백금 핀서 화합물의 합성 및 Silylcyanation 촉매반응에 대한 응용

김윤태* · 윤명식*,**,†

*호서대학교 제약공학과, **호서대학교 기초과학연구소 (2016년 4월 4일 접수, 2016년 5월 1일 심사, 2016년 5월 24일 채택)

Abstract
A platinum(II) pincer complex composed of two six-membered fused metallacycles was directly synthesized using 1,3-bis(2-pyridyloxy)benzene and K₂PtCl₄. The structure of the complex was elucidated via NMR and X-ray crystallography analysis. The stable complex was formed due to the six-membered fused cycle structure around the Pt(II) center which reduced the bond angle strain. The complex was applied to the silylcyanation reaction of aldehydes and imines and showed an efficient catalytic activity with 99% yield.

Keywords: platinum, x-ray structure, catalyst, silylcyanation, pincer complex

1. Introduction
A variety of organometallic complexes have been prepared by combining terdentate, monoaonic NCN-pincer ligand (NCN = 2,6-bis[(dimethylamino)methyl]phenyl anion)[1]. These pincer complexes have found in numerous applications, such as catalysis, catalyst immobilisation, optical devices and sensor materials[2-6]. The pincer complexes are mainly composed of a bicyclic, fused metallacyle in which the metal (Ni, Pd, Pt, Fe, etc.) is coordinated by two donor heteroatoms such as N and a central anionic benzene ligand, depicted as 1 (Figure 1)[7-11]. These pincer complexes having two five-membered fused metallacycles suffer severe bond angle strain around the metal center.

As a result, this bond angle strain sometime affects the catalytic properties of the pincer complexes. On the other hand, less strained pincer complexes can be synthesized by inserting of “X” species such as O, S, and CH₂ between the central benzene and pyridine rings; as type complex 2 (Figure 1)[12-16]. Thereby, the bond angle strains around the metal center decrease. Previously, we synthesized Pd(II) pincer complex 3 where the bond angle strain around the metal center is minimal[17]. The bond angles between C-Pd-N and N-Pd-Cl are 88.54 and 91.46° respectively which are very close to 90°. This Pd(II) pincer complex 3 showed remarkable catalytic activity in the Heck reaction. On the basis of the minimal angle strain and catalytic activity of the complex, now we have changed the metal center from Pd(II) to Pt(II) to form new pincer complexes 4. Lam and his co-workers have synthesized a series of cyclometalated Pt(II) complexes containing meta-bis(2-pyridoxy)benzene and measured their spectroscopic property[18]. The catalytic activities of the metal complexes, however, were not reported in their study. Furthermore, we have replaced the halide ligand by water to form Pt(II) complex 8 and evaluated its catalytic activity in the silylcyanation reaction of both aldehydes and imines.
2. Materials and Methods

All reactions were carried out under inert atmosphere in dried flask equipped with rubber septum as inlet. Solvent and liquid reagents were transferred by argon flushed syringe or cannula. All reactions were monitored by TLC Merck 60 F 254 pre-coated silica gel plate. Silica gel (Merck 60, 230-400 mesh) was used for column chromatography in air. Nuclear magnetic resonance (NMR) spectra (1H, 13C, 19F NMR) were recorded on a Brucker AM-300 spectrometer. Chemical shifts were reported in δ (ppm) referenced to an internal SiMe4 standard for 1H NMR and chloroform-d (δ 7.26) for 13C NMR. Multiplicities were given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (doublet of triplet), and m (multiplet). HR El-mass spectra were conducted on a JMSAX505WA (JEOL, Tokyo, Japan) and were reported in unit of m/z.

Single crystal X-ray diffraction data for the complex were collected by a Siemens CCD area diffractometer using graphite mono-chromatized Mo-Kα (λ = 0.71073Å) radiation. The structure of the complex was solved by direct methods and refined by full matrix least-squares methods using the SHELX program package with anisotropic thermal parameters for all non-hydrogen atoms.

2.1. Preparation of Pt(II) complexes

The general method adopted for the preparation of the Pt(II) pincer complex 8 is shown in Scheme 1. The synthesis procedure and spectral characterizations of the complexes are described below.

[1,3-Bis(2-pyridyloxy)phenyl]platinum chloride (4). A mixture of 1,3-bis(2-pyridyloxy)benzene (0.14 g, 0.53 mmol), K2PtCl4 (0.22 g, 0.53 mmol), and acetic acid (3 mL) was refluxed for 72 h. The reactions were monitored by TLC. The reaction mixture was cooled to room temperature and the bright yellow solid was filtered off. The pure compound 3 was obtained by sequential washing with H2O, MeOH, and Et2O.

Yield : 0.21 g (80%); Mp: 285-289 °C; 1H NMR (CDCl3, 300 MHz) : δ 7.02 (m, 5H), 7.27 (m, 2H), 7.87 (t, J = 7.2 Hz, 2H), 9.51 (m, 2H); 13C NMR (CDCl3, 75 MHz) : δ 159.7, 153.2, 153.1, 141.2, 125.5, 119.7, 113.3, 102.4; HRMS (FAB) calcd for C16H11N2O2PtCl+ 458.0468, found 458.0471.

[1,3-Bis(2-pyridyloxy)phenyl]aqoplatinum(II) trifluoromethansulfonate (8). A mixture of compound 3 (0.17 g, 0.34 mmol) and silver triflate (88 mg, 0.34 mmol) in dichloromethane (10 mL) was stirred at room temperature. The stirring was continued for 5-7 h to complete the reaction. To remove AgCl, the mixture was filtered through Celite and was washed with CH2Cl2. The filtrate was evaporated by rotary evaporator to give compound 8 as a pale yellow solid.

Yield : 0.19 g (89%); Mp: 238-240 °C; 1H NMR (CDCl3, 300 MHz) : δ 6.93 (d, J = 7.9 Hz, 2H), 7.21 (m, 5H), 7.94 (t, J = 7.1 Hz, 2H), 8.87 (m, 2H); 13C NMR (CDCl3, 75 MHz) : δ 159.5, 153.2, 153.1, 142.2, 125.5, 120.6, 116.1, 113.9, 102.4; HRMS (FAB) calcd for C16H11N2O2Pt(M-H2O-OTf)+ 458.0468, found 458.0473.

2.2. Standard procedure of the Pt(II)-catalyzed silylcyanation of aldehyde and imine

To a mixed solution of the aldehyde or imine (3.6 mmol) and catalyst 8 (0.023 g, 0.036 mmol, 1 mol%) in CH2Cl2 (10 mL) was added trimethylsilyl cyanide (TMSCN) (0.6 mL, 4.5 mmol), and the resulting solution was stirred at room temperature for 5 h. Next, 3N hydrochloric acid solution (10 mL) was added slowly to the mixture and the resulting mixture was stirred for another 1-2 h. Next, it was extracted using CH2Cl2, and the organic part was separated, dried over MgSO4 and evaporated in vacuo. The residue was purified by column chromatography (ethylacetate/petroleum ether) to give a pure cyanohydrin. The conversion was determined by integrating the proton singlets of cyanohydrin and aldehyde, respectively, in the 1H NMR spectrum. The enantiomeric excess was determined by 1H NMR spectroscopy using Eu(hfc)3 as the chiral shift reagent.

3. Results and Discussion

The Pt(II) pincer complex 8 was synthesized according to our previous report[17]. Ligand 7 was treated with K2PtCl4 in refluxing glacial acetic acid for 72 h, which was cooled to give Pt(II) complex 3 as yellow

Figure 1. Pincer complexes composed of five and six-membered metallacycles.
precipitates. The precipitates were isolated by filtration in 80% yield (Scheme 1). The chloroplatinum complex 3 thus obtained was converted to its triflate analogue 8 by treating with silver triflate in dichloromethane for 5-7 h. The platinum complex 8 was characterized by NMR spectroscopic and mass analysis. The CH proton of central benzene ring of ligand 7 disappeared as pincer complex 3 formed, together with concomitant chemical shift changes. A solid structure of the pincer complex 8 was resolved by single-crystal X-ray crystallography for single crystals obtained by slow evaporation of the solvent (dichloromethane/n-hexane = 1/10) (Figure 2a), which clearly shows that its molecular geometry is very similar to the designed structure except for the triflate part. The solid structure of 8 clearly shows that both the pyridine rings and central phenyl are out of the coordination plane and twisted 68.1° as well as 28.6° respectively. The bond angles involving the metal center (89.0-90.3°) are close to 90°, which indicates that the bond angle strain around the metal center expected for the complex type 1 is reduced here in pincer complexes 8.

Interestingly, we found that two water molecules are coordinating to the platinum complex 8. One water molecule is coordinating to Pt(II) center, and another water molecule is also coordinating to this first water molecule bound to the Pt(II). Thereby, it forms a dimeric structure bridging through triflate ion (Figure 2b).

The catalytic activity of pincer complexes 8 was evaluated in the silylcyanylation reaction of aldehydes and imine. A wide variety of Lewis acids including ZnI2, AlCl3, TMSOTf and lanthanides; La(III), Yb(III), Sm(III) complexes were found to catalyze the cyanation of aldehydes and ketones to give cyanohydrins[19-24]. Asymmetric variants of this reaction have been successfully developed using titanium based chiral Lewis acids, which both activate and control the facial selectivity of a metal coordinated aldehyde[25].

Extensive studies were carried out using benzaldehyde as the substrate and TMSCN for silylcyanylation agent with catalyst 8. There was no cyanohydrin formation in the absence of catalyst 8. The effect of solvents on the reaction was also investigated using cyclohexane, CH3Cl, CH3CN, THF, diethyl ether, toluene, benzene, acetone, DMF and DMSO. It was found that CH3Cl was the solvent of choice, and

Table 1. Catalytic Activity of Pt(II) Complex 8 in the Silylcyanylation Reaction of Aldehydes

| Entry | Substrate                      | Conversion (%) |
|-------|--------------------------------|----------------|
| 1     | Benzaldehyde                   | 97             |
| 2     | 4-Methoxybenzaldehyde          | 99             |
| 3     | 4-Methylbenzaldehyde           | 83             |
| 4     | 4-Nitrobenzaldehyde            | 23             |
| 5     | Salicylaldehyde                | 52             |
| 6     | Cinnamaldehyde                 | 96             |
| 7     | Cyclohexanecarboxyaldehyde     | 85             |
| 8     | Isobutyraldehyde               | 99             |
| 9     | Propionaldehyde                | 99             |

Reactions conditions: 3.6 mmol of the substrate in CH2Cl2 (10 mL), 4.5 mmol of TMSCN, 1 mol% of catalyst 8, conversion determined by 1H NMR analysis for the diagnostic peaks: 9.60-10.15 (1H, s, RCHO), 4.30-5.79 (1H, s, RCH(NCN)OH).

1 mol% of catalyst 8 was enough for quantitative transformation of cyanohydrins within 5 h. Reducing the catalyst loading to 0.1 mol% resulted in the lower conversion to cyanohydrins. Under optimized reaction conditions (1 mol% catalyst 8, 1.3 equiv. of TMSCN in CH2Cl2), the silylcyanylation reaction was performed with a variety of aldehydes (Table 1). The results reveal a significant difference in the conversion of aldehyde containing electron donating substituent (entry 2) versus aldehyde substituted with an electron withdrawing nitro group (entry 4); the latter provides less conversion in this procedure. Salicylaldehyde, containing an intramolecular hydrogen bonded carbonyl, also gives a very low conversion of cyanohydrin (entry 5). The aliphatic aldehydes work well (entry 8, 9). Cinnamaldehyde (α,β-unsaturated aldehyde) gives exclusively the 1, 2-addition product with good conversion (entry 6).

To test the catalytic behavior of [Pt] complex 8 for other addition reactions, we investigated the silylcyanylation to imines (Table 2). As
Table 2. Catalytic Activity of 8 in Silylcyanation Reaction of Imine*

| Entry | Substrate | Conversion (%) | Ref. of characterization |
|-------|-----------|----------------|--------------------------|
| 1     |           | 91 (80)        | 31                       |
| 2     |           | 99 (87)        | 32                       |
| 3     |           | 69 (55)        | 33                       |
| 4     |           | 29 (22)        | 34                       |
| 5     |           | 91 (78)        | 35                       |

*Reaction conditions: 3.6 mmol of the substrate in CH₂Cl₂ (10 mL), 4.5 mmol of TMSCN, 1 mol% of catalyst 8, i) aqueous HCl.

found in the case of the aldehydes, an imine containing electron-donating substituent (entry 2) is superior to that of electron-withdrawing substituent, either para to the imine (entry 3) or attached directly to the nitrogen (entry 4). N-Benzylamine gives a good yield of the corresponding α-amino nitrile (entry 1), and the use of the related (R)-α-methylbenzylamine derived imine results in a moderate selectivity (4:1) for the (R,R)-diastereoisomer (entry 5). In the present study, the results indicates that the good to excellent yields obtained with 1 mol% catalyst within 5 h at room temperature, which is comparable to those reported reactions catalyzed by transition metal and lanthanides complexes[26-30]. The X-ray crystal structure further confirmed that there is slight bond angle distortion around the metal center.

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Appendix

Supplementary crystallographic data associated with this paper (CCDC 1063590) can be found in the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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