Novel cycloaurated gold(III) complexes and their effects on styrene polymerization

Murat Emre Hanhan

Published online: 8 February 2011

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Abstract Novel cycloaurated gold(III) complexes were prepared by using Schiff bases with different substituents. Effects of the synthesized gold(III) complexes and substituent groups on styrene polymerization were investigated. As a result of these investigations, it was observed that gold(III) complexes could not catalyze polymerization reaction without addition of a co-catalyst like NaBAR'_4 ($\text{Ar}'=3,5\text{-bis(trifluoromethyl)phenyl}$). All ligands and complexes were characterized by using ^1H nuclear magnetic resonance (NMR), ^{13}C -NMR, LC-MS, elemental analysis and FT-IR techniques. The architecture of the polymer was determined as an atactic or syndiotactic polymer by using ^{13}C -NMR and DSC techniques. Molecular weights of the polymers were analyzed by using gel permeation chromatogram (GPC).

Keywords Gold(III) · Cycloauration · Styrene polymerization

Introduction

Cyclometallation reaction of gold(III) is one of the most important reactions of direct C-H bond activation. In 1989, Constable and Leese discovered first cycloauration by using 2-phenylpyridine [1]. Applications of organogold chemistry have been explored by Hashmi [2–4]. Organic derivatives of both Au(I) and (III) ions were reported in the review and in more recent papers [5–13].

Polystyrene is a hard plastic and more common in our everyday life. The stereoregular state of the polymer is important because it determines the crystallinity and physical properties of the resulting polymer. In general, transition metals are used for styrene polymerization in radicalic polymerization reaction and polystyrene obtained are generally isotactic reach atactic form [14]. But syndiotactic polystyrene (s-PS) is more useful than atactic polystyrene (a-PS) with a high melting point of $\sim 270^\circ\text{C}$, a glass transition temperature similar to atactic polystyrene, a fast crystallization rate, a high modulus of elasticity and an excellent resistant to heat and chemical agents [15]. Because of these properties, an immediate commercialization of syndiotactic polystyrene was successfully performed by the Idemitsu Kosan Company in a semi-commercial plant of approximately 5,000 t/year in Chiba/Japan and by The Dow Chemical Company, based on a pilot plant in Midland, Michigan. The first commercial s-PS plant worldwide at a capacity of about 36,000 t/year in Schkopau, Germany opened in 1999, and continued by Idemitsu Kosan in a modernized production facility in Chiba, Japan, in 2006 [16]. In automotive systems, s-PS can be applied in power distribution centers under the hood, in electrical lighting, and electronics, s-PS can be used successfully for connectors, plugs and sockets, glass-fiber-reinforced and color-stabilized s-PS grades are materials for iron skirts and at least very promising markets of s-PS are food and water contact applications [17]. Especially half-metallocene transition metal complexes are very effective catalysts to synthesize s-PS [18, 19]. Although, gold complexes used for a wide array of transformations, there are few reports on the usage of gold complexes for polymerization reactions. In 2008, Perez and co-workers highlighted that polymerization mechanism of styrene with gold—carbene complexes is not working without using a co-catalyst like NaBAR'_4 . Their

M. Emre Hanhan (✉)
Department of Chemistry, Zonguldak Karaelmas University,
Zonguldak 67100, Turkey
e-mail: emrehanhan@karaelmas.edu.tr

M. Emre Hanhan
e-mail: emrehanhan@hotmail.com

reaction results showed that their polymerization mechanism was cationic type [20]. But they did not explain the role of gold center.

In this work, we synthesized three cycloaurated gold(III) complexes to investigate their catalytic activity and reaction mechanism on styrene polymerization with using NaBAR'_4 as a co-catalyst. As a result, when styrene is alone with NaBAR'_4 , reaction resulted with isotactic to reach atactic polystyrene, but when gold(III) complexes are added to the reaction, the polymer we gained was syndiotactic which is more valuable than atactic form.

Synthesis and characterization

All of the synthesized ligands and complexes (Fig. 1) were characterized with a combination of elemental analysis, LC-MS, ^1H and ^{13}C nuclear magnetic resonance (NMR) techniques. All compounds elemental analysis results and mass analysis results are suitable with theoretical values.

FT-IR spectra of the complexes gave us important information about complexation. A comparison was made between ligands and their complex forms. Shifting frequency of $\text{C}=\text{N}$ double bond of ligands with complexation, ranging from $\sim 1,600$ to $\sim 1,700\text{ cm}^{-1}$ displays out the coordination of ligand to the metal. ^1H -NMR gave us more important evidences about complexation than FT-IR. After complexation, H(4) proton shifts to downfield because H(4) proton is located near to the halogens. In the spectrums of L1 and AuL1, $\text{R}=\text{CH}_3$ peak was seen at 2.1 ppm. In AuL2's spectrum, the effect of strongly electronegative CF_3 group was seen clearly. H(1) proton, which is patient from CF_3 group, split up into two shifts from 7.89 to 7.72 ppm. This shifting implies that after coordination to metal center, electronegativity effect of CF_3 decreases. In the spectrum of L3 and AuL3, $\text{R}=\text{H}$ peak is seen at 8.22 ppm in the ligand and 9.12 ppm in the complex. Shifting of proton to downfield displays the coordination of the ligand to the central metal atom.

Catalytic effects of complexes on styrene polymerization

In the first series of experiments, L1Au–L3Au complexes were employed in catalytic amounts in bulk polymerization

Fig. 1 Synthesized Au(III) complexes

reactions involving styrene. Under these reaction conditions, no polymerization was observed. When 1 equiv of NaBAR'_4 was added to neat styrene solution as a halide scavenger, sudden polymerization was observed. To determine the effect of NaBAR'_4 , blank experiments were carried out. No reaction was observed when L1–L3 ligands were used as catalyst without metal center. Interestingly, NaBAR'_4 alone with styrene gave polystyrene with high yield a-PS (Table 1; run nos., 1–5). When gold complexes added to the reaction media s-PS was formed (Fig. 2; Table 1; run nos., 6–20)

After these results were evaluated, series of experiments were conducted at room temperature with different solvents and results. Bulk polymerization was carried out at different catalyst concentrations but conversion did not pass 25% yield. Polymerization reactions were traced for 48 h and it was observed that polymerization reactions finalized at the end of 24th hour. Therefore we carried out several experiments in the presence of co-solvent. When toluene and chloroform was used as a co-solvent, conversion occurred in 24 h. When toluene was used, PDI value of polymers were recorded under 2.0 but yields of polymerization reactions were pretty less (ranging from 2% to 5% within 5 h; Table 1, run nos., 10, 15, 20). Maximum yields of polymerization reactions were ranging from 35% to 50% after 24 h. When chloroform was used as a co-solvent, conversion increased to 100%, although the polydispersity was also higher than both bulk and toluene containing experiments. Conversion was inhibited completely after 24 h when THF or acetonitrile was added to the polymerization media. All complexes yielded syndiotactic polystyrene.

Characterization of polymers

The number and weight-average molecular weights (M_n and M_w) were determined by GPC in CHCl_3 as calibrated with polystyrene standards. The triad tacticities of polymers were determined by ^{13}C -NMR spectra in deuterated chloroform.

^1H -NMR is very useful to identify polystyrene. Chemical shifts between 6.39 and 7.42 ppm are aromatic hydrogen signals. The 1.72–2.43 ppm are methyne hydrogen signals and chemical shifts between 0.97 and 1.76 ppm are methylene hydrogen signals in polystyrene [21].

Figure 3 shows the comparison ^{13}C -NMR spectrums of polystyrene in CDCl_3 solution with catalyst and without catalyst. All spectrums were analyzed in terms of triads. Three main peaks left to right in Fig. 3 were assigned to isotactic triad (mm), heterotactic triad (mr), and syndiotactic triad (rr), respectively [22]. When we did not use a catalyst, the isotactic peak (mm) seen as a major peak and the polymer obtained as isotactic reach atactic. On the other hand, when

Table 1 Styrene polymerization datas^a induced by L1Au–L3Au and NaBAR₄

Run no.	Catalyst	Styrene/ml	Co-solvent	TON ^b	TOF	M _n ^c	M _w ^c	PDI ^c	Tacticity
1	–	2	None	77	385	9184	20205	2.2	a-PS
2	–	5	None	128	640	11254	30116	2.7	a-PS
3	–	10	None	149	745	13194	31666	2.4	a-PS
4	–	2	PhMe	92	460	6428	16713	2.6	a-PS
5	–	2	CHCl ₃	254	1270	10142	25355	2.5	a-PS
6	L1Au	2	None	80	450	11216	26918	2.4	s-PS
7	L1Au	5	None	100	500	14772	32388	2.2	s-PS
8	L1Au	10	None	125	625	16391	29504	1.8	s-PS
9	L1Au	2	PhMe	75	375	7732	14691	1.9	s-PS
10	L1Au	2	CHCl ₃	375	1875	12713	40682	3.2	s-PS
11	L2Au	2	None	105	525	19388	40715	2.1	s-PS
12	L2Au	5	None	118	590	21617	49719	2.3	s-PS
13	L2Au	10	None	145	725	23916	55007	2.3	s-PS
14	L2Au	2	PhMe	125	625	9721	19442	2.0	s-PS
15	L2Au	2	CHCl ₃	625	3125	17530	50837	2.9	s-PS
16	L3Au	2	None	102	510	9152	20134	2.2	s-PS
17	L3Au	5	None	109	545	10322	19612	1.9	s-PS
18	L3Au	10	None	116	580	10932	24051	2.2	s-PS
19	L3Au	2	PhMe	50	250	7122	12820	1.8	s-PS
20	L3Au	2	CHCl ₃	125	325	11367	32584	2.8	s-PS

^a Equimolar mixtures of L1Au–L3Au and NaBAR₄ (1×10^{-3} mmol), [Styrene]/[Au]=2,500 when 2 ml of styrene employed

^b Isolated yield after precipitation with methanol
Determined by GPC using polystyrene standards.

we used Au catalyst, the stereoregularity of polymer changed and syndiotactic (rr) peak seen as a major peak.

Figure 4 shows the DSC thermogram of PS obtained by using L2Au as catalyst (Table 1, entry 13) and using without catalyst (Table 1, entry 3). Experiment without catalyst, the glass transition temperature ($T_g=105^\circ\text{C}$) was obtained from the curve. No sharp melting peak above 200°C was observed. This indicates that the resulting polymer is amorphous. Also the melting points at 270 and 240°C were observed in the syndiotactic and isotactic polystyrene, respectively. No melting point was observed for polystyrene

suggesting that the obtained polymer was atactic. Moreover, polystyrene obtained with using catalysts, a melting point at 266°C was observed which indicates that the synthesized polystyrene is in crystalline and syndiotactic form.

Experimental

General

All reactions were performed under dry, oxygen-free, nitrogen atmosphere. ^1H and ^{13}C -NMR spectra were recorded at room temperature in CDCl_3 on a Bruker/BioSpin NMR 300 MHz with SiMe_4 (0.0 ppm) as internal reference. Elemental analysis was performed on a LECO CHNS-932. Melting points were measured on a Buchi Melting Point B-540 apparatus and they are uncorrected. FT-IR spectra were recorded on a Jasco 300E spectrometer with KBr palletes in the $4,000\text{--}400\text{ cm}^{-1}$ range. Atmospheric pressure chemical ionization mass spectra were recorded with an AGILENT 1100 MS LC-MS mass spectrometer. Molecular weights and molecular weight distributions were determined with a Knauer model gel permeation chromatograph (GPC) with CHCl_3 as eluent and calibration was conducted with polystyrene standards. Differential scanning calorimetry (DSC) was obtained on Perkin Elmer Diamond DSC instrument under a nitrogen atmosphere with a heating/cooling rate of $20^\circ\text{C}/\text{min}$ of NaBAR₄ was synthesized according to the reference [23].

Fig. 2 Effect of Au(III) catalyst on styrene polymerization

Fig. 3 Comparative ^{13}C -NMR spectrum of polystyrene

Preparation of ligands, general procedure

One millimole of acetylpyridine, pyridinecarboxyaldehyde, or acetophenone was dissolved in 2 ml ethanol. Two millimoles aniline and 30 ml of toluene were added dropwise to the above solution. In order to remove water from the solution, a Dean–Stark apparatus was used and resulting solution was refluxed for 2 h. Precipitation was accomplished by cooling the mixture to room temperature. The precipitate (L1–L3) was isolated by filtration and then it was washed with cold methanol and finally it was dried under vacuum.

(*E*)-*N*-(1-Phenylethylidene)benzenamine (L1)

Yield 79%. M.p. 122°C. Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{N}$: C, 86.43; H, 6.51; N, 7.06. Found, C, 86.12. H, 6.71. N, 7.17. ^1H -NMR (DMSO- d_6): δ 2.11 (s, 3H), 6.90 (m, 2H), 7.12 (m, 2H), 7.25 (m, 2H), 7.39 (m, 2H), 7.48 (m, 2H) ppm. ^{13}C -NMR (DMSO- d_6): δ 17.531, 119.44, 124.64, 123.21, 127.25, 128.35, 128.65, 130.45, 139.55, 151.83, 165.36 ppm. FT-IR (KBr, ν , cm^{-1}) 1630 (C=N). LC-MS m/z 218 (+ Na^+).

(*Z*)-*N*-(2,2,2-Trifluoro-1-phenylethylidene)aniline (L2)

Yield 84%. M.p. 138°C. Anal. Calcd for $\text{C}_{14}\text{H}_9\text{F}_3\text{N}$: C, 67.11; H, 4.41; N, 5.61. Found, C, 67.47. H, 4.04. N, 5.62. ^1H -NMR (DMSO- d_6): δ 6.75 (m, 2H), 6.86 (m, 2H), 6.95 (m, 1H), 7.24 (m, 1H), 7.58 (m, 2H), 7.89 (m, 2H) ppm. ^{13}C -NMR (DMSO- d_6): δ 120.25, 120.94, 125.18, 128.51, 129.88, 130.53, 131.25, 132.04, 151.51, 158.04 ppm. FT-IR (KBr, ν , cm^{-1}) 1598 (C=N). LC-MS m/z 272 (+ Na^+).

(*E*)-*N*-Benzylideneaniline (L3)

Yield 79%. M.p. 114°C. Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}$: C, 85.31; H, 6.88; N, 7.81. Found, C, 85.68. H, 6.64. N, 7.69. ^1H -NMR (DMSO- d_6): δ 7.18 (m, 6H), 7.37 (m, 2H), 7.48 (m, 2H), 8.22 (s, 1H) ppm. ^{13}C -NMR (DMSO- d_6): δ 126.62, 129.42, 129.51, 132.53, 137.18, 153.47, 161.11 ppm. FT-IR (KBr, ν , cm^{-1}) 1645 (C=N). LC-MS m/z 204 (+ Na^+).

Preparation of complexes, general procedure

A solution of the ligand (L1–L3; 1.00 mmol) in CH_3CN (5 ml) was added to a solution of HAuCl_4 (1.00 mmol) in H_2O (20 ml), forming a yellow suspension (Fig. 1). The suspension was stirred at room temperature for 2 h and a yellow solid was collected by filtration. After the precipitate was washed with H_2O and a small amount of diethyl ether, it was suspended in mixed $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (50 ml; 1/5, v/v). The suspension was stirred at room temperature for 10 min, and then it was heated at reflux for an hour. The reaction mixture was cooled to room temperature. After the filtration of this mixture, obtained precipitate was washed with H_2O . The precipitate was extracted with hot acetone or CH_2Cl_2 , and the extract was filtered through filter paper. The solvent was removed by evaporation under vacuum and the

Fig. 4 Comparative DSC curve of polystyrene

residual solid (AuL1–AuL3) was soaked with a small amount of pre-cooled acetone and then hexanes.

[AuL1], [AuCl₂(L1)], yield 58%. M.p. 233°C (decomposition). Anal. Calcd for C₁₄H₁₂AuCl₂N: C, 36.39; H, 2.62; N, 3.03. Found, C, 37.14. H, 2.33. N, 3.41. ¹H-NMR (DMSO-d₆): δ 2.11 (s, 3H), 7.07 (m, 2H), 7.33 (m, 2H), 7.49 (m, 2H), 7.63 (m, 2H), 7.91 (d, 1H) ppm. ¹³C-NMR (DMSO-d₆): δ 18.51, 121.24, 124.64, 128.31, 129.89, 129.30, 130.93, 135.63, 141.16, 152.09, 166.42 ppm. FT-IR(KBr, ν, cm⁻¹) 1702 (C=N). LC-MS *m/z* 484 (+Na⁺).

[AuL2], [AuCl₂(L2)], yield 69%. M.p. 212–214°C (decomposition). Anal. Calcd for C₁₄H₉AuCl₂F₃N: C, 32.58; H, 1.76; N, 2.71. Found, C, 32.82. H, 1.54. N, 2.44. ¹H-NMR (DMSO-d₆): δ 6.89 (m, 1H), 6.97 (m, 2H), 7.12 (t, 1H), 7.59 (m, 1H), 7.83 (d, 2H), 8.07 (d, 2H) ppm. ¹³C-NMR (DMSO-d₆): δ 160.31, 153.74, 134.26, 133.22, 132.92, 131.25, 130.97, 130.32, 126.27, 122.93, 122.14 ppm. FT-IR(KBr, ν, cm⁻¹) 1716 (C=N). LC-MS *m/z* 514 (+Na⁺).

[AuL3], [AuCl₂(L3)], yield 77%. M.p. 247°C (decomposition). Anal. Calcd for C₁₃H₁₀AuCl₂N: C, 34.84; H, 2.25; N, 3.13. Found, C, 35.02; H, 1.99; N, 3.38. ¹H-NMR (DMSO-d₆): δ 9.12 (s, 1H), 7.92(d, 1H), 7.76 (d, 1H), 7.57 (m, 4H), 7.38 (m, 3H) ppm. ¹³C-NMR (DMSO-d₆): δ 163.72, 154.21, 138.10, 135.61, 133.70, 131.21, 130.88, 130.11, 127.22 ppm. FT-IR(KBr, ν, cm⁻¹) 1708 (C=N). LC-MS *m/z* 446 (+Na⁺).

Polymerization reactions

In a 50 ml ampoule, equipped with a magnetic stir bar, 1 × 10⁻³ mmol of L1Au–L3Au were introduced along with 1 equivalent of NaBAR₄. The co-solvent and styrene were added via syringe and the mixture was stirred at room temperature. The initial brownish color mixture readily converted into a colorless mixture. At the end of the reaction, addition of 20 ml of methanol into this colorless mixture induced the precipitation of the polymer. The polymer was separated by filtration and washed with two portions of MeOH. Finally, the polymer was dried first under vacuum and later in the oven at 100°C for 12 h before isolated yield was calculated.

Conclusions

It's already known that, gold is very effective for both homogeneous and heterogeneous catalysis. But effects of gold on polymerization reactions are not explored. In conclusion, we have found that styrene can be polymerized

in the presence of gold(III) complexes and NaBAR₄. Collected results seem very interesting because gold catalysts did not affect the yield of reaction. But significantly they affect to the stereoregularity of the polymer. The problem is high polydispersity values and low yields of the resulting polymers. This problem can be achieved by using different ligand systems. Results are very promising to use gold catalysts in polymerization reactions.

Acknowledgments We gratefully acknowledge financial support for this work from TUBITAK, 108T240, Turkey.

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