48}BN_2PPd\cdot H_2O$: C, 70.81; H, 6.06; N, 3.37. Found: C, 70.89; H, 5.94; N, 3.50. FAB-MS: m/z 493 ([Pd(C_3H_5)(NNP)]$^+$); 452 ([Pd(NNP)]$^+$). $^{31}P\{^1H\}$NMR (121.5 MHz, acetone-d_6): δ 35.4. ^1H NMR (300.13 MHz, acetone-d_6): δ 8.70 (br, 1 H, CH=N), 8.04−7.71 (m, 14 H, C_6H_4, PPh_2), 7.52−6.90 (m, 24 H, BPh_4), 5.94 (m, 1 H, CH_2=CH), 4.83−4.71 (m, 2 H, CH_2=CH), 4.52 (s, br, 1 H, NH), 4.09 (s, br, 2 H, CH_2N=), 3.14 (s, br, 2 H, CH_2NH), 3.02 (m, 3 H, CH_3), 2.23 (m, 2 H, CH_2Pd). $^{13}C\{^1H\}$ NMR (75.5 MHz, acetone-d_6): δ 165.5 (d, J(PC) = 3.8 Hz, CH=N), 165.2 (1:1:1:1 quartet, J(BC) = 49.2 Hz, ipso BPh_4), 141.1 (s, HC=CH_2), 139.4 (d, J (PC) = 9.0 Hz, C_6H_4), 137.4−126.4 (m, C_6H_4, PPh_2), 110.0 (s, HC=CH$_2$), 62.9 (s, CH_2N=), 53.8 (s, CH_2NH), 38.2 (s, CH_3), 25.1 (s, CH_2Pd).

CDNNP (5). *o*-$Ph_2PC_6H_4CHO$ (0.13 g, 0.45 mmol) was added to a suspension of 6-$NH_2CH_2CH_2NH$-β-CD (0.50 g, 0.42 mmol) in 50 mL of methanol. The mixture was stirred for 24 h at room temperature to afford a yellow solution. The solvent was then removed under vacuum to give a pale yellow solid, which was washed with acetone and dried under vacuum. Yield: 0.52 g, 86%. FAB-MS: m/z 1449 (M$^+$). $^{31}P\{^1H\}$ NMR (121.5 MHz, DMSO-d_6): δ −14.1 (s, predominant, CDNNP), −20.6 (s, minor, could be due to 6-(*o*-$Ph_2PC_6H_4CH(OH)NHCH_2$-CH_2NH)-β-CD). ^1H NMR (300.13 MHz, CD_3OD): δ 9.51 (d, J(PH) = 4.1 Hz, 1 H, CH=N), 8.09−7.41 (m, 14 H, C_6H_4, PPh_2), 5.16 (s, 7 H, H-1), 5.0 (br, OH of CD and methanol), 3.95−2.8 (m, other protons). $^{13}C\{^1H\}$ NMR (100.40 MHz, DMSO-d_6): δ 160.1 (d, J(PC) = 16.4 Hz, CH=N), 139.4−124.5 (m, C_6H_4, PPh_2), 102.3 (br, C-1), 83.5−81.9 (m, C-4), 73.5−68.9 (m, C-2, C-3, C-5), 60.9 (s, CH_2N=), 60.3 (m, C-6), 50.9 (s, CH_2NH, 46.7 (CH_2NH).

[PdCl(CDNNP)]Cl (6). A solution of CDNNP (200 mg, 0.14 mmol) in 30 mL of methanol was added dropwise to a solution of $PdCl_2(PhCN)_2$ (53 mg, 0.14 mmol) in 10 mL of methanol. A brown precipitate was formed immediately. The reaction mixture was stirred for 1 h at room temperature. The solvent was then removed under vacuum to afford a brown solid, which was washed with acetone, ether, and dichloromethane and dried under vacuum. Yield: 0.21 g, 91%. The compound could also be prepared from the reaction of $PdCl_2$(COD) with CDNNP. FAB-MS: m/z 1589 ([PdCl(CDNNP)]$^+$), 1553 ([Pd(CDNNP)]$^+$). Anal. Calcd for $C_{63}H_{89}Cl_2N_2O_{34}PPd\cdot 9H_2O$: C, 42.30; H, 6.03; N, 1.57. Found: C, 41.66; H, 5.62; N, 1.34. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3OD): δ 31.3 (s), 31.4 (s). ^1H NMR (300.13 MHz, DMF-d_7): δ 9.07 (br, 1 H, CH=N), 8.29−7.48 (m, 14 H, C_6H_4, PPh_2), 5.87 (m, br, OH), 4.97 (m, 7 H, H-1), 4.8−2.7 (m, other protons); $^{13}C\{^1H\}$ (100.40 MHz, DMSO-d_6): δ 164.6 (d, J(PC) = 7.0 Hz, CH=N), 145.4−125.4 (m, C_6H_4, PPh_2), 101.9 (C-1), 81.7 (C-4), 73.1−72.6 (C-2, C-3, C-5), 66.1 (CH_2N=), 60.1 (C-6), 51.0 (CH_2N), 47.1 (CH_2NH).

[Pt(CDNNP)Cl]Cl (7). A mixture of $PtCl_2$(COD) (0.10 g, 0.27 mmol) and CDNNP (0.38 g, 0.27 mmol) in methanol (50 mL) was stirred at room temperature for 3 h to give a pale yellow solution. The solvent was then removed under vacuum to afford a white solid, which was collected by filtration, washed with acetone, ether, and dichloromethane, and dried under vacuum. Yield: 0.20 g, 45%. FAB-MS: 1679 ([PtCl(CDNNP)]$^+$), 1643 ([Pt(CDNNP)]$^+$). Anal. Calcd for $C_{63}H_{89}Cl_2N_2O_{34}PPt\cdot 9H_2O$: C, 40.30; H, 5.78; N, 1.49. Found: C, 39.64; H, 5.26; N, 1.40. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3OD): δ 4.59(s), 4.52 (s with Pt satellites, J(Pt−P) = 3389 Hz). ^1H NMR (300.13 MHz, CD_3OD): δ 9.28 (d, J(PH) = 3.6 Hz, 1 H, N=CH), 8.09−7.66 (m, 14 H, C_6H_4, PPh_2), 5.39 (m, 7 H, H-1), 4.7−3.0 (m, other protons).

[Pd(η^1-C_3H_5)(CDNNP)]Cl (8). A mixture of [PdCl(η^3-C_3H_5)]$_2$ (51 mg, 0.14 mmol of Pd) and CDNNP (0.20 g, 0.14 mmol) in 20 mL of methanol was stirred for 1 h at room temperature. The solvent was then evaporated to dryness under vacuum. A yellowish solid was obtained when 50 mL of acetone was added to the reaction flask. The solid was collected by filtration, washed with acetone and dichloromethane, and then dried under vacuum. Yield: 0.21 g, 92%. FAB-MS: m/z 1631 ([Pd(C_3H_5)(CDNNP)]$^+$), 1554 ([Pd(CDNNP)]$^+$). Anal. Calcd for $C_{66}H_{94}ClN_2O_{34}PPd\cdot 9H_2O$: C, 44.18; H, 6.29; N, 1.56. Found: C, 44.03; H, 5.68; N, 1.83. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3OD): δ 31.6 (s), 31.5 (s). ^1H NMR (300.13 MHz, DMF-d_7): δ 8.90 (br, 1 H, N=CH), 8.28−7.40 (m, 14 H, C_6H_4, PPh_2), 5.67 (m, 1 H, CH=CH_2), 5.25−5.16 (m, 7 H, H-1), 4.75 (br, OH and

NH), 4.22 (m, 2 H, C*H*=CH_2), 3.10 (m, 2 H, CH_2Pd), 4.09−3.0 (m, other protons). The [1]H signals of the allyl group were assigned on the basis of a H−H COSY experiment. $^{13}C\{^1H\}$ NMR (100.40 MHz, DMF-d_7): δ 164.2 (s, CH=N), 140.6 (s, H*C*=CH_2), 138.2−123.8 (m, C_6H_4, PPh_2), 108.2 (s, HC=*C*H_2), 102.8−102.0 (m, C-1), 84.4−81.7 (m, C-4), 73.8−72.7 (m, C-2, C-3, C5), 66.6 (s, CH_2N=), 61.8−60.6 (m, C-6), 50.0 (CH_2NH), 48.3 (CH_2NH), 25.0 (s, CH_2Pd).

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