

백금 핀서 화합물의 합성 및 Silylcyanation 촉매반응에 대한 응용

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Synthesis of a Platinum-Pincer Complex and Application to Catalytic Silylcyanation

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초 록

본 연구에서는 1,3-bis(2-pyridyloxy)benzene과 K_2PtCl_4 를 이용하여 백금을 중심으로 2개의 6원환을 이루는 백금 핀서 화합물을 합성하였다. NMR과 X-ray를 이용하여 구조를 규명하였고 백금원자를 중심으로 이루는 6원환 구조는 angle strain을 감소시켜 안정한 화합물을 형성하였다. 이 화합물을 알데하이드와 이민의 silylcyanation 반응에 적용하여 본 결과 수율 99%까지 나타내는 효과적인 촉매작용을 보여주었다.

Abstract

A platinum(II) pincer complex composed of two six-membered fused metallacycles was directly synthesized using 1,3-bis(2-pyridyloxy)benzene and K_2PtCl_4 . 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, monoanionic 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 metallacycle 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 CH_2 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 similar 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.

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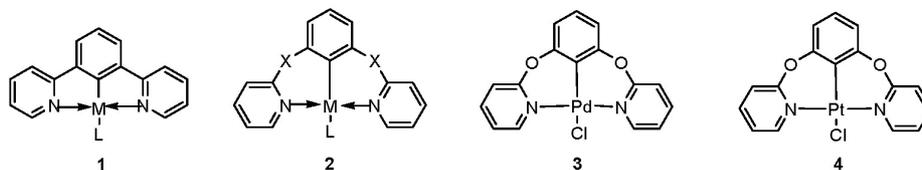


Figure 1. Pincer complexes composed of five and six-membered metallacycles.

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 F₂₅₄ 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 Bruker AM-300 spectrometer. Chemical shifts were reported in δ (ppm) referenced to an internal SiMe₄ standard for ¹H NMR and chloroform-*d* (δ 77.36) 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 EI-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 monochromatized Mo-K α (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.

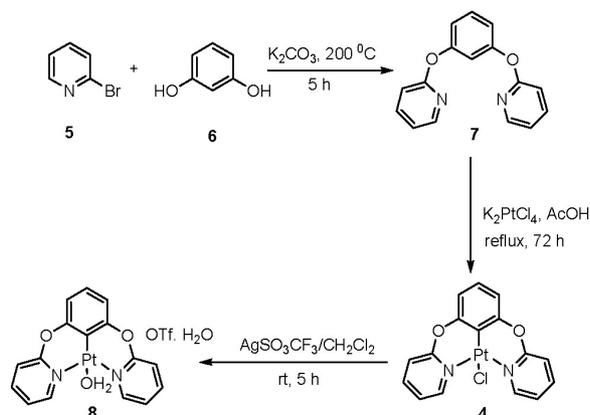
2.1. Preparation of Pt(II) complexes

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, 115.6, 113.3, 102.4; HRMS (FAB) calcd for C₁₆H₁₁N₂O₂Pt(M-Cl)⁺ 458.0468, found 458.0471.

[1,3-Bis(2-pyridyloxy)phenyl]aquaplatinum(II) trifluoromethanesulfonate (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



Scheme 1. Synthesis of Pt(II) pincer complex of 1,3-bis(2-pyridyloxy)benzene.

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 C₁₆H₁₁N₂O₂ Pt(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

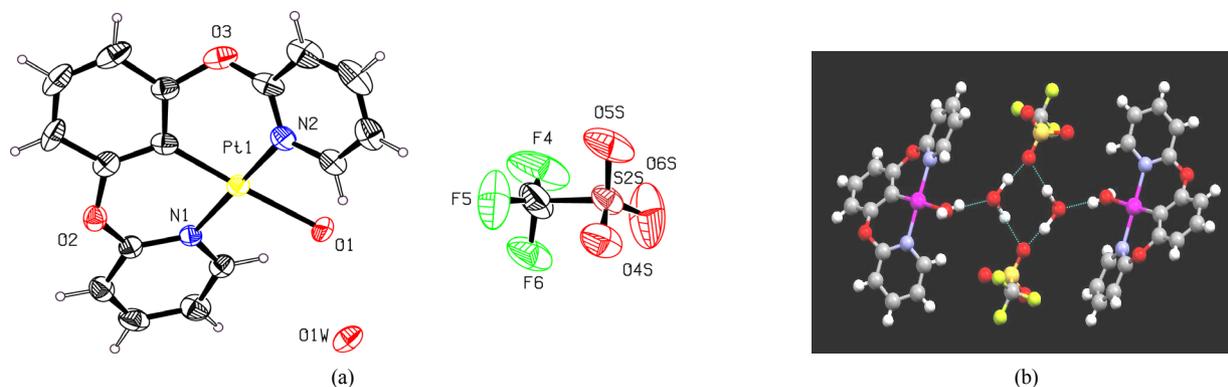


Figure 2. X-ray single crystal structure of the Pt(II) complex **8**; (a) ORTEP plot (50% probability ellipsoids), and (b) ball and stick plot; dimeric structure. The hydrogen atoms are omitted for clarity. Selected bond length (Å) : Pt(1) - C(6) = 1.926(10), Pt(1) - N(2) = 2.004(8), Pt(1) - N(1) = 2.029(7), Pt(1) - O(1) = 2.157(6); selected bond angles (deg) : C(6) - Pt(1) - N(2) = 89.0(4), C(6) - Pt(1) - N(1) = 90.3(4), N(2) - Pt(1) - N(1) = 176.9(3), C(6) - Pt(1) - O(1) = 177.8(4), N(2) - Pt(1) - O(1) = 89.6(3), N(1) - Pt(1) - O(1) = 91.2(3).

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 silylcyanation 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 silylcyanating 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, CH₂Cl₂, CH₃CN, THF, diethyl ether, toluene, benzene, acetone, DMF and DMSO. It was found that CH₂Cl₂ was the solvent of choice, and

Table 1. Catalytic Activity of Pt(II) Complex **8** in the Silylcyanation Reaction of Aldehydes^a

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

^aReaction conditions : 3.6 mmol of the substrate in CH₂Cl₂ (10 mL), 4.5 mmol of TMSCN, 1 mol% of catalyst **8**, ^bconversion determined by ¹H NMR analysis for the diagnostic peaks : 9.60-10.15 (1H, s, RCHO), 4.30-5.79 (1H, s, RCH(CN)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 silylcyanation 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 silylcyanation to imines (Table 2). As

Table 2. Catalytic Activity of 8 in Silylcyanation Reaction of Imine^a

Entry	Substrate	Conversion (%) ^{b,c}	Ref. of characterization
1		91 (80)	31
2		99 (87)	32
3		69 (55)	33
4		29 (22)	34
5		91 (78) (R,R : R,S = 4 : 1)	35

^aReaction conditions : 3.6 mmol of the substrate in CH₂Cl₂ (10 mL), 4.5 mmol of TMSCN, 1 mol% of catalyst 8, ^bconversion determined by ¹H NMR analysis for the diagnostic peaks : 8.38-9.10 (1H, s, ArCH₂NH), 4.40-5.58 (1H, s, ArCH₂(CN)NHR). ^cIsolated yield are given in parenthesis.

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 lanthanide complexes[26-30].

4. Conclusion

In conclusion, we have synthesized a new NCN-Pt(II) pincer complex of 1,3-bis(2-pyridyloxy)benzene by direct cycloplatination with K₂PtCl₄ as the metal source. This Pt(II) pincer complex is composed of two six-membered fused cycles with reduced bond angle strain around the Pt(II) center. The complex enabled catalytic silylcyanation of aldehyde and imine, with a comparable efficiency (up to 99% yield) to the highest values obtained by related transition metal catalysts 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.

References

- G. V. Koten, Tuning the reactivity of metals held in a rigid ligand environment, *Pure Appl. Chem.*, **61**, 1681-1694 (1989).
- M. P. H. Rietveld, D. M. Grove, and G.V. Koten, Recent advances in the organometallic chemistry of aryldiamine anions that can function as n,c,n'- and c,n,n'-chelating terdentate "pincer" ligands : a n overview, *New J. Chem.*, **21**, 751-771 (1997).
- M. Albrecht and G. V. Koten, Platinum group organometallics based on "pincer" complexes: Sensors, switches, and catalysts, *Angew. Chem. Int. Ed.*, **40**, 3751-3781 (2001).
- S. W. Botchway, M. Charnley, J. W. Haycock, A. W. Parker, D. L. Rochester, J. A. Weinstein, and J. A. G. Williams, Time-resolved and two-photon emission imaging microscopy of live cells with inert platinum complexes, *Proc. Natl. Acad. Sci. USA*, **105**, 16071-16076 (2008).
- W. P. To, K. T. Chan, G. S. M. Tong, C. Ma, W. M. Kwok, X. Guan, K. H. Low, and C. M. Che, Strongly luminescent gold(III) complexes with long-lived excited states: High emission quantum yields, energy up-conversion, and nonlinear optical properties, *Angew. Chem. Int. Ed.*, **52**, 6648-6652 (2013).
- H. Zhang, B. Zhang, Y. Li, and W. Sun, Acid-sensitive Pt(II) 2,6-Di(pyridin-2-yl)pyrimidin-4(1H)-one complexes, *Inorg. Chem.*, **48**, 3617-3627 (2009).
- B. Soro, S. Stoccoro, G. Minghetti, A. Zucca, M. A. Cinellu, S. Gladiali, M. Manassero, and M. Sansoni, Synthesis of the first C-2 cyclopalladated derivatives of 1,3-Bis(2-pyridyl)benzene. Crystal structures of [Hg(N-C-N)Cl], [Pd(N-C-N)Cl], and [Pd₂(N-C-N)₂(μ -OAc)]₂[Hg₂Cl₆]. Catalytic activity in the Heck reaction, *Organometallics*, **24**, 53-61 (2005).
- D. J. Cardenas and A. M. Echavarren, Divergent behavior of palladium(II) and platinum(II) in the metalation of 1,3-Di(2-pyridyl)benzene, *Organometallics*, **18**, 3337-3341 (1999).
- M. Q. Slagt, G. R. Miguez, M. M. P. Grutters, R. J. M. K. Gebbink, W. Klopper, L. W. Jenneskens, M. Lutz, A. L. Spek, and G. V. Koten, Synthesis and properties of para-substituted NCN-pincer palladium and platinum complexes, *Chem. Eur. J.*, **10**, 1331-1344 (2004).
- L. A. V. D. Kuil, D. M. Grove, R. A. Gossage, J. W. Zwikker, L. W. Jenneskens, W. Drenth, and G. V. Koten, Mechanistic as-

- pects of the Kharasch addition reaction catalyzed by organonickel(II) complexes containing the monoanionic terdentate aryldiamine ligand system $[C_6H_2(CH_2NMe_2)_2-2,6-R-4]$, *Organometallics*, **16**, 4985-4994 (1997).
11. N. Selander and J. K. Szab, Catalysis by palladium pincer complexes, *Chem. Rev.*, **111**, 2048-2076 (2010).
 12. D. J. D. Geest, B. J. O. Keefe, and P. J. Steel, Cyclometallated compounds. XIII. Cyclopalladation of 2-phenoxy pyridine and structurally-related compounds *J. Organomet. Chem.*, **579**, 97-105 (1999).
 13. B. J. O. Keefe and P. J. Steel, Cyclometallated compounds. XVI. Double cyclopalladations of bis(2-pyridyloxy)naphthalenes. Kinetic versus thermodynamic control of regioselectivity, *Organometallics*, **22**, 1281-1292 (2003).
 14. A. J. Canty, N. J. Minchin, B. W. Skelton, and A. H. White, Cyclopalladation to form planar tridentate [N-C-N]- intramolecular co-ordination systems involving pyridine donor groups, including ligand synthesis and X-ray structural studies, *J. Chem. Soc. Dalton Trans.*, **1987**(6), 1477-1483 (1987).
 15. M. S. Yoon, R. Ramesh, J. Kim, D. Ryu, and K. H. Ahn, Chiral Pt(II)/Pd(II) pincer complexes that show C-H...Cl hydrogen bonding: Synthesis and applications to catalytic asymmetric aldol and silylcyanation reactions, *J. Organomet. Chem.*, **691**, 5927-5934 (2006).
 16. J. S. Fossey and C. J. Richards, Catalysis of aldehyde and imine silylcyanation by platinum and palladium NCN-pincer complexes, *Tetrahedron Lett.*, **44**, 8773-8776 (2003).
 17. M. S. Yoon, D. Ryu, J. Kim, and K. H. Ahn, Palladium pincer complexes with reduced bond angle strain: efficient catalysts for the Heck reaction, *Organometallics*, **25**, 2409-2411 (2006).
 18. B. K.-W. Chiu, M. H.-W. Lam, D. Y.-K. Lee, and W.-Y. Wong, Synthesis, characterization and spectroscopic studies of cyclometallated platinum(II) complexes containing meta-bis(2-pyridoxy) benzene, *J. Organomet. Chem.*, **689**, 2888-2899 (2004).
 19. W. C. Groutas and D. Felker, Synthetic applications of cyano-trimethylsilane, iodotrimethylsilane, azidotrimethylsilane, and methylthiotrimethylsilane, *Synthesis*, **1980**(11), 861-868 (1980).
 20. W. Lidy and W. Sundermeyer, Spaltungsreaktionen des trimethylsilylcyanids, eine neue darstellungsmethode für O-(Trimethylsilyl)cyanhydrine, *Chem. Ber.*, **106**, 587-593 (1973).
 21. R. Noyori, S. Murata, and M. Suzuki, Trimethylsilyl triflate in organic synthesis, *Tetrahedron*, **37**, 3899-3910 (1981).
 22. A. E. Vougioukas and H. B. Kagan, Lanthanides as Lewis-acid catalysts in aldol addition, cyanohydrin-forming and oxirane ring opening reactions, *Tetrahedron Lett.*, **28**, 5513-5516 (1987).
 23. J. A. Vale, W. M. Faustino, P. H. Menezes, and G. F. de Sa, Lanthanide dithiocarbamate complexes: Efficient catalysts for the cyanosilylation of aldehydes, *J. Braz. Chem. Soc.*, **17**, 829-831 (2006).
 24. J. M. Brunel and I. P. Holmes, Chemically catalyzed asymmetric cyanohydrin syntheses, *Angew. Chem. Int. Ed.*, **43**, 2752-2778 (2004).
 25. M. North, Synthesis and applications of non-racemic cyanohydrins, *Tetrahedron Asymmetry*, **14**, 147-176 (2003).
 26. N. H. Khan, R. I. Kureshy, S. H. R. Abdi, S. Agrawal, and R. V. Jasra, Metal catalyzed asymmetric cyanation reactions, *Coord. Chem. Rev.*, **252**, 593-623 (2008).
 27. M. Hayashi, Y. Miyamoto, and T. Inoue, Oguni, N. Enantioselective trimethylsilylcyanation of some aldehydes catalyzed by chiral Schiff base-titanium alkoxide complexes, *J. Org. Chem.*, **58**, 1515-1522 (1993).
 28. Y. Jiang, X. Zhou, W. Hu, L. Wu, and A. Mi, Asymmetric synthesis XXII: Asymmetric catalytic trimethylsilylcyanation of benzaldehyde by novel Ti(IV)-chiral schiff base complexes, *Tetrahedron Asymmetry*, **6**, 405-408 (1995).
 29. Y. Jiang, L. Gong, X. Feng, W. Hu, W. Pan, Z. Li, and A. Mi, Salen-Ti(OR)₄ complex catalyzed trimethylsilylcyanation of aldehydes, *Tetrahedron*, **53**, 14327-14338 (1997).
 30. P. Pitchaimani, K. M. Lo, and K. P. Elango, Synthesis, crystal structures, luminescence properties and catalytic application of lanthanide(III) piperidine dithiocarbamate complexes, *Polyhedron*, **93**, 8-16 (2015).
 31. J. Xia, J. Xu, Y. Fan, T. Song, L. Wang, and J. Zheng, Indium metal-organic frameworks as high-performance heterogeneous catalysts for the synthesis of amino acid derivatives, *Inorg. Chem.*, **53**, 10024-10026 (2014).
 32. V. V. R. Reddy, B. Saritha, R. Ramu, R. Varala, and A. Jayashree, Zn(OAc)₂ · 2H₂O-catalyzed one-pot efficient synthesis of amino nitriles, *Asian. J. Chem.*, **26**, 7439-7442 (2014).
 33. B. Karmakar and J. Banerji, K₂PdCl₄ catalyzed efficient multi-component synthesis of α-aminonitriles in aqueous media, *Tetrahedron Lett.*, **51**, 2748-2750 (2010).
 34. M. L. Kantam, K. Mahendar, B. Sreedhar, and B. M. Choudary, Synthesis of α-aminonitriles through Strecker reaction of aldimines and ketoimines by using nanocrystalline magnesium oxide, *Tetrahedron*, **64**, 3351-3360 (2008).
 35. Y.-L. Hou, R. W.-Y. Sun, X.-P. Zhou, J.-H. Wang, and D. A. Li, Copper(I)/copper(II)-salen coordination polymer as a bimetallic catalyst for three-component Strecker reactions and degradation of organic dyes, *Chem. Commun.*, **50**, 2295-2297 (2014).