Synthesis and characterization of Zr(IV) and Y(III) complexes with monocyclopentadienyl ligands containing an additional site tethered by a coordinating 2,6-pyridine bridge. X-ray crystal structures of the zirconium complexes

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Abstract

A new monocyclopentadienyl ligand containing an additional site tethered by a coordinating 2,6-pyridine unit has been prepared, *rac*-2-(1′-hydroxy-2′,2′-dimethylpropyl)-6-(1″,1″-dimethyl-cyclopentadienylmethyl) pyridine dilithium salt, LLi$_2$ (*rac*-**4**) that is analogous to the ligands present in CGC. After reacting the dilithium salt of the ligand with ZrCl$_4$ in a molar ratio of 1:1 in THF the complex LZrCl$_2$·THF (*rac*-**5**) was obtained which forms an insoluble oligomeric species after the loss of THF upon purification. From the mater liquor two crystalline species of the formula LHZrCl$_3$ (*rac*-**6**) and LH$_2$ZrCl$_4$·THF (*rac*-**7**) were isolated, whose X-ray crystal structures are reported. The reaction of LLi$_2$ with Y(OTf)$_3$ afforded the probably dimeric species [LYOTf]$_2$ (*rac*-**8**) from which the complex [LY(CH$_2$Si(CH$_3$)$_3$)]$_2$ (*rac*-**9**) was obtained after reaction with LiCH$_2$Si(CH$_3$)$_3$.
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1. Introduction

In the last few years, group IIIB and IVB metallocenes and *ansa*-metallocenes have shown interesting properties as homogeneous catalysts in the Ziegler–Natta polymerization of α-olefins. Electronically more deficient zirconium, titanium and lanthanide species with only one cyclopentadienyl ligand containing an additional site tethered via a non-coordinating or a coordinating bridge (CGC), are currently attracting considerable interest [1,2]. The higher activity of these CGC species compared to the corresponding metallocenes and *ansa*-metallocenes can be assigned to their increased electronic deficiency and decreased steric bulk around the metal ion.

With the aim to prepare trigonal bipyramidal zirconium(IV) complexes similar to *ansa*-zirconocenes [3] and *ansa*-lanthanocenes [4], synthesized previously by our group, we report herein the synthesis of the new ligand *rac*-2-(1′-hydroxy-2,2′-dimethylpropyl)-6-(1″,1″-dimethylcyclopentadienylmethyl)pyridine (*rac*-**2**) and its corresponding zirconium(IV) (*rac*-**5**, *rac*-**6** and *rac*-**7**) and yttrium(III) (*rac*-**8** and *rac*-**9**) complexes.

2. Results and discussion

2.1. Synthesis of the ligand (rac-2)

Usually the tridentate monocyclopentadienyl ligands used in CGC contain the additional donor (N or O) atoms in flexible chains bonded to the cyclopentadienyl ring, making possible equilibrium between species where the ligand acts both in a bidentate and a tridentate
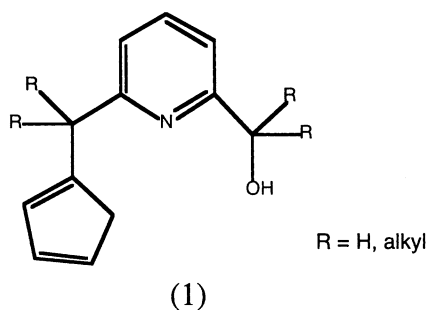
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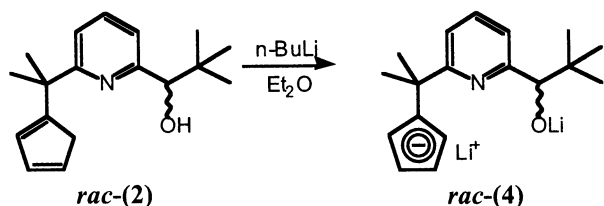*E-mail address:* paolucci@unive.it (G. Paolucci).
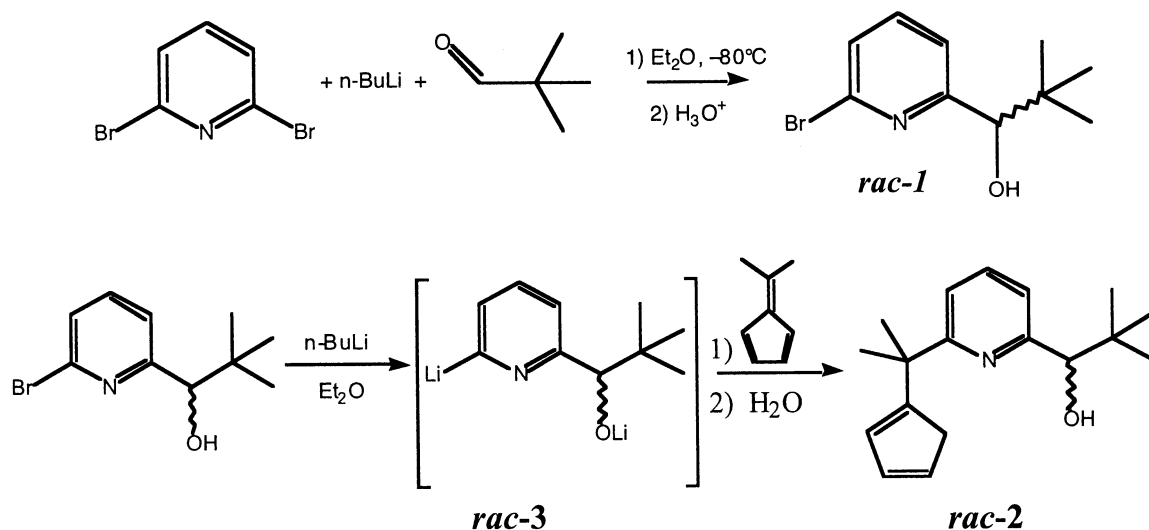
Scheme 1.

mode. To obtain more rigid structures affording co-ordination geometries suitable of inducing steric effects on the metal ion, and by considering our previous results [3,4], we considered ligands of the type:

R = H, alkyl

(1)

The synthetic approach to a racemic mixture of a ligand of the type (1) is reported on Scheme 1.

The first two steps of the synthesis affording *rac*-1 were made sequentially according to the literature method [5]. The successive steps have been carried out without protecting the alcoholic group (we tested a protection with 3,4-dihydro-2H-pyrane) as the overall yields of the two methods (with and without OH-protection) were about the same. The final dilithium salt derivative (*rac*-4) was hardly purified from the impurity due to the lithium salt initially formed by reaction of *rac*-1 and *n*-BuLi (*rac*-3) present, as both salts have similar solubility. To obtain the ligand *rac*-2

in a pure form, the crude dilithium salt (*rac*-4) was protonated by a brine solution and extracted with diethyl ether. The solvent removed under vacuum and the oily residue purified by flash chromatography affording *rac*-2 in pure form, from which the pure dilithium salt *rac*-4 was obtained by reaction with *n*-BuLi (Scheme 2).
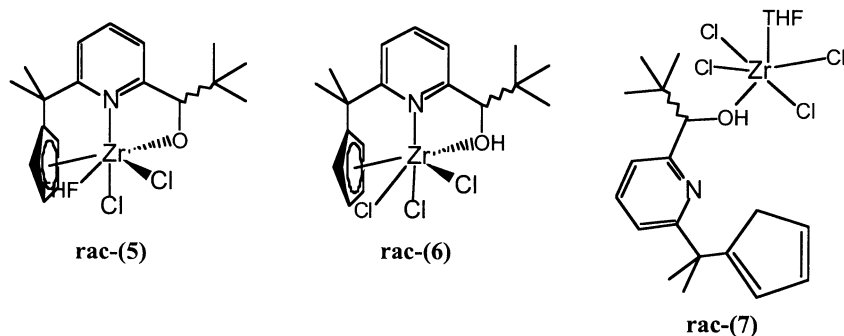
2.2. Zirconium complexes

The reaction of the dilithium salt (*rac*-2) with $ZrCl_4$ in THF at low temperature ($-30\ ^\circ C$) afforded a clear yellow solution. The solvent was removed under vacuum and the solid residue extracted with three portion of dichloromethane. LiCl was filtered off and the removal of volatile under vacuum gave a yellow solid. After this process the solid product is no more soluble in dichloromethane probably as a consequence of the loss of coordinated THF molecules to the complex giving rise to oligomeric species through oxygen bridges such as suggested in Scheme 3.

In particular, by extraction of the crude product with toluene a solid residue, as main product, remained. By slow diffusion of *n*-hexane into the toluene solution the compounds *rac*-5, *rac*-6 and *rac*-7 have been isolated,
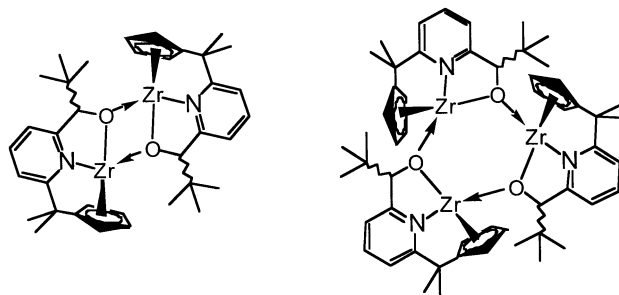
Scheme 2.

Scheme 3. Chlorine atoms are omitted for clarity.

whose elemental analyses are in agreement with the formulas $L_N^O ZrCl_2 \cdot THF$ (*rac*-**5**), $L_N^{OH} ZrCl_3$ (*rac*-**6**) and $L_N^{OH} ZrCl_4 \cdot THF$ (*rac*-**7**), respectively. The formation of the last two compounds can be probably due to the addition of an *n*-BuLi solution with a title lower than measured by titration during the synthesis of the dilithium salt (*rac*-**4**).

experiment (scalar coupling) and from the NOE inter-action with the methyl groups (15 and 16), the triplet at δ 7.99 is assigned to the pyridine-4H (H4), while the NOESY (scalar couplings) experiment showing the interaction between the proton in position-3 of the pyridine ring with the t-Butyl group allows the assign-ment of the doublet centered at δ 7.41 to the pyridine-3

rac-(5)   **rac-(6)**

rac-(7)

In fact, by reacting the ligand *rac*-**2** with $ZrCl_4$ in THF, the compound *rac*-**7** was obtained in good yields. Any attempt to deprotonate the complex *rac*-**7** did not afford complex *rac*-**6** but a complex mixture of pro-ducts, thus excluding that *rac*-**7** was the first product formed in the reaction from which *rac*-**5** and *rac*-**6** were successively formed.

All the compounds were fully characterized by elemental analysis, NMR and, in the case of complexes *rac*-**6** and *rac*-**7**, by X-ray diffractometry. While the formation of *rac*-**7** could be explained by considering a lack of *n*-BuLi and the affinity of the Zr ion to the oxygen to form strong Zr–O bonds, the formation of compound *rac*-**6** is rather surprising by considering the relative acidities of the –OH and CpH groups.

2.3. Characterization of (rac-6)

The IR spectrum of compound *rac*-**6** showed two absorption in the O–H stretching region at 3450 cm^{-1} and 3180 cm^{-1} assignable to the free and associated –OH stretching. The NMR study of the compound *rac*-**6** (^{1}H, ^{13}C, HMQC, COSY, NOESY, NOEDS experi-ments) allowed the complete assignment of all the proton and carbon atoms following the numbering of the proton and carbon atoms in Scheme 4.

On the basis of their chemical shifts and integrations, the singlets at δ 1.80, δ 1.64 are assigned to the methyl protons bonded to the methyl carbons (15 and 16), and the singlet at δ 1.16 to the methyl protons of the ^{t}Bu group (17, 18, 19). From the multiplicity and COSY

proton (H3). Thus the doublet at δ 7.55 must be assigned to the pyridine-5 proton (H5) on the basis of the NOE interaction with the two singlets of the bonded dimethyl-substituted methylcyclopentadienyl group (15 and 16). In addition both the signals at δ 7.41 and δ 1.16 show a NOE interaction with the signal at δ 5.54 (H13) which, from the HMQC experiment, results to be bonded to the carbon at δ 89.4 ppm, corresponding to the carbon-13 atom. The signals at δ 7.31, δ 6.67, δ 6.49 and δ 6.45, show several COSY interactions revealing the reciprocal coupling H9–H10, H9–H11, H9–H12, H10–H11, H10–H12, H11–H12, assignable to the cyclopentadienyl protons. From NOESY experiments several (positive) overhauser interactions and some signals due to unterhauser interactions (confirmed by NOEDS experiments) are observed. These negative signals together with the low resolution of the multi-
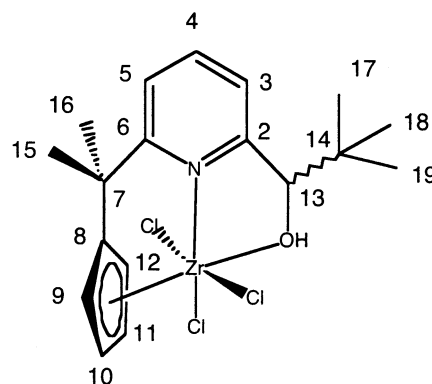
Scheme 4.

plicity of the signals can be due to the dynamism of the alcoholic proton. In fact the rapid change of the bond order of O–H implies a change of the coordinative availability of the oxygen atom on the zirconium ion and a consequent change of the electronic density on metal ion. The resulting effect could be both a change of the electronic density on the Cp-protons with a modulation of the scalar coupling of their protons and a fast change of the geometry about the central ion with little changes in the chemical shift values. The phenomena could produce the peak broadening. The signal at δ 6.06, integrating for one proton, does not show any coupling with the other signals (from COSY experiments), shows a NOE interaction with the t-butyl protons, it reveals an unterhauser effect with the proton at δ 5.54 (H13) and the HMQC experiment shows that this proton is not bonded to any carbon atom. All these data are in agreement with the assignment of the singlet at δ 6.06 to the –OH proton.

2.4. Solid-state single crystal structures

The solid-state structures of $[L_N^{OH}ZrCl_3]$ (*rac*-**6**) and $[L_N^{OH}ZrCl_4 \cdot THF]$ (*rac*-**7**) determined by single-crystal X-ray diffraction are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are listed in Tables 1 and 2, respectively.

The species $[L_N^{OH}ZrCl_3]$ (*rac*-**6**) is monomeric and shows the typical geometry for pseudo octahedral zirconium(IV) monocyclopentadienyl derivative, with the chlorine ligands in *mer* position. The cyclopentadienyl ring bound to the metal in a η^5 mode shows asymmetry in the metal bond. The Zr–C bond lengths progressively increase from C(7) to C(11) in the range 2.478(5)–2.531(6)Å. The L_N^{OH} ligand is bound to the zirconium center through the nitrogen and oxygen with the formation of a five-membered chelate ring having
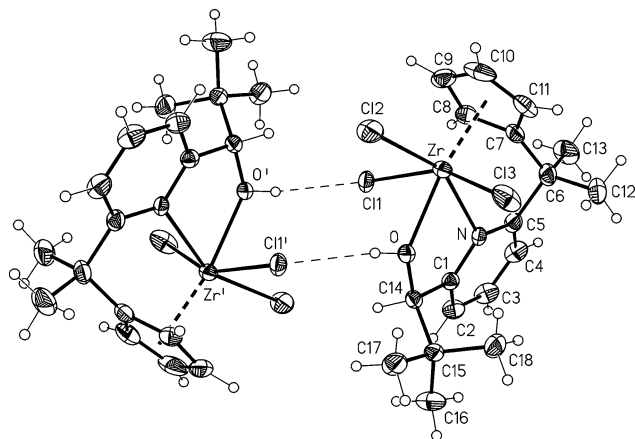
Fig. 2. Molecular structure of $[L_N^{OH}ZrCl_4 \cdot THF]$ (*rac*-**7**).

the oxygen atom *trans* to the Cp ring. The zirconium ion is out of the plane defined by N, Cl(1), Cl(2) and Cl(3) of 0.537(1)Å. The Zr–Cl(1) bond distance of 2.596(2) is longer than the Zr–Cl(2) and Zr–Cl(3) (2.482(2) and 2.469(2) Å respectively and it is significantly longer than the values found for terminal Zr(IV)–Cl bonds in monocyclopentadienyl complexes (av. 2.473 Å) [6], probably due to the intermolecular hydrogen bond O–H⋯Cl(1)′ of 2.343(6) Å, O–H⋯Cl(1)′ 171.5(6)° (at $2 - x$, $-y$, $-z$) that determines the formation of a pseudo

Fig. 1. Molecular structure of $[L_N^{OH}ZrCl_3]$ (*rac*-**6**). Primed atoms are related to unprimed ones by the symmetry operation $2 - x$, $-y$, $-z$.
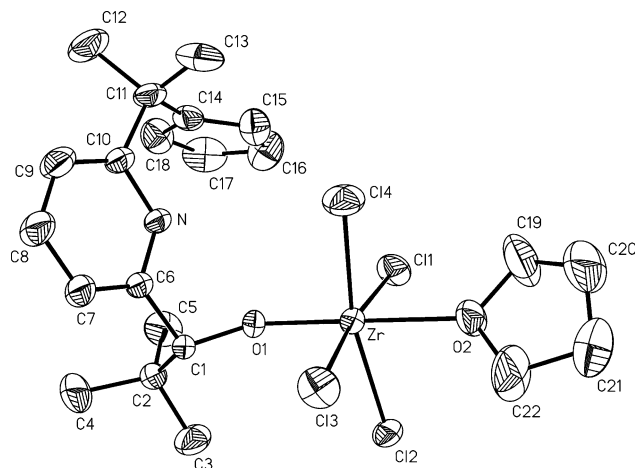
Table 1
Selected bond lengths (Å) and bond angles (°) for $[L_N^{OH}ZrCl_3]$ (*rac*-**6**)

Bond lengths			
Zr–Cl(1)	2.596(2)	Zr–Cl(2)	2.469(2)
Zr–Cl(3)	2.482(2)	Zr–O	2.254(3)
Zr–N	2.352(4)	Zr–C(7)	2.484(6)
Zr–C(8)	2.478(6)	Zr–C(9)	2.497(7)
Zr–C(10)	2.528(8)	Zr–C(11)	2.531(6)
Zr–X	2.200(4)	O–C(14)	1.444(6)
N–C(5)	1.364(7)	N–C(1)	1.347(6)
C(1)–C(2)	1.395(7)	C(5)–C(6)	1.528(8)
C(6)–C(7)	1.503(8)	C(7)–C(11)	1.417(8)
C(7)–C(8)	1.417(7)	C(8)–C(9)	1.395(9)
C(9)–C(10)	1.410(9)	C(10)–C(11)	1.392(9)
Bond angles			
Cl(1)–Zr–Cl(2)	87.2(1)	Cl(1)–Zr–Cl(3)	155.2(1)
Cl(1)–Zr–O	76.0(1)	Cl(1)–Zr–N	80.2(1)
O–Zr–X	165.8(1)	Cl(1)–Zr–X	100.7(1)
Cl(2)–Zr–Cl(3)	90.9(1)	Cl(2)–Zr–O	85.4(1)
N–Zr–X	97.0(2)	Cl(2)–Zr–N	153.4(1)
Cl(2)–Zr–X	108.3(1)	Cl(3)–Zr–O	79.2(1)
Cl(3)–Zr–N	91.0(1)	Cl(3)–Zr–X	103.4(1)
O–Zr–N	69.0(1)	O–C(14)–C(1)	107.4(4)
C(14)–C(1)–N	118.5(4)	N–C(5)–C(6)	115.9(5)
C(5)–C(6)–C(7)	108.8(5)	Zr–O–C(14)	123.5(5)

X is the centroid of the Cp ring C(7) C(8) C(9) C(10) C(11).

Table 2
Selected bond lengths (Å) and bond angles (°) for $[L_N^{OH}ZrCl_4 \cdot THF]$
(rac-**7**)

| Bond lengths			
Zr–Cl1	2.461(2)	Zr–Cl2	2.466(2)
Zr–Cl3	2.452(2)	Zr–Cl4	2.455(2)
Zr–O1	1.924(3)	Zr–O2	2.280(5)
O1–C1	1.400(7)		
Bond angles			
Cl1–Zr–Cl2	87.6(1)	Cl1–Zr–Cl3	173.3(1)
Cl1–Zr–Cl4	90.6(1)	Cl1–Zr–O1	97.4(1)
Cl1–Zr–O2	87.7(1)	Cl2–Zr–Cl3	88.0(1)
Cl2–Zr–Cl4	167.6(1)	Cl2–Zr–O1	98.2(1)
Cl2–Zr–O2	84.0(1)	Cl3–Zr–Cl4	92.7(1)
Cl3–Zr–O1	88.2(1)	Cl3–Zr–O2	86.8(1)
Cl4–Zr–O1	94.2(1)	Cl4–Zr–O2	83.7(1)
O1–Zr–O2	174.5(2)	Zr–O1–C1	146.4(3)
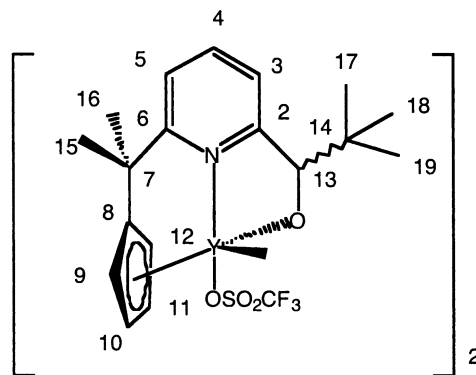
Scheme 6.

centrosymmetric dimer as evidenced in Fig. 1. The Zr–O (2.254(3)) bond distance is comparable to that found in $[(\eta^5C_5Me_5Si(Me)_2OCH_2C_4H_7NH)ZrCl_3]$ (2.244(6) Å) [7]. The Zr–N bond length 2.352(4)Å, is in the normal range of distances found in several examples of pyridine-bonded derivatives (Zr–N bond lengths range from 2.34 to 2.38 Å) [8,9]. The pyridine ring is orthogonal to the coordination plane (89.8(4)°) and forms an angle of 74.3(2)° with the cyclopentadienyl moiety.

The $[L_N^{OH}ZrCl_4 \cdot THF]$ (rac-**7**) derivative obtained in absence of ^nBuLi in the reaction path is characterized by a distorted Zr(IV) octahedral coordination geometry with four equatorial chlorines and two axial oxygen donors. This distortion of the O(1)–Zr–O(2) (174.5(2)°) from linearity most likely arise from interactions between equatorial chlorines and the hydrogens of the coordinated THF molecule, the non-bonding contacts of the chlorines to O(2) range from 3.16 to 3.29 Å. The Zr–O(2) bond lengths of 2.280(5)Å is consistent with Zr–O single bond and its is comparable to that reported

in $ZrCl_4(THF)_2$ [10] and the Zr–Cl bond distance, 2.458(2) Å v.s. is in agreement with that found in the previously quoted structure. The most prominent feature of the structure is the short Zr–O_{allyl} bond distance (Zr–O(1) 1.924(3) Å) indicating a prevalent covalent character of this bond.

2.5. Yttrium complexes (rac-**8**, rac-**9**)

The reaction of rac-**4** with $Y(OTf)_3$ was carried out in THF initially at −10 °C and then at room temperature overnight affording the product rac-**8** in a reasonable yield. On the contrary any attempt to prepare the analogous complexes of Pr, Nd, Sm and Yb following the same reaction conditions as for rac-**8**, always afforded complex mixtures hardly separable. The product rac-**8** was spectroscopically and analytically fully characterized and was then reacted with $LiCH_2SiMe_3$ to afford compound rac-**9** in good yield according to the Scheme 5.
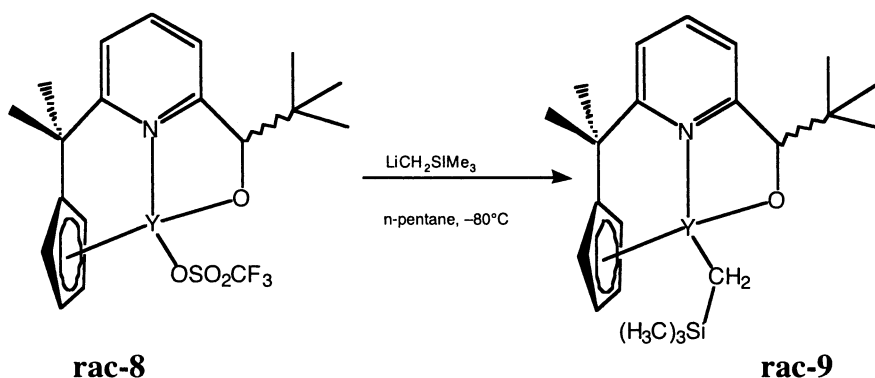
Scheme 5.
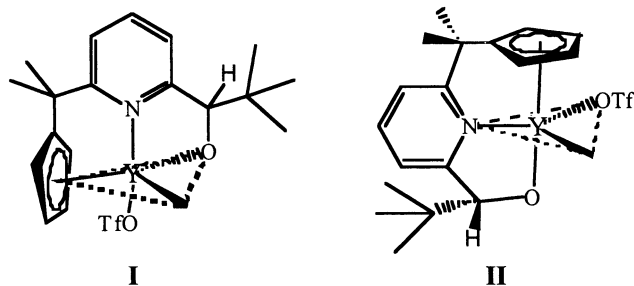
Scheme 7. Possible isomers of *rac*-**8**.

2.6. NMR characterization of complex rac-8

The characterization of probably dimeric *rac*-**8** has been made by NMR experiments (^{1}H, ^{13}C, COSY, NOESY). For the assignments we used the same numbering as reported in Scheme 6.

By integration the singlets at δ 1.76 and δ 1.63 are assigned to the methyl protons H16 and H15 respectively, and the singlet at δ 0.87 to *t*-butyl protons (H17, H18, H19). The triplet at δ 7.80 is assigned to the H4 while the signal at δ 7.45 is assigned, by means of the NOESY experiment, to the H5 due to the interactions with the methyl protons H15 and H16. The NOESY experiment allows the assignment of the signal at δ 7.08 to H3 due to its interaction with the *t*-butyl group. In addition both the signals at δ 7.08 and δ 0.87 show NOE interaction with the singlet at δ 5.05, that could be assigned to the H13 proton. The signals at δ 6.33, δ 6.26, and δ 6.05 show many COSY interactions from which the reciprocal couplings are deduced and suggesting their cyclopentadienyl nature. From the NOESY spectrum, which allows non-perturbative analysis, has been possible to assign to the protons H9 and H10 the unresolved signal at δ 6.05. The dipolar interactions of the signals at δ 1.76 and d 1.63 (H15 and H16 methyl protons) with the signal at δ 6.05 are indicative of the spatial proximity of H15 with H9 and H16 with H12. As a confirmation of the last assignment, the signals at δ 6.33 and δ 6.26 assignable to the H10 and H11 show NOE interaction. According to the two possible isomers reported in Scheme 7, differing for the geometry of the metal center, the chemical non-equivalence of the cyclopentadienyl protons cannot confirm the structure **I** as also in the structure **II** the same non-equivalence of these protons is present due to the presence of the chiral carbon atom which modifies their chemical neighboring.

However in the isomer **II**, the fragment PyCMe$_2$Cp must be highly symmetric, with a consequent identical spatial distance between the H5 proton and the two methyl groups H15 and H16. On the contrary, from NOESY experiments we observed a strong difference in intensity of these signals, thus excluding the structure **II**. In fact by calculation (Spartan pro) of the minimized structure I the different spatial distance between H5 proton and H15 and H16 methyls has been confirmed (H5–H15 = 3.37 Å; H5–H16 = 2.83 Å) and allowed the final assignments of the cyclopentadienyl and methyl protons: δ 1.76 = H16, δ 6.05 = H12, δ 6.26 = H11, δ 6.33 = H10, δ 6.05 = H9, δ 1.63 = H15.

3. Experimental

3.1. General details

3.2. rac-1′-(6-Bromopyridine-2-yl)-2′,2′-dimethylpropanol (rac-1)

A solution of *n*-BuLi (93.5 mmol, 55 ml of a 2.5 M solution in *n*-hexane) was added to a suspension of 2,6-dibromo-pyridine (20.18 g, 85.2 mmol) in diethyl ether (400 ml) at −78 °C and the mixture stirred at this temperature for 100 min. To the solution, 2,2′-dimethylpropional (10.2 ml, 93.6 mmol) was added slowly and the mixture was slowly warmed up to room temperature (r.t.) in 40 min. The reaction was quenched with HCl 30% (43 ml) and the aqueous solution was extracted with diethyl ether. The organic phase was washed with brine and then several times with water. The organic phase, dried overnight on anhydrous MgSO$_4$, was evaporated to dryness under vacuum. The solid residue was crystallized from diethyl ether–*n*-hexane giving 18.67 g of white crystals (88% yield).

Anal. Calc. for $C_{10}H_{14}NOBr$: C, 49.19; H, 5.78; N, 5.73; Br, 32.7. Found C, 49.50; H, 6.00; N, 5.50; Br, 33.1%. Main IR bands (NuJol mull on KBr disks; cm^{-1}): 3400, 2960, 1572, 1548, 1430, 1127, 1045, 762. ^{1}H-NMR, $CDCl_3$, 200 MHz, 25 °C, δ (ppm), J (Hz): 7.49 (t, 1H, $J = 7.6$, Py-4), 7.37 (dd, 1H, $J = 7.6$, $J = 1.0$, Py-5), 7.17 (dd, 1H, $J = 7.6$, $J = 1.0$, Py-3), 4.33 (d, 1H, $J = 7.6$, –CH–OH), 3.60 (d, 1H, $J = 7.6$, –CH–OH), 0.91 (s, 9H, t-Bu).

3.3. rac-2-(1′-Hydroxy-2′,2′-dimethylpropyl)-6-(1″,1″-dimethyl-cyclopentadienylmethyl) pyridine (rac-2)

A n-hexane solution of n-BuLi 2.5 M (7.2 ml, 18 mmol) was added to a solution of rac-1-(6-Bromopyridin-2-yl)-2′,2′-dimethylpropanol (rac-1) (2.188 g, 8.96 mmol) in diethyl ether (70 ml) in 40 min at −80 °C under magnetic stirring. The reaction mixture was slowly warmed up to 0 °C in 40 min and left to react at this temperature for 150 min. Then the mixture was cooled down to –80 °C and 6,6-dimethylfulvene (1.2 ml, 9.85 mmol) in n-hexane (5 ml) was slowly added. The mixture was warmed up to –23 °C and maintained at this temperature for 3 h. The temperature was then slowly raised to r.t. (in about 5 h) and stirred overnight. The reaction mixture was then quenched with brine/ice, the organic layer was separated and the aqueous layer extracted with diethyl ether (three portions of 20 ml). The organic fractions were dried over anhydrous $MgSO_4$ and the solvents removed under vacuum. The residue was purified by flash chromatography by using n-hexane–ethyl acetate 9:1 as eluent, giving a yellow oil (1.266 g, 52% yield).

Anal. Calc. for $C_{18}H_{25}NO$: C, 79.65; H, 9.28; N, 5.16. Found: C, 80.00; H, 9.50; N, 5.00%.

$J = 7.59$, Py-3 or Py-5), 6.95 (d, 1H, $J = 7.59$, Py-3 or Py-5), 6.40 (dq, 1H, $J = 5.30$, $J = 1.41$, H11 or H12), 6.34 (dq, 1H, $J = 5.30$, $J = 1.41$, H11 or H12), 6.15 (m, 1H, $J = 1.73$, H9), 4.78 (d, 1H, $J = 7.26$, OH), 4.31 (d, 1H, $J = 7.26$, H13), 3.01 (m, 2H, $J = 1.52$, H10), 1.61 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 0.90 (s, 9H, t-Bu).

^{13}C-NMR, $CDCl_3$, 100 MHz, 25 °C, δ (ppm): 165.28 (C8), 157.89 (C2 or C6), 154.22 (C2 or C6), 135.73 (C4), 133.65 (C11 or C12), 133.40 (C11 or C12), 124.89 (C9), 119.89 (C3 or C5), 119.45 (C3 or C5), 79.83 (C13), 40.91 (C10), 27.85 (CH_3), 27.83 (CH_3), 25.85 ($C(CH_3)_3$).

^{1}H-NMR, $CDCl_3$, 400MHz, 25 °C, δ (ppm), J (Hz):(less abundant tautomer) 7.50 (t, 1H, $J = 7.82$, Py-4), 7.05 (d, 1H, $J = 7.82$, Py-3 or Py-5), 6.95 (d, 1H, $J = 7.82$, Py-3 or Py-5), 6.43 (dq, 1H, $J = 6.58$, $J = 1.62$, H10 or H11), 6.27 (dq, 1H, $J = 5.68$, $J = 1.62$, H10 or H11), 6.32 (sext, 1H, $J = 1.09$, H9), 4.77 (d, 1H, $J = 7.21$, OH), 4.31 (d, 1H, $J = 7.21$, H13), 2.80 (m, $J = 1.45$, H12), 1.63 (s, 3H, CH_3), 1.61 (s, 3H, CH_3), 0.89 (s, 9H, t-Bu)

^{13}C-NMR, $CDCl_3$, 100MHz, 25 °C, δ (ppm): 165.96 (C8), 157.79 (C2 or C6), 156.59 (C2 or C6), 135.79 (C4), 131.82 (C11 or C10), 131.61 (C11 or C10), 126.26 (C9), 119.82 (C3 or C5), 119.20 (C3 or C5), 79.81 (C13), 40.93 (C12), 28.71 (CH_3), 28.60 (CH_3), 28.85 (t-Bu).

3.4. rac-2-(1′-Hydroxy-2′,2′-dimethylpropyl)-6-(1″,1″-dimethyl-cyclopentadienylmethyl) pyridine di lithium salt (rac-4)

A solution of n-BuLi (5.78 ml, solution 2.5 M in n-hexane, 14.4 mmol) under magnetic stirring was added to a solution of (rac-2) (1.784 g, 6.57 mmol) in diethyl

^{1}H-NMR, $CDCl_3$, 400 MHz, 25 °C, δ (ppm), J (Hz): (main tautomer) 7.50 (t, 1H, $J = 7.59$, Py-4), 7.05 (d, 1H,

ether (40 ml) at −80 °C. The reaction mixture was stirred at –80 °C for 1 h and then warmed up to r.t. and

stirred overnight. The solvent was removed under vacuum and the residue washed with *n*-hexane (three portions 10 ml) giving 1.62 g of white product (87% yield).

Anal. Calc. for $C_{18}H_{23}Li_2NO$: C, 76.32; H, 8.18; N, 4.94. Found: C, 76.05; H, 8.20; N, 5.05%. ^{1}H-NMR, THF-d_8, 200 MHz, 25 °C, δ (ppm), *J* (Hz): 7.50 (t, 1H, *J* = 7.6, Py-4), 7.32 (d, 1H, *J* = 7.5, Py-3 or Py-5), 6.69 (d, 1H, *J* = 7.4, Py-3 or Py-5), 5.80 (bs, 4H, Cp), 4.45 (s, 1H, 1′H), 1.82 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 0.82 (s, 9H, *t*-Bu).

3.5. Reaction of the dilithium salt (rac-4) with ZrCl₄

To a magnetically stirred solution of $ZrCl_4$ (270 mg, 1.16 mmol) in THF (35 ml) at −30 °C, a solution of (*rac*-4) (305 mg, 1.07 mmol) in THF (8 ml) was added. The reaction mixture was slowly warmed up to r.t. and stirred overnight. The solvent was removed under vacuum and the solid residue was washed with dichloromethane (three portions of 30 ml each). The organic solution was evaporated to dryness and the residue was extracted with toluene. The treatment of the solid with toluene was repeated three times. The toluene solution was concentrated under vacuum. By slow diffusion of *n*-hexane a first light brow product, precipitated (*rac*-5).

Anal. Calc. for $C_{22}H_{31}NO_2Cl_2Zr$: C, 52.47; H, 6.20; N, 2.78. Found: C, 52.00; H, 5.85; N, 2.55%. ^{1}H-NMR, CDCl₃, 200 MHz, 25 °C, δ (ppm), *J* (Hz): 7.96 (t, 1H, *J* = 8.0, Py-4), 7.53 (d, 1H, *J* = 7.9, Py-3 or Py-5), 7.40 (d, 1H, *J* = 8.2, Py-3 or Py-5), 6.84 (bs, 1H, Cp), 6.74 (pq, 1H, *J* = 3.5, Cp), 6.57 (pq, 1H, *J* = 3.7, Cp), 6.46 (pq, 1H, *J* = 3.7, Cp), 5.54 (s, 1H, C*H*-CMe₃), 4.52 (m, 4H, THF), 2.05 (m, 4H, THF), 1.81 (s, 3H, C*H₃*), 1.77 (s, 3H, C*H₃*), 1.18 (s, 9H, C*Me₃*).

The mother liquor of (*rac*-5) was concentrated in vacuo and after 2 days in the refrigerator a crystalline product was formed (*rac*-6).

Anal. Calc. for $C_{18}H_{24}NOCl_3Zr$: C, 46.19, H, 5.16, N, 2.99. Found: C, 46.85, H, 5.30, N, 3.10%. ^{1}H-NMR, CD₂Cl₂, 400 MHz, 25 °C, δ (ppm), *J* (Hz): 7.99 (t, 1H, *J* = 8.2, Py-4), 7.55 (d, 1H, *J* = 8.2, Py-3), 7.41 (d, 1H, *J* = 8.2, Py-5), 7.31 (bs, 1H, Cp), 6.67 (bs, 1H, Cp), 6.49 (bs, 1H, Cp), 6.45 (bs, 1H, Cp), 6.06 (bs, 1H, -O*H*), 5.54 (s, 1H, C*H*-CMe₃), 1.80 (s, 3H, C*H₃*), 1.64 (s, 3H, C*H₃*), 1.16 (s, 9H, C*Me₃*). [13]C CD₂Cl₂, 100 MHz, 25 °C, δ (ppm): 141.4 (Py-C4), 137.4 (Py-C2, Py-C6), 124.2 (Cp-1) 121.1 (Py-C3), 120.5 (Py-C5), 120.3 (Cp-2) 118.3 (Cp-3), 117.0 (Cp-4), 89.4 (CH–O), 44.6, 37.8, 29.9, 29.3, 27.1.

By further addition of *n*-hexane to the liquor mother of (*rac*-6) pale yellow crystals precipitated (*rac*-7).

Anal. Calc. for $C_{22}H_{32}NO_2Cl_4Zr$: C, 45.91; H, 5.60; N, 2.43; Cl, 24.63. Found: C, 46.15; H, 5.85; N, 2.55; Cl, 24.10%.

^{1}H-NMR, CDCl₃, 200 MHz, 25 °C, δ (ppm), *J* (Hz): 8.33 (t, 1H, *J* = 8.1, Py-4), 7.76 (d, 1H, *J* = 8.1, Py-3), 7.60 (d, 1H, *J* = 8.1, Py-5), 6.8-6.16 (m, 3H, Cp protons), 5.72 (s, 1H, –O*H*), 5.65 (s, 1H, –C*H*–CMe₃), 4.6 (m, 4H, THF), 3.23 (m, 2H, Cp protons), 2.03 (m, 4H, THF), 1.91 (s, 3H, C*H₃*), 1.88 (s, 3H, C*H₃*), 1.0 (s, 9H, C*Me₃*).

3.6. bis{[rac-2-(2′,2′-Dimethylpropan-1′-olate)-6-(1″,1″-dimethyl-h5-cyclopentadienylmethyl]-N-yttrium(III) (rac-8)

A solution of *rac*-4 (0.335 g, 1.18 mmol) in THF (11 ml) was slowly added to a THF (45 ml) solution of Y(OTf)₃ (0.652 g, 1.24 mmol) at −10 °C under magnetic stirring. The temperature was left to raise to r.t. and the reaction mixture was stirred overnight. The yellow solution was evaporated to dryness under vacuum. The solid residue was washed several times with CH_2Cl_2 portions (4 × 20 ml) and the solution separated by centrifuge. The solution volume was reduced until the precipitation takes place. The precipitate was recrystallized from CH_2Cl_2–*n*-hexane (0.365 g, 58% yield).

Anal. Calc. for $C_{19}H_{23}F_3NO_4SY$: C, 44.98; H, 4.56; N, 2.76; F, 11.23. Found: C, 45.35; H, 4.75; N, 2.85; F, 11.50%. ^{1}H-NMR, CD₂Cl₂, 400 MHz, 25 °C, δ (ppm), *J* (Hz): 7.78 (t, 1H, *J* = 7.8, Py-4), 7.43 (d, 1H, *J* = 7.9, Py-3), 7.07 (d, 1H, *J* = 7.8, Py-5), 6.40 (q, 1H, *J* = 2.8, Cp protons), 6.28 (q, 1H, *J* = 2.8, Cp protons), 6.03 (t, 2H, *J* = 2.6, Cp protons), 5.05 (s, 1H, –C*H*–CMe₃), 1.78 (s, 6H, C*H₃*), 0.88 (s, 9H, C*Me₃*). ^{13}C-NMR, CD₂Cl₂, 100 MHz, 25 °C, δ (ppm): 138.2, 122.2, 120.2, 115.8, 111.6, 111.4, 110.5, 91.9, 68.2, 37.4, 32.9, 29.5, 27.2, 25.9.

3.7. bis{[rac-2-(2′,2′-Dimethylpropan-1′-olate)-6-(1″,1″-dimethyl-h5-cyclopentadienylmethyl]-N-yttrium(III) trimethylsilylmethylate (rac-9)

A solution of 0.60 ml of LiCH₂SiMe₃ 0.61 M in *n*-pentane, further diluted with 2 ml of *n*-pentane, was slowly added to a suspension of *rac*-8 (0.160 g, 0.315 mmol) in *n*-pentane (12 ml) and toluene (1 ml) at −80 °C under magnetic stirring. The temperature was left to raise to 0 °C in 90 min and the reaction mixture was left to react a this temperature for one additional hour; the temperature was slowly raised to r.t. and the reaction continued for 40 h. The yellow solution was separated by centrifugation and volume reduced under vacuum until the precipitation occurs. The pale yellow product was recrystallized from *n*-pentane at −30 °C (0.085 g, 61% yield).

Anal. Calc. for $C_{22}H_{34}NOSiY$: C, 59.31; H, 7.69; N, 3.14. Found: C, 59.80; H, 8.00; N, 3.05%. ^{1}H-NMR, CD₂Cl₃, 400 MHz, 25 °C, δ (ppm), *J* (Hz): 7.05 (t, 1H,

Table 3
Crystal data and structure refinement

Compound	$[L_N^{OH}ZrCl_3]$ (rac-6)	$[L_N^{OH}ZrCl_4 \cdot THF]$ (rac-7)
Chemical formula	$C_{18}H_{24}NOCl_3Zr$	$C_{22}H_{31}NO_2Cl_4Zr$
Formula weight	467.95	574.50
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pbca$
Unit cell dimensions		
a (Å)	9.896(3)	15.954(3)
b (Å)	16.070(4)	30.323(4)
c (Å)	13.511(3)	11.239(2)
β (°)	109.38(4)	
V (Å^3)	2027(1)	5437(2)
Z	4	8
T (°C)	293(2)	293(2)
D_{calc} (g cm^{-3})	1.534	1.401
$F(000)$	952	2352
Crystal size (mm^3)	$0.12 \times 0.40 \times 0.46$	$0.20 \times 0.42 \times 0.44$
μ(Mo–K$_\alpha$) (cm^{-1})	9.43	8.15
No. reflections collected	5635	4624
No. observed [$I \geq 2\sigma(I)$]	3385	4532
R (F_o) [a]	0.050	0.067
R_w (F_o^2) [b]	0.114	0.141
Goodness of fit	1.28	1.32

[a] $R(F_o) = ?|F_o| - |F_c|/?|F_o|$.
[b] R_w (F_o^2) = $[?(F_o^2 - F_c^2)^2/? w(F_o^2)^2]^{1/2}$.

$J = 8.0$, Py-4), 6.80 (bd, 2H, $J = 8.1$, Py-3,5), 6.51 (q, 1H, $J = 2.7$, Cp protons), 6.41 (q, 1H, $J = 2.8$, Cp protons), 6.35 (q, 1H, $J = 2.7$, Cp protons), 6.02 (q, 1H, $J = 2.7$, Cp protons), 4.79 (s, 1H, $-CH-CMe_3$), 1.69 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 0.83 (s, 9H, CMe_3), 0.31 (s, $SiMe_3$), -1.17 (dd, 1H, $J1 = 10.2$, $J2 = 3.7$, $Y-CH_2-SiMe_3$), -1.90 (dd, 1H, $J1 = 10.2$, $J2 = 3.7$, $Y-CH_2-SiMe_3$).

4. X-ray crystallographic studies

Single crystals of rac-**6** suitable for X-ray analysis were obtained by slow diffusion of n-hexane in a saturated toluene solution maintained at -20 °C of the crude product formed by reaction of rac-**4** and $ZrCl_4$. Single crystals of rac-**7** were obtained by slow diffusion of n-hexane to the liquor mother of rac-**6**.

Crystals were lodged in Lindemann glass capillaries and centred on a four circle Philips PW1100 diffractometer using graphite monochromated Mo–K$_\alpha$ radiation (0.71073 Å), following the standard procedures. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The diffraction data were corrected for Lorentz-polarization effects and for absorption, as described by North et al. [12].

The structures were solved by standard direct methods [13] and subsequently completed by Fourier synth-

eses. Non-hydrogen atoms were refined anisotropically in all the structures. The hydrogen atoms were introduced at the calculated positions with fixed isotropic thermal parameters (1.2 U_{equiv} of the parent carbon atom), except for the hydrogen bound to O of $[L_N^{OH}ZrCl_3]$(rac-**6**) located from Fourier maps and refined isotropically. The hydrogens of the THF ligand of the $[L_N^{OH}ZrCl_4(THF)]$ (rac-**7**) derivative were omitted due to disordering in the THF moiety.

Structure refinement and final geometrical calculations were carried out with SHELXL-97 [14] program, implemented in the WINGX package [15]; drawings were produced using ORTEP II [16]. Experimental data are listed in Table 3.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 207285–207286. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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