

Bis-(thio)ethers as chelating ligands for the Pd-catalyzed alternating CO/4-*tert*-butylstyrene copolymerization

Abstract

We synthesized and characterized new neutral and cationic palladium (II) complexes containing bis-(thio)ether ligands. Depending on the rigidity of the ligand backbone and on the chelating ring size, single diastereoisomers or mixtures were obtained. The cationic compounds catalyzed the alternating CO/4-*tert*-butylstyrene copolymerization leading to polyketones with different degree of stereoregularity depending on the nature of the S-S ligand.

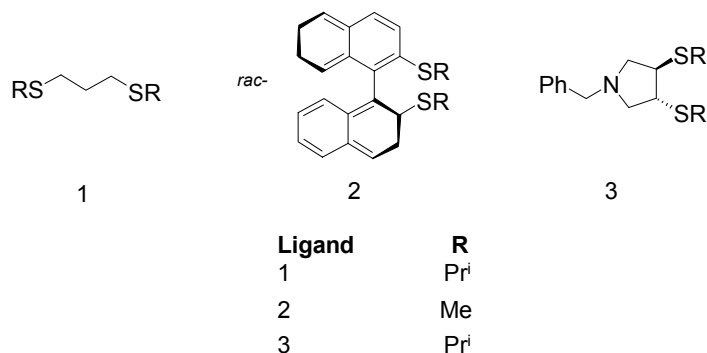
3.1. Introduction

In the last few years there has been much interest in the copolymerization of alkenes with carbon monoxide for yielding perfectly alternating polyketones.^{1,2,3} The main topics of interest today are the search for new catalytic systems and the study of the steps of the catalytic cycle.⁴ Several types of cationic palladium (II) precatalysts (isolated or “in situ”) containing chelating ligands have been reported. Bisnitrogen ligands have been successful in CO/styrene copolymerization⁵ as well as P-N ligands.⁶ There are only a few examples of phosphorous ligands that have proved to be active in this reaction.^{3,7}

Sulfur-containing ligands have been rarely used in this process. It was reported that bis-(alkylthio)ethers are active ligands for the CO/styrene copolymerization process,^{2,8} but they have received less attention than N-N or P-P ligands because they involve a loss of stereochemical control. An example with a hemilabile bis-phosphine monosulfide P-P(S) has recently been reported for the CO/ethylene copolymerization.⁹ Our experience with thioether ligands in different catalytic processes¹⁰ prompted us to test several bis-(thio)ethers as modifying ligands for palladium copolymerization precatalysts.

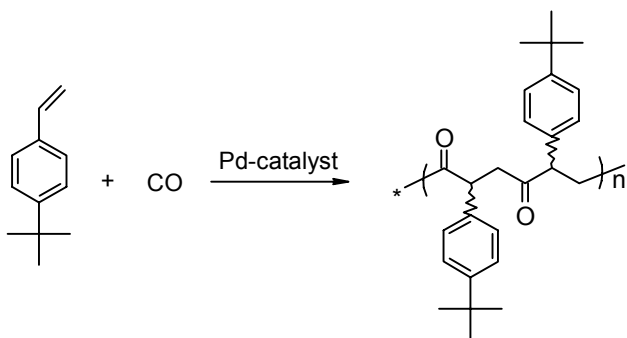
Although P-P ligands with relatively large bite angles and flexible backbones, such as dppp, enhance the rate of CO and alkene-insertion reactions, the best N-N ligands are those with small bite angles and rigid backbones, such as bipy or phen.^{11,12} We therefore proposed a comparative

study with bis-(thio)ethers that have different rigidities and coordinate to palladium to form five-, six-, and seven-membered ring chelates (Scheme 1).



Scheme 1. Bis-(thio)ethers used in this study

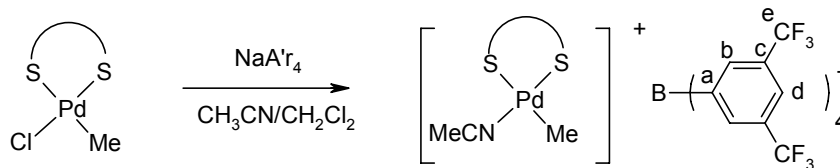
Here we report on the synthesis and characterization of the neutral [PdClMe(S-S)] (**1a-3a**) and cationic [PdMe(NCMe)(S-S)][BAR'₄] (**1b-3b**) (Ar' = 3,5-(CF₃)₂C₆H₃) palladium(II) complexes. The activity and stereocontrol provided by the cationic ones as catalysts in the CO/4-*tert*-butylstyrene copolymerization is also described (Scheme 2).



Scheme 2. Copolymerization reaction of *tert*-butylstyrene with CO

3.2. Results and discussion

In this work three bis-(thio)ethers -1,3-bis-(isopropylthio)propane (**1**), *rac*-1,1' binaphthalene-2,2'-dimethylthiol (binasMe₂) (**2**) and (-)-1-benzyl-3,4-bis (isopropylsulfanyl)pyrrolidine ((-)-degusprⁱ) (**3**)- were coordinated to palladium to obtain the neutral and cationic complexes (**1a-3a**, **1b-3b**). The neutral complexes [PdClMe(S-S)] (**1a-3a**) were obtained by reaction of [PdClMe(cod)] (cod = 1,5-cyclooctadiene) with an equimolar amount of the corresponding bis-(thio)ether ligands in dichloromethane. Displacement of the chloro ligand using NaBAR'₄ in the presence of acetonitrile gave the cationic derivatives (**1b-3b**) (Scheme 3). The ligand with the more flexible backbone (**1**) led to broad signals in the NMR spectra of **1a** and **1b**. This was probably because there were several diastereomeric species in equilibrium in solution, since the sulfur atoms became stereogenic centers upon coordination to palladium.¹⁶ There was no evidence of similar behavior with the complexes containing ligands **2** and **3**, whose ¹H NMR signals at room temperature remained sharp. However it was reported the fluxional behaviour of complex [Pd(Cl)₂(**2**)] in solution, due to the different spatial arrangements of the S-methyl substituents and the different conformations of a seven-membered chelate ring.¹⁷ In the case of hindered ligand **3** the more rigid backbone together with the five-membered chelate ring may account for the presence of a give single diastereomeric species in solution, which agrees with the behavior observed in the related complex [Pd(Cl)₂(**3**)], which gives a single diastereomer in solution.¹⁸



S-S	Neutral	Cationic
1	1a	1b
2	2a	2b
3	3a	3b

Scheme 3. Synthesis of the cationic complexes **1b-3b**

Complexes **1b-3b** were tested as catalysts for the alternating CO/4-*tert*-butylstyrene (TBS) copolymerization and turned out to be active (Table 1). In general an increase of CO pressure led to a faster decomposition of the catalyst to palladium metal together with increasing amounts of poly-(4-*tert*-butyl)styrene. All the experiments were performed at room temperature and reaction times were varied between 24–64 hours. To avoid decomposition of the catalyst also one experiment at low temperature (273 K) was done, but in this case inhibition of activity was observed. Although **1b** had the lowest activity at atmospheric pressure (entry 1), it was active at higher pressures (entries 4 and 6). It is remarkable that **1b** is more active at 5 atm. than at 1 atm. unlike what happens with N-N donor ligands.⁶ Precursor **3b** decomposed so readily under CO atmosphere that no experiments at higher pressures were performed.

Table 1. Comparative activity of precursors [PdMe(NCMe)(S-S)][BAr'₄] (**1b**-**3b**) as copolymerization catalysts.

Entry	Precursor	PCO (atm)	TBS/cat	M _n (M _w /M _n)	Prod (g CP/g Pd.h)
1	1b	1	300	3300 (1.1) ^a	0.8
2	2b	1	250	10080 (1.4) ^b	2.4
3	3b	1	400	7950 (1.8) ^b	3.4
4	1b	5	300	15700 (1.3) ^a	6.9
5	2b	5	250	7700 (1.5) ^b	1.4
6	1b	10	300	10100 (1.5) ^b	1.8

Reaction conditions: 0.025 mmol catalyst, 5 mL chlorobenzene, room temperature, 24 hours. ^a Determined by SEC-MALLS measurements. ^b Determined by GPC measurements relative to polystyrene standards.

We were able to study the behavior of **1b** and **2b** over time because of their greater stability under CO atmosphere (Table 2). When we increased the ratio of substrate to catalyst we observed higher productivity (entries 1-2, 4-5). This could be attributed to the higher stability of the catalysts when we increased the amount of styrene.⁴ⁱ For both precursors longer reaction times led to a decrease in productivity. This was probably

due to the increasing difficulty of the monomers to access the catalytic site and the decomposition of the catalysts.

Table 2. Influence of time and amount of alkene in catalytic experiments.

Entry	Precursor	t (h)	TBS/cat	M_n (M_w/M_n)	Prod (gCP/gPd.h)
1	1b	24	300	3300 (1.1) ^a	0.8
2	1b	24	600	11000 (1.4) ^a	2.9
3	1b	64	600	8600 (1.4) ^a	1.6
4	2b	24	250	10080 (1.4) ^b	2.4
5	2b	24	1600	5900 (1.8) ^b	5.3
6	2b	64	1600	9600 (1.6) ^b	4.3

Reaction conditions: 0.025 mmol catalyst, 5 mL chlorobenzene, room temperature, 1 atm CO. ^a Determined by SEC-MALLS measurements. ^b Determined by GPC measurements, relative to polystyrene standards.

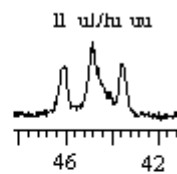
Although the activities and molecular weights with bis-(thio)ethers as chelating ligands were not as high as with planar N-N ligands (bipy, phen, etc.), they were similar to those with chiral P-OP, N-N or P-N ligands.^{3,5a,7} However with these S-S ligands molecular weights up to 15700 g/mol have been obtained in milder conditions. The rather high

polydispersity values together with a non linear relationship between time and molecular weight of the copolymers show that these system do not behave as living ones.¹⁹

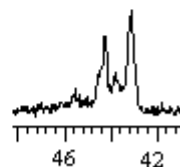
It has been suggested that the bis-(thio)ethers produce atactic copolymers probably because their structure in the donor atom is flexible.² Comparison of the ¹³C NMR spectra of the copolymers obtained with **1b-3b** and an epimerized copolymer suggested us that the tacticity of the materials strongly depended on the structure of the S-S ligand (Figure 1).

The reference spectrum shows in the region of the methylenic carbon the broad signals attributed to the four triads *ll*, *ul*, *lu* and *uu* in a ratio 1:2:1 due to the overlapping of the two heterotactic triads. The palladium precursor substituted with the achiral bis-(thio)ether **1** showed a major signal in the region of the *uu*-triad relative to a tendency to syndiotacticity, as observed for achiral N-N ligands.^{5a} However the copolymer produced with the catalyst **2b** modified with a chiral racemic ligand was atactic, as previously reported for S-S ligands. Finally the copolymer obtained with **3b** showed a main signal relative to the *ll*-triad which is an evidence for the prevailing isotactic structure.^{5c}

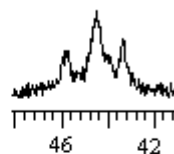
Reference



1b



2b



3b

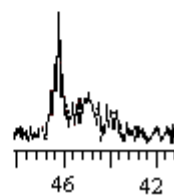


Figure 1. Methylene carbon atom-region of the copolymers obtained with precursors **1b**, **2b** and **3b**. The reference spectrum is epimerized poly (4-tert-butylstyrene- alt- CO)

3.3. Conclusions

We have shown that palladium (II) complexes with bis-(thio)ether ligands (**1-3**) are active in the alternating CO/4-*tert*-butylstyrene copolymerization under mild conditions of pressure and temperature. Additionally we have proved that, in contrast with what has been proposed for bis-(thio)ethers, choosing the right S-S ligand a control on stereoregularity can be achieved.

3.4. Experimental

3.4.1. General procedures

All syntheses were carried out in a nitrogen atmosphere at room temperature using standard Schlenk techniques. Solvents were distilled and deoxygenated prior to use unless otherwise stated. The salt NaBAr'₄ (Ar' = 3,5-(CF₃)₂-C₆H₃) and the palladium precursor [PdClMe(cod)] (cod = 1,5-cyclooctadiene) were prepared according to reported method.^{13,14} Ligands **1**, **2** and **3** were prepared according to literature.^{10b,15} Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108. ¹H NMR spectra were recorded on a Varian Gemini spectrometer with a ¹H resonance frequency of 300 MHz. Chemical shifts were reported relative to tetramethylsilane as internal standard. IR spectra were recorded on a Bruker Equinox 55 FT-IR spectrophotometer. Molecular weight of the copolymers and molecular weight distributions were determined by size exclusion chromatography (SEC - MALLS) measurements made in THF on a Waters 510-GPC device using a SHODEX K-800P precolumn and a three-serial column system (SHODEX K80M and PLGEL MIXED-D and MIXED-E linear columns) with

a Wyatt mini-DAWN Light Scattering and a SHIMADZU RID-6A refractive index detector or on a Waters 515-GPC device using a lineal Waters Ultrastyrigel column with a Waters 2410 refractive index detector using polystyrene standards.

3.4.2. Synthesis of the neutral complexes

[PdClMe(1)] (1a) (1 = 1,4-bis(isopropylthio)propane)

A solution of [PdClMe(cod)] in CH₂Cl₂ was added to a solution of **1** (in 10% excess) in CH₂Cl₂ and the mixture was stirred for an hour. After the solvent evaporated to 1 ml, the addition of Et₂O gave a yellow compound. Yield: 67%. Anal. Found for C₁₀H₂₃ClPdS₂: C, 34.45; H, 6.55; S, 18.57; Calc.: C, 34.41; H, 6.59; S, 18.37. ¹H NMR (300 MHz, CDCl₃): δ 3.64 (sp, ³J = 6.6 Hz, 1H, CH), 3.36 (sp, ³J = 6.6 Hz, 1H, CH), 2.8 (m, 2H, CH₂S), 2.61 (m, 2H, CH₂S), 2.22 (m, 2H, CH₂), 1.43 (d, ³J = 6.6 Hz, 6H, CH₃), 1.37 (d, ³J = 6.6 Hz, 6H, CH₃), 0.77 (s, 3H, Pd-CH₃).

[PdClMe(2)] (2a) (2 = binasMe₂)

A similar synthesis as for **1a** was performed using hexane to precipitate an orange compound. Yield: 80%. Anal. Found for C₂₃H₂₁ClPdS₂: C, 54.16; H, 4.33; S, 11.14; Calc.: C, 54.89; H, 4.17; S, 12.74. ¹H NMR (300 MHz, CDCl₃): δ 8.14- 6.97 (12H, Harom.), 2.66 (s, 3H, CH₃S), 2.43 (m, 3H, CH₃S), 1.04 (Pd-CH₃).

[PdClMe(3)] (3a) (3 = degusPri₂)

A similar synthesis as for **2a** was performed. This yielded a white-brownish oily compound. ¹H NMR (300 MHz, CDCl₃): δ 7.7- 7.32 (m, 5H,

Harom.), 4.75 (d, $^2J = 12.8$ Hz, 1H, CH₂), 4.21 (m, 1H, CH₂N), 3.53 (d, $^2J = 12.8$ Hz, 1H, CH₂), 3.45 (m, 1H, CH₂N), 3.2 (m, 1H, CH₂N), 3.0 (sp, $^3J = 6.7$ Hz, 1H, CH), 2.86 (sp, $^3J = 6.7$ Hz, 1H, CH), 2.6 (d, $^3J = 10.1$ Hz, 1H, CHS), 2.43 (d, $^3J = 10.1$ Hz, 1H, CHS), 2.15 (m, 1H, CH₂N), 1.3 (d, $^3J = 6.7$ Hz, 12H, CH₃), 1.25 (s, 3H, Pd-CH₃).

3.4.3. Synthesis of the cationic complexes

[PdMe(NCMe)(1)][BAr'₄] (1b)

A solution of **1a** in 2 ml of CH₂Cl₂ was added to a solution of NaBAr'₄ in the minimum volume of CH₃CN and allowed to react for one hour. The suspension was filtered over Kieselghur, the solvent reduced to 1 ml and pentane added to give a white-brownish compound. Yield: 74%. Anal. Found for C₄₄H₃₈BF₂₄NPdS₂: C, 43.57; H, 3.30; N, 1.05; S, 5.61; Calc.: C, 43.39; H, 3.12; N, 1.15; S, 5.27. ¹H NMR (300 MHz, CDCl₃): δ 7.69 (s, 8H, H_b), 7.54 (s, 4, H_d), 3.25 (sp, $^3J = 6.8$ Hz, 1H, CH), 3.06 (sp, $^3J = 6.8$ Hz, 1H, CH), 2.79 (m, 4H, CH₂S), 2.24 (s, 3H, Pd-NCCH₃), 2.16 (m, 2H, CH₂), 1.42 (d, $^3J = 6.8$ Hz, 6H, CH₃), 1.32 (d, $^3J = 6.8$ Hz, 6H, CH₃), 1.01 (s, 3H, Pd-CH₃).

[PdMe(NCMe)(2)][BAr'₄] (2b)

Complex **2b** was synthesized in a similar way. A dark red compound was obtained. Yield: 64%. Anal. Found for C₅₇H₃₆BF₂₄NPdS₂: C, 48.60; H, 2.39; N, 1.02; S, 4; Calc.: C, 49.88; H, 2.63; N, 1.02; S, 4.7. ¹H NMR (300 MHz, CDCl₃): δ 8.18- 6.99 (m, 24H, Harom.), 2.5 (s, 3H, Pd-NCCH₃), 2.4 (s, 3H, CH₃S), 2.06 (s, 3H, CH₃S), 1.25 (s, 3H, Pd-CH₃).

[PdMe(NCMe)(3)][BAr'₄] (3b)

Complex **2b** was synthesized in a similar way. An orange oil was obtained. ¹H NMR (300 MHz, CDCl₃): δ 7.71 (s, 8H, H_b), 7.54 (s, 8H, H_d), 7.39 (m, 5H, Harom.), 4.26 (d, ²J= 13.4 Hz, 1H, CH₂), 3.99 (m, 1H, CH₂N), 3.65 (d, ²J= 13.4 Hz, 1H, CH₂), 3.28 (m, 2H, CH₂N), 2.98 (sp, ³J= 6.8 Hz, 2H, CH), 2.7 (d, ³J= 10.7 Hz, 1H, CHS), 2.55 (d, ³J= 10.7 Hz, 1H, CHS), 2.36 (m, 1H, CH₂N), 2.2 (s, 3H, Pd-NCCH₃), 1.32 (d, ³J= 6.8 Hz, 6H, CH₃), 1.26 (s, 1H, Pd-CH₃), 1.25 (d, ³J= 6.8 Hz, 6H, CH₃).

3.4.4. CO/4-tert-butylstyrene copolymerization experiments

The 4-tert-butylstyrene was passed through a small column of Al₂O₃ prior to use. Chlorobenzene was used as purchased from Aldrich. In a typical procedure, the cationic precursor **1b**, **2b** or **3b** (0.025 mmol) was dissolved in 5 ml of chlorobenzene in a previously purged Schlenk and placed under CO atmosphere. 4-tert-butylstyrene was then introduced and the reaction was allowed to take place at room temperature and 1 atm of CO. The experiments under higher CO pressure were carried out in a 100 mL stainless steel Berghoff autoclave. The reaction mixture was introduced into the autoclave by suction and the pressure level was kept constant by continuous feeding from a gas reservoir. Reaction times varied from 24 to 64 hours. Workup included filtration of the reaction mixture through Kieselghur and precipitation of the polymeric material by adding the reaction solution dropwise into 100 ml of rapidly stirring methanol. The off-white powder was collected by filtration and then purified by column chromatography through silica. The homopolymer impurity was eluted first with CH₂Cl₂, and pure copolymer was then obtained by elution with ethyl

acetate. The product was then washed with methanol and dried in a vacuum oven at 70° C overnight.

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