

Synthesis of 2,6-Bis(dicyclohexylphosphinomethyl)phenyl Platinum(II) Complexes (2,6-(Cy₂CH₂)₂C₆H₃)PtX (X=Cl, I, OTf)

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Recently late transition metal complexes with PCP pincer ligands have been reported to be active catalysts for aliphatic dehydrogenation,¹ Stille coupling,² and Heck coupling,³ as well as useful in the studies of C-H, C-C and C-O activation.⁴ The terdentate ligand inhibits both phosphine dissociation and reductive elimination of the aryl group. Consequently, these complexes stabilized with the rigid ligand framework are to be remarkably thermally stable and inert to air, showing good catalysts.

The chelating diphosphines of the type 1,3-(R₂PCH₂)₂C₆H₄, with various substituents R, readily reacted with divalent group 10 metals giving square planar cyclometallated compounds of (2,6-(R₂PCH₂)₂C₆H₃)MX (Scheme 1).⁵ In particular, the compound with bulky substituents 1,3-(Cy₂PCH₂)₂C₆H₄ was reported to undergo cyclometallation with Ni(II) and Pd(II) *via* C-H activation to give monomeric square planar complexes.⁶ However, an analogous platinum compound has not been reported due to formation of dimeric species [PtCl₂(1,3-(Cy₂PCH₂)₂C₆H₄)₂], which is exceedingly thermally stable.^{6b}

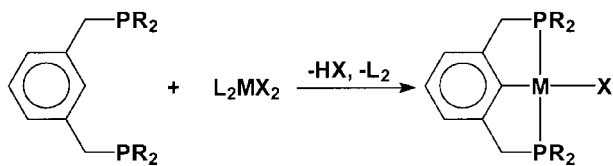
As a part of our studies on the use of the sterically demanding pincer ligand 2,6-(Cy₂PCH₂)₂C₆H₃ to stabilize platinum group metal complexes of unusual reactive species with hard-base ligands,⁷ we have synthesized the complexes of (2,6-(Cy₂PCH₂)₂C₆H₃)PtX (X=Cl, I, OTf) by the reaction of 1,3-(Cy₂PCH₂)₂C₆H₄ with the platinum(II) precursor (COD)PtX₂ under suitable reaction conditions.

In the precedents, attempts at preparations of cyclometallated monomeric nickel triads (2,6-(Cy₂PCH₂)₂C₆H₃)MX from the reactions of 1,3-(Cy₂PCH₂)₂C₆H₄ with appropriate metal precursors in refluxing 2-methoxyethanol gave the targeted complexes only for nickel and palladium species.⁶ In the case of palladium, a mixture of monomeric and oligomeric species was produced from the reaction, in which the oligomeric species can be thermally converted into cyclometallated monomeric compounds. For the platinum case, however, only dimeric species was formed from the reaction, showing severe resistance to thermal conversion to yield a cyclo-

metallated monomer, even at refluxing temperatures for a prolonged period of reaction time.

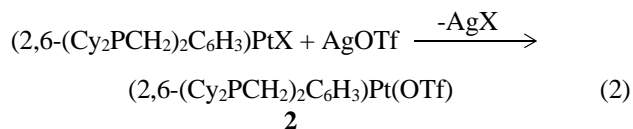
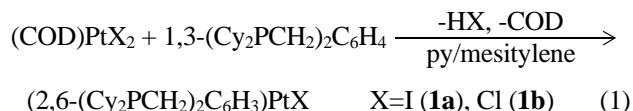
When we have attempted at preparation of cyclometallated palladium complexes from reaction of (COD)PdBr₂ with 1,3-(Cy₂PCH₂)₂C₆H₄ in the presence of a base such as pyridine, we have found that the pure monomeric complex (2,6-(Cy₂PCH₂)₂C₆H₃)PdBr was produced in good yields without formation of any oligomeric product.⁸ These results prompted us to prepare analogous platinum complexes employing mesitylene as solvent of a higher boiling point (b.p. 163 °C) than that of 2-methoxyethanol (b.p. 124 °C) in the presence of a base.

Reaction of (COD)PtI₂ with a stoichiometric amount of 1,3-(Cy₂PCH₂)₂C₆H₄ in refluxing mesitylene for 2 h gave a pale-yellow solution. When pyridine (*ca.* equimolar) was introduced into this solution, the color of solution suddenly changed to dark olive and then gradually to brownish orange.⁹ The reaction mixture was stirred for additional 24 h, resulting in a brownish solution along with formation of a small amount of black solids. It is worth noting that the use of an excess amount of base gave an increased amount of black solid, thus resulting in low yield of product. After appropriate work-up from the resulting solution, the colorless crystalline compound (2,6-(Cy₂PCH₂)₂C₆H₃)PtI (**1a**) was obtained in moderate yield. The chloro complex (2,6-(Cy₂PCH₂)₂C₆H₃)PtCl (**1b**) was similarly prepared by reaction of the corresponding chloro precursor (COD)PtCl₂ with 1,3-(Cy₂PCH₂)₂C₆H₄. From these reactions, neither dimeric nor oligomeric species was produced. Treatment of the platinum halide with silver triflate readily afforded the triflate complex (2,6-(Cy₂PCH₂)₂C₆H₃)Pt(OTf) (**2**) (Eq. 2). This complex with the labile triflate ligand, particularly bearing the rigid ligand framework, may serve as a good precursor for studying on many stoichiometric and catalytic reactions relevant to amination, alkoxylation, dehydrogenation, and cross-couplings.^{1-4,5de,7,10}



R = Me, Ph, *t*-Bu ; M = Ni, Pd, Pt ; X = halide

Scheme 1



The formation of cyclometallated platinum(II) complexes can be readily verified by the observation of the pseudo-tri-

plet resonance for the benzylic methylene protons (PCH_2) in the ^1H -NMR spectrum, due to the "virtual trans-phosphorus couplings".¹¹ This methylene protons resonate in a distinctive region of the ^1H -NMR spectrum at around δ 3.0 and when the ligand is coordinated to metal in a terdentate mode, they appear as a diagnostic pseudo-triplet (*ca.* 8.0 Hz).^{6,11} The methylene resonances of **1a** in the ^1H -NMR spectrum (CDCl_3) displayed at δ 3.17 as a pseudo-triplet ($|^2J(\text{PH}) + ^4J(\text{PH})| = 8.5$ Hz) along with platinum satellites ($^3J(\text{PtH}) = 18.5$ Hz). The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **1a** in CDCl_3 clearly displayed a sharp single resonance at δ 48.1 ($^1J(\text{PtP}) = 2766$ Hz). The ^1H - and $^{31}\text{P}\{^1\text{H}\}$ -NMR parameters for **1b** and **2** have been similarly observed as for those of **1a** (see Experimental Section). These observed resonances for the benzylic methylene protons and phosphorus as well as all coupling constants are well consistent with previously reported data.^{5,6} It is worth noting that the molar conductivity value ($\Lambda_{\text{M}} = 94 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) measured for **2** shows that the complex is a type of 1 : 1 electrolyte, indicating the triflate ligand being dissociative in solution.¹²

In the reported work, the failure to obtain cyclometallated platinum monomers would seem to be in the formation of an extremely stable dimeric product $[\text{PtCl}_2(1,3\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_4)]_2$, in which the bidentate ligand spans two metal centers, resisting to rearrange to *trans*-spanning monomeric species prior to undergoing cyclometallation. In this work, the cyclometallated platinum complexes particularly bearing the sterically hindered pincer have been successfully prepared. The facile formation of these complexes can be probably explained by the use of a base which facilitates cyclometallation of the ligand by readily eliminating HX and simultaneously acts as a competing ligand to inhibit the formation of dimeric species.

Experimental Section

All preparations of air sensitive compounds were carried out on a standard Schlenk line or in an inert atmosphere glove box under argon. Tetrahydrofuran and diethyl ether were freshly distilled from sodium/benzophenone ketyl under nitrogen, and then stored over molecular sieve. Benzene, *n*-hexane, and *n*-pentane were distilled from sodium/benzophenone ketyl with tetraglyme (tetraethylene glycol dimethyl ether). All chlorinated solvents such as CHCl_3 and CH_2Cl_2 were dried by refluxing over lithium aluminum hydride or calcium hydride under nitrogen. K_2PtCl_4 was supplied by Kojima Chemicals Co., Ltd., and used without purification. Silver triflate, 1,5-cyclooctadiene, α, α' -dibromo-*m*-xylene, and deuterated solvents such as CDCl_3 and C_6D_6 were purchased from Aldrich Chemical Company, and used as supplied. Dicyclohexylphosphine was supplied by Strem Chemicals Inc. All other reagents were from various commercial companies. $(\text{COD})\text{PtX}_2$ ¹³ and $1,3\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_4$ ^{6a} were prepared according to the literature methods.

IR spectra were recorded on a Bomem FT-IR spectrometer (Michelson 100), as pressed KBr pellets. ^1H -, $^{31}\text{P}\{^1\text{H}\}$ - and $^{19}\text{F}\{^1\text{H}\}$ -NMR spectra were measured on a Varian Gemini-

2000 spectrometer, using the deuterium signal of the solvent as an internal lock frequency. Chemical shifts for ^1H -NMR are reported in ppm (δ) relative to TMS. Chemical shifts for $^{31}\text{P}\{^1\text{H}\}$ - and $^{19}\text{F}\{^1\text{H}\}$ -NMR were measured in ppm relative to external 85% H_3PO_4 ($\delta = 0$) and perfluoromethylbenzene ($\delta = -63.73$), in a sealed capillary, respectively. Conductivity measurements were obtained with a TOA conductivity meter (CM-40S). Nitromethane was used as solvent in a cell containing platinized electrodes (cell constant = 1.014 cm^{-1}). Elemental analyses were performed at the Korea Basic Science Institute in Seoul, Korea.

Preparation of Pt(2,6-(Cy₂PCH₂)₂C₆H₃)I (1a). A 30 mL mesitylene solution of $(\text{COD})\text{PtI}_2$ (1.00 g, 1.80 mmol) and $1,3\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_4$ (0.896 g, 1.80 mmol) was stirred for 2 h at refluxing temperatures, resulting in a pale-yellow solution. The reaction mixture was cooled to room temperature. To this cooled solution was added pyridine (0.142 g, 1.80 mmol). The reaction mixture was stirred for additional 24 h at refluxing temperatures, resulting in a brownish solution with a small amount of decomposed black metal. After cooling the solution at ambient temperature, all volatiles were removed *in vacuo* to give a deep-orange residue. The resulting residue was extracted with benzene (3×20 mL) and filtered to give an orange solution. The volume of the solution was reduced to *ca.* 15 mL. Addition of ethanol (*ca.* 30 mL) into the concentrated solution gave pale-yellow precipitates, which were isolated by vacuum filtration, and dried *in vacuo* for 24 h. An analytically pure compound of **1** can be obtained by column chromatography on silica gel with a benzene eluent to give colorless crystals from *n*-hexane. Yield 856 mg (58%). ^1H -NMR (in CDCl_3): δ 1.0-2.5 m (44H, Cy), δ 3.17 t (4H, CH_2 , $|^2J(\text{PH}) + ^4J(\text{PH})| = 8.5$ Hz, $^3J(\text{PtH}) = 18.5$ Hz), δ 7.02 m (3H, Ph). ^1H -NMR (in d_6 -benzene): δ 1.0-2.5 m (44H, Cy), δ 2.93 t (4H, CH_2 , $|^2J(\text{PH}) + ^4J(\text{PH})| = 8.44$ Hz, $^3J(\text{PtH}) = 18.4$ Hz), δ 7.21 m (3H, Ph). $^{31}\text{P}\{^1\text{H}\}$ -NMR (in CDCl_3): δ 48.1 s ($^1J(\text{PtP}) = 2766$ Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (in d_6 -benzene): δ 48.4 s ($^1J(\text{PtP}) = 2771$ Hz). Anal. Calc. for $\text{C}_{32}\text{H}_{51}\text{IPt}$: C, 46.9; H, 6.27. Found: C, 47.3; H, 6.52%.

The chloro complex $(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{PtCl}$ (**1b**) was similarly prepared by using $(\text{COD})\text{PtCl}_2$ (1.00 g, 2.67 mmol) and $1,3\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_4$ (1.33 g, 2.67 mmol). Yield 1.05 g (54%). ^1H NMR (CDCl_3): δ 1.0-2.5 m (44H, Cy), δ 3.10 t (4H, CH_2 , $|^2J(\text{PH}) + ^4J(\text{PH})| = 8.4$ Hz, $^3J(\text{PtH}) = 18.0$ Hz), δ 6.93 m (3H, Ph). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): δ 49.7 s ($^1J(\text{PtP}) = 2835$ Hz). Anal. Calc. for $\text{C}_{32}\text{H}_{51}\text{ClPt}$: C, 52.8; H, 7.06. Found: C, 53.3; H, 7.32%.

Preparation of Pt(2,6-(Cy₂PCH₂)₂C₆H₃)(OSO₂CF₃) (2). To a solution of $\text{Pt}(2,6\text{-(Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{I}$ (300 mg, 0.37 mmol) in CH_2Cl_2 (20 mL) was added a THF solution of silver triflate (126 mg, 0.48 mmol, in 2 mL THF). After filtration of AgI formed in the reaction mixture, the solution volume was reduced to *ca.* 3 mL. Addition of *n*-hexane (10 mL) to the concentrated solution gave white crystalline compounds. Complex **2** for satisfactory microanalysis can be obtained by column chromatography on silica gel with an eluent of CH_2Cl_2 to give colorless crystals from *n*-hexane. The isolated yield of **2** after column chromatography was

87% (268 mg). IR (KBr): $\nu(\text{SO}) = 1174, 1260 \text{ cm}^{-1}$. $^1\text{H-NMR}$ (CDCl_3): δ 1.0-2.5 m (44H, Cy), δ 3.11 t (4H, CH_2 , $|^2J(\text{PH}) + ^4J(\text{PH})| = 8.0 \text{ Hz}$, $^3J(\text{PtH}) = 20.0 \text{ Hz}$), δ 6.94 m (3H, Ph). $^1\text{H-NMR}$ (d_6 -benzene): δ 1.0-2.5 m (44H, Cy), δ 2.71 t (4H, CH_2 , $|^2J(\text{PH}) + ^4J(\text{PH})| = 8.4 \text{ Hz}$, $^3J(\text{PtH}) = 21.2 \text{ Hz}$), δ 6.92 m (3H, Ph). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): δ 53.7 ($^1J(\text{PtP}) = 2749 \text{ Hz}$). $^{31}\text{P}\{^1\text{H}\}$ -NMR (d_6 -benzene): δ 54.3 ($^1J(\text{PtP}) = 2878 \text{ Hz}$). $^{19}\text{F}\{^1\text{H}\}$ -NMR (CDCl_3): δ -78.8 s. $^{19}\text{F}\{^1\text{H}\}$ -NMR (d_6 -benzene): δ -78.4 s. Λ_M (in CH_3NO_2 , $[\text{Pt}] = 1.0 \times 10^{-3} \text{ mol} = 94 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. Anal. Calc. for $\text{C}_{33}\text{H}_{51}\text{F}_3\text{O}_3\text{P}_2\text{PtS}$: C, 47.1; H, 6.11; S, 3.81. Found: C, 46.8; H, 6.43; S, 3.67%.

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