Zirconocenes as Photoinitiators for Free-Radical Polymerisation of Acrylates

Eleonora Polo,*[a] Andrea Barbieri,[a] Silvana Sostero,[a] and Malcolm L. H. Green[b]

Keywords: Metallocenes / Zirconium / Photolysis / Homogeneous catalysis / Polymerizations

This paper reports the photochemical behaviour of unbridged (**1**–**6**) and bridged zirconocenes (**7r**, **7m**), whose substituents differ in both electron-donor and steric properties. The study of the electronic spectra and EPR spin-trapping experiments showed the photogeneration of ligand- and zirconium-centred radicals at wavelengths higher than 350 nm. This feature makes these complexes suitable as photoinitiators for radical polymerisation processes. *tert*-Butyl acrylate polymerisation has been studied in detail and the results are particularly encouraging as far as the reaction yields and the stereochemistry are concerned. In particular, the complexes **4**–**6**, due to the tuneability of their structure and their stability in solution, look the most promising reagents.

Introduction

Photochemical or photoinitiated polymerisations play a central role in several commercial technologies[1−3] and they are largely employed today in the areas of surface coatings, photoresists, adhesives, and holography. In particular, a growing area of interest is the design of new photoinitiators for use in pigmented coatings. Among those, initiators showing absorption peaks at wavelengths higher than 350 nm[4] are of particular interest since they can be used with the visible light produced by continuous wave lasers.

Photoinitiated reactions offer several potential advantages over conventional thermally activated processes since the absorption of a photon generates an electronic excited state whose chemical reactivity can differ substantially from that of the ground state. As a consequence, the involvement of an excited state can induce a reaction pathway that does not occur thermally or occurs only at very high temperatures.

Light is a clean, tuneable and versatile "reagent", since it allows the selective activation of a photoinitiator also in the presence of organic solvents and chemical contaminants. Regulation of light intensity affords a convenient means of controlling reaction kinetics and photoinitiation can also be spatially directed and turned on or off simply by switching the light source. Other potential advantages of the photochemical reactions include reduced energy requirements, increased shelf life of substrate formulations, and greater compatibility with heat-sensitive materials. Other commendable features are low toxicity and friendly environmental impact.

The desire to expand the application of photoinitiated chemistry beyond organic systems has led recently to the discovery of several classes of inorganic and organometallic photoinitiators.[5−9] Among them, metallocenes have attracted increasing interest because it is possible to tailor the polymer microstructure by systematic, rational variation of the cyclopentadienyl ligand substituents, whether they are connected by an interannular bridge or not. Moreover, they leave low-toxic residues and they photobleach with high efficiency, thus leaving clear or colourless coatings after exposure to argon lasers.[5]

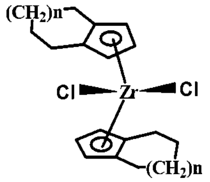
Despite their importance in organometallic chemistry and catalysis, to now few studies have been performed on the photochemistry of metallocene complexes of Ti, Zr, and Hf.[10−17] Moreover, while the relationship between the catalytic activity of Group IV metallocenes and their structure has been thoroughly studied, very little is known about its correlation with their electronic properties.

In this paper we report the photochemical behaviour of zirconocenes, whose substituents differ in both electron-donor and steric properties. Several unbridged zirconium complexes have been studied: bis(η^5-cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2, **1**), bis(η^5-pentamethylcyclopentadienyl)zirconium dichloride ($Cp^*{}_2ZrCl_2$, **2**), bis(η^5-indenyl)zirconium dichloride (Ind_2ZrCl_2, **3**), bis(η^5-tetrahydroindenyl)zirconium dichloride (THI_2ZrCl_2, **4**), bis(η^5-hexahydroazulenyl)zirconium dichloride [$(C7)_2ZrCl_2$, **5**], and bis[η^5-(4,5,6,7,8,9-hexahydro-1*H*-cyclopentacyclooctenyl)]zirconium dichloride [$(C8)_2ZrCl_2$**6**].

They have been also compared with two bridged complexes, *rac*-[ethylenebis(4,7-dimethyl-η^5-1-indenyl)]zirconium dichloride (*rac*-$EBDMIZrCl_2$, **7r**), and its *meso* isomer *meso*-$EBDMIZrCl_2$ (**7m**), in order to check if some of the

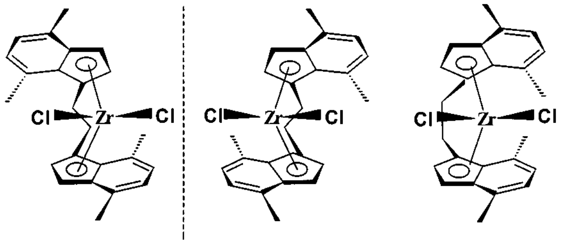
---

[a] Dipartimento di Chimica, Centro di Studio su Fotoreattività e Catalisi del C. N. R.,
Via L. Borsari 46, 44100 Ferrara, Italy
Fax: (internat.) + 39-0532/240709
E-mail: tr3@unife.it
[b] Inorganic Chemistry Laboratory, University of Oxford
South Parks Road, Oxford OX1 3QR, United Kingdom
Fax: (internat.) + 44-1865/272690
E-mail: malcolm.green@chem.ox.ac.uk



n = 1 **(4)**, 2 **(5)**, 3 **(6)**

original stereocontrol properties were retained after irradiation and could be applied in catalysis.



7r **7m**

Preliminary olefin photopolymerisation tests have also been carried out to verify their activity as photoinitiators for α-olefins.

Results and Discussion

Photochemistry

UV/Vis spectra of the zirconocenes under study were recorded in benzene, THF and CH_2Cl_2. No solvent effect was observed, neither on the λ_{max}, or on the ε_{max} values. The results are reported in Table 1. All complexes exhibit at least one electronic transition in the visible range of the spectrum (at $\lambda > 320$ nm) with ε values of the order of 10^3 $mol^{-1}\cdot L\cdot cm^{-1}$. The progressive red-shift of the bands as the electron-donor activity of the cyclopentadienyl substituents increases supports the hypothesis of LMCT character for the low-energy electronic transition.

Selective photolysis was carried out on the complexes at the wavelength corresponding to their LMCT transition, in order to ascertain if they can be employed as initiators in radical photopolymerisation and to optimise the reaction conditions. The primary quantum yield corresponding to the metal-ring cleavage is of the order of 0.28 for all the unbridged compounds, and of 0.11 for $EBDMIZrCl_2$ (**7r** and **7m**). Long-time photolysis led to the bleaching of the solutions due to evolution of the complexes, as determined by NMR analysis.

Table 1. Spectral band maxima of zirconocene complexes in solution (benzene, THF or CH_2Cl_2)

Zirconocene	λ_{max} [nm]	ε_{max} ($mol^{-1}\cdot L\cdot cm^{-1}$)
Cp_2ZrCl_2	290	2400
	340	620
$Cp^*_2ZrCl_2$	350	1580
	370	1990
Ind_2ZrCl_2	310	1475
	380	720
THI_2ZrCl_2	310	1600
	350	1100
$(C7)_2ZrCl_2$	310	2380
	345	1540
$(C8)_2ZrCl_2$	305	2920
	345	1720
meso-$EBDMIZrCl_2$	380	1130
rac-$EBDMIZrCl_2$	425	1350

The solvent nature strongly affects the stability of the complexes in solution, and it emphasises the differences among the metallocenes; in particular, in benzene and in toluene, (Figure 1) after 1 h of irradiation, only the 5−10% (by UV/Vis spectroscopy) of the complexes **4−6** were decomposed and the degradation rates were $Ind_2ZrCl_2 > Cp^*_2ZrCl_2 > Cp_2ZrCl_2 >> (THI)_2ZrCl_2 > (C7)_2ZrCl_2/(C8)_2ZrCl_2$.

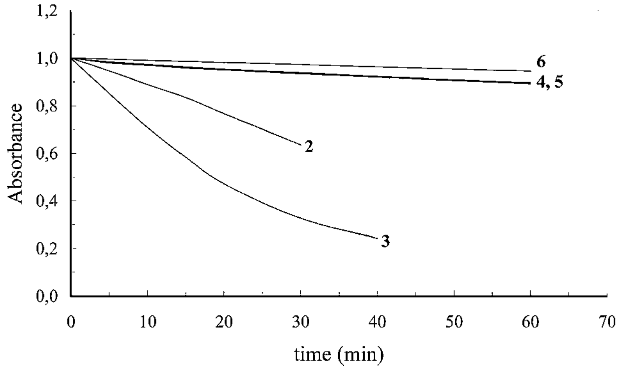


Figure 1. Absorption maxima decay of the zirconocenes **2−6** in benzene as a function of time

Pure solutions of **4−6** in benzene or in toluene were more stable and the photodecomposition was reversed after 24 h of storage in the dark. The initial spectral pattern and absorbance values were almost completely recovered.

Figure 2 shows that in THF the photodecomposition of the compounds **1−6** was faster (30−70%) and followed the same trend as in benzene solution. The increased rate of decomposition may be due to stronger coordinating properties of THF. We note that the UV/Vis spectra in THF have a different shape from those in toluene or benzene.

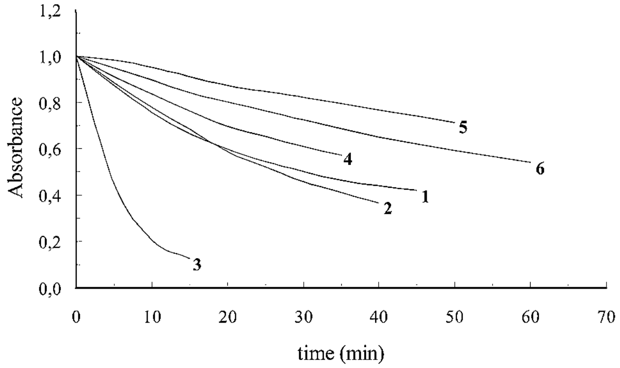


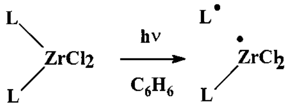
Figure 2. Absorption maxima decay of the zirconocenes **1−6** in THF as a function of time

EPR Spin Trapping Investigation

In order to assess the nature of the primary photochemical act, EPR/spin trapping experiments have been carried out by direct irradiation of benzene solutions of the zirconocenes inside the spectrometer cavity. Different spin traps, i.e. *N*-*tert*-butyl-α-phenylnitrone (PBN), nitrosodurene (ND), and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), were used in order to identify unambiguously the nature of the radical species.[18−19] By comparison with NIEHS Spin Trap Database data,[20] the hyperfine coupling constants (*hfcc*) of the spin adducts detected and reported in Table 2, could be assigned to cyclopentadienyl-type radicals. Therefore, the primary photochemical act can be described by Scheme 1.

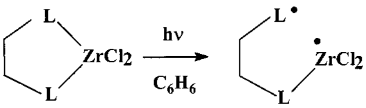
Table 2. Hyperfine coupling constants of cyclopentadienyl-type spin adducts (all values are expressed in Gauss)

Zirconocene	ND	PBN	DMPO
Cp_2ZrCl_2	a_N = 13.7 a_H = 15.3	a_N = 14.6 a_H = 2.9	a_N = 14.0 a_H = 20.2
$Cp^*{}_2ZrCl_2$	a_N = 13.5	a_N = 14.6 a_H = 4.0	a_N = 14.8 a_H = 20.3
Ind_2ZrCl_2	a_N = 13.8 a_H = 15.4	a_N = 14.6 a_H = 2.5	a_N = 14.0 a_H = 20.0
THI_2ZrCl_2	a_N = 13.8 a_H = 13.8	a_N = 14.6 a_H = 3.2	a_N = 14.2 a_H = 20.8
$(C7)_2ZrCl_2$	a_N = 13.8 a_H = 15.9	a_N = 14.5 a_H = 2.9	a_N = 14.2 a_H = 20.4
$(C8)_2ZrCl_2$	a_N = 13.8 a_H = 21.3	a_N = 14.7 a_H = 3.0	a_N = 14.0 a_H = 20.3
$EBDMIZrCl_2$	a_N = 14.0 a_H = 9.8	a_N = 14.6 a_H = 2.3	a_N = 14.3 a_H = 20.4



Scheme 1

The case of the bridged *rac*- and *meso*-metallocenes is rather complicated since the photodissociation of one of the two L−Zr bonds gives a biradical species as a consequence of the bridge and because the light causes also a partial interconversion between the two isomeric forms.[17] In this case, the primary photochemical act can be described by Scheme 2.



Scheme 2

The presence of radical intermediates in the zirconocenes' photochemical reactions suggests a possible use as photoinitiators for radical polymerisation processes. In order to test the effectiveness of these organometallic photoinitiators, similar EPR/spin trapping experiments were performed in the presence of different alkenes, i.e. 1-pentene, methyl methacrylate (MMA) and *tert*-butyl acrylate (*t*BA), and in different solvents, benzene and dichloromethane. During irradiation of the zirconocene/alkene mixtures the growth of a new EPR signal characteristic of a carbon-centred radical has been detected (a_N = 14.7−14.9 G; a_H = 3.0−3.6 G). The results are reported in Table 3.

Removal of the solvent left a polymeric film, while no polymer formation was observed even after prolonged irradiation in the absence of metallocenes. This observation supports the proposal that the radical species produced upon irradiation can add to the double bond of the monomers, thus initiating the radical polymerisation process. When the same experiments were carried in CH_2Cl_2, the $^{\cdot}CH_2Cl$ radical was also detected (a_N = 14.2 G; a_H = 3.1 G) (see Table 3, last column). This species can act as a second photoinitiator and this accounts for the higher monomer conversions obtained when the polymerisations were carried in halogenated solvents.[21−23]

The stability of the complexes in the presence of the monomers has been also determined. We found that in benzene and in toluene only 10% of the complexes was decomposed after 1 h of irradiation, whilst in THF the decomposition was more rapid and ca. 60% of the complexes **4−6** was decomposed, while the other metallocenes were completely decomposed in the same period.

Polymerisation Studies

On the basis of these findings, polymerisation tests were performed on *tert*-butyl acrylate, since the polymerisation of acrylates is of industrial interest and has been the subject of intensive experimental investigations and practical application. Recently, zirconocene complexes were introduced as catalysts or catalyst precursors for methyl methacrylate polymerisation.[24−27] We tested the most promising metallocenes in benzene and in CH_2Cl_2, and we can compare our data with what reported[28−34] for similar systems. We have also determined whether there is evidence for stereochemical control by the *ansa*-zirconocenes **7r** and **7m** (Table 4). The tacticity of the poly(*t*BA) formed has been estimated by deconvolution of the methine peaks which occurs at δ ≈ 42 in the ^{13}C NMR spectra (Figure 3).

The EPR data (vide supra) for the polymerisations in CH_2Cl_2 with the complexes **4−6** gave higher product yields than in benzene solutions due to the synergistic effect of the $^{\cdot}CH_2Cl$ radical. This effect was quite negligible with the *ansa*-bridged metallocenes **7r** and **7m**. The stereochemical outcome of the reaction was independent of the solvent and of stereochemistry of the compounds **7r** and **7m.**

The polymer yields shown in Table 4 compare favourably with the yields reported for polymerisations using chiral metallocenes with alumoxanes.[28] For example, after only 1 h, we have 22−36% polymer yield, when the literature values were only 13% after 17 h. The stereochemical properties of the polymers (Table 4) are comparable to those reported for other catalysts,[30−34] even though the latter had more complex and rigid stereochemical features.

Table 3. Hyperfine coupling constants of cyclopentadienyl-type spin adducts (all values are expressed in Gauss)

Zirconocene[a]	1-pentene in C_6H_6	MMA in C_6H_6	*t*BA in C_6H_6	*t*BA in CH_2Cl_2	
Cp_2ZrCl_2	a_N = 14.7	a_N = 14.7			
	a_H = 3.0	a_H = 3.6			
$Cp^*_2ZrCl_2$	a_N = 14.6	a_N = 14.7			
	a_H = 2.9	a_H = 3.7			
Ind_2ZrCl_2	a_N = 14.8				
	a_H = 2.9				
THI_2ZrCl_2	a_N = 14.8	a_N = 14.7	a_N = 14.9	a_N = 15.0	a_N = 14.0
	a_H = 3.0	a_H = 3.5	a_H = 3.4	a_H = 3.1	a_H = 3.1
$(C7)_2ZrCl_2$	a_N = 14.7	a_N = 14.6	a_N = 14.9	a_N = 15.2	a_N = 14.2
	a_H = 3.0	a_H = 3.5	a_H = 3.4	a_H = 3.4	a_H = 3.0
$(C8)_2ZrCl_2$	a_N = 14.7	a_N = 14.5	a_N = 14.9	a_N = 15.2	a_N = 14.3
	a_H = 3.0	a_H = 3.4	a_H = 3.4	a_H = 3.4	a_H = 3.2
$EBDMIZrCl_2$ *meso*			a_N = 15.0	a_N = 15.1	a_N = 14.2
			a_H = 3.5	a_H = 3.5	a_H = 3.0
$EBDMIZrCl_2$ *rac*			a_N = 15.2	a_N = 15.1	a_N = 14.2
			a_H = 3.6	a_H = 3.5	a_H = 3.0

[a] 8 mg of metallocene in 4 mL of a 20% solution of the monomer in benzene or dichloromethane.

Table 4. *tert*-Butyl acrylate polymerisation data

Zirconocene	20% *t*BA in C_6H_6				20% *t*BA in CH_2Cl_2			
	Yield[a]	Stereochemistry[b] (%)			Yield[a]	Stereochemistry[b] (%)		
		[rr]	[mr]	[mm]		[rr]	[mr]	[mm]
THI_2ZrCl_2	24	37	52	11	29	40	47	13
$(C7)_2ZrCl_2$	22	40	45	15	27	44	45	11
$(C8)_2ZrCl_2$	24	35	50	15	31	39	49	12
$EBDMIZrCl_2$ *meso*	36	41	47	12	38	41	48	10
$EBDMIZrCl_2$ *rac*	35	40	48	12	39	40	49	11

[a] Weight of polymer obtained/weight of monomer added. [b] Percent of syndiotactic [rr], isotactic [mm], and atactic [mr] triads in the isolated polymer, calculated from the deconvolution of the ^{13}C NMR peaks at δ = 41−43.

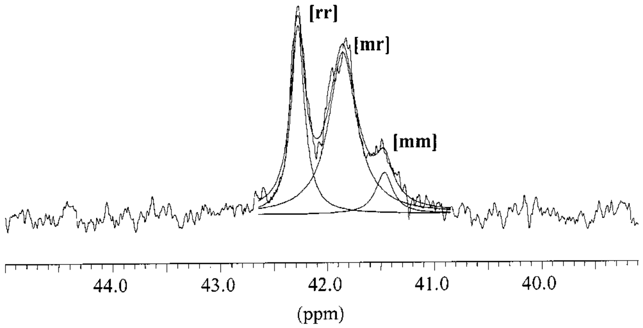


Figure 3. Methine region in the ^{13}C NMR spectrum of poly(*t*BA) obtained in CH_2Cl_2 (the single deconvoluted peaks are also represented)

Conclusion

Known and new zirconocene complexes are described here to be photoinitiators for radical polymerisation processes. *tert*-Butyl acrylate polymerisation has been studied in detail with both bridged (**7r** and **7m**) and unbridged complexes (**4−6**) and the results are particularly encouraging as far as the reaction yields and the stereochemistry are concerned. Also the use of non-halogenated solvents is environmentally desirable.

We propose to take advantage of the ability to modify the structure of the complexes **4−6**,[35] in order to tune the optical properties and radical stability.

Experimental Section

General Remarks: All manipulations of air- and/or moisture-sensitive materials were carried out under an inert gas using a dual vacuum/argon line and standard Schlenk techniques. All solvents were thoroughly dehydrated and deoxygenated under argon before use. They were dried and purified by refluxing under argon over a suitable drying agent (benzene, toluene and THF over Na/benzophenone ketyl; CH_2Cl_2 over CaH_2) followed by distillation, and stored under argon in Young's ampoules. Solvents and solutions were transferred, using a positive pressure of argon, through stainless-steel cannulae (diameter 0.5−2.0 mm) and mixtures were filtered in a similar way using modified cannulae which could be fitted with glass-fibre filter disks (Whatman GFC).

Preparation of the Complexes: Metallocenenes THI_2ZrCl_2 (**4**),[35] $(C7)_2ZrCl_2$ (**5**),[35] $(C8)_2ZrCl_2$ (**6**),[35] Ind_2ZrCl_2 (**3**),[36] and $EBDMIZrCl_2$ [37] were prepared as described previously; Cp_2ZrCl_2 (**1**), and $Cp^*_2ZrCl_2$ (**2**) were purchased from Sigma-Aldrich Chem. Co. and used without further purification.

NMR Spectra: ^1H (200.13 MHz) and ^{13}C (50.32 MHz) nuclear magnetic resonance spectra were recorded at room temperature with a Bruker AC200 spectrometer. Spectra were referenced internally using the residual protio solvent resonance relative to tetramethylsilane ($\delta = 0$). Deuterated solvents were dried and distilled under argon over a suitable drying agent (CaH_2 for $CDCl_3$ and K for C_6D_6) and stored under argon in Young's ampoules.

EPR Studies: The spin traps PBN, ND and DMPO were purchased from Sigma-Aldrich Chem. Co. and used without further purification, except from DMPO, which was distilled under vacuum below 40 °C to remove paramagnetic impurities. The EPR/spin trapping experiments were performed with a Bruker EMX spectrometer, operating in the X-band (microwave frequency: 9.6 GHz; microwave power: 2 mW; modulation frequency: 100 kHz; modulation amplitude: 1 G; sweep rate: 50 G/min; time constant: 20 ms). Sample solutions were irradiated with a 350-W medium-pressure Hg lamp directly into the EPR spectrometer (Bruker ER-4104OR, TE102) cavity. Solid α,α'-diphenyl-β-picrylhydrazyl was used as external reference for *g* values. The *hfcc* values were calculated by best-fit simulation of experimental spectra using the NIEHS WinSim software.[38]

Photochemical Experiments: Irradiation was performed using an Oriel 500-W high-pressure Hg lamp using either a grating monochromator (Jasco CT-25A) or cut-off filters for wavelength selection. UV/Vis spectra were recorded with a Jasco UVIDEC-610 double-beam spectrophotometer.

Polymerisation Tests: 1-Pentene, methyl methacrylate and *tert*-butyl acrylate were dehydrated over molecular sieves (4Å) and freed from the stabilisers by filtration before use. In a typical experiment a 20% monomer solution in a 4-mL cuvette was irradiated for 1 h in the presence either of 7 mg of an unbridged metallocene at $\lambda = 350$ nm, or of 3 mg of an *ansa*-bridged metallocene at $\lambda = 410$ nm. After 1 h, the polymerisation was quenched with methanol and HCl, and the polymer was recovered after removal of the solvents under reduced pressure.

Acknowledgments

We thank the C. N. R. Short Term Fellowship Program (1996/97) for supporting the stay of E. P. in Oxford and Prof. O. Traverso of the University of Ferrara for helpful discussion.

---

[1] N. S. Allen (Ed.), *Photopolymerization and Photoimaging Science and Technology*, Elsevier, Amsterdam, **1989**.

[2] S. P. Pappas (Ed.), *Radiation Curing: Science and Technology*, Plenum Press, New York, **1992**.

[3] A. B. Scranton, C. N. Bowman, R. W. Peiffer (Eds.), *Photopolymerization: Fundamentals and Applications* (ACS Symp. Ser., no. 673), American Chemical Society, Washington, DC, **1997**.

[4] Ciba (Ed.), *Photoinitiators for UV curing. Key Products Selection Guide. Additives*, **1998** (brochure available at http://www.cibasc.com).

[5] B. M. Monroe, G. C. Weed, *Chem. Rev.* **1993**, *93*, 435−448.

[6] R. S. Davidson, *J. Photochem. Photobiol., A* **1993**, *69*, 263−275

[7] R. S. Davidson, *J. Photochem. Photobiol., A* **1993**, *73*, 81−96

[8] C. Kutal, *Coord. Chem. Rev.* **2001**, *211*, 353−368

[9] Y. Yamaguchi, B. J. Palmer, C. Kutal, *Macromolecules* **1998**, *31*, 5155−5157.

[10] W. Kaminsky, A. M. Schauwienold, F. Freidanck, *J. Mol. Catal. A: Chem.* **1996**, *112*, 37−42.

[11] A. L. Rheingold, N. P. Robinson, J. Whelan, B. Bosnich, *Organometallics* **1992**, *11*, 1869−1876.

[12] K. Schmidt, A. Reinmuth, U. Rief, J. Diebold, H. H. Brintzinger, *Organometallics* **1997**, *16*, 1724−1728.

[13] E. Vitz, C. H. Brubaker, Jr., *J. Organomet. Chem.* **1974**, *82*, C16.

[14] R. W. Harrigan, G. S. Hammond, M. B. Gray, *J. Organomet. Chem.* **1974**, *81*, 79−85.

[15] E. Vitz, P. J. Wagner, C. H. Brubaker Jr., *J. Organomet. Chem.* **1976**, *107*, 301−306.

[16] G. L. Lee, C. H. Brubaker, Jr., *Inorg. Chim. Acta* **1977**, *25*, 181−184.

[17] A. Barbieri, A. Droghetti, S. Sostero, O. Traverso, *J. Photochem. Photobiol., A* **1999**, *129*, 137−142.

[18] S. Sostero, D. Rehorek, O. Traverso, E. Polo, *Inorg. Chim. Acta* **1993**, *209*, 171−176.

[19] S. Di Martino, S. Sostero, O. Traverso, D. Rehorek, T. J. Kemp, *Inorg. Chim. Acta* **1990**, *176*, 107−112.

[20] A. S. W. Li, K. B. Cummings, H. P. RoethLing, G. R. Buetner, C. F. Chignell, *J. Magn. Reson.* **1988**, *79*, 140−142.

[21] H.-G. Woo, J.-Y. Park, L.-Y. Hong, S.-Y. Yang, H. You, H.-S. Ham, *Bull. Korean Chem. Soc.* **1996**, *17*, 582−585.

[22] H.-G. Woo, J.-Y. Park, H.-S. Ham, H.-R. Park, S.-D. Cho, Y.-H. Ko, W.-G. Kim, *Bull. Korean Chem. Soc.* **1997**, *18*, 444−447.

[23] H.-G. Woo, J. Y. Park, L.-Y. Hong, S.-Y. Yang, H. You, H.-S. Ham, *Bull. Korean Chem. Soc.* **1996**, *17*, 412−414.

[24] W. B. Farnham, W. R. Hertler, US Patent 4,728,706, **1988**.

[25] K.-H. Thiele, H.-J. Timpe, D. Schenke, B. Strehmel, DD Patent 297018, **1991**.

[26] C. Albrecht, W. Frass, R. Zertani, EP 573805, **1993**.

[27] R. Zertani, D. Mohr, K. Rode, EP 447930, **1991**.

[28] H. Deng, K. Soga, *Macromolecules* **1996**, *29*, 1847−1848.

[29] Y. Li, D. G. Ward, S. S. Reddy, S. Collins, *Macromolecules* **1997**, *30*, 1875−1883.

[30] P. A. Cameron, V. C. Gibson, A. J. Graham, *Macromolecules* **2000**, *33*, 4329−4335.

[31] M. H. Lee, J.-W. Hwang, Y. Kim, J. Kim, Y. Han, Y. Do, *Organometallics* **1999**, *18*, 5124−5129.

[32] C. Qian, W. Nie, J. Sun, *Organometallics* **2000**, *19*, 4134−4140.

[33] H. Frauenrath, H. Keul, H. Höcker, *Macromolecules* **2001**, *34*, 14−19.

[34] J. Q. Sun, Z. D. Pan, Y. Zhong, W. Q. Hu, S. L. Yang, *Eur. Polym. J.* **2000**, *36*, 2375−2380.

[35] E. Polo, R. M. Bellabarba, G. Prini, O. Traverso, M. L. H. Green, *J. Organomet. Chem.* **1999**, *577*, 211−218.

[36] E. Samuel, *Bull. Soc. Chim. Fr.* **1966**, *11*, 3548−3564.

[37] L. Resconi, F. Piemontesi, I. Camurati, D. Balboni, A. Sironi, M. Moret, H. Rychlicki, R. Ziegler, *Organometallics* **1996**, *15*, 5046−5059.

[38] D. R. Duling, *J. Magn. Reson. Ser. B* **1994**, *104*, 105−110.

Received August 3, 2001
[I01291]