DOI: 10.1002/ejic.200600399

Substituted Ring-Fused Yttrium Derivatives – X-ray Crystal Structures of [(L′YCl$_2$·THF)$_2$LiCl·2THF] and [{L′YCl(OH)}$_6$·2THF] (L′ = 2-Phenyl-4,5,6,7,8-hexahydroazulenyl)

Gino Paolucci,*[a] Manuela Vignola,[a] Alessandra Zanella,[a] Valerio Bertolasi,[b] Eleonora Polo,*[c] and Silvana Sostero[c]

Keywords: Yttrium / Fused-ring systems / Olefin polymerization

The reaction of lithium salts of ring-fused ligands (L), where the ring fused to the cyclopentadienyl moiety is a saturated one (six, seven, or eight carbon atoms), with YCl$_3$ in THF in 2:1 and 1:1 molar ratios affords complexes of formula [L$_2$YCl]$_2$ and [(LYCl$_2$·THF)$_2$LiCl·2THF], respectively. Here we report the synthesis, spectroscopic characterization, and X-ray crystal structure of [(L′YCl$_2$·THF)$_2$LiCl·2THF] (L′ = 2-phenyl-4,5,6,7,8-hexahydroazulenyl), together with the crystal structure of the hexameric species [{L′YCl(OH)}$_6$·2THF], which was quite unexpectedly isolated during the attempted crystallization of the latter complex and is probably formed by partial hydrolysis of that complex. The activity of the new complexes towards ethylene and 1-hexene polymerization reactions was also tested.

Introduction

The chemistry of group 3 organometallics has undergone a spectacular growth in the past two decades.[1] Besides their activity as catalysts and reagents for a number of reactions,[2] they are also reckoned to be excellent models[3] and very active catalysts for Ziegler–Natta polymerizations of olefins, often without the aid of activators or co-catalysts.

Lanthanide chemistry has been dominated mainly by cyclopentadienyl complexes[4] because this family of ligands allows a wide range of modifications of the environment at the metal center through simple variation of the substitution pattern. Despite the interesting results thus far obtained, their high sensitivity to air and moisture, polar solvents,[5] and reagents[5,6] makes their application on an industrial scale still quite difficult. Furthermore, lanthanides with unsubstituted cyclopentadienyl ligands are almost insoluble in hydrocarbon solvents and usually show low activity.[7] Due to the delicate balance required in the ligand substitution pattern, it is advisable to find a family of cyclopentadienyl ligands provided with a more versatile structure and also capable of imparting higher stability and better solubility in most common organic solvents. In the framework of our research for metallocenes suitable for application in homogeneous catalysis, we have recently[8] synthesized several froup 4 ring-fused metallocenes where the ring (six, seven, or eight carbon atoms) fused to the cyclopentadienyl moiety is a saturated one. Besides their higher solubility, stability, and resistance to hydrolysis in comparison with the corresponding unsaturated counterparts, these complexes proved to be interesting polymerization catalysts,[9] since their particular structure introduces a conformational flexibility that can be finely tuned by varying the size of the cycloalkyl-ring and by introducing different substituents on the cyclopentadienyl ring. Here, we report the reactions of some ligands of this family with yttrium trichloride in 1:1 and 2:1 molar ratios as a test for lanthanides to check if they can produce more stable and soluble complexes for catalytic applications.

Results and Discussion

Synthesis and Characterization of Yttrium Complexes

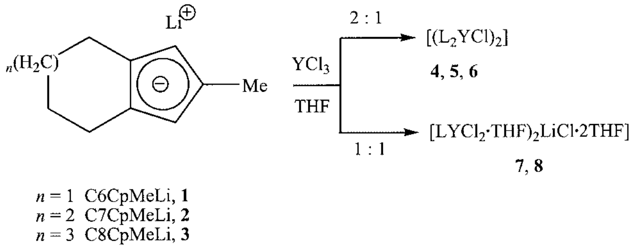
The lithium salts (C6CpMe)Li (**1**; HL = 2-methyl-4,5,6,7-tetrahydro-1*H*-indene), (C7CpMe)Li (**2**; HL = 2-methyl-1,4,5,6,7,8-hexahydroazulene, and (C8CpMe)Li (**3**; HL = 2-methyl-4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulene, prepared according to the literature procedures,[9a] were treated with YCl$_3$ in a 2:1 molar ratio to afford the corresponding complexes [L$_2$YCl]$_2$ with L = C6CpMe (**4**),

---

[a] Dipartimento di Chimica, Università Ca'Foscari di Venezia,
Dorsoduro 2137, 30123 Venezia, Italy
E-mail: paolucci@unive.it
[b] Centro di Strutturistica Diffrattometrica and Dipartimento di Chimica, Università di Ferrara,
44100 Ferrara, Italy
Fax: +39-053-224-0709
E-mail: m38@unife.it
[c] C.N.R.I.S.O.F., sez. Ferrara, Dipartimento di Chimica, Università di Ferrara,
Ferrara, Italy
Fax: +39-053-224-0709
E-mail: tr3@unife.it

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

C7CpMe (**5**), and C8CpMe (**6**), and in a 1:1 ratio to give the complexes [(LYCl$_2$·THF)$_2$LiCl·2THF] with L = C7CpMe (**7**) and C8CpMe (**8**); see Scheme 1.



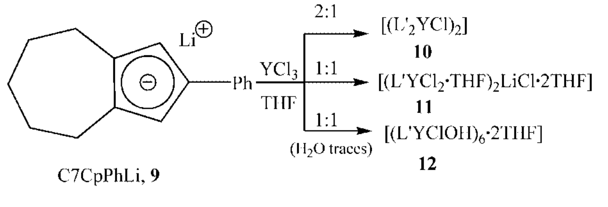
Scheme 1. Synthesis of the 2-methyl-substituted complexes.

The resulting complexes, which were isolated as dusty solids by precipitation with *n*-hexane from toluene or CH$_2$Cl$_2$ solutions, are also completely soluble in diethyl ether and THF. Analytical (elemental analyses and MS data) and NMR (^{1}H and ^{13}C; assignments by HMQC and HMBC experiments) data were consistent with the given formulations.

Crystal Structures

Crystals of complexes **4**, **6**, **7**, and **8** were obtained by slow evaporation of concentrated CH$_2$Cl$_2$ solutions, but, despite repeated attempts, they were not suitable for X-ray analysis. This difficulty in obtaining ordered structures is probably due both to the flexibility of the saturated ring and to the small size of the methyl group. Only complex **5** gave crystals suitable for X-ray diffraction, but they did not withstand the treatment (Fomblin F06206R or dehydrated Nujol) necessary to protect them from air and moisture during X-ray data acquisition.

Since the reactivity, stability, and solubility of lanthanide compounds are highly dependent on the steric hindrance of the ligand preventing oligomer formation, we decided to substitute the methyl group in the 2-position of the ligands for a phenyl group in order to obtain more ordered crystals. We chose the ligand with a saturated ring of seven carbon atoms since it was the only one that gave acceptable crystals for **5** and **7**. Treatment of lithium 2-phenyl-1,4,5,6,7,8-hexahydroazulenyl (L′, **9**)[9b] with YCl$_3$ in a 2:1 or 1:1 molar ratio, afforded complexes [(L′$_2$YCl)$_2$] (**10**) and [(L′YCl$_2$·THF)$_2$LiCl·2THF] (**11**), respectively (Scheme 2).



Scheme 2. Synthesis of the 2-phenyl-substituted complexes.

Crystals suitable for X-ray diffractometry studies were obtained only in the case of complex **11**. While attempts to protect the crystals with Fomblin failed, the use of anhydrous Nujol allowed X-ray data collection at 150 K; this confirmed the analytical and NMR spectroscopic data, which correspond to a complex of formula [(L′YCl$_2$·THF)$_2$LiCl·2THF] (L′ = C7CpPh; Figure 1).

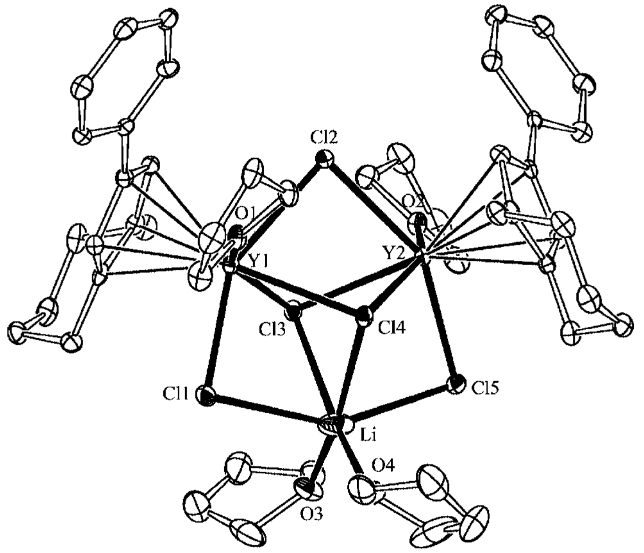


Figure 1. ORTEP[10] view of complex **11** displaying the thermal ellipsoids at 30% probability. The hydrogen atoms have been omitted for sake of clarity.

The structure (Figure 1, and Tables S1 and S2 in the Supporting Information) consists of a trimetallic complex where two atoms of yttrium and one atom of lithium, in a distorted octahedral coordination, are bridged by three μ-Cl (Cl1, Cl2, and Cl5) and two μ$_3$-Cl (Cl3 and Cl4) anions. Each Y atom is coordinated to four chloride ions, an η^5-cyclopentadienyl ring of the 2-phenyl-1,4,5,6,7,8-hexahydroazulenyl ligand, and a molecule of THF, while the lithium cation is coordinated to four Cl ions (Cl1, Cl3, Cl4, and Cl5) and two molecules of THF. The six Y–Cl bonds involved in the formation of Y–Cl–Y bridges display distances in the range 2.677(1)–2.860(1) Å (2.77 Å on average), and are slightly longer than those observed in dimeric bis[(μ-Cl)Y^{III}(cyclopentadienyl)] complexes (2.66–2.70 Å).[11–13] This Y–Cl lengthening can be justified by the presence of a μ-Cl bridge between yttrium atoms and two μ$_3$-Cl bridges which involve all three metal centers. The remaining μ-Cl1 and μ-Cl5 chlorides connecting yttrium atoms with lithium display shorter Y–Cl distances of 2.607(2) and 2.627(1) Å, in agreement with those found in the range 2.62–2.65 Å in similar Y–Cl–Li fragments.[14,15]

During our attempts to finding the appropriate crystallization solvents for complex **11**, in one crop we isolated several crystals stable to Fomblin treatment which allowed crystal data collection. Quite unexpectedly, they turned out to be the partial hydrolysis product of **11**, most probably caused by slight traces of water in the crystallization solvent. The results of the fast X-ray data collection at 120 K revealed the structure of an organometallic yttrium cluster, namely [{L′YCl(OH)}$_6$·2THF] (**12**; Figure 2 and Tables S3 and S4 in the Supporting Information). It is well known that hydrolysis and oxidation reactions are a common mode of decomposition for organometallic complexes of yttrium and the f elements, giving in most cases organometallic species containing M–OH or M–O–O–M bonds.[16–18]

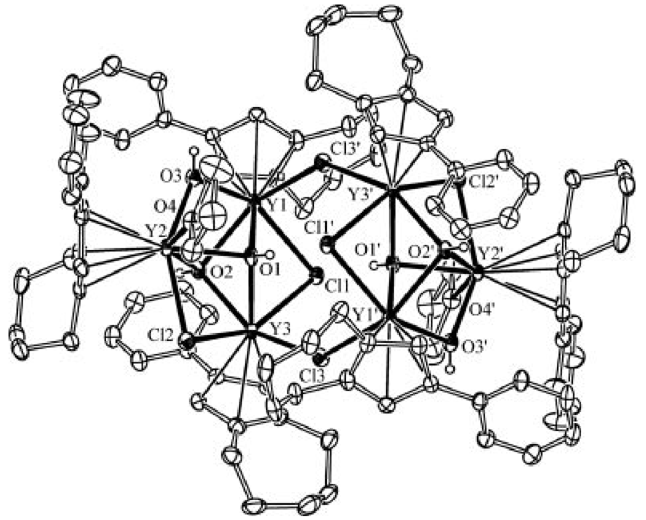


Figure 2. ORTEP view of complex **12** displaying the thermal ellipsoids at 30% probability. The hydrogen atoms have been omitted for sake of clarity.

The ^{1}H NMR spectrum of crystals of complex **12** is quite similar to that of **11** except for the presence of a very broad singlet at δ = 2.73 ppm that can be attributed to the OH group. The IR spectrum in CH_2Cl_2 solution shows an OH stretch at 3540 cm^{1}.

Complex **12** is a hexamer where two trimetallic clusters of yttrium atoms are held together, around a center of symmetry, by two μ-Cl3 chlorides between Y1 and Y3 (Figure 3). In each trimer the yttrium atoms are surrounded by an η^5-bonded cyclopentadienyl ring belonging to a 2-phenyl-1,4,5,6,7,8-hexahydroazulenyl ligand and bridged by chloride and hydroxy groups. In particular, the three Cl1, Cl2, and O3H anions span the three edges of the triangles formed with the Y atoms, while the μ_3-O1H and μ_3-O2H hydroxy groups triply bridge above and below the triangle formed by the yttrium atoms. The sixfold coordination around Y2 is completed by the oxygen atom of a THF molecule.

Accordingly, the overall geometry about each yttrium atom can be described as a distorted octahedral coordination. The Y–(μ-Cl) distances (2.66–2.74 Å) are in agreement with those observed in dimeric bis[(μ-Cl)Y^{III}(cyclopentadienyl)] complexes. Furthermore, as observed in other compounds,[16–19] the Y–(μ-OH) distances of 2.230(6) and 2.216(4) Å for Y1–O3 and Y2–O3, respectively, are shorter than those of Y–(μ_3-OH), which are in the range 2.34–2.43 Å. In both complexes the Y–Cp(cyclopentadienyl centroid) bond length (2.37–2.40 Å) and the Y–O(THF) distance of 2.338(6) Å are in accordance with the respective values observed in other cyclopentadienylyttrium derivatives.[20–23]

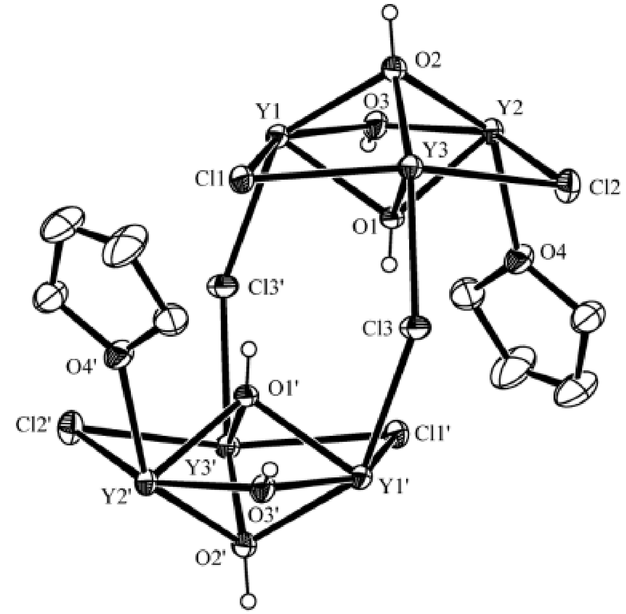


Figure 3. Diagram of the metal, halogen, and hydroxy framework of complex **12**, including the coordinated THF molecules.

Polymerization Studies

We have examined the activity of the new yttrium complexes, with MAO as co-catalyst, as a preliminary test for their polymerization activity. It is known[2] that organolanthanide complexes often do not require a co-catalyst or an activator to show high activity, but they must be previously converted into the corresponding sterically demanding alkyl derivatives [(trimethylsilyl)methyl or bis(trimethylsilyl)methyl], to prevent β-alkyl elimination, and as intermediates to the more unstable, but much more active, hydrides.

The bis(cyclopentadienyl) complexes **4**, **5**, **6**, and **10** did not show any activity towards ethene polymerization, while the mono(cyclopentadienyl) complexes **7** and **11**, which have a more open coordination sphere around the metal center, show a moderate activity (Table 1). This result can be interpreted by taking into account the fact that only a limited number of mono(cyclopentadienyl) half-sandwich rare-earth complexes of the type $[(\eta^5\text{-}C_5R_5)LnX_2(L)_n]$ have been synthesized, and their catalytic performance is often hampered by "ate complex" formation with concomitant alkali metal salt incorporation.[24] We also noticed some differences between the polymers obtained with the methyl-substituted (**7**) and phenyl-substituted (**11**) derivatives. While with the methyl-substituted complex **7**, after the usual work-up, a single fraction of highly linear polyethylene was produced (single peak at δ = 27.7 ppm in the ^{13}C NMR spectrum), with the phenyl-substituted complex **11** the yield was almost twice as high but the solid consisted of two fractions, the first (43%) of which is similar to the polymer isolated with the catalyst **7** and the second (57%) of which contains a mixture of oligomers. Apparently this different behavior can be attributed to the influence of the substituent in the ancillary ligand. It is likely that the methyl group, which exerts a symmetrical steric hindrance around the metal center, produces a more homogeneous material than the phenyl with its different space occupancy. We also tried the polymerization of a more sterically demanding monomer, 1-hexene, but we could not get any polymer. In structurally similar achiral lanthanocenes,[2e,25] which are also inactive towards 1-alkene polymerization, this negative result has been attributed to the formation of stable η^3-allyl type complexes.[26]

Table 1. Results of ethane and 1-hexene polymerizations.

Complex	Monomer	Activity[a]	Oligomers [%]
4, **5**, **6**, **10**	ethene[b]	–	–
7	ethene[b]	820	7
11	ethene[b]	1650	57
7	1-hexene[c]	–	–
11	1-hexene[c]	–	–

[a] $g_{Pol}(mmol_y\,h\,atm)^{-1}$. [b] Reaction conditions: toluene: 100 mL, [Y] = 8×10^{-6} M, [MAO]/[Y] = 1100, t_{rxn} = 24 h, room temp. [c] Reaction conditions: toluene: 100 mL, [Y] = 8×10^{-6} M, [MAO]/[Y] = 1875, t_{rxn} = 24 h, room temp.

Conclusions

Novel unbridged bicyclic yttrium complexes containing six-, seven-, and eight-membered saturated rings fused to a cyclopentadienyl moiety substituted in position 2 (CH_3, Ph) have been synthesized with 2:1 and 1:1 ligand/metal ratios, and fully characterized. Unlike their analogous cyclopentadienyl derivatives, these complexes are very soluble in most common organic solvents but are highly sensitive to air and moisture. The crystal structure of complex **11** shows its dimeric nature, thus confirming that the high coordinative unsaturation of the monomer in the absence of high steric hindrance favors the formation of dimeric yttrium species. Quite unexpectedly, we have been able to isolate and fully characterize the hexameric yttrium organometallic cluster **12**, which is probably formed by the reaction of **11** with traces of water in the crystallization solvent. The yttriocenes **4**, **5**, **6**, and **10**, in combination with MAO as cocatalyst, are inactive in the polymerization of ethylene and 1-hexene, while complexes **7** and **11** show a low reactivity towards ethene polymerization and are also inactive towards 1-hexene. These unsatisfactory results can be attributed to the probably dimeric nature of the complexes, which is maintained after MAO activation, thus preventing access of the olefin to the reactive center due to steric hindrance. Further studies are necessary to modify the chloro complexes (i.e., by substitution with bulky alkyl groups) in order to produce monomeric yttrium species, which should be more efficient polymerization catalysts.

Experimental Section

General procedures: All manipulations were carried out under an oxygen- and moisture-free atmosphere in a Braun MB 200 GII glove box. All solvents were thoroughly deoxygenated and dehydrated under argon by refluxing and distillation over a suitable drying agent (*n*-hexane, toluene, and THF over Na or K/benzophenone ketyl; CH_2Cl_2, CD_2Cl_2, and $CDCl_3$ over CaH_2; C_6D_5N over KOH). YCl_3 (Aldrich) was used as received. Nujol (Aldrich) was degassed and dehydrated by reflux over potassium. Fomblin (ABCR) F06206R, viscosity 1600cSt, was degassed prior to use. The ligands C6CpMeH,[8] C6CpMeLi (**1**),[8] C7CpMeH,[8] C8CpMeH,[8] and C7CpPhH[9a] were prepared according to literature methods. Microanalyses were performed at the Istituto di Chimica Inorganica e delle Superfici, CNR, Padova. The Li contents of the complexes were determined by ICP using an ICP-MS Agilent 7500 apparatus. Mass spectra were recorded with a Finnigan Trace MS equipped with a probe for the direct introduction of the sample (EI = 70 eV, T_{probe} = 120–150 °C). ^{1}H and ^{13}C NMR spectra were obtained for $CDCl_3$ or CD_2Cl_2 solutions with a Bruker AMX 300 spectrometer operating at 300 and 100.61 MHz, respectively. 2D-Heterocorrelated COSY experiments (HMQC and HMBC) allowed the identification of all ^{1}H and ^{13}C resonances.

Lithium Salts of the Ligands. General Synthetic Procedure: The starting diene (14 mmol) was suspended in *n*-hexane at –80 °C. *n*-Butyllithium (14 mmol) was then added dropwise, whilst stirring, and the solution was slowly allowed to reach room temperature (about 4 h) and stirred overnight. The lithium salt that separated from the solution was isolated by centrifugation, washed several times with *n*-hexane, and dried under vacuum to give a dusty solid.

2-Methyl-1,4,5,6,7,8-hexahydroazulenyllithium (2): White solid. Yield: 1.94 g (90%). ^{1}H NMR ([D$_5$]pyridine): δ = 1.73–1.94 (m, 6 H, C-CH$_2$-CH_2-), 2.43 (s, 3 H, CH_3), 2.85 (br. s, 4 H, -C-CH_2-CH$_2$-), 5.86 (s, 2 H, -CH-,Cp) ppm.

2-Methyl-4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulenyllithium (3): White solid. Yield: 2.22 g (88%). ^{1}H NMR ([D$_5$]pyridine): δ = 1.57–1.74 (m, 8 H, C-CH-CH_2-), 2.41 (s, 3 H, CH_3), 2.68–2.74 (m, 4 H, -C-CH_2-CH$_2$-), 5.86 (s, 2 H, -CH-, Cp) ppm.

2-Phenyl-1,4,5,6,7,8-hexahydroazulenyllithium (9): Pink-white solid. Yield 1.82 g (60%). ^{1}H NMR ([D$_5$]pyridine): δ = 1.47–1.65 (m, 6 H, C-CH-CH_2-), 2.48 (m, 4 H, -C-CH_2-CH$_2$-), 6.11 (s, 2 H, -CH-, Cp), 6.50 (t, $^{3}J_{H,H}$ = 7.7 Hz, 1 H, *meta*-C_5H_6), 6.90 (t, $^{3}J_{H,H}$ = 7.7 Hz, 2 H, *para*-C_5H_6), 7.42 (d, $^{3}J_{H,H}$ = 7.6 Hz, 2 H, *ortho*-C_5H_6) ppm.

Yttrium Complexes. General Synthetic Procedure: YCl_3 (1.0 mmol) was dissolved in warm THF (30 mL) and cooled to room temperature. A solution of the lithium salt (2.0 or 1.0 mmol) dissolved in THF (20 mL) was then added with vigorous stirring at room temperature, and the reaction mixture stirred overnight. The solvent was then removed under reduced pressure, the residue washed with dichloromethane (3 × 10 mL), and separated from LiCl, when necessary, by centrifugation. The yellow solution was concentrated (to about 10 mL) and left at –25 °C for several days to give microcrystals.

Bis[(μ-chloro){bis[η^5-(2-methyl-4,5,6,7-tetrahydro-1*H*-indenyl)]-yttrium}] (4): Yellow solid. Yield: 0.508 g (65%). $C_{40}H_{52}Cl_2Y_2$ (781.57): calcd. C 61.47, H 6.71, Cl 9.07; found C 61.05, H 6.95, Cl 8.90. ^{1}H NMR ($CDCl_3$): δ = 1.65–1.80 (m, 8 H, C-CH$_2$-CH_2-), 2.05 (s, 6 H, CH_3), 2.50–2.90 (m, 8 H, -C-CH_2-CH$_2$-), 5.90 (s, 4 H, -CH-, Cp) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.9 (CH_3), 29.9 (-C-CH$_2$-CH_2-), 33.1(-C-CH_2-CH$_2$-), 114.6 (-CH, Cp), 125.7 (-C-CH$_3$), 132.8 (-CH$_2$-C=CH-, Cp) ppm. MS (T_{probe} = 120 °C): *m*/*z* (%) 766 (18) $[M^{+\cdot} - CH_3]^+$, 751 (22) $[M^{+\cdot} - 2CH_3]^+$, 746 (12) $[M^{+\cdot} - Cl]^+$, 731 (10) $[M^{+\cdot} - CH_3 - Cl]^+$.

Bis[(μ-chloro){bis[η^5-(2-methyl-1,4,5,6,7,8-hexahydroazulenyl)]-yttrium}] (5): Yellow solid. Yield: 0.611 g (73%). $C_{44}H_{60}Cl_2Y_2$ (837.68): calcd. C 63.09, H 7.22, Cl 8.46; found C 62.75, H 6.95, Cl 8.65. ^{1}H NMR ($CDCl_3$): δ = 1.35–1.70 (m, 8 H, C-CH$_2$-CH_2-

CH$_2$-), 1.70–1.95 (m, 4 H, C-CH$_2$-CH$_2$-C*H*$_2$-), 2.08 (s, 6 H, C*H*$_3$), 2.50–2.90 (m, 8 H, -C-C*H*$_2$-CH$_2$-CH$_2$-), 5.95 (s, 4 H, -C*H*-, Cp) ppm. ^{13}C NMR (CDCl$_3$): δ = 14.9 (*C*H$_3$), 29.9 (-C-CH$_2$-*C*H$_2$-CH$_2$-), 31.6 (-C-*C*H$_2$-CH$_2$-CH$_2$-), 33.2 (C-CH$_2$-CH$_2$-*C*H$_2$), 114.4 (-*C*H, Cp), 120.3 (-*C*-CH$_3$), 129.8 (-CH$_2$-*C*=CH-, Cp) ppm. MS (T_{probe} = 120 °C): *m*/*z* (%) 837 (1) $[M]^{+\cdot}$, 822 (21) $[M^{+\cdot} - CH_3]^+$, 807 (25) $[M^{+\cdot} - 2CH_3]^+$, 802 (15) $[M^{+\cdot} - Cl]^+$, 690 (42) $[C_{33}H_{45}Cl_2Y_2]^+$, 403 (44) $[C_{21}H_{27}ClY]^+$, 388 (100) $[C_{20}H_{24}ClY]^+$, 368 (37) $[C_{21}H_{27}Y]^+$.

Bis[(μ-chloro){bis[η^5-(2-methyl-4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulenyl)]yttrium}] (6): Yellow solid. Yield: 0.590 g (66%). C$_{48}$H$_{68}$Cl$_2$Y$_2$ (893.78): calcd. C 64.50, H 7.67, Cl 7.93; found C 64.15, H 7.25, Cl 7.80. ^{1}H NMR (CDCl$_3$): δ = 1.10–1.25 (m, 12 H, -C*H*$_2$-), 1.25–1.50 (m, 4 H, -C*H*$_2$-), 2.00 (s, 6 H, C*H*$_3$), 2.30–2.45 (m, 4 H, -C-C*H*$_2$-CH$_2$-), 2.55–2.75 (m, 4 H, -C-C*H*$_2$-CH$_2$-), 5.95 (s, 4 H, s, 4 H, -C*H*-, Cp) ppm. ^{13}C NMR (CDCl$_3$): δ = 14.9 (*C*H$_3$), 26.3 (C-CH$_2$-*C*H$_2$–CH$_2$-), 27.4 (-C-*C*H$_2$-CH$_2$-CH$_2$-), 33.4 (C-CH$_2$-CH$_2$-*C*H$_2$), 112.3 (-*C*H, Cp), 122.0 (-*C*-CH$_3$), 128.3 (-CH$_2$-*C*=CH-, Cp) ppm. MS (T_{probe} = 10 °C): 893 (3) $[M]^{+\cdot}$, 878 (27) $[M^{+\cdot} - CH_3]^+$, 863 (31) $[M^{+\cdot} - 2CH_3]^+$, 858 (15) $[M^{+\cdot} - Cl]^+$, 446 (8) $[C_{24}H_{34}ClY]^+$, 431 (100) $[C_{23}H_{31}ClY]^+$, 416 (65) $[C_{22}H_{28}ClY]^+$, 396 (37) $[C_{23}H_{31}Y]^+$.

Complex 7: Yellowish solid. Yield: 0.803 g (85%). C$_{38}$H$_{62}$Cl$_5$LiO$_4$Y$_2$ (944.92): calcd. C 48.30, H 6.61, Cl 18.76, Li 0.73; found C 47.95, H 6.55, Cl 18.45, Li 0.80. ^{1}H NMR (CDCl$_3$): δ = 1.25–1.95 (m, 12 H, -C*H*$_2$-), 1.90 (br. s, 16 H, THF), 2.00 (s, 6 H, C*H*$_3$), 2.45–2.80 (m, 8 H, -C-C*H*$_2$-CH$_2$-), 3.80 (br. s, 16 H, THF), 5.95 (s, 4 H, -C*H*-, Cp) ppm.

Complex 8: Yellow solid. Yield: 0.807 g (83%). C$_{40}$H$_{66}$Cl$_5$O$_4$LiY$_2$ (972.96): calcd. C 49.38, H 6.84, Cl 18.22, Li 0.71; found C 49.15, H 6.75, Cl 18.45, Li 0.80. ^{1}H NMR (CDCl$_3$): δ = 1.10–1.85 (m, 16 H, -C*H*$_2$-), 1.98 (br. s, 16 H, THF), 2.05 (s, 6 H, C*H*$_3$), 2.10–2.65 (m, 8 H, -C-C*H*$_2$-CH$_2$-), 4.04 (br. s, 16 H, THF), 5.72 (s, 4 H, -C*H*-, Cp) ppm. ^{13}C NMR (CDCl$_3$): δ = 16.28 (*C*H$_3$), 25.81 (THF), 26.47 (-C-CH$_2$-*C*H$_2$-CH$_2$-), 27.71 (-C-*C*H$_2$-CH$_2$-CH$_2$-), 33.33 (C-CH$_2$-CH$_2$-*C*H$_2$-), 71.02 (THF), 114.16 (-*C*H, Cp), 123.0 (-*C*–CH$_3$), 129.91 (-CH$_2$-*C*=CH-, Cp) ppm.

Bis[(μ-chloro){bis[η^5-(2-phenyl-1,4,5,6,7,8-hexahydroazulenyl)]-yttrium}] (10): Deep-yellow solid. Yield: 0.847 g (78%). C$_{64}$H$_{68}$Cl$_2$Y$_2$ (1085.9): calcd. C 70.78, H 6.31, Cl 6.53; found C 70.45, H 6.15, Cl 6.75. ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.12–2.10 (m, 12 H, -C*H*$_2$-), 2.25–2.85 (m, 8 H, -C-C*H*$_2$-CH$_2$-CH$_2$-), 6.14 (s, 4 H, -C*H*-, Cp), 7.12 (t, $^3J_{H,H}$ = 7.23 Hz, 2 H, *para*-C$_5$H$_6$), 7.33 (t, $^3J_{H,H}$ = 7.62 Hz, 4 H, 4 H, *meta*-C$_5$H$_6$), 7.46 (d, $^3J_{H,H}$ = 7.23, 4 H, *ortho*-C$_5$H$_6$) ppm. MS (T_{probe} = 120 °C): *m*/*z* (%) 1085 (1) $[M]^{+\cdot}$, 877 (44) $[C_{48}H_{51}Cl_2Y_2]^+$, 667 (2) $[C_{32}H_{34}Cl_2Y_2]^+$, 543 (1) $[C_{32}H_{34}ClY]^+$, 528 (100) $[C_{31}H_{31}ClY]^+$, 493 (28) $[C_{31}H_{31}Y]^+$, 298 (1) $[C_{16}H_{16}Y]^+$, 210 (20) $[C_{16}H_{18}]^+$.

Complex 11: Deep-yellow solid. Yield: 0.823 g (77%). C$_{48}$H$_{66}$Cl$_5$LiO$_4$Y$_2$ (1069.05): calcd. C 53.93, H 6.22, Cl 16.58, Li 0.65; found C 54.10, H 6.05, Cl 16.80, Li 0.70. ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.65 (m, 8 H, C-CH$_2$-C*H*$_2$-CH$_2$-), 1.78 (m, 4 H, C-CH$_2$-CH$_2$-C*H*$_2$-), 1.89 (br. s, 16 H, THF), 2.40–2.53 (m, 8 H, -C-C*H*$_2$-CH$_2$-CH$_2$-), 3.99 (br. s, 16 H, THF), 6.65 (s, 4 H, -C*H*-, Cp), 7.11 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, *para*-C$_5$H$_6$), 7.27 (t, $^3J_{H,H}$ = 7.3 Hz, 4 H, *meta*-C$_5$H$_6$), 7.43 (d, $^3J_{H,H}$ = 7.3 Hz, 4 H, *ortho*-C$_5$H$_6$) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ = 25.7 (THF), 28.3 (-C-CH$_2$-*C*H$_2$-CH$_2$-), 28.4 (-C-CH$_2$-*C*H$_2$-CH$_2$-), 30.1 (-C-*C*H$_2$-CH$_2$-CH$_2$-), 30.7 (-C-*C*H$_2$-CH$_2$-CH$_2$-), 31.9 (-C-CH$_2$-CH$_2$-*C*H$_2$-), 70.4 (THF), 124.7 (*ortho*-C$_5$H$_6$), 126.1 (*para*-C$_5$H$_6$), 128.7 (*meta*-C$_5$H$_6$), 133.0 (-*C*H, Cp), 142.0 (*ipso*-C$_5$H$_6$), 142.8 (-*C*–C$_5$H$_6$), 143.6 (-CH$_2$-*C*=CH-, Cp) ppm. Crystals suitable for X-ray analysis were obtained from a very concentrated CH$_2$Cl$_2$ solution after four days at –26 °C.

Complex 12: Yellow solid, C$_{104}$H$_{108}$Cl$_6$O$_8$Y$_6$ (2232.12): calcd. C 55.96, H 5.73, Cl 9.53; found C 55.80, H 5.60, Cl 9.40. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3540 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.55–1.71 (m, 8 H, C-CH$_2$-C*H*$_2$-CH$_2$-), 1.71–1.83 (m, 4 H, C-CH$_2$-CH$_2$-C*H*$_2$-), 1.89 (br. s, 2.7 H, THF), 2.37–2.55 (m, 8 H, -C-C*H*$_2$-CH$_2$-CH$_2$-), 2.73 (br. s, 1 H, OH), 3.97 (br. s, 2.7 H, THF), 6.66 (s, 4 H, -C*H*-, Cp), 7.12 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H, *para*-C$_5$H$_6$), 7.27 (t, $^3J_{H,H}$ = 7.0 Hz, 4 H, *meta*-C$_5$H$_6$), 7.44 (d, $^3J_{H,H}$ = 7.0 Hz, 4 H, *ortho*-C$_5$H$_6$) ppm.

X-ray Crystallographic Structure Determinations for 11 and 12: The crystal data for compounds **11** and **12** (Table 2) were collected at 120 and 150 K, respectively, using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation. The data sets were integrated with the Denzo-SMN package[27] and corrected for Lorentz, polarization, and absorption (SORTAV[28]) effects. The structures were solved by direct methods (SIR97[29]) and refined using full-matrix least-squares with all non-hydrogen atoms anisotropic and hydrogens included at calculated positions as riding on their carrier atoms. All calculations were performed using SHELXL97[30] and PARST[31] implemented in WINGX[32] system of programs.

Table 2. Crystal data for complexes **11** and **12**.

Compound	**11**	**12**
Formula	C$_{48}$H$_{66}$Cl$_5$LiO$_4$Y$_2$	C$_{104}$H$_{108}$Cl$_6$O$_8$Y$_6$
MW	1069.02	2520.56
Space group	$P2_12_12_1$	$P\bar{1}$
Crystal system	orthorhombic	triclinic
a [Å]	11.6874(3)	14.0415(3)
b [Å]	19.9579(5)	14.4971(3)
c [Å]	21.3214(4)	15.4855(5)
α [°]	90	76.886(1)
β [°]	90	86.128(1)
γ [°]	90	65.722(2)
T [K]	120	150
Z	4	1
D_c [g cm^{-3}]	1.428	1.496
F(000)	2200	1286
μ(Mo-K_α) [cm^{-1}]	26.313	33.940
Measured reflections	29098	42244
Unique reflections	9657	12718
R_{int}	0.101	0.050
Obs. reflns [$I \geq 2\sigma(I)$]	7677	9484
$\Theta_{\min}$, $\Theta_{\max}$ [°]	2.85–26.00	4.00–27.50
hkl ranges	–13,14; –24,24; –26,26	–18,18; –16,18; –19,20
$R(F^2)$(obs. reflns.)	0.0537	0.0701
$wR(F^2)$ (all reflns.)	0.0961	0.1781
No. variables	541	625
Goodness of fit	1.054	1.218
$\rho_{\min}$, $\rho_{\max}$ [e Å^{-3}]	–0.686, 0.379	–0.750, 1.180

CCDC-297382 (for **11**) and -297383 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Selected interatomic distances and angles are given in Tables S1–S4.

General Polymerization Conditions: All manipulations of air- and/or moisture-sensitive materials were carried out under inert atmosphere using either a dual vacuum/nitrogen line and standard Schlenk techniques or in a dry-box under nitrogen atmosphere

(<10 ppm oxygen, <20 ppm water). MAO (Witco, 10 wt.-% solution in toluene) was used after drying in vacuo (5 h, 50 °C, 0.1 mbar) to remove the solvent and unreacted $AlMe_3$, and was stored under nitrogen. Nitrogen and ethylene were purified by passage through columns of BASF RS-11 (Fluka) and Linde 4-Å molecular sieves. 1-Hexene was deoxygenated and dehydrated under nitrogen by refluxing and distillation over $LiAlH_4$, and stored under nitrogen.

Ethylene Polymerizations: A 250-mL glass reactor equipped with a magnetic stirrer was charged with anhydrous toluene (100 mL) and MAO (8.8 mmol) from a syringe. Ethylene was then added until saturation. The polymerization was started by adding a solution of the catalyst (**7** or **11**) (8 µmol; [Al]/[Y] ratio: 1100) in toluene (5 mL) with a syringe under ethylene pressure. After 24 h the reaction was terminated by addition of a small amount of ethanol, and the polymer was precipitated by pouring the whole reaction mixture into ethanol (600 mL) to which concentrated hydrochloric acid (5 mL) had been added. The organic phase was separated, washed with $NaHCO_3$ saturated solution, deionized water, and dried with $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure and the last traces of toluene were eliminated by azeotropic distillation with absolute ethanol (three times). Absolute ethanol was added again and the polymer was collected by filtration, washed with absolute ethanol, and dried overnight under vacuum at 70 °C. If oligomers were produced (as with catalyst **7**), they were retrieved as an oily residue after evaporation of the ethanol from the filtered solution, extraction with pentane, and evaporation of the solvent.

1-Hexene Polymerizations: A 250-mL glass reactor equipped with a magnetic stirrer was charged with anhydrous toluene (100 mL), 1-hexene (1 mol/L), and MAO (15 mmol). The polymerization was started by adding a solution of the catalyst (**7** or **11**) (8 µmol; [Al]/[Y] ratio: 1875) in toluene (5 mL) with a syringe under nitrogen pressure. After 24 h the polymerization was quenched by adding a small amount of ethanol. The contents of the reactor were poured into a conical flask, and a solution of concentrated HCl in ethanol (200 mL; 15% by volume) was added. After 30 min stirring, the mixture was transferred into a separating funnel, the organic phase was separated, washed once with $NaHCO_3$ saturated solution, twice with deionized water, and dried with $MgSO_4$. After filtration, the solvent was removed under reduced pressure. No polymer was obtained.

Acknowledgments

The authors warmly thank Dr. F. Forlini of ISMAC-C.N.R. (Milano, Italy) for performing the polymerization tests. This work was funded by the MURST PRIN-2004 (prot. 2004030307_3).

---

[1] a) W. J. Evans, *Polyhedron* **1987**, *6*, 803–835; b) C. J. Schaverien, *Adv. Organomet. Chem.* **1994**, *36*, 283–362; c) F. T. Edelmann, in *Comprehensive Organometallic Chemistry* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson, M. F. Lappert), Pergamon, Oxford, **1995**, vol. 4; d) H. Schumann, J. A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865–986; e) G. A. Molander, J. A. C. Romero, *Chem. Rev.* **2002**, *102*, 2161–2186; f) R. Anwander, in *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**, vol. 2, p. 866; g) *Lanthanides: Chemistry and Use in Organic Synthesis* (Ed.: S. Kobayashi), Springer, Berlin, **1999**.

[2] a) T. R. Jensen, J. J. O'Donnel III, T. J. Marks, *Organometallics* **2004**, *23*, 740–754; b) M. Nishiura, Z. Hou, *J. Mol. Catal. A* **2004**, *213*, 101–106; c) Z. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* **2002**, *231*, 1–22 and references cited therein; d) G. Lanza, I. L. Fragalà, T. J. Marks, *Organometallics* **2002**, *21*, 5594–5612; e) G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann, T. J. Marks, *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103.

[3] a) P. L. Watson, *J. Am. Chem. Soc.* **1982**, *104*, 337–339; b) P. L. Watson, G. W. Parshall, *Acc. Chem. Res.* **1985**, *18*, 51–56.

[4] J. Okuda, T. Eberle, in *Metallocenes* (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, Weinheim, Germany, **1998**; vol. 1, p. 415.

[5] a) P. L. Watson, *J. Chem. Soc., Chem. Commun.* **1983**, 276–277; b) W. J. Evans, L. R. Chamberlain, T. A. Ulibarri, J. W. Ziller, *J. Am. Chem. Soc.* **1988**, *110*, 6423–6432; c) B. J. Deelman, M. Booij, A. Meetsma, J. H. Teuben, H. Kooijman, A. L. Spek, *Organometallics* **1995**, *14*, 2306–2317.

[6] W. E. Piers, P. J. Shapiro, E. E. Bunel, J. E. Bercaw, *Synlett* **1990**, 74–84.

[7] a) J. L. Namy, P. Girard, H. B. Kagan, P. E. Caro, *Nouv. J. Chim.* **1981**, *5*, 479–484; b) R. E. Maginn, S. Manastyrskyj, M. Dubeck, *J. Am. Chem. Soc.* **1963**, *85*, 672; c) W. J. Evans, J. H. Meadows, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1984**, *106*, 1291–1300.

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

[9] a) E. Polo, S. Losio, F. Forlini, P. Locatelli, A. Provasoli, M. C. Sacchi, *Macromol. Chem. Phys.* **2002**, *203*, 1859–1865; b) E. Polo, A. Barbieri, S. Sostero, M. L. H. Green, *Eur. J. Inorg. Chem.* **2002**, 405–409; c) E. Polo, A. Barbieri, O. Traverso, *Eur. J. Inorg. Chem.* **2003**, 324–330; d) E. Polo, A. Barbieri, O. Traverso, *New J. Chem.* **2004**, *28*, 652–656; e) E. Polo, F. Forlini, P. Locatelli, M. C. Sacchi, *Macromol. Chem. Phys. Macrom. Symp.* **2004**, *213*, 89–99; f) E. Polo, S. Losio, G. Zecchi, F. Bertini, M. C. Sacchi, *Macromol. Rapid. Commun.* **2004**, *25*, 1845–1850; g) S. Losio, G. Zecchi, F. Bertini, M. C. Sacchi, V. Bertolasi, E. Polo, *Macromolecules* **2005**, *38*, 7231–7240; h) M. C. Sacchi, I. Tritto, F. Bertini, S. Losio, G. Zecchi, E. Polo, *Kinet. Catal.* **2006**, *47*, 268–273.

[10] M. N. Burdett, C. K. Johnson, *ORTEP III, Report ORNL6895*, Oak Ridge National Laboratory, Oak Ridge, TN, **1996**.

[11] W. J. Evans, M. S. Sollberger, J. S. Shreeve, J. M. Olofson, J. H. Hain Jr, J. W. Ziller, *Inorg. Chem.* **1992**, *31*, 2492–2501.

[12] R. Broussier, G. Delmas, P. Perron, B. Gautheron, J. L. Petersen, *J. Organomet. Chem.* **1996**, *511*, 185–192.

[13] H. Schumann, H. Heim, J. Damtschuk, S. H. Mühle, *Organometallics* **2003**, *22*, 118–128.

[14] W. E. Evans, T. J. Boyle, J. W. Ziller, *Inorg. Chem.* **1992**, *31*, 1120–1122.

[15] H. Schumann, J. Loebel, J. Pickardt, C. Qian, Z. Xie, *Organometallics* **1991**, *10*, 215–219.

[16] W. E. Damrau, G. Paolucci, J. Zanon, E. Siebel, R. D. Fischer, *Inorg. Chem. Commun.* **1998**, *1*, 424–426.

[17] H. Schumann, F. H. Görlitz, F. E. Hahn, J. Pickardt, C. Qian, Z. Xie, *Z. Anorg. Allg. Chem.* **1992**, *609*, 131.

[18] W. J. Evans, M. A. Hozbor, S. G. Bott, G. H. Robinson, J. L. Atwood, *Inorg. Chem.* **1988**, *27*, 1990–1993.

[19] E. H. Barash, P. S. Coan, E. B. Lobkovsky, W. E. Streib, K. G. Coulton, *Inorg. Chem.* **1993**, *32*, 497–501.

[20] H. Schumann, H. Heim, J. Damtschuk, S. H. Mühle, *Organometallics* **2002**, *21*, 3323–3334.

[21] R. A. L. Gendron, D. J. Berg, P. Shao, T. Barclay, *Organometallics* **2001**, *20*, 4279–4286.

[22] K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228–243.

[23] E. Ihara, S. Yoshioka, M. Furo, K. Katsura, H. Yasuda, S. Mohri, N. Kanehisa, Y. Kai, *Organometallics* **2001**, *20*, 1752–1761.

[24] a) P. J. Shapiro, E. Bunel, W. P. Schaefer, J. E. Bercaw, *Organometallics* **1990**, *9*, 867869; b) P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **1994**,

116, 46234640; c) C. J. Schaverien, *Organometallics* **1994**, *13*, 6982; d) I. Albrecht, H. Schumann, *J. Organomet. Chem.* **1986**, *310*, C29; e) H. Schumann, I. Albrecht, J. Pickardt, E. Hahn, *J. Organomet. Chem.* **1984**, *276*, C5.

[25] a) G. Jeske, L. E. Schock, P. N. Swepston, H. Schumann, T. J. Marks, *J. Am. Chem. Soc.* **1985**, *107*, 81038110; b) W. J. Evans, T. A. Ulibarri, J. W. Ziller, *J. Am. Chem. Soc.* **1990**, *112*, 2314–2324.

[26] a) C. P. Casey, T.-Y. Lee, J. A. Tunge, D. W. Carpenetti II, *J. Am. Chem. Soc.* **2001**, *123*, 210763; b) C. P. Casey, J. F. Klein, M. A. Fagan, *J. Am. Chem. Soc.* **2000**, *122*, 4320–4330; c) C. P. Casey, S. L. HallenBeck, J. M. Wright, C. R. Landis, *J. Am. Chem. Soc.* **1997**, *119*, 9680–9690.

[27] Z. Otwinowski, W. Minor, in *Methods in Enzymology* (Eds.: C. W. Carter, R. M. Sweet), vol. 276, part A, Academic Press, London, **1997**, 307–326.

[28] R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33–38.

[29] SIR97: A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[30] G. M. Sheldrick, *SHELX97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

[31] M. Nardelli, *J. Appl. Crystallogr.* **1995**, *28*, 659–661.

[32] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

Received: May 2, 2006