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On the structural features of the chiral organometallic Lewis-acid catalyst "(dibornacyclopentadienyl)zirconiumtrichloride" *

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Abstract

2-Bornenyllithium (**3**) was prepared from camphor by a variant of the Shapiro reaction and then reacted with 0.5 molar equivalents of ethylformate to give the dibornenylcarbinol **4**. Subsequent acid-catalyzed cyclization of **4** yielded "dibornacyclopentadiene" as a mixture of two diastereoisomers; their deprotonation with n-butyllithium produced a single "dibornacyclopentadienyllithium" reagent (**6**). Reaction of **6** with MCl_4 (M = Zr, Hf, Ti) gave the chiral organometallic Lewis-acids "(diborna-Cp)MCl_3". "(+)-(Dibornacyclopentadienyl)zirconiumtrichloride" (**7a**) was characterized by X-ray diffraction. The molecular structure of **7a** provides a basis for discussing the stereochemical characteristics of the enantioselective arene hydroxyalkylation process catalyzed by the optically active organometallic Lewis-acid "(dibornacyclopentadienyl)zirconiumtrichloride".

1. Introduction

Chiral organometallic Lewis-acids are of ever increasing practical importance as efficient catalysts in the asymmetric synthesis of organic target molecules. The high effectiveness they show for transfer and consequent multiplication of their inherent chirality information in asymmetric carbon–carbon coupling and related reactions has made chiral organometallic Lewis-acid mediated organic synthesis of great significance for the future development of synthetic methods in organic chemistry [1].

Most currently used organometallic catalyst systems are based on a combination of heteroatom-containing ligands with a main group or transition metal centre. However, there are a few systems known where simple heteroatom-free hydrocarbyl systems have been attached to a suitable metal/ligand combination to create a catalytically active and synthetically useful organometallic Lewis-acid catalyst system [2,3]. We have recently contributed such a specific organometallic Lewis-acid which is based on a chirally modified η^5-cyclopentadienyl ligand attached to the zirconiumtrichloride moiety [4].

The chiral "dibornacyclopentadienyl" ligand system was prepared in optical purity starting from either enantiomer of camphor. The chiral bicyclic ketone **1** was converted to the respective bornenyl lithium reagent **3** by a variant of the Shapiro reaction [5]. Subsequent addition to formic ester in 2:1 stoichiometry gave the chiral dialkenylcarbinol (**4**) which was then subjected to acid catalyzed cyclization to yield the dibornacyclopentadiene system (**5**) [6]. A mixture of two diastereomers was formed (7:1 ratio). These originate from the facile shifting of double bonds in the central cyclopentadienyl ring system. Apart from this, the overall synthetic sequence is completely stereoselective: using the enantiomerically pure bornenyl lithium reagent **3** has allowed the formation of only one type of annulated "diborna-Cp" carbon framework. Consequently, deprotonation produced only a

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* Dedicated to Professor E.O. Fischer on the occasion of his 75th birthday.

[1] Work done during their stay with G.E. at the Universität Würzburg.

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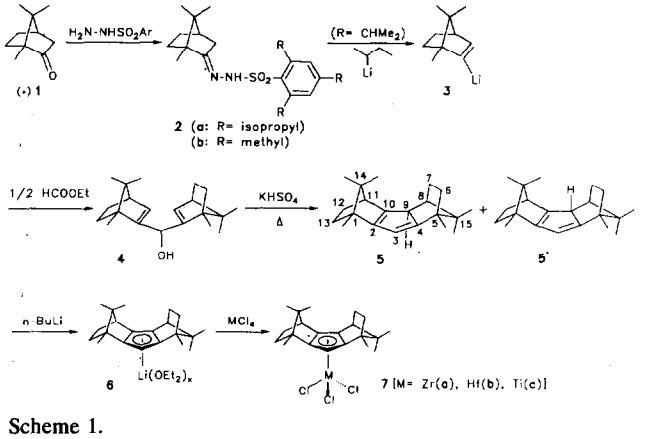
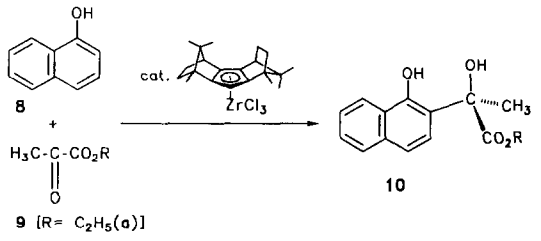
single "dibornacyclopentadienyl lithium" isomer (**6**). Its reaction with zirconiumtetrachloride then gave the chiral organometallic Lewis-acid "(dibornacyclopentadienyl)zirconiumtrichloride" (**7a**) in good yield. Both enantiomers were easily made available separately. Their optical purity depended only on the enantiomeric purity of the camphor starting material employed. The corresponding (dibornacyclopentadienyl) hafnium- and titaniumtrichloride Lewis-acids (**7b**, **7c**) were prepared in an analogous manner (Scheme 1), although the latter was not obtained analytically pure.

Optically active "(dibornacyclopentadienyl)zirconiumtrichloride" (**7a**) effectively catalyzes the asymmetric hydroxyalkylation of α-naphthol with alkylpyruvates and related reagents. The resulting 2-(1-hydroxy-2-naphthyl)alkyllactates (**10**) are of pharmaceutical interest when they can be prepared at least in a highly enantiomerically enriched state [7]. The hydroxyalkylation of α-naphthol with ethylpyruvate catalyzed by 5 mol percent of the "(diborna-Cp)$ZrCl_3$" Lewis-acid gave optically active 2-(1-hydroxy-2-naphthyl)ethyllactate (**10a**) with > 84% enantiomeric excess on a preparative scale (0.95 g, 56% isolated product). The reaction on a preparative scale required the presence of a small amount of water (*ca.* 20 mol percent) in order to maintain a high asymmetric induction throughout the catalytic reaction. In the absence of added H_2O a steady decrease was observed of the (2-aryl)ethyllactate enantiomeric excess in step with increasing product formation. In this catalytic process of the aldol addition type the "(diborna-Cp)$ZrCl_3$" Lewis-acid catalyst derived from (1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one [(+)-camphor] induced the formation of the *R*-configured hydroxyalkylation product [(+)-**10a**]. We ensured by experiment that the (−)-camphor derived catalyst system (ent-**7a**) produced the 2*S*-(1-hydroxy-2-naphthyl)ethyllactate enantiomer [(−)-**10a**] in excess.



Scheme 1.



Scheme 2.

We have now obtained crystals of "(+)-(diborna-Cp)$ZrCl_3$" that could be used for X-ray crystal structure analysis of this interesting example of a chiral organometallic Lewis-acid catalyst. Knowing the molecular structure led us to attempt to describe some of the features of the action of this electrophilic catalyst system on an experimentally sound basis.

2. Results and discussion

The "(+)-(diborna-Cp)$ZrCl_3$" complex **7a** was crystallized from methylene chloride. In the crystal the zirconium atom of **7a** is tetrahedrally coordinated to three chloride ligands and to the bis-bornene-annulated η^5-cyclopentadienyl ligand. The Zr–C(Cp) bond distances range from 2.45 to 2.61 Å which makes this particular cyclopentadienyl ligand rather asymmetrically bonded to zirconium. Both the Zr–C(10) and Zr–C(9) bonds are rather long at 2.609(3) and 2.577(3) Å. The "diborna-Cp" ligand is slightly tilted towards the "front side" (*i.e.* the sector where the single methine unit of the tetrasubstituted cyclopentadienyl ring is oriented). The corresponding metal–C(Cp) distances are 2.447(4) [Zr–C(4)], 2.453(3) [Zr–C(3)], and 2.506(2) Å [Zr–C(2)].

Attaching the $ZrCl_3$ unit to the "diborna-Cp" anion-equivalent has broken the C_2 ligand-symmetry. Bonding of the zirconiumtrichloride moiety to one of the formerly homotopic cyclopentadienyl ligand faces has resulted in a structural differentiation between the two annulated bornene ring systems. For ease of description we will look at the monocyclopentadienylzirconiumtrichloride complex **7a** from the "front", *i.e.* from the side to which the cyclopentadienyl-methine group is directed, with the annulated η^5-cyclopentadienyl system oriented at the top. The "left" annulated bornene ring system is then oriented so that its endo-side is facing the coordinated $ZrCl_3$ unit, with the methyl groups at C(14) being oriented away from the metal centre, whereas the "right" annulated bornene system is oriented in the opposite way with the methyl groups at C(15) pointing to the side where the zirconium centre is located (exo-side). Making these very

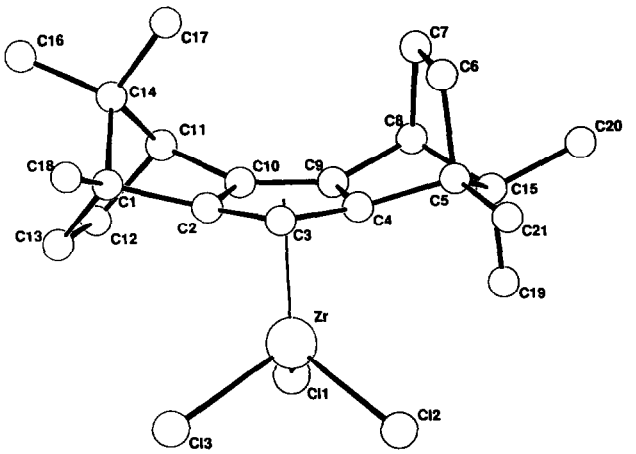


Fig. 1. A view of the molecular geometry of "(+)-(diborna-Cp)$ZrCl_3$" (**7a**). Selected bond lengths (Å) and angles (deg): Zr–Cl(1) 2.358(1), Zr–Cl(2) 2.377(1), Zr–Cl(3) 2.372(1), Zr–C(2) 2.506(2), Zr–C(3) 2.453(3), Zr–C(4) 2.447(3), Zr–C(9) 2.577(3), Zr–C(10) 2.609(3), C(2)–C(3) 1.420(4), C(2)–C(10) 1.420(4), C(3)–C(4) 1.425(4), C(4)–C(9) 1.428(4), C(9)–C(10) 1.407(3), Cl(3)–Zr–Cl(2) 93.2(1), Cl(3)–Zr–Cl(1) 103.3(1), Cl(2)–Zr–Cl(1) 111.2(1). For additional structural data see Table 1.

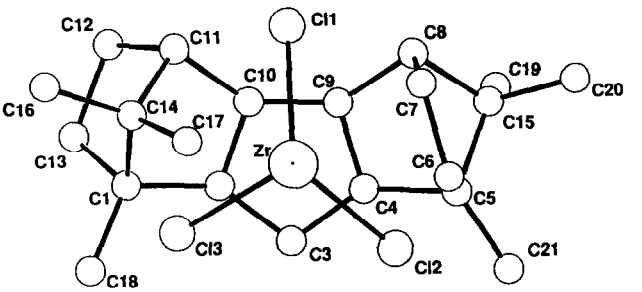


Fig. 2. Top view of the molecular geometry of complex **7a** in the crystal.

bulky bicyclic systems part of the cyclopentadienyl ligand has created some steric strain. We notice that all four carbon–carbon bonds of the central Cp-ring system, pointing towards the annulated hydrocarbyl substituents, are located markedly outside the average Cp-ring plane. They are all oriented away from the attached metal atom [dihedral angles C(4)–C(3)–C(2)–C(1) 157.6°, C(4)–C(9)–C(10)–C(11) 157.3°. C(2)–C(3)–C(4)–C(5) 152.8°, C(2)–C(10)–C(9)–C(8) 152.3°, see Fig. 1]. The bonding features of the bornenyl moieties included in complex **7a** are unexceptional as can be seen from a comparison of bond lengths and angles between **7a** and the (+)camphor-2,4,6-trimethylbenzenesulfonylhydrazone (**2b**), whose molecular structure was determined in the course of this study for the purpose of comparison (see Table 1 and Fig. 3).

In the crystalline state complex **7a** appears to adopt a specific orientation of groups along the metal–cyclopentadienyl vector that seems to minimize unfavourable steric interactions in this rather congested situation. In Fig. 2 a projection from the top of the molecule indicates that the Zr–Cl(1) bond [2.358(1) Å] bisects the C(10)–C(9) vector. This leads to a conformation where the Zr–Cl(2) and Zr–Cl(3) bonds are arranged almost bisecting the carbon–carbon bonds of the front sector of the cyclopentadienyl ring. In the top projection shown in Fig. 2 it becomes apparent that complex **7a** favours in the solid state a conformation where the Zr–Cl(1) and C(3)–H(3) vectors have be-

TABLE 1. A comparison of selected bond lengths (Å) and angles (deg) of the bornane frameworks of **7a** and **2b** (for **2b** averaged values over the four independent molecules per unit cell are given)

7a				**2b**	
C(1)–C(2)	1.530(4)	C(4)–C(5)	1.530(4)	C(1)–C(2)	1.508(7)
C(2)–C(10)	1.420(4)	C(4)–C(9)	1.428(4)	C(2)–C(3)	1.492(7)
C(10)–C(11)	1.499(4)	C(8)–C(9)	1.504(4)	C(3)–C(4)	1.538(8)
C(1)–C(14)	1.589(4)	C(5)–C(15)	1.580(4)	C(1)–C(7)	1.548(7)
C(1)–C(18)	1.511(4)	C(5)–C(21)	1.513(6)	C(4)–C(7)	1.538(8)
C(11)–C(14)	1.567(4)	C(8)–C(15)	1.555(4)	C(1)–C(10)	1.502(9)
C(14)–C(17)	1.531(4)	C(15)–C(19)	1.519(4)	C(7)–C(9)	1.503(10)
C(14)–C(16)	1.537(4)	C(15)–C(20)	1.545(5)	C(7)–C(8)	1.536(8)
C(11)–C(12)	1.561(4)	C(8)–C(7)	1.550(4)	C(4)–C(5)	1.49(1)
C(12)–C(13)	1.545(6)	C(7)–C(6)	1.551(8)	C(5)–C(6)	1.53(1)
C(1)–C(13)	1.558(4)	C(5)–C(6)	1.570(4)	C(1)–C(6)	1.51(1)
C(1)–C(2)–C(10)	106.8(2)	C(5)–C(4)–C(9)	106.2(2)	C(1)–C(2)–C(3)	107.4(8)
C(1)–C(2)–C(3)	140.7(2)	C(5)–C(4)–C(3)	140.0(2)	C(1)–C(2)–N(2)	122.2(4)
C(2)–C(10)–C(11)	106.9(2)	C(4)–C(9)–C(8)	107.3(2)	C(2)–C(3)–C(4)	100.8(4)
C(9)–C(10)–C(11)	142.3(3)	C(8)–C(9)–C(10)	141.1(3)	N(1)–N(2)–C(2)	117.0(4)
C(1)–C(14)–C(11)	93.4(2)	C(5)–C(15)–C(8)	94.5(2)	C(1)–C(7)–C(4)	92.8(4)
C(16)–C(14)–C(17)	107.4(2)	C(19)–C(15)–C(20)	106.5(2)	C(8)–C(7)–C(9)	107.8(6)
C(2)–C(1)–C(18)	115.6(2)	C(4)–C(5)–C(21)	118.0(3)	C(2)–C(1)–C(10)	115.3(4)

come oriented anti-periplanarly relative to the zirconium–cyclopentadienyl axis and where the C(3)–H(3) vector bisects the Cl(2)–Zr–Cl(3) angle.

The changes in orientations of both annulated bornene substituent systems, with the metal facing the endo-side of the "left" and the exo-side of the "right" bornene framework, has resulted in different steric environments of the sectors to "left" and "right" of the metal–cyclopentadienyl vector. Understanding this difference in steric "dibornacyclopentadienyl"-ML_n interaction is probably basic to describing and understanding the principles of discrimination between enantiotopic pyruvate faces during the catalytic process initiated by the "(diborna-Cp)$ZrCl_3$" chiral Lewis-acid catalyst. The different steric features of these two sectors in the vicinity of the zirconium atom, which are induced by the characteristic differences of the bornene sectors arranged above them at the central cyclopentadienyl unit, can probably best be described by looking at non-bonded interactions between the $ZrCl_3$ unit and the nearest dibornacyclopentadienyl-hydrogen atoms.

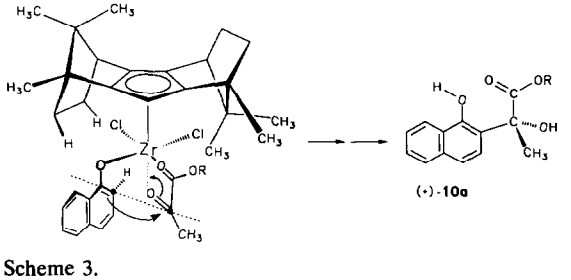
First it will be noticed that the methyl substituents at the bornene bridgehead positions are not oriented in such a way that major interactions with the $ZrCl_3$ group are to be expected. The C(18) methyl group at the "left" bornene moiety is clearly pointing away from zirconium. The C(21) methyl group is oriented more towards the metal centre. Due to the stereochemical characteristics of the camphor-derived "diborna-Cp" ligand system the C(19) methyl group must be pointing towards the side of the zirconium centre. The corresponding chloride-methyl interaction seems to be of some importance for controlling stereochemical features of the above-mentioned catalytic process since substrates and reagents will be bonded to the electrophilic zirconium centre and thus will be present at a distance from the zirconium which is similar to that of the chloride ligands in **7a**. The endo-hydrogen atoms at carbon centres C(13) and C(12) of the "left" bornene moiety are oriented towards the zirconium centre. The corresponding H(12-endo)–Cl(1) interaction is of the usual order of magnitude at 2.9 Å, whereas the H(13-endo)–Cl(3) separation is shorter, at *ca.* 2.6 Å. This leads to the conclusion that the overall steric interaction of $ZrCl_3$ with the "right" bornene moiety of the coordinated "diborna-Cp" ligand system is less pronounced than that with the "left" annulated bicyclic substituent framework. It appears that the special ligand geometry is such that on tetrahedral coordination at zirconium the bornene endo-hydrogen interaction with the additional ligands at the central metal atom is more pronounced than their repulsive interaction with the proximal methyl group [C(19)] at the "right" bornene framework.

This structure may serve as a basis for a brief discussion of the stereochemical characteristics of the asymmetric naphthol hydroxyalkylation process catalyzed by the "(diborna-Cp)$ZrCl_3$" Lewis-acid as mentioned above (see Scheme 2). From our experimental studies it is clear that one chloride ligand is exchanged for naphtholate during the catalytic process [4]. The pyruvate molecule is then coordinated at the remaining two vacant coordination sites at zirconium. The active species probably contains octahedrally coordinated zirconium with the pyruvate chelate bonded through its carbonyl groups in positions *cis* and *trans* to the "apical" η^5-dibornacyclopentadienyl ligand. Since the bornene frameworks are both oriented towards the "back side" of the molecule (the designations "left", "right", "back" and "front" are used for simplification as defined above using molecular projections analogous to those depicted for the parent complex in Fig. 1) it can be assumed that addition, coupling, and replacement of reagents and substrates during the catalytic process take place exclusively at the "front" sector of the bulky "(dibornacyclopentadienyl)zirconium" catalyst system. The formal analysis reveals that three pairs of optional arrangements of reagents have to be taken into account for describing the stereochemical course taken in this aldol addition type coupling reaction at the "front" section of the chiral electrophilic zirconium catalyst. The pyruvate can be chelating in two orientations, the reacting keto group being exposed either in a *cis* or *trans* position in relation to the Cp-ring system. The naphtholate can be arranged with its annulated phenylene moiety pointing either away from the centre of the complex and towards the outside ("distal" orientation) or arranged facing inside ("proximal" orientation), and the zirconium bound naphtholate nucleophile may approach the coordinated pyruvate electrophile from the "left" or "right" side at the octahedral metal complex. Taken together these combinations then lead to a total of eight possible transition state geometries for the catalytic carbon–carbon coupling reaction in the coordination sphere of the zirconium atom. Four of these combinations result in the formation of boat-shaped transition states which lead to severely unfavourable steric interactions and thus may be regarded as being less likely to be adopted. The other four combinations result in chair-like geometries, and they require closer inspection. Two of these are characterized by having the pyruvate keto group in a position *cis* to the Cp ligand and the naphtholate phenylene moiety arranged in the "proximal" orientation. These two transition states are then distinguished by having the naphtholate carbon nucleophile oriented at the "left" or "right" side of the prochiral pyruvate electrophile. At the

(+)-camphor derived catalyst system the former corresponds to si-face attack and would yield the S-configured arene-hydroxyalkylation product, contrary to what is observed experimentally. The latter transition state would correctly lead to the production of 2R-(1-hydroxy-2-naphthyl)ethyllactate [(+)-**10a**]. However, a close inspection of the geometry of both transition states revealed no major differences in steric interaction such as would be expected to lead to an appreciable energetic discrimination between them. This is different for the remaining two possible transition state geometries of the catalytic CC-coupling process. Both have the pyruvate keto group positioned *trans* to the Cp-ring at the octahedral zirconium complex and the naphtholate oriented with its annulated phenylene part in the "distal" arrangement. In the (+)-camphor derived catalyst system, attack of the naphtholate carbon nucleophile from the "left" (re-face attack) then leads to the observed *R*-configured product (see Scheme 2). This transition state does not show any substantial steric interference between the participating groups either, whereas the alternative naphtholate attack from the "right" side (si-face attack leading to the *S*-configured product (−)-**10a**) clearly suffers a repulsive steric interaction between the naphtholate C(8)–H and the bridgehead methyl group at the "right" bornene moiety of the controlling chiral Cp-ligand. As this seems to be the only major steric discrimination among the four possible chair-like transition states we must assume that the asymmetric induction of this catalytic process is due to a combination of two major controlling factors, namely an electronic component, which favours an orientation of the pyruvate substrate with its keto-functionality coordinated in a position *trans* to the Cp-ring system, and a steric component which favours naphtholate attack from the side of the endo-oriented annulated bornene moiety (see Scheme 3).

What remains to be discussed is the role of the added stoichiometric amount of water which is essential to maintain high catalyst activity throughout the catalytic process independent of the degree of substrate conversion. Our present structural study has revealed that in the crowded situation at the active "(dibornacyclopentadienyl)zirconiumtrichloride" catalyst there is probably no room for the intervention of an H_2O molecule to become an active part of the asymmetric carbon–carbon coupling process. In addition, the X-ray crystal structure analysis has revealed that the very bulky "diborna-Cp" ligand in **7a** is more loosely bound than in a number of related monocyclopentadienylzirconium complexes exhibiting less sterically demanding cyclopentadienyl ligands [8]. It is therefore conceivable that the "diborna-Cp" ligand in this specific system has a slightly higher tendency of getting protonated under the rather acidic conditions of the catalytic arene-hydroxyalkylation process as compared to a number of "ordinary" $(RCp)ZrCl_3$ type complexes. Protolytic cleavage of "dibornacyclopentadiene" (**5**) probably leads to the formation of an achiral electrophilic zirconium complex of much higher catalytic activity than the original chiral organometallic Lewis-acid (**7a**). We assume that the added amount of water simply serves very effectively to convert this subsequently formed achiral catalytically active decomposition product of the initial catalyst system into unreactive di- or polynuclear oxygen-bridged zirconium complexes.

We are confident that our increased knowledge of the structural and reactivity features of **7a** will be of help in the process of developing other related asymmetric carbon–carbon coupling reactions that are effectively catalyzed by "(dibornacyclopentadienyl)zirconiumdichloride" (**7a**) and related chiral organometallic Lewis-acids.



Scheme 3.

3. Experimental details

3.1. General conditions

All reactions with organometallic reagents were carried out in an inert atmosphere (argon) using Schlenk-type glassware. Solvents were dried and distilled under argon prior to use. NMR spectra were measured on Bruker AC 200 P (200 MHz ^1H; 50 MHz ^{13}C) or WM 300 (300 MHz ^1H) NMR spectrometers. IR spectra were recorded on a Nicolet 5 DXC FT IR spectrometer. Optical rotation: Perkin-Elmer polarimeter model 241 MC, sodium vapour lamp ($\lambda = 589$ nm), ambient temperature, concentration c in g/100 ml. Melting points: Büchi SMP 20 or DuPont DSC 910, melting points are uncorrected. Elemental analyses: Perkin-Elmer model 240 or Foss-Heraeus CHNO-RAPID. 2,4,6-Triisopropylbenzenesulfonylhydrazine, 2,4,6-trimethylbenzenesulfonylhydrazine, and $TiCl_4(THF)_2$ were synthesized as described in the literature [9]. The preparation of enantiomerically enriched (+)-2*R*-(1-hydroxy-2-naphthyl)ethyllactate [(+)-**10a**] (84% ee,

TABLE 2. Atomic coordinates of **7a**

Atom	x	y	z
Zr	0.9722(1)	0.0338(1)	0.8422(1)
Cl(1)	0.7243(2)	0.0916(1)	0.7747(1)
Cl(2)	1.1832(2)	0.1378(1)	0.8840(1)
Cl(3)	1.1921(2)	−0.0138(1)	0.7569(1)
C(1)	0.9305(4)	−0.1955(2)	0.8393(1)
C(2)	0.9311(4)	−0.1138(2)	0.8798(1)
C(3)	1.0370(4)	−0.0712(2)	0.9318(1)
C(4)	0.9099(4)	−0.0123(2)	0.9620(1)
C(5)	0.8782(4)	0.0341(2)	1.0307(1)
C(6)	0.7761(5)	−0.0348(2)	1.0750(1)
C(7)	0.5757(5)	−0.0435(2)	1.0413(2)
C(8)	0.5837(4)	0.0180(2)	0.9792(2)
C(9)	0.7261(4)	−0.0216(1)	0.9308(1)
C(10)	0.7402(4)	−0.0844(2)	0.8801(1)
C(11)	0.6232(4)	−0.1460(2)	0.8402(2)
C(12)	0.6817(6)	−0.1419(2)	0.7616(2)
C(13)	0.8864(6)	−0.1775(2)	0.7610(2)
C(14)	0.7266(5)	−0.2274(2)	0.8637(1)
C(15)	0.7009(5)	0.0901(2)	1.0116(2)
C(16)	0.6580(6)	−0.3062(2)	0.8263(2)
C(17)	0.7148(5)	−0.2436(2)	0.9424(2)
C(18)	1.0998(5)	−0.2514(2)	0.8521(2)
C(19)	0.7388(6)	0.1611(2)	0.9614(2)
C(20)	0.6058(6)	0.1285(2)	1.0769(2)
C(21)	1.0493(6)	0.0734(2)	1.0656(2)

0.95 g, 56% isolated yield) from α-naphthol and ethylpyruvate catalyzed by 5 mol percent of "(+)-(dibornacyclopentadienyl)zirconiumtrichloride" (**7a**) was recently described by us in a preliminary communication [4]. In an analogous experiment α-naphthol (542 mg, 3.76 mmol) was coupled with excess ethylpyruvate (13.2 mmol) in the presence of "(−)-(dibornacyclopentadienyl)zirconiumtrichloride" (ent-**7a**, 90.0 mg, 0.19 mmol = 5 mol percent catalyst) to give 610 mg (67%) of (−)-2*S*-(1-hydroxy-2-naphthyl)ethyllactate [(−)-**10a**] with an enantiomeric excess of 84%.

3.2. Preparation of (+)-(1R,4R)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-one-(2,4,6-triisopropylbenzene-sulfonylhydrazone) (2a)

A mixture of 56.4 g (0.19 mol) of 2,4,6-triisopropylbenzenesulfonylhydrazine and 26.1 g (0.17 mol) of (+)-camphor was suspended in 88 ml of acetonitrile. Conc. HCl (17 ml) was added and the mixture stirred for 24 h at ambient temperature. The mixture was then kept at −30°C for 12 h. The precipitated product was collected by filtration while still cold, washed with a small amount of mother liquor, and then dried *in vacuo* to yield 61.6 g (83%) of **2a**, m. p. 178°C (dec.); $[\alpha]_D = +43.0°$ (c 0.40, CH_2Cl_2). ^1H NMR (C_6D_6): $\delta = 0.44$ and 0.53 (2s, 6H, 7-CH_3), 0.89 (s, 3H, 1-CH_3), 1.05 (d, 6H, *p*-CH(CH_3)$_2$), 1.43 (d, 12H, *o*-CH(CH_3)$_2$), 0.77–1.59 (m, 6H, CH_2), 1.97 (m, 1H, bridgehead CH), 2.61 (sept., 1H, CHMe$_2$), 4.77 (sept., 2H, CHMe$_2$), 7.21 (s, 2H, arom. CH). ^{13}C NMR (C_6D_6): $\delta = 11.2$ (1-CH_3), 18.4 and 19.3 (7-CH_3), 23.6 (*p*-CH(CH_3)$_2$), 25.1 and 25.2 (*o*-CH(CH_3)$_2$), 30.2 (*o*(CHMe$_2$), 27.3 and 32.5 (C-5, C-6), 33.4 (C-3), 34.4 (*p*-CHMe$_2$), 44.1 (C-4), 47.8 (C-7), 52.8 (C-1), 123.8 (arom. CH), 132.9 (arom. *ipso*-C, *p*), 152.1 (arom. *ipso*-C, *o*), 153.2 (arom. *ipso*-C), 163.2 (C-2). IR (KBr): $\tilde{\nu} = 3238$, 2959, 2929, 2870, 1670, 1601, 1565, 1459, 1427, 1391, 1382, 1335, 1322, 1031, 672, 655 cm^{-1}. Anal. calcd. for $C_{25}H_{40}N_2O_2S$ (432.7) C 69.40, H 9.32, N 6.47; found: C 69.03, H 9.50, N 6.13%.

(−)-Camphor (31.2 g, 0.21 mol) was treated in an analogous manner with 66.5 g (0.22 mol) of 2,4,6-triisopropylbenzenesulfonylhydrazine in 200 ml of acetonitrile in the presence of 20 ml of conc. HCl to yield 76.3 g (86%) of ent-**2a**.

3.3. Preparation of (+)-(1R, 4R)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-one-(2,4,6-trimethylbenzenesulfonylhydrazone) (2b)

The compound **2b** was prepared for the purpose of structural comparison with the trimethylbicyclo[2.2.1]-heptane frameworks of complex **7a**. Analogous to the preparation of **2a** as described above 18.7 g (0.12 mol) of (+)-camphor was allowed to react with 28.9 g (0.14 mol) of 2,4,6-trimethylbenzenesulfonylhydrazine in 100 ml of acetonitrile and 10 ml of conc. aqueous hydrochloric acid. Workup as described above yielded 33.9 g (79%) of **2b**, m.p. 153–155°C; $[\alpha]_D = 45.5°$ (*c* 0.44, CH_2Cl_2). The arenesulfonylhydrazone **2b** was characterized spectroscopically and by X-ray diffraction (see Tables 1, 3, 4 and Fig. 3). ^1H NMR (C_6D_6): $\delta = 0.36$, 0.53 (2s, 6H, 7-CH_3), 0.86 (s, 3H, 1-CH_3), 0.60–1.50 (m, 6H, CH_2), 1.85 (s, 3H, arom. *p*-CH_3), 2.00 (m, 1H, 4-H), 2.90 (s, 6H, arom. *o*-CH_3), 6.61 (s, 2H, arom.

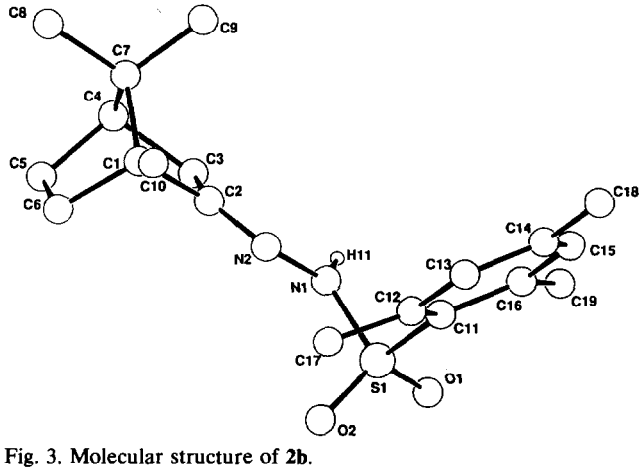


Fig. 3. Molecular structure of **2b**.

CH), 7.82 (broad s, 1H, NH). ^{13}C NMR (C_6D_6): δ = 11.3 (1-CH_3), 18.6, 19.4 (7-CH_3), 20.9 (arom. *p*-CH_3), 23.8 (arom. *o*-CH_3), 27.4, 32.6, 33.7 (CH_2), 44.3 (C-4), 48.1, 53.3 (C-1, C-7), 132.2 (arom. CH), 134.0 (arom. *ipso*-C, *p*), 140.9 (arom. *ipso*-C), 142.6 (arom. *ipso*-C, *o*), 170.9 (C-2). IR (KBr): $\tilde{\nu}$ = 3213, 2962, 2941, 2874, 1669, 1605, 1566, 1341, 1150, 912, 669, 614, 529 cm^{-1}. Anal. calcd. for $C_{19}H_{28}N_2O_2S$ (348.5) C 65.48, H 8.10, N 8.04; found C 65.40, H 8.13, N 8.16%.

3.4. Preparation of di[2-(1R, 4R)-1,7,7-trimethylbicyclo-[2.2.1]hept-2-enyl]carbinol (4)

To a suspension of 41.6 g (96.1 mmol) of **2a** in 200 ml of tetrahydrofuran was added dropwise at −78°C 163 ml of a 1.3 M sec-butyllithium solution (212 mmol) in cyclohexane/n-hexane (98/2) during 2 h. The mixture was stirred for an additional 2 h at −78°C and then warmed to 0°C. The reaction mixture was kept at 0°C for *ca.* 20 min until evolution of nitrogen had ceased. The clear, red solution was cooled to −60°C. To the solution was then added dropwise during 15 min 3.55 g (48.0 mmol) of ethylformate dissolved in 10 ml of tetrahydrofuran. The yellow-orange solution was stirred for 30 min, allowed to warm to ambient temperature overnight and then hydrolyzed by the addition of 10 ml of water. Solvents were removed *in vacuo* and the yellow residue dissolved with vigorous stirring by adding 200 ml of petrol and 300 ml of water. Phases were separated and the aqueous layer extracted with three 100 ml portions of petrol. The combined organic layers were dried over sodium sulfate. Solvent was then removed in vacuo and the crystalline, slightly yellowish product dried *in vacuo* to yield 11.5 g (80%) of **4**, m.p. = 59–60°C, $[\alpha]_D$ = +8.3° (*c* 0.40, CH_2Cl_2). ^{1}H NMR (C_6D_6): δ = 0.70, 0.73, 0.88, 0.91 (4s, 12H, 7-CH_3), 0.99, 1.08 (2s, 6H, 1-CH_3), 0.50–1.32, 1.52, 1.78 (4m, 2H each, CH_2), 2.22 (m, 2H, 4-H), 4.63 (d, 1H, CH(OH)), 5.63 (br. d, 1H, OH), 5.77, 5.88 (2d, 2H, 3-H). ^{13}C NMR (C_6D_6): δ = 11.6, 11.9 (1-CH_3), 19.8 (double intensity), 20.0, 20.1 (7-CH_3), 25.7, 25.9 (C-5), 31.8, 32.6 (C-6), 51.7, 52.0 (C-4), 54.2, 54.5, 56.2, 57.9 (C-1, C-7), 66.0 (CH(OH)), 130.1, 130.3 (C-3), 150.4 (double intensity, C-2). IR (film): $\tilde{\nu}$ = 3450, 3055, 2986, 2950, 2869, 1620, 1600, 1474, 1459, 1441, 1384, 1374, 1104, 1094, 1012, 972 cm^{-1}. Anal. calcd. for $C_{21}H_{32}O$ (300.5) C 83.95, H 10.73; found C 81.53, H 10.76%.

TABLE 3. Selected data concerning the data collection and structure solution of **7a** and **2b** [10].

	7a	**2b**
formula	$C_{21}H_{29}Cl_3Zr$	$C_{19}H_{28}O_2N_2S$
mol wt	479.0	348.5
crystal size, mm	0.27×0.33×0.37	0.32×0.49×0.60
a, Å	7.006(1)	10.945(1)
b, Å	16.149(1)	19.832(1)
c, Å	19.122(1)	18.145(1)
β, deg		90.45(1)
V, Å^3	2163.6	3938.3
D_{calcd}, g cm^{-3}	1.47	1.18
μ, cm^{-1}	8.76	15.16
F(000), e	984	1504
Z	4	8
space group [no.]	$P2_12_12_1$ [19]	$P2_1$ [4]
diffractometer	Enraf-Nonius CAD4	
$K\alpha$ radiation, λ, Å	0.71069	1.54178
abs correction	none	none
no. of measd reflcns	2839 (+*h*, +*k*, +*l*)	8637 (+*h*, +*k*, +*l*)
$[(\sin\theta)/\lambda]_{max}$, Å^{-1}	0.65	0.63
R_{av}	–	0.01
no. of indep reflcns	2812	8364
no. of obsd reflcns ($I > 2\sigma(I)$)	2642	7632
no. of refined params	227	866
R	0.026	0.061
R_w ($w = 1/\sigma^2(F_o)$)	0.033	0.075
max. resid electron dens, e Å^{-3}	0.38	0.29

Structures were solved using heavy-atom methods, H-atom positions were calculated and kept fixed in the final refinement stages.

TABLE 4. Atomic coordinates of **2b** (only the representative data of one of the four independent molecules per unit cell are given)

Atom	*x*	*y*	*z*
S(1)	0.3552(1)	0.0005(1)	0.8050(1)
O(1)	0.2934(3)	0.0563(2)	0.8384(2)
O(2)	0.3433(3)	−0.0629(2)	0.8418(2)
N(1)	0.4983(3)	0.0246(2)	0.8006(2)
N(2)	0.5750(3)	−0.0275(2)	0.7761(2)
C(1)	0.7804(4)	−0.0741(3)	0.7660(3)
C(2)	0.6879(3)	−0.0206(2)	0.7885(2)
C(3)	0.7573(4)	0.0351(3)	0.8250(3)
C(4)	0.8885(5)	0.0077(3)	0.8193(5)
C(5)	0.8973(6)	−0.0482(6)	0.8732(4)
C(6)	0.8217(6)	−0.1057(4)	0.8385(5)
C(7)	0.8907(4)	−0.0292(3)	0.7471(3)
C(8)	1.0090(5)	−0.0688(5)	0.7327(5)
C(9)	0.8661(8)	0.0144(6)	0.6816(5)
C(10)	0.7357(6)	−0.1265(5)	0.7132(5)
C(11)	0.3132(3)	−0.0098(2)	0.7119(2)
C(12)	0.3209(3)	−0.0735(2)	0.6786(2)
C(13)	0.2856(4)	−0.0780(2)	0.6051(2)
C(14)	0.2448(4)	−0.0242(3)	0.5646(3)
C(15)	0.2401(4)	0.0379(3)	0.5989(3)
C(16)	0.2719(4)	0.0475(2)	0.6720(2)
C(17)	0.3645(5)	−0.1372(3)	0.7134(3)
C(18)	0.2081(5)	−0.0315(4)	0.4855(3)
C(19)	0.2574(6)	0.1166(3)	0.7018(3)

The analogous reaction of 68.5 g (158 mmol) of ent-**2a** with 2.2. molar equiv of sec.-butyllithium followed by addition of 5.41 g (73.0 mmol) of ethylformate gave 19.3 g (88%) of ent-**4**.

*3.5. Preparation of (1R,5R,8R,9S,11S)- and (1R,5R,8R,9R,11S)-1,5,14,14,15,15-hexamethylpentacyclo[9.2.1.1^{5,8}0^{2,10}0^{4,9}]pentadeca-3,Δ^{2,10}-diene (**5**, **5'**, "dibornacyclopentadiene")*

(+)Di(2-bornenyl)carbinol (**4**, 14.0 g, 46.3 mmol) was mixed with 400 mg (2.94 mmol) of potassium hydrogensulfate and heated for 3 h *in vacuo* with stirring at 110–120°C. Subsequent distillation *in vacuo* (10^{-2} torr) at 150–160°C gave 12.2 g (93%) of a mixture of the two diastereoisomers **5** and **5'** in a 7:1 ratio (m.p. = 87°C). Recrystallization from methanol gave the major isomer as a colourless solid, m.p. 107–108°C, $[\alpha]_D = +157.5°$ (*c* 0.40, CH_2Cl_2). ^1H NMR (C_6D_6): $\delta = 0.79$, 1.09 (2s, 6H, 1-CH_3, 5-CH_3), 0.83, 0.84, 1.04, 1.11 (4s, 12H, 14-CH_3, 15-CH_3), 0.69–1.99 (m, 8H, CH_2), 2.37, 2.64 (2m, 2H, 8-H, 11-H), 3.70 (s, 1H, 9-H), 5.56 (s, 1H, 3-H). ^{13}C NMR (C_6D_6): $\delta = 12.1$, 15.6, 18.6, 20.0, 20.3, 21.0 (1-, 5-, 14-, 15-CH_3), 27.8, 30.2, 33.9, 36.2 (CH_2), 48.6, 49.8 (C-8, C-11), 50.8, 52.6, 54.0 (double intensity) (C-1, C-5, C-14, C-15), 74.7 (C-9), 112.8 (C-3), 147.1, 147.2 (C-2, C-4), 164.6 (C-10). IR (film): $\tilde{\nu} = 3052$, 2951, 2869, 2843, 1663, 1472, 1451, 1441, 1386, 1374, 1287, 1270, 1120, 998, 768 cm^{-1}. Anal. calcd. for $C_{21}H_{30}$ (282.5) C 89.29, H 10.71; found C 88.91, H 10.56%.

The (−)di(2-bornenyl)carbinol ent-**4** (12.0 g, 39.9 mmol) was similarly dehydrated and cyclized with $KHSO_4$ (200 mg) to yield 10.6 g (94%) of the ent-**5**, ent-**5'** mixture, m.p. = 89°C.

*3.6. Preparation of (1R,5R,8S,11S)-1,5,14,14,15,15-hexamethylpentacyclo[9.2.1.1^{5,8}0^{2,10}0^{4,9}]pentadeca-3, Δ^{2,10}-dienyllithium (**6**, "dibornacyclopentadienyllithium")*

To a solution of 6.62 g (23.4 mmol) of (+)"dibornacyclopentadiene" (**5**) in 70 ml of ether was added dropwise at −78°C 15.7 ml (25.1 mmol) of a 1.6 M n-butyllithium solution in n-hexane. The reaction mixture was allowed to warm to room temperature and stirred for 2 days. Solvent was removed *in vacuo* to give the lithium compound **6** as an oil containing an undefined quantity of coordinated ether. Characterization was therefore only carried out by NMR spectroscopy. ^1H NMR (C_6D_6): $\delta = 0.80$, 1.00, 1.01, 1.06, 1.37, 1.41 (6s, 18H, 1-, 5-, 14-, 15-CH_3), 0.69–1.50 and 1.82–2.39 (4m, 8H, CH_2), 2.74, 2.90 (2m, 2H, 8-H, 11-H), 5.43 (s, 1H, 3-H) and coordinated diethylether signals at $\delta = 0.74$ (CH_3) and 2.82 (CH_2). ^{13}C NMR (C_6D_6): $\delta = 13.7$, 14.3 (1-, 5-CH_3), 20.8, 21.2, 21.6, 22.0 (14-, 15-CH_3), 30.9, 31.5, 37.7, 38.3 (CH_2), 50.2, 51.3 (C-8, C-11), 51.1, 52.0 (C-14, C-15), 55.5, 63.5 (C-1, C-5), 85.2 (C-3), 121.7, 121.8, 124.9, 136.2 (C-2, C-4, C-9, C-10) and signals of coordinated ether at $\delta = 14.6$ (CH_3) and 66.1 (CH_2).

Deprotonation of ent-**5** with n-butyllithium in n-hexane proceeded in an analogous way to give the lithium reagent ent-**6** in almost quantitative yield.

*3.7. Preparation of {(1R,5R,8S,11S)-η^5-1,5,14,14,15,15-hexamethylpentacyclo[9.2.1.1^{5,8}0^{2,10}0^{4,9}]pentadeca-3, Δ^{2,10}-dienyl}zirconiumtrichloride (**7a**, "(dibornacyclopentadienyl)zirconiumtrichloride")*

Dibornacyclopentadienyllithium (**6**; prepared from 23.4 mmol of **5** as described above) was dissolved in 70 ml of toluene and added at ambient temperature to a suspension of 8.18 g (35.1 mmol) of freshly sublimed zirconiumtetrachloride in 70 ml of toluene. The mixture was stirred at 90°C for 4 days and then cooled to room temperature. The remaining solid was filtered off and the residue washed with 10 ml of toluene. Solvent was removed from the clear filtrate *in vacuo* and the residue extracted with two portions (80 and 20 ml) of methylene chloride. Solvent was removed *in vacuo*, the residue washed with 30 ml of pentane and dried *in vacuo* to yield 8.12 g (73%) of **7a**, m.p. = 137°C, $[\alpha]_D = +51.0°$ (*c* = 0.30, CH_2Cl_2). Single crystals suitable for the X-ray crystal structure analysis of **7a** were obtained from methylene chloride. ^1H NMR (C_6D_6): $\delta = -0.01$, 0.54, 0.58, 0.96, 1.02, 1.34 (6s, 18H, CH_3), 0.40–1.72, 2.10, 2.90 (m, 8H, CH_2), 2.35, 2.66 (2m, 2H, 8-H, 11-H), 5.71 (s, 1H, 3-H). ^{13}C NMR (C_6D_6): $\delta = 11.6$, 12.4 (1-CH_3, 5-CH_3), 19.6, 20.3, 20.4, 29.6 (14-CH_3, 15-CH_3), 26.0, 28.6, 32.4, 38.5 (CH_2), 50.5, 51.6 (C-8, C-11), 55.7 (double intensity), 55.8, 68.5 (C-1, C-5, C-14, C-15), 106.5 (C-3), 144.5, 146.8, 152.7, 158.9, (C-2, C-4, C-9, C-10). IR (KBr): $\tilde{\nu} = 3004$, 2971, 2955, 2889, 2870, 1610, 1481, 1473, 1447, 1389, 1379, 1367, 810 cm^{-1}. The analogous reaction of the lithium reagent ent-**6** (9.3 mmol) with 2.45 g (10.5 mmol) of freshly sublimed $ZrCl_4$ yielded 2.58 g (58%) of "(−)-(dibornacyclopentadienyl)zirconiumtrichloride" (ent-**7a**), m.p. = 136°C, $[\alpha]_D = -53.0°$ (c = 1.1, CH_2Cl_2). Anal. calcd. for $C_{21}H_{29}Cl_3Zr$ (479.0) C 52.65, H 6.10; found C 52.79, H 6.01%.

The "(+)-(dibornacyclopentadienyl)hafniumtrichloride" complex **7b** was prepared analogously by reacting a solution of 2.00 g (7.08 mmol) of "(+)-dibornacyclopentadiene" (**5**) in 40 ml of ether with 4.44 ml (7.10 mmol) of a 1.6 M n-butyllithium solution, followed by 2.31 g (7.20 mmol) of hafniumtetrachloride in 100 ml of toluene. Workup as described above gave 1.64 g (41%) of **7b**, m.p. 145°C (dec.), $[\alpha]_D = +34.0°$ (*c* = 0.30, CH_2Cl_2). ^1H NMR (C_6D_6): $\delta = 0.01$, 0.56, 0.58, 1.02, 1.03, 1.33 (6s, 18H, CH_3), 0.55–1.93, 2.09, 2.87 (several

m, 8H, CH_2), 2.37, 2.70 (2m, 2H, 8-H, 11-H), 5.57 (s, 1H, 3-H). ^{13}C NMR (C_6D_6): $\delta = 11.7$, 12.4 (1-CH_3, 5CH_3), 19.9, 20.5, 20.7, 28.5 (14-CH_3, 15-CH_3), 26.4, 29.1, 32.8, 39.1 (CH_2), 50.3, 51.4 (C-8, C-11), 104.2 (C-3), 142.0, 145.4, 150.3, 156.4 (C-2, C-4, C-9, C-10). IR (KBr): $\tilde{\nu} = 3065$, 2956, 2928, 2871, 1670, 1552, 1545, 1477, 1450, 1389, 1261, 819 cm^{-1}. Anal. calcd. for $C_{21}H_{29}Cl_3Hf$ (566.3) C 44.54, H 5.16; found C 43.30, H 5.33%.

The "(+)-(dibornacyclopentadienyl)titaniumtrichloride" complex **7c** was prepared in a similar way. It was isolated but as yet has not been obtained analytically pure: a cold solution (−78°C) of 1.61 g (5.61 mmol) of "dibornacyclopentadienyllithium" (**6**) in 40 ml of toluene was added dropwise to a yellow suspension of 1.70 g (5.10 mmol) of bis(tetrahydrofuran)titaniumtetrachloride in 40 ml of toluene at −78°C. The mixture was allowed to warm to ambient temperature overnight. The dark-violet solution was filtered from some precipitate. Solvent was removed from the clear filtrate and the remaining solid extracted with 50 ml of methylene chloride. Solvent was removed *in vacuo* and the residue solidified by vigorous stirring with pentane (20 ml). The solid crude product (1.0 g, 46%) was collected by filtration and recrystallized from boiling n-heptane to give 0.5 g (23%) of the red-brown amorphous titanium complex **7c** m.p. 232°C (dec.). ^1H NMR (C_6D_6): $\delta = -0.10$, 0.57 (double intensity), 1.05, 1.13, 1.45 (5s, 18H, CH_3), 0.50–1.90 (several m, 8H, CH_2), 2.39, 2.76 (2m, 2H, 8-H, 11-H), 6.00 (s, 1H, 3-H). ^{13}C NMR (C_6D_6): $\delta = 11.4$, 12.2 (1-CH_3, 5-CH_3), 20.4, 20.5, 26.4 (double intensity) (14-CH_3, 15-CH_3), 26.0, 27.8, 33.6, 38.5 (CH_2), 51.4 (double intensity) (C-8, C-11), 52.2, 52.3, 55.5 (double intensity) (C-1, C-5, C-14, C-15), 111.5 (C-3), 153.2 (cyclopent. *ipso*-C). IR (KBr): $\tilde{\nu} = 3007$, 2962, 2917, 2871, 1596, 1451, 1386, 1262, 1104, 1097, 1031, 1022, 1016, 802 cm^{-1}.

Acknowledgments

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