

이민에 기초한 질소주개 리간드의 전이금속 착물 합성, 화학적 특성 및 촉매활성

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Synthesis, Chemical Characterization and Catalytic Activity of Transition Metal Complexes Having Imine Based Nitrogen Donor Ligand

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요약. Schiff 리간드인 (Z)-N-((Z)-2-(sec-butylimino)-1,2-diphenylethylidene)butan-2-amine을 벤질과 sec-부틸아민과의 축합반응에 의해 합성하였다. 일 주기 전이금속인 망간(II) 및 니켈(II)과 리간드와의 착물반응을 시도하였다. 리간드 및 착물의 특성을 FTIR, 원소분석 및 열무게분석으로 고체 상태에서, 그리고 NMR (^1H , ^{13}C)로 용액 상태에서의 각각 조사하였다. 두 착물 모두 온화한 조건에서 methylaluminoxane (MAO) 존재 하에 부타디엔 올리고화 반응의 조촉매로 좋은 촉매활성을 보였다.

주제어: Schiff 염기, 올리고화 반응, Methylaluminoxane

ABSTRACT. A Schiff base ligand (Z)-N-((Z)-2-(sec-butylimino)-1,2-diphenylethylidene)butan-2-amine was synthesized by condensation of benzil with sec-butyl amine. Complexation of the ligand was carried out with first row transition elements, manganese(II) and nickel(II). Ligand and complexes were characterized by FTIR, elemental analysis and thermogravimetric analysis in solid state and by NMR (^1H , ^{13}C) in solution form. Both the complexes demonstrate good catalytic activity for butadiene oligomerization under mild conditions with methylaluminoxane (MAO) as co-catalyst.

Keywords: Schiff base, Oligomerization, Methylaluminoxane

INTRODUCTION

Over the past years, there has been much development of the application in homogeneous catalysis of transition metal complexes containing nitrogen-donor chelating ligands. Among them, 2,2'-bipyridine,¹ 1,10-phenanthroline,² oxazoline-based ligands,³ 8-iminoquinoline derivatives,⁴ 2,6-bis(imino)pyridine ligands,⁵ 2,6-bis(imino)phenoxy ligands,⁶ N-(2-pyridyl)benzamide based ligands⁷ and naphthalene based ligands,⁸ have attracted particular attention.

From the literature, a correlation between the transition metal and the nature of the ancillary ligand spontaneously arises, i.e. ligands with a cyclopentadienyl moiety are generally associated with early transition metals, while non-carbon donor ligands are preferentially related to late transition metals.⁹

Ziegler in 1954 proposed first time the selective dimerization reaction.¹⁰ Later the selectivity was improved by the modification of the catalyst and the optimization of reaction conditions.¹¹⁻¹⁴ The production of polyolefins is one of the most important areas in chemical industry, which estimated worldwide

annual production of 80 million tons (in 2000). World has witnessed a 100% increase in production volume over the past decade only.¹⁵

SHOP-process (Shell Higher Olefin Process) accounts for about 35% of the annual worldwide production of α -olefins made through ethylene oligomerization.¹⁶ Nickel and palladium complexes based on α -diimines ligands have been reported to have good activity and selectivity for oligomerization of ethylene. But Nickel is a better catalyst as compared to palladium.¹⁷

In 1998 extremely active iron and cobalt based catalysts bearing 2,6-bis(imino)pyridyl ligands for the linear polymerization of ethylene were independently reported by Brookhart and Gibson.¹⁸ By tuning the steric and electronic properties of

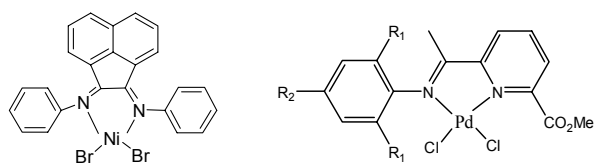


Fig. 1. Complex models of ethylene oligomerization catalysts

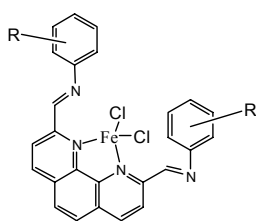


Fig. 2. Iron complex investigated for Oligomerization of ethylene.

the ligand, the catalytic product of these metal complexes varied from polyethylene to oligomers in which both the catalytic activity and selectivity of α -olefins were highly interesting.

Extending the iron complexes including other tridentate ligands, however, commonly lead to lower catalytic activity for ethylene oligomerization and polymerization.¹⁹ In scanning for suitable metal complexes, the late transition metal complexes ligated by 2,9-bis(imino)-1,10-phenanthrolyl ligands have also been investigated. Nickel and cobalt complexes show good catalytic activities as compared to iron and palladium.

EXPERIMENTAL

General

Melting points were determined in a capillary tube using elector-thermal melting point apparatus model MP-D Mitamura Riken Kogyo (Japan). Infrared spectra were recorded as KBr discs on Bio-Rad Elmer 16 FPC FT-IR. ¹H and ¹³C NMR spectra were recorded on Jeol JNM-LA 500 FT-NMR. Si(CH₃)₄ was used as internal reference. GC-MS analysis was carried out by Agilent GC-MS. Thermal analysis was carried out on Perkin-Elmer Thermal Analyzer.

Synthesis

(Z)-N-((Z)-2-(sec-butylimino)-1,2-diphenylethylidene)butan-2-amine. Ligand was synthesized by mixing 2.1 g (0.01 mol) of benzil, 2.02 mL (0.02 mol) of secondary butyl amine and catalytic amount of para toluene sulphonic acid in acetone.²¹ Reaction was carried out in two neck round bottom flask for 48 hours under refluxing and constant stirring. Thick liquid was obtained which was treated at low temperature to have a white solidified material with 73% yield. Washing was given with acetone/dichloromethane (1:1) mixture. M.p 184 °C; Elemental analysis % Calc. (found): Carbon 82.5 (81.5), Nitrogen 8.75 (7.81), Hydrogen 8.75 (7.91); ¹H-NMR (CD₃OD): δ (ppm) 7.75-7.60 (m), 3.04-2.94 (m), 1.65 (q, 4H), 1.21 (d, 6H), 0.83 (t, 6H); ¹³C-NMR (CD₃OD): δ (ppm) 173.1, 132.7, 132.6, 129.3, 128.7, 59.2, 30.5, 20.3, 10.0; FT-IR (KBr): ν (cm⁻¹) 3054, 2960, 2926, 1636, 1590; Thermogravimetric analysis: T_i, 180 °C T_f, 460 °C, Residual mass % Calc. (found) 0.00 (0.056).

[LMnCl₂(H₂O)₂]. Manganese complex was synthesized by

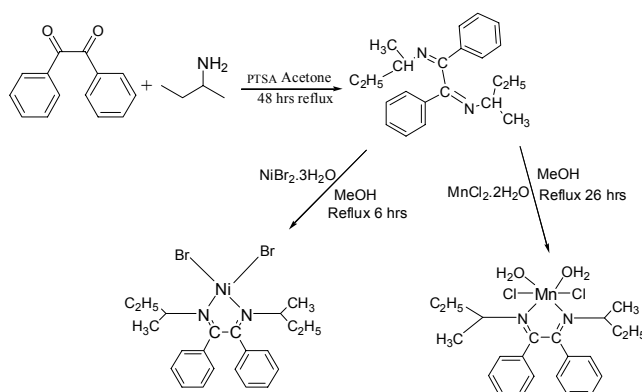


Fig. 3. Synthetic scheme of ligand and its complexes

mixing 0.3 g (0.93 mmol) of ligand with 0.151 g (0.93 mmol) of MnCl₂·2H₂O in dry methanol and argon atmosphere. Color change was observed after 3 hours and reaction was proceeded for further 23 hours to completion. Reaction was carried out in two neck round bottom flask with constant magnetic stirring under reflux. Resulting brown colored solution was rotary evaporated to get a brown colored solid which was purified with dichloromethane. Yield 71%; M.p 153 °C; Elemental analysis % Calc. (found): Carbon 54.77 (54.82), Nitrogen 5.8 (4.98), Hydrogen 6.8 (5.96); ¹³C-NMR (CD₃OD): δ (ppm) 175.6, 132.6, 131.5, 129.1, 127.8, 56.9, 29.2, 20.4, 10.8; FT-IR (KBr): ν (cm⁻¹) 3510-3245, 3057, 2967, 2926, 1655, 1586; Thermogravimetric analysis: T_i, 100 °C T_f, 820 °C, Residual mass % Calc. (found) 26.16 (26.09).

[LNiBr₂]. Nickel complex was synthesized by mixing 0.3 g (0.93 mmol) of ligand with 0.255 g (0.93 mmol) of NiBr₂·3H₂O in methanol and was refluxed for 6 hours. Light green colored product was separated as filtrate and unreacted material was separated as residue. After rotary evaporation washing was given with dichloromethane. Yield 80%; M.p 215 °C; Elemental analysis % Calc. (found): Carbon 49.02 (49.53), Nitrogen 5.19 (5.30), Hydrogen 5.19 (5.74); ¹³C-NMR (CD₃OD): δ (ppm) 175.8, 132.8, 132.3, 129.0, 127.8, 57.2, 28.8, 19.9, 10.5; FT-IR (KBr): ν (cm⁻¹) 3073, 2966, 2930, 1657, 1589; Thermogravimetric analysis: T_i, 207 °C T_f, 860 °C, Residual mass % Calc. (found) 13.87 (15.33).

Catalytic Activity

Oligomerization of Butadiene. Oligomerization of butadiene was carried out in 200 mL Schlenk-type glass reactor equipped with a magnetic stirrer.²² 5 μ mol of nickel complex was added in the reactor and it was made airtight with the help of rubber septum. After evacuating air and moisture from the reactor for about 30 minutes with argon, methylaluminoxane (MAO) and 30 mL toluene were added with syringe. Activity was carried out at room temperature and pressure with Al/M ratio of 500.

Butadiene was continuously flown through the glass reactor for about 30 minutes and then first sample was taken for analysis on GC-MS. Second sample was taken after 60 minutes and the third after 90 minutes. After 90 minutes the reaction was stopped with acidified ethanol. Same procedure was adopted for manganese complex.

RESULTS AND DISCUSSION

^1H NMR data of the ligand was recorded in deuterated methanol. In the ligand there are basically two types of protons, aliphatic and aromatic. Aromatic protons give a multiplet in the region 7.60 - 7.75 ppm. The peak of protons present at carbon 9 split into a doublet at 1.21 ppm with coupling constant value of 6.3 Hz due to protons present in vicinity of these protons. Protons of the methyl group at carbon number 8 provide a triplet at 0.83 ppm with coupling constant 7.5 Hz due to the presence of two methylenic protons at carbon 7. Protons of carbon 7 and 6 offer a quintet and multiplet respectively. ^1H NMR data of complexes give overlapping signals due to paramagnetic behaviour of the metals involved so their structure was evaluated with ^{13}C NMR data and other techniques.

^{13}C NMR spectra of the ligand as well as complexes were recorded in deuterated methanol. Nine different carbon atoms are present in the ligand, maximum downfield carbon is C-9 because it is attached with electronegative nitrogen atom of the ligand which will withdraw electron density from the carbon atom and will force it downfield, downfield shielding will also increase due to the attachment with electron withdrawing phenyl group and will provide a signal downfield at 173.1 ppm. All the other carbon atoms in the ligand appear at the normal positions. ^{13}C NMR spectra of the complexes show characteristic differences from the ligand. C-6 which gives a signal at 59.2 ppm moves up field 2 - 3 ppm in both the complexes due to increased electron density around this carbon after the complexation of nitrogen to the metal. As the nitrogen donates the electron density to the metal it becomes bare from electron density as a result the electron donating methyl and ethyl groups will donate extra electron density to compensate the loss.

Infrared spectroscopic data was determined with the help of KBr disk and recorded with a range of $400\text{ cm}^{-1} \sim 4000\text{ cm}^{-1}$. FT-IR data was recorded for starting material i.e. benzil, ligand

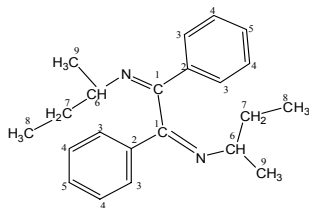


Fig. 4. ^1H and ^{13}C -NMR numbering scheme of L.

and its complexes. Benzil gives a characteristic carbonyl peak at 1681 cm^{-1} which disappears in the ligand proving the conversion of both the carbonyl groups. There are no aliphatic protons in the benzil but they appear in the ligand due to attachment of sec butyl group. Ligand gives a peak of imine group at 1636 cm^{-1} conforming the formation of imine bond. Absence of any peak in the region $3300\text{ cm}^{-1} \sim 3500\text{ cm}^{-1}$ conforms the purity of the ligand from any impurity of sec butyl amine. In manganese and nickel complexes the peak at 1636 cm^{-1} is shifted toward higher wave number 1655 cm^{-1} and 1674 cm^{-1} values respectively indicating the strengthening of carbon nitrogen double bond. This happens because, as the nitrogen donates its electron density to the metal it becomes electron deficient, to fulfill this loss of electrons, electrons come from electron donating methyl and ethyl groups present on imine carbon resulting in the increased strength of carbon nitrogen double bond. Another reason may be the donation of electron density from metal to π^* orbitals of the ligand which are empty, resulting in an increased strength of carbon nitrogen bond.²⁰

Manganese complex contains coordinated water and gives a broad band in the 3500 cm^{-1} region and for the nickel complexes with no coordinated water this region is clear from any kind of peak. The peaks for Aromatic-H are present in the region above 3000 cm^{-1} in both the complexes ligand and starting material. The peaks for resonating $-\text{C}=\text{C}-$ of the ring are present in the region $1581\text{ cm}^{-1} - 1599\text{ cm}^{-1}$ in all the compounds. Aliphatic-H of the sec butyl group gives peaks in the region around 2900 cm^{-1} .

TGA data was recorded at $20\text{ }^\circ\text{C}/\text{min}$. The ligand and complexes were heated at $50\text{ }^\circ\text{C}$ for 0.1 minute to remove any absorbed moisture. All the thermograms were recorded in an oxidizing atmosphere of oxygen. At the end the residual mass of metal oxides gave best information about the amount of the metals in the complexes.

Catalytic activity of both the complexes was carried out at room temperature and pressure using toluene as a solvent and methylaluminoxane (MAO) as cocatalyst in respect of oligomerization of butadiene. Concentration of the catalyst used was $5\text{ }\mu\text{mol}$ and Al/M ratio was selected to be 500. GC was first calibrated for butadiene and toluene peaks. After carrying out the activity toluene was checked for oligomers. Mass spectrum of the new peaks in gas chromatogram gave molecular ion peaks at m/z 281, 279, 120, and 108 values conforming the formation of oligomers. Catalytic activity of the sample taken after 30 minutes is $1.1786 \times 10^5\text{ g h}^{-1}\text{mol}^{-1}$, it decreases to $5.2924 \times 10^4\text{ g h}^{-1}\text{mol}^{-1}$ after 60 minutes and after 90 minutes it was found to be $3.0951 \times 10^4\text{ g h}^{-1}\text{mol}^{-1}$. Activity of the manganese complex was found to be $4.9482 \times 10^4\text{ g h}^{-1}\text{mol}^{-1}$, $2.8549 \times 10^4\text{ g h}^{-1}\text{mol}^{-1}$ and $1.1464 \times 10^4\text{ g h}^{-1}\text{mol}^{-1}$ after 30, 60 and 90 minutes respectively.

SUMMARY

Newly synthesized complexes were checked for their catalytic activities in respect of butadiene oligomerization using methylaluminumoxane as co-catalyst at room temperature and pressure. It was observed that nickel complex shows better catalytic activity than manganese complex. Catalytic activities of both the complexes decrease from 30 to 90 minutes. Higher temperature and pressure may improve the activity and selectivity in future studies.

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