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

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Received 12 February 2002; accepted 18 April 2002

We synthesized and characterized new neutral and cationic palladium(II) complexes containing bis-(thio)ether ligands. The cationic compounds catalyzed the alternating CO/*tert*-butylstyrene copolymerization leading to polyketones with different degrees of stereoregularity depending on the nature of the S-S ligand.

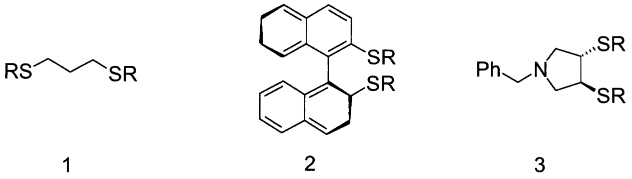
KEY WORDS: bis-(thio)ether; copolymerization; palladium; carbon monoxide; catalysis.

1. Introduction

In the past few years there has been much interest in the copolymerization of olefins with carbon monoxide for yielding perfectly alternating polyketones [1–3]. 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 copolymerization [5] 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 rarely been 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 processes [10] prompted us to test several bis-(thio)ethers as modifying ligands for palladium copolymerization precatalysts.

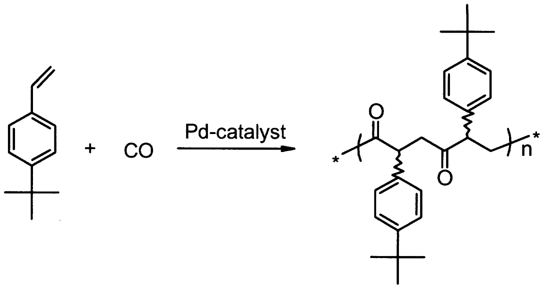
Although P-P ligands with relatively large bite angles and flexible backbones, such as dppp, enhance the rate of CO and alkene-insertion reactions, the best N-N ligands are those with small bite angles and rigid backbones, such as bipy or phen [11,12]. We therefore proposed a comparative study with bis-(thio)ethers that have different rigidities and coordinate to palladium to form five-, six- and seven-membered ring chelates (scheme 1).



Ligand	R
1	Pr^i
2	Me
3	Pr^i

Scheme 1.

Here we report on the synthesis and characterization of the neutral [PdClMe(S-S)] (**1a**–**3a**) and cationic $[\mathrm{PdMe(NCMe)(S\text{-}S)}][\mathrm{BAr}'_4]$ (**1b**–**3b**) (Ar$'$ = 3,5-$(\mathrm{CF_3})_2\mathrm{C_6H_3}$) palladium(II) complexes. The activity and stereocontrol provided by the cationic ones as catalysts in the CO/*tert*-butylstyrene copolymerization is also described (scheme 2).



Scheme 2.

2. Experimental

2.1. General procedures

All syntheses were carried out in a nitrogen atmosphere at room temperature using standard Schlenk

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techniques. Solvents were distilled and deoxygenated prior to use unless otherwise stated. The salt $NaBAr'_4$ ($Ar' = 3,5\text{-}(CF_3)_2\text{-}C_6H_3$) and the palladium precursor [PdClMe(cod)] (cod = 1,5-cyclooctadiene) were prepared according to reported methods [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 Brucker Equinox 55 FTIR spectrophotometer. The 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 linear Waters Ultrastyragel column with a Waters 2410 refractive index detector using polystyrene standards.

2.2. Synthesis of the neutral complexes

2.2.1. Synthesis of [PdClMe(S-S)] (S-S = **1**, 1,4-bis(isopropylthio)propane (**1a**); **2**, binasMe$_2$ (**2a**); **3**, degusPr$^i_2$ (**3a**))

A solution of [PdClMe(cod)] in CH_2Cl_2 was added to a solution of **1** (in 10% excess) in CH_2Cl_2 and the mixture was stirred for 1 h. After the solvent evaporated to 1 ml, the addition of Et_2O gave a yellow compound.

Yield: 67%. Anal. Found for $C_{10}H_{23}ClPdS_2$: C, 34.5; H, 6.6; S, 18.6; Calc.: C, 34.4; H, 6.6; S, 18.4. ^1H NMR (300 MHz, $CDCl_3$): δ 3.64 (sp, $^3J = 6.6$ Hz, 1H, CH), 3.36 (sp, $^3J = 6.6$ Hz, 1H, CH), 2.8 (m, 2H, CH_2S), 2.61 (m, 2H, CH_2S), 2.22 (m, 2H, CH_2), 1.43 (d, $^3J = 6.6$ Hz, 6H, CH_3), 1.37 (d, $^3J = 6.6$ Hz, 6H, CH_3), 0.77 (s, 3H, Pd-CH_3).

Complexes **2a** and **3a** were synthesized in a similar way. **2a**: A similar synthesis as for **1a** was performed using hexane to precipitate an orange compound. Yield: 80%. Anal. Found for $C_{23}H_{21}ClPdS_2$: C, 54.2; H, 4.3; S, 11.1; Calc.: C, 54.9; H, 4.2; S, 12.7. ^1H NMR (300 MHz, $CDCl_3$): δ 8.14–6.97 (12H, Harom.), 2.66 (s, 3H, CH_3S), 2.43 (m, 3H, CH_3S), 1.04 (Pd-CH_3). **3a**: A similar synthesis as for **2a** was performed. This yielded a brownish-white oily compound. ^1H NMR (300 MHz, $CDCl_3$): δ 7.7–7.32 (m, 5H, Harom.), 4.75 (d, $^2J = 12.8$ Hz, 1H, CH_2), 4.21 (m, 1H, CH_2N), 3.53 (d, $^2J = 12.8$ Hz, 1H, CH_2), 3.45 (m, 1H, CH_2N), 3.2 (m, 1H, CH_2N), 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, CH_2N), 1.3 (d, $^3J = 6.7$ Hz, 12H, CH_3), 1.25 (s, 3H, Pd-CH_3).

2.3. Synthesis of the cationic complexes

2.3.1. Synthesis of [PdMe(NCMe)(S-S)][NaBAr$'_4$] (S-S = **1,** 1,4-bis(isopropylthio) propane (**1b**); **2**, binasMe$_2$ (**2b**); **3**, degusPr$^i_2$ (**3b**))

A solution of **1a** in 2 ml of CH_2Cl_2 was added to a solution of $NaBAr'_4$ in the minimum volume of CH_3CN and allowed to react for 1 h. The suspension was filtered over Kieselghur, the solvent reduced to 1 ml and pentane added to give a brownish-white compound. Yield: 74%. Anal. Found for $C_{44}H_{38}BF_{24}NPdS_2$: C, 43.6; H, 3.3; N, 1.0; S, 5. 6; Calc.: C, 43.4; H, 3.1; N, 1.2; S, 5.3. ^1H NMR (300 MHz, $CDCl_3$): 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, CH_2S), 2.24 (s, 3H, Pd-$NCCH_3$), 2.16 (m, 2H, CH_2), 1.42 (d, $^3J = 6.8$ Hz, 6H, CH_3), 1.32 (d, $^3J = 6.8$ Hz, 6H, CH_3), 1.01 (s, 3H, Pd-CH_3).

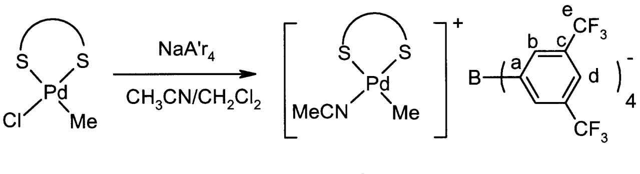
Complexes **2b** and **3b** were synthesized in a similar way. **2b**: A dark red compound was obtained. Yield: 64%. Anal. Found for $C_{57}H_{36}BF_{24}NPdS_2$: C, 48.6; H, 2.4; N, 1.0; S, 4; Calc.: C, 49.9; H, 2.6; N, 1.0; S, 4.7. ^1H NMR (300 MHz, $CDCl_3$): δ 8.18–6.99 (m, 24H, Harom.), 2.5 (s, 3H, Pd-$NCCH_3$), 2.4 (s, 3H, CH_3S), 2.06 (s, 3H, CH_3S), 1.25 (s, 3H, Pd-CH_3). **3b**: An orange oil was obtained. ^1H NMR (300 MHz, $CDCl_3$): 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, CH_2), 3.99 (m, 1H, CH_2N), 3.65 (d, $^2J = 13.4$ Hz, 1H, CH_2), 3.28 (m, 2H, CH_2N), 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, CH_2N), 2.2 (s, 3H, Pd-$NCCH_3$), 1.32 (d, $^3J = 6.8$ Hz, 6H, CH_3), 1.26 (s, 1H, Pd-CH_3), 1.25 (d, $^3J = 6.8$ Hz, 6H, CH_3).

2.4. *CO*/tert-*butylstyrene copolymerization experiments*

The 4-*tert*-butylstyrene was passed through a small column of Al_2O_3 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 h. 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 CH_2Cl_2, 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.

3. Results and discussion

In this work three bis-(thio)ethers, 1,3-bis-(iso-propylthio)propane (**1**), *rac*-1,1′ binaphtalene-2,2′-dimethylthiol (binasMe$_2$) (**2**) and (−)-1-benzyl-3,4-bis (isopropylsulfanyl)pyrrolidine ((−)-degusPr^i) (**3**), were coordinated to palladium to obtain the neutral and cationic complexes (**1a**–**3a**, **1b**–**3b**). The neutral complexes [Pd(CH$_3$)(Cl)(S-S)] (**1a**–**3a**) were obtained by reaction of [Pd(CH$_3$)(Cl)(cod)] 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 ^{1}H NMR signals remained sharp. It seems that more rigid backbones 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 [17].



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

Scheme 3.

Complexes **1b**–**3b** were tested as catalysts for the alternating CO/*tert*-butylstyrene (TBS) copolymerization and turned out to be active at 1 atm of CO and room temperature (table 1). In general an increase of CO pressure led to a faster decomposition of the catalyst to palladium metal. To avoid decomposition also low-temperature experiments (273 K) were 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 [Pd(Me)(NCMe)(S-S)][BAr$'_4$] (**1b**–**3b**) as copolymerization catalysts

Entry	Precursor	pCO (atm)	sust/cat	M_n (M_w/M_n) (g/mol)	Prod (grCP/gPd·h)
1	**1b**	1	300	3 300 (1,1)[a]	0.8
2	**2b**	1	250	10 080 (1,4)[b]	2.4
3	**3b**	1	400	7 950 (1,8)[b]	3.4
4	**1b**	5	300	15 700 (1,3)[a]	6.9
5	**2b**	5	250	7 700 (1,5)[b]	1.4
6	**1b**	10	300	10 100 (1,5)[b]	1.8

Reaction conditions: 0.025 mmol catalyst, 5 ml chlorobenzene, room temperature, 24 h.

[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 1 atm of CO atmosphere (table 2). When we increased the ratio of substrate to catalyst we observed higher productivity (entries 1 *versus* 2, 4 *versus* 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.

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 15 700 g/mol have been obtained in milder conditions. The rather high polydispersity values (M_w/M_n) together with a nonlinear relationship between time and molecular weight of the copolymers show that these system do not behave as living ones [18].

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 ^{13}C NMR spectra of the copolymers obtained with **1b**–**3b** and an

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

Entry	Precursor	T (h)	subs/cat	M_n (M_w/M_n) (g/mol)	Prod (gCP/gPd·h)
1	**1b**	24	300	3 300 (1,1)[a]	0.8
2	**1b**	24	600	11 000 (1,4)[a]	2.9
3	**1b**	64	600	8 600 (1,4)[a]	1.6
4	**2b**	24	250	10 080 (1.4)[b]	2.4
5	**2b**	24	1600	5 900 (1.8)[b]	5.3
6	**2b**	64	1600	9 600 (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.

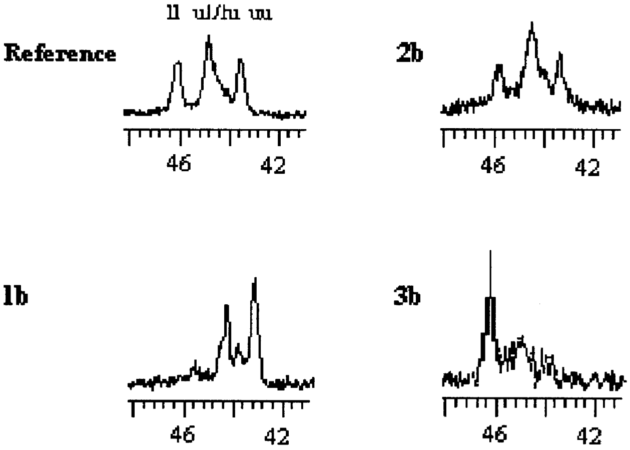


Figure 1. Methylene carbon atom-region of the copolymers obtained with precursors **1b**, **2b** and **3b**. The reference spectrum is epimerized poly(4-*tert*-butylstyrene-alt-CO).

epimerized copolymer suggested 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 evidence for the prevailing isotactic structure [5c].

4. Conclusions

We have shown that palladium(II) complexes with bis-(thio)ether ligands (**1**–**3**) are active in the alternating CO/*tert*-butylstyrene copolymerization under mild conditions of pressure and temperature. The copolymerization results depend on the nature of the ligands used. It is important to note that, in contrast to what has been previously proposed for bis-(thio)ethers, by choosing the right S-S ligand a control on stereoregularity can be achieved.

Acknowledgments

We acknowledge Prof. S. Gladiali for the gift of *rac*-1,1′ binaphthalene-2,2′-dimethylthiol. We thank the Spanish Ministerio de Educación, Cultura y Deporte for financial support (DGES PB-97-0407-C05-01 and 2FD97-1565) and the Ministerio de Ciencia y Tecnología for awarding a research grant (to A. Bastero).

References

[1] A. Sen, Acc. Chem. Res. 26 (1993) 303.
[2] E. Drent and P.H.M. Budzelaar, Chem. Rev. 96 (1996) 663.
[3] K. Nozaki and T. Hiyama, J. Organomet. Chem. 576 (1999) 248.
[4] *For new catalytic systems see*: (a) F.J. Parlevliet, M.Z. Zuideveld, C. Kiener, H. Kooijman, A.L. Spek, P.C.J. Kamer and P.W.N.M. van Leeuwen, Organometallics 18 (1999) 3394; (b) J. Schwarz, E. Herdtweck and W.A. Herrmann, Organometallics 10 (2000) 3154; (c) C. Gambs, S. Chaloupka, G. Consiglio and A. Togni, Angew. Chem. Int. Ed. 39 (2000) 2486; (d) C. Bianchini, H.M. Lee, A. Meli, W. Oberhauser, F. Vizza, P. Brüggeller, R. Haid and C. Langes, Chem. Comm. (2000) 777; (e) J.C. Yuan and S.J. Lu, Organometallics 20 (2001) 2697; (f) C.R. Baar, M.C. Jennings and R.J. Puddephatt, Organometallics 20 (2001) 3459. *For mechanistic studies see*: (g) F.C. Rix, M. Brookhart and P.S. White, J. Am. Chem. Soc. 118 (1996) 4746; (h) M.A. Zuideveld, P.C.J. Kamer, P.W.N.M. van Leeuwen, P.A.A. Klusener, H.A. Stil and C.F. Roobeek, J. Am. Chem. Soc. 120 (1998) 7977; (i) B. Milani, G. Corso, G. Mestroni, C. Carfagna, M. Formica, R. Seraglia, Organometallics 19 (2000) 3435; (j) G.K. Barlow, J.D. Boyle, N.A. Cooley, T. Ghaffar and D.F. Waas, Organometallics 19 (2000) 1470; (k) C.S. Shultz, J. Ledford, J.M. DeSimone and M. Brookhart, J. Am. Chem. Soc. 122 (2000) 6351; (l) K. Nozaki, H. Komaki, Y. Kawashima, T. Hiyama and T. Matsubara, J. Am. Chem. Soc. 123 (2001) 534; (m) W.P. Mul, E. Drent, P.J. Jansens, A.H. Kramer and M.H.W. Sonnemans, J. Am. Chem. Soc. 123 (2001) 5350.
[5] (a) M. Brookhart, M.I. Wagner, G.G.A. Balavoine and H.A. Haddou, J. Am. Chem. Soc. 116 (1994) 3641; (b) B. Milani and G. Mestroni, Comments Inorg. Chem. 20 (1999) 301; (c) M.T. Reetz, G. Haderlein and K. Angermund, J. Am. Chem. Soc. 122 (2000) 996; (d) A. Bastero, A. Ruiz, J.A. Reina, C. Claver, A.M. Guerrero, F.A. Jalón and B.R. Manzano, J. Organomet. Chem. 619 (2001) 287; (e) C. Carfagna, G. Gatti, D. Martini and C. Pettinari, Organometallics 20 (2001) 2175; (f) A. Bastero, S. Castillón, C. Claver and A. Ruiz, Eur. J. Inorg. Chem. 12 (2001) 3009.
[6] A. Aeby and G. Consiglio, Inorg. Chim. Acta 296 (2000) 45.
[7] J.C. Yuan and S.J. Lu, J. Polym. Sci. A: Polym. Chem. 38 (2000) 2919.
[8] J.A. Van Doorn and E. Drent, Eur. Pat. Appl. 345 847 (1989), Chem. Abst. 112 (1990) 199339.
[9] G.P. Suranna, P. Mastrorilli, C.F. Nobile and W. Keim, Inorg. Chim. Acta 305 (2000) 151.
[10] (a) M. Diéguez, A. Orejón, A.M. Masdeu-Bultó, R. Echarri, S. Castillón, C. Claver and A. Ruiz, J. Chem. Soc., Dalton Trans. (1997) 4611; (b) M. Diéguez, A. Ruiz, C. Claver, M.M. Pereira and A.M. d'A Rocha Gonsalves, J. Chem. Soc., Dalton Trans. (1998) 3517; (c) O. Pàmies, M. Diéguez, G. Net, A. Ruiz and C. Claver, J. Chem. Soc., Dalton Trans. (1999) 3439; (d) J.C. Bayón, C. Claver and A.M. Masdeu-Bultó, Coord. Chem. Rev. 193-195 (1999) 73; (e) O. Pàmies, G. Net, A. Ruiz, C. Claver and S. Woodward, Tetrahedron: Asymmetry 11 (2000) 871; (f) S. Jansat, M. Gómez, G. Muller, M. Diéguez, A. Aghmiz, C. Claver, A.M. Masdeu-Bultó, L. Flores-Santos, E. Martin, M.A. Maestro and J. Mahía, Tetrahedron: Assymetry 12 (2001) 1469.
[11] H.A. Ankersmit, N. Veldman, A. Spek, K. Eriksen, K. Goubitz, K. Vrieze and G. van Koten, Inorg. Chim. Acta 252 (1996) 203.
[12] P.W.N.M. van Leeuwen, P.C.J. Kamer, J.N.H. Reek and P. Dierkes, Chem. Rev. 100 (2000) 2741.
[13] S.R. Bahr and P.J. Boudjouk, J. Org. Chem. 57 (1992) 5545.
[14] R.E. Rülke, J.M. Ernsting, A.L. Spek, C.J. Elsevier, P.W.N.M. van Leeuwen and K. Vrieze, Inorg. Chem. 32 (1993) 5769.
[15] (a) Ligand **1**: A. Gomis, G. Net, A. Ruiz, C. Claver and A. Alvarez-Larena, Inorg. Chim. Acta 325 (2001) 58; (b) Ligand **2**: D. Fabbri, S. Pulacchini and S. Gladiali, Synlett 11 (1996) 1019.
[16] E.W. Abel, S.K. Bhargava and K.G. Orrell, Prog. Inorg. Chem. 32 (1984) 1.
[17] M. Diéguez, A. Ruiz, A.M. Masdeu-Bultó and C. Claver, J. Chem. Soc., Dalton Trans. (2000) 4154.
[18] M. Brookhart, F.C. Rix and J.M. DeSimone, J. Am. Chem. Soc. 114 (1992) 5894.