DALTON
FULL PAPER

Zirconium complexes of cyclopenta[*b*]pyridine: synthesis, structure, and olefin polymerization catalysis †

Alexey N. Ryabov,[a] **Vyatcheslav V. Izmer,**[a] **Anatoly A. Borisenko,**[a] **Jo Ann M. Canich,**[b] **Lyudmila G. Kuz'mina,**[c] **Judith A. K. Howard**[d] **and Alexander Z. Voskoboynikov** *[a]

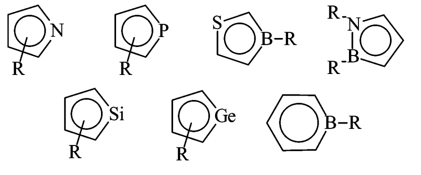
[a] *Department of Chemistry, Moscow State University, V-234, Moscow, GSP, 119899, Russian Federation. E-mail: voskoboy@org.chem.msu.su*
[b] *Baytown Polymer Center, ExxonMobil Chemical Company 5200 Bayway Drive, Baytown, Texas 77520, U.S.A.*
[c] *N. S. Kurnakov Institute of General and Inorganic Chemistry, 31 Leninsky Avenue, Moscow 117907, Russian Federation*
[d] *Department of Chemistry, Durham University, South Road, Durham, UK DH1 3LE*

Received 20th February 2002, Accepted 23rd May 2002

By treatment of Cp^*ZrCl_3 with the lithium salt of cyclopenta[*b*]pyridine ($LiCp^{Py}$) in toluene, the unsymmetrical complex $Cp^*(\eta^5\text{-}Cp^{Py})ZrCl_2$ was prepared in 32% yield. On the evidence of X-ray crystal structure analysis, the bifunctional Cp^{Py} ligand coordinates Zr in an η^5-manner rather than *via* nitrogen. Cyclopenta[*b*]pyridine turned out to react with $Zr(NMe_2)_4$ in toluene to form mono-cyclopentadienyl complex $(\eta^5\text{-}Cp^{Py})Zr(NMe_2)_3(Me_2NH)$ in 70% yield. The polymerization of ethylene and the copolymerization of ethylene with 1-hexene or propene catalyzed by $Cp^*(\eta^5\text{-}Cp^{Py})ZrCl_2$ activated with MAO was studied in detail.

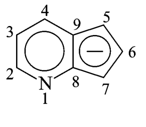
Introduction

Common single-site propene polymerization catalysts involve various alkyl/aryl substituted cyclopentadienyl, indenyl, and fluorenyl fragments in the coordination shell of an early transition metal.[1] Studies of these catalysts have resulted in the development of very effective stereospecific olefin polymerization processes. For the last few years, a number of early transition metal complexes with η^5-heterocyclic ligands, isoelectronic and isostructural to Cp and containing nitrogen,[2] phosphorus,[3] sulfur and boron,[4] silicon, and germanium,[5] as well as with η^6-borabenzene ligand[6] were synthesized and characterized.

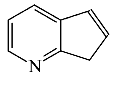


The catalytic activity of these complexes in olefin polymerization has been studied. However, to date, only limited information on early transition metal complexes involving cyclopentadienyl ligands with fused heterocycles (thiophene and pyrrole)[7] has been available.

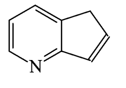
This paper is devoted to the chemistry of zirconium complexes including the cyclopenta[*b*]pyridinyl ligand:



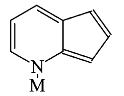
The parent compound, cyclopenta[*b*]pyridine, can be easily prepared from 6,7-dihydro-5*H*-cyclopenta[*b*]pyridine[8] to exist as a *ca.* 3 to 2 mixture of 7*H*- and 5*H*-cyclopenta[*b*]pyridines (**I** and **II**)[9] in equilibrium with the minor third isomer 1*H*-cyclopenta[*b*]pyridine (**III**, M = H), which is responsible for the apparent orange color of the substance even though there is less than 0.1% of **III** in the equilibrium mixture of the isomers.[10]



I



II



III

Similar to alkyl-substituted cyclopentadienyls, cyclopenta[*b*]pyridinyl ligand can give σ- or η^5-cyclopentadienyl–metal derivatives. For instance, complexes of Cp^{Py} with late transition metals, such as Fe, Ru, and Mn, possess an η^5 coordination mode.[11] On the other hand, it is obvious that a σ-bonded ligand can be expected to occur in the complexes of main group metals. Alternatively, with such hard Lewis acids as silicon or zirconium(IV) this ligand can form η^1 element–nitrogen bonding (**III**, M = Si, Zr). We have performed preliminary geometrical and energy calculations for several zirconium complexes including η^1-N- and η^5-cyclopenta[*b*]pyridinyl ligands using the semiempirical ZINDO/1 method. In all cases we have found that complexes involving the ligand bonded in an η^5-manner should be more stable than the respective compounds with Zr–N bonding. Thus, we aimed to gain experimental evidence in favor of this hypothesis and to study possible bonding modes of cyclopenta[*b*]pyridine in the respective Zr(IV) complexes. Finally, we have assayed the catalytic activities of zirconium complexes with η^5-cyclopenta[*b*]pyridinyl ligand to compare them with the known catalysts and understand the place of this ligand among common cyclopentadienyl ligands used in olefin polymerization.

---

† Electronic supplementary information (ESI) available: characterization data for **1**–**3**, $Cp^{Py}Li$ and Cp^*ZrCl_3; computational data for **3**. See http://www.rsc.org/suppdata/dt/b2/b201829b/

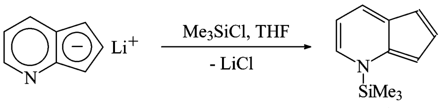
DOI: 10.1039/b201829b

Results and discussion

Synthesis and structure of zirconium complexes of cyclopenta[*b*]pyridine

Our first attempts to synthesize individual zirconium complexes of cyclopenta[*b*]pyridine failed. In spite of a lot of work, only two zirconium complexes of cyclopenta[*b*]pyridine could be isolated in an analytically pure form. For instance, on the evidence of NMR spectroscopy, the simplest reaction of 1–3 equivalents of cyclopenta[*b*]pyridinyl lithium ($Cp^{Py}Li$) with either $ZrCl_4$, $ZrCl_4(THF)_2$ or $(C_5H_5)ZrCl_3$ (or similar titanium compounds) usually gave intractable mixtures. When the reaction between $ZrCl_4$ and 2 equiv. of $Cp^{Py}Li$ was carried out in toluene, it gave a dark brown solution and a red precipitate. The latter consists of LiCl and three zirconium complexes (on the evidence of NMR). Two of them in 1 : 1 ratio are likely to be isomeric $(Cp^{Py})_2ZrCl_2$ complexes.[12] Unfortunately, we could not isolate these compounds in analytically pure form since this precipitate contained one more zirconium complex (up to 10% of the precipitate). As the total yield of these complexes was very low (less than 5%), the main products of this reaction are likely to be compounds with Zr–N bonding (probably, oligomeric compounds with bridging Zr–N–Zr fragments). The formation of such compounds can be judged from the characteristic UV-Vis spectrum of the liquid phase.[13]

Some insight into the chemistry of the interaction of $Cp^{Py}Li$ with Zr(IV) salts can be obtained from the analogy of Zr(IV) and Si, both of which are considered hard Lewis acids.[14] The treatment of $Cp^{Py}Li$ with an excess of Me_3SiCl gave 1-(trimethylsilyl)-1*H*-cyclopenta[*b*]pyridine (**1**) as a dark red oil in 94% yield [eqn. (1)].

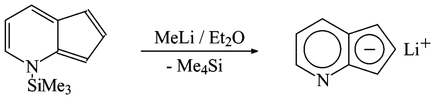


1

(1)

The fulvenoid structure of **1** can be confirmed by the data from electronic absorption spectroscopy. Indeed, **1** possesses an absorption band in the visual region at 480 nm, similar to the bands of the minor isomer of cyclopenta[*b*]pyridine (**III**, M = H, λ_{max} = 471 nm) and 1-methyl-1*H*-cyclopenta[*b*]pyridine (**III**, M = Me, λ_{max} = 456 nm).[10]

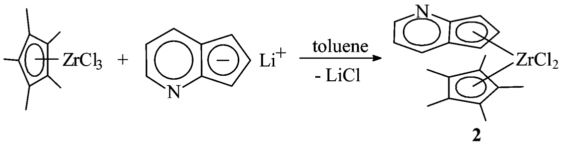
We have found that the reaction of **1** with MeLi in ether gives the lithium salt of cyclopenta[*b*]pyridine in almost quantitative yield [eqn. (2)]. Thus, **1** can be considered as a convenient source of this lithium salt. Whereas cyclopenta[*b*]pyridine itself must be freshly prepared, as it is unstable to decomposition after several hours at rt, **1** is stable at rt for at least a week and can be safely stored in a refrigerator indefinitely.



(2)

Further on, we turned our attention to attempts to obtain η^5-Cp^{Py} zirconium complexes, as soon as our theoretical calculations revealed that the $(\eta^5\text{-}Cp^{Py})Zr$ structure should be more stable than the respective η^1-complex, we expected that η^5-complexes can be synthesized using either softer reagents or a reversible reaction.

It is well known that the metal center in Cp^*ZrCl_3 possesses softer Lewis acid character due to the electron-rich Cp* ligand. The treatment of this compound with $Cp^{Py}Li$ in toluene yields a new zirconium complex **2** [eqn. (3)], which was isolated in 32% yield as extremely moisture sensitive white needles. As can be guessed from the lack of absorbance in the visual region in the UV-Vis spectrum of **2** in toluene, the coordination mode of Cp^{Py} in this complex is not η^1 fulvenoid, but rather is closer to the expected η^5 sandwich.[15]



2

(3)

Indeed, this hypothesis was confirmed by resolving the molecular structure by X-ray crystal structure analysis. The general view and atom labeling scheme are shown in Fig. 1. The molecule has the bent sandwich geometry, with two Cl ligands in the bisecting plane. The angle between two σ-bonds is equal to 98.0(1)°; the angle between the planes of the η^5-cyclopentadienyl groups is 126.7°. Both these values agree well with such parameters observed for other members of the zirconocene family.[1]

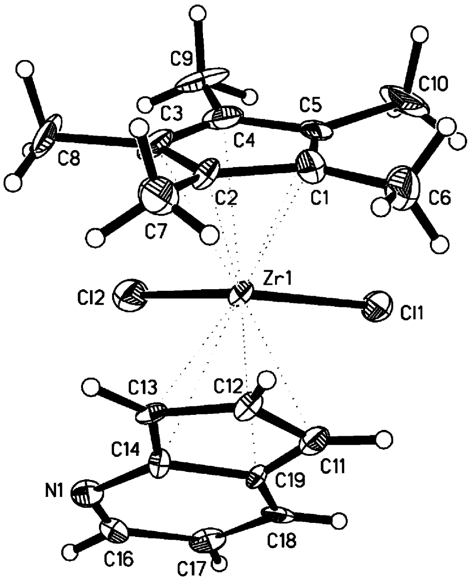


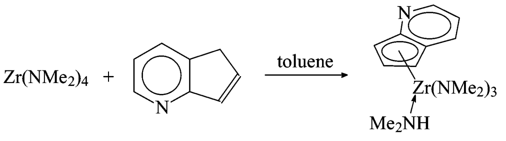
Fig. 1 View of complex **2**.

The coordination of pentamethylcyclopentadienyl ligand corresponds to an almost regular η^5 mode. The Zr–C distances vary within the range 2.50–2.53 Å. The angle between the normal from Zr to the cyclopentadienyl ring and the Zr–centroid cyclopentadienyl line is equal to 0.7°. The cyclopentadienyl ring is planar within 0.01 Å. All methyl substituents are displaced from the cyclopentadienyl least squares mean plane in the opposite direction from the metal atom. The displacements vary within a rather wide range of 0.04–0.23 Å. The displacements of three methyl groups [C(6), C(8), and C(9)] do not exceed 0.09 Å, whereas the displacements of the other two methyl groups [C(7) and C(10)] are significantly greater, 0.23 and 0.19 Å. This distortion is due to a short contact of both C(7) methyl with the C(12)–H fragment of an adjacent ligand, and C(10) with the Cl(1) ligand. Actually, the C(7) ··· C(12) non-bonding distance of 3.20 Å is the shortest amongst all distances between carbon atoms of Cp* and Cp^{Py} ligands, and the C(10) ··· Cl(1) distance of 3.14 Å is the shortest distance of Cl ligands to any carbon atom in the molecule.

The coordination of the cyclopenta[*b*]pyridinyl ligand is rather irregular. While three Zr–C distances vary within 2.50–2.53 Å, the distances from Zr(1) to the C(14) and C(19) atoms are longer, equal to 2.66 and 2.60 Å, respectively. It should be noted that the latter two atoms belong to the fused pyridine ring. The cyclopentadienyl fragment of the ligand is planar within 0.04 Å. The angle between the normal from Zr to the cyclopentadienyl ring and the Zr–centroid cyclopentadienyl line is equal to 4.2°. The bicyclic ligand is bent around the fusion C(14)–C(19) bond by 3.5°. The pyridine ring is bent in the opposite direction from the Cl(1)–Zr(1)–Cl(2) plane due to overcrowding in the Zr coordination sphere. To minimize this hindrance, two cyclopentadienyl fragments are in a staggered configuration.

The distance between Zr(1) and N(1) (3.644 Å) is too long to correspond to a chemical bond. Thus, the X-ray structural investigation unambiguously shows that the cyclopenta[*b*]pyridinyl ligand has the η^5-cyclopentadienyl coordination mode rather than monodentate bonding through the N atom.

An alternative synthetic procedure for Group IV metallocenes involves the use of $Zr(NMe_2)_4$[16–19] which has a much softer metal center than $ZrCl_4$. Furthermore, in contrast to exchange reactions with $Cp^{Py}Li$, the reaction of substituted cyclopentadienes with $Zr(NMe_2)_4$ is a reversible transformation which should result in more thermodynamically stable products. We found that a pink precipitate is rapidly formed upon treatment of $Zr(NMe_2)_4$ with 1 equiv. of cyclopenta[*b*]pyridine in toluene at rt [eqn. (4)]. This precipitate is sparingly soluble in toluene and highly soluble in CH_2Cl_2. This dichloromethane solution has a deep red color, which is accounted for by an unresolved broad absorption in the 350–500 nm region lacking any characteristic bands. This color is likely to be caused by minor decomposition products. Nevertheless, on the evidence of NMR spectroscopy, the precipitate is an individual zirconium complex **3**, which includes one Cp^{Py} ligand and a coordinated dimethylamine molecule (see also ref. 16*c*). It should be noted that **3** does not react with the second equiv. of cyclopenta[*b*]pyridine to form the respective zirconocene. On the evidence of NMR spectroscopy, less than 5% decomposition of **3** occurred at room temperature in CD_2Cl_2 after 1.5 h. However, on keeping overnight a considerable decomposition of **3** took place to give a white precipitate probably because of slow NMe_2/Cl exchange with the chlorinated solvent.



(4)

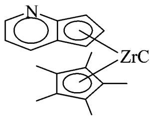
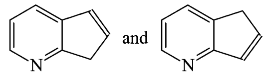
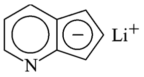
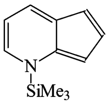
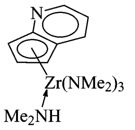
3

A considerable broadening of resonances attributed to 4-H ($\Delta\nu_{1/2}$ = 12.0 Hz), 5-H ($\Delta\nu_{1/2}$ = 8.4 Hz) in Cp^{Py}, and Me_2N protons (doublet, $^3J_{N-H}$ = 6.5 Hz, $\Delta\nu_{1/2}$ = 3.8 Hz) of the coordinated dimethylamine appears in the ^1H NMR spectrum of **3** in CD_2Cl_2 at rt. At −75 °C, this spectrum displays broad resonances for the protons of the cyclopentadienyl ring of Cp^{Py}, *i.e.* 5-H ($\Delta\nu_{1/2}$ = 7.8 Hz), 6-H ($\Delta\nu_{1/2}$ = 9.8 Hz), and 7-H ($\Delta\nu_{1/2}$ = 8.6 Hz), and the protons of Me_2N ($\Delta\nu_{1/2}$ = 4.8 Hz) and Me_2NH ($\Delta\nu_{1/2}$ = 7.2 Hz) ligands. In the last case, N–H coupling in the Me_2NH fragment was not observed. On the other hand, we found no broadening of the resonance attributed to 4-H of Cp^{Py}. A theoretical calculation of **3** using the semiempirical ZINDO/1 method resulted in the following stable conformation of this sterically strained compound (hydrogen atoms of Me_2N ligands are not shown) with close contacts of the Me_2NH group and 4-/5-protons of the η^5-cyclopenta[*b*]pyridinyl ligand.

Thus, the observed dynamic behavior of **3** in solution is probably due to the hindered rotation of Cp^{Py} or/and Me_2NH ligands in the coordination sphere of zirconium. Another possible explanation is a reversible dissociation of the $Zr \leftarrow NHMe_2$ fragment.

Unfortunately, the crystal structure analysis of **3** could not be performed. This compound decomposed after *ca.* 1 h in CH_2Cl_2 solution at rt to give a polymeric material with no characteristic NMR resonances. Obviously, the evidence of ^1H and ^{13}C NMR spectra of **3** is not sufficient to provide reliable information on bonding modes of ligands in this compound. Both possible isomers (with η^5-Cp^{Py} ligand or with direct Zr–N bonding) should have had similar NMR spectra. However, it might be expected that ^{15}N NMR spectra might be more sensitive to the changes or bonding in the complexes under study (Table 1).

Table 1 ^{15}N NMR chemical shifts at 25 °C[a]

Compound	δ/ppm
	305.7[b]
	302.5 and 296.4[c]
	253.3[d]
	162.2[c]
$Zr(NMe_2)_4$	145.6 (br)[b,e]
$Me_2NH{\cdot}HCl$	23.6[f]
Me_2NH	10.7[f]
	239.6 175.9 30.4 (br)[b,g]

[a] Relatively liquid NH_3 at 25 °C. [b] In CD_2Cl_2. [c] In $CDCl_3$. [d] In THF-d_8. [e] 143.0 (br, $\Delta\omega$ = 375 Hz) in ^{14}N spectrum in benzene-d_6. [f] In MeOH.[19] [g] At −55 °C.

Whereas the ^{15}N resonance of unsubstituted pyridine appears at 317.3 ppm,[20] the spectrum of cyclopenta[*b*]pyridine shows two resonances at 302.5 and 296.4 ppm attributed to two isomers **I** and **II**, respectively. It is of interest that the coordination with zirconium in **2** does not result in a considerable shift of the resonance. Thus, bonding between η^5-Cp^{Py} ligand and zirconium in **2** is almost covalent. Actually, the ^{15}N resonance of ionic $Cp^{Py}Li$ exhibits a *ca.* 50 ppm upfield shift relative to the resonances attributed to uncharged cyclopenta[*b*]pyridine or η^5-Cp^{Py} in **2**. On the other hand, direct Si–N bonding in **1** results in a *ca.* 140 ppm upfield shift.

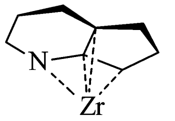
In the ^{15}N NMR spectrum of **3**, three resonances at 239.6, 175.9, and 30.4 ppm were found. A broad line at 30.4 ppm was attributed to the coordinated Me_2NH molecule. The most intense line at 175.9 ppm was attributed to three NMe_2 ligands bonded to zirconium. It is of interest to note that $Zr(NMe_2)_4$, which in the solid state was found to have a dimeric structure with two NMe_2 bridges,[21] displays a broad resonance at 145.6 ppm in the ^{15}N NMR spectrum in CD_2Cl_2 at rt. As zirconium amides are known to react slowly with CH_2Cl_2, we

Table 2 Preliminary results of polymerization experiments in the presence of **2**/MAO

Entry	Olefin	T/°C	Ethene/psi	Polymer yield/g	Activity/ kg P (mol Zr)$^{-1}$ atm^{-1} h^{-1}	M_w	M_n	M_w/M_n	Co-monomer/ mol%
1	C2	60	52	0.8	370				
2	C2	60	52	0.5	230				
3	C2	80	65	2.0	750	611,000	241,000	2.53	
4	C2	80	65	3.4	1270	545,000	212,000	2.57	
5	C2/C6	60	49	1.6	400	678,000	358,000	1.89	1.1
6	C2/C6	60	49	1.2	300	645,000	256,000	2.52	1.5
7	C2/C6	80	65	8.1	1510	203,000	65,000	3.12	2.1
8	C2/C6	80	65	7.9	1480	200,000	54,000	3.70	2.3
9	C2/C3	115	148	7.5	310	103,000	13,000	7.92	2.1
10	C2/C3	115	148	6.4	260	84,000	10,000	8.40	1.9

decided to repeat this experiment using C_6D_6 as solvent. Unfortunately, in this case at room temperature we observed no resonance at all, probably because of a very broad signal. However, the ^{14}N NMR spectrum of this benzene solution was found to display a broad resonance at 143.0 ppm.

The third resonance at 239.6 ppm in the ^{15}N NMR spectrum of **3** was attributed to the cyclopenta[*b*]pyridinyl fragment. This resonance has a *ca.* 65 ppm upfield shift relative to the ^{15}N resonance in **2**. On the other hand, it exhibits a *ca.* 80 ppm downfield shift relative to the resonance attributed to compound **1** with direct N–Si bonding. Thus, bonding modes for Cp^{Py} fragments in compounds **3**, **2**, and **1** are different. The most likely explanation of this phenomenon is that bonding between Cp^{Py} and zirconium in **3** is close to ionic, *i.e.* as in $Cp^{Py}Li$. The following considerations speak in favor of this conclusion. The resonance of $Cp^{Py}Li$ appears at 253.3 ppm. Secondly, **3** is a highly sterically strained compound (see NMR spectra and the calculated geometry). Therefore, the η^5-Cp^{Py}–Zr bond length should be larger than the respective bond length in **2**. This is likely to result in a weaker orbital overlap between Cp^{Py} and Zr, and, therefore, lead to a shift towards more ionic interaction. Another possible explanation is associated with a possibility of η^3- or η^4-Cp^{Py} coordination to Zr, *e.g.*



It should be noted that this coordination mode is quite different from that with direct Zr–N bonding similar to Si–N bonding observed for **1**. Lack of any characteristic bands in the 350–500 nm region of the electronic spectrum of **3** speaks in favor of the polydentate bonding mode.

Olefin polymerization catalyzed by 2 activated with MAO

Compound **2** when activated with methylaluminoxane is an active catalyst for the polymerization of ethylene and the copolymerization of ethylene with 1-hexene and propene. The preliminary results of this study are shown in Table 2. Ethylene homopolymers with weight average molecular weights up to 610 kDa were produced at 80 °C with a relatively narrow polydispersity of 2.53–2.57 (entries 3 and 4), indicating traditional single-site behavior. Incorporation of propene or 1-hexene was rather low with copolymers containing from 1.1 to 2.3 mol% of co-monomer. Polymer molecular weight is highly dependent on polymerization temperature, with significantly lower molecular weights being produced at 60 °C (entries 5 and 6) than at 80 °C (entries 7 and 8). It should be noted that this catalyst exhibits moderate activity for ethylene–propylene copolymerization producing polymers with a relatively broad polydispersity of 7.92–8.40 (entries 9 and 10). The results of the polymerization experiments are summarized in Table 2.

A comparison of the activity of **2**/MAO with the activities of well-known polymerization catalysts reveals that **2** is a precursor of a highly active catalyst.[22] However, the activities of other metallocene catalysts are nevertheless considerably higher, *e.g.* the values for Cp_2ZrCl_2 and $(Indenyl)_2ZrCl_2$ activated by MAO in PE polymerization were found to be 123 and 355 tons P (mol Zr)$^{-1}$ atm^{-1} h^{-1}, respectively.[23] It is of interest to note that the activities of other systems based on cyclopentadiene fused to thiophene or pyrrole rings are also considerably higher.[7] As ligand electronegativities are known to correlate both with the calculated energy of the LUMO orbitals of activated catalysts and with the experimental activities of the selected zirconocene catalysts,[24] the observed relatively lower activity of **2**/MAO could be anticipated. Whereas the electronegativity of the cyclopenta[*b*]pyridinyl anion is equal to −0.315 Hartrees, cyclopenta[*b*]thiophenyl and indenyl anion are less electronegative (−0.302 and −0.304 Hartrees, respectively). However, the main explanation of the observed activity can be associated with a possibility of coordination of Al in MAO to the nitrogen atom of the pyridine fragment. This can change counterion interaction during the polymer chain growth to result in an additional steric screening of the active site of the catalyst.

Experimental

All manipulations were performed either on a high-vacuum line in all-glass apparatus equipped with PTFE stopcocks or in an atmosphere of thoroughly purified argon using a standard Schlenk technique. Tetrahydrofuran and ether for synthesis (and THF-d_8 for NMR measurements) were purified by distillation over $LiAlH_4$ and kept over sodium benzophenone ketyl. Hydrocarbon solvents (including toluene-d_8 for NMR measurements) were distilled and stored over CaH_2 or Na/K alloy. Dichloromethane (and CD_2Cl_2) was distilled and stored over CaH_2. Chloroform-*d* was distilled over P_4O_{10} and stored over molecular sieves (3 Å). Anhydrous $ZrCl_4$ (Aldrich) was used as obtained. Cyclopenta[*b*]pyridine,[8] pentamethylcyclopentadiene,[25] and $Zr[NMe_2]_4$[18] were prepared according to the published methods. $Cp^{Py}Li$ and Cp*Li were prepared by the treatment of the corresponding cyclopentadienes in toluene with 2.4 M solution of ^{n}BuLi in hexanes. Alternatively, $Cp^{Py}Li$ was prepared from **1** and MeLi in ether as described below. ^{1}H, ^{13}C, and ^{15}N spectra were recorded with a Varian VXR 400 for 1–10% solutions in deuterated solvents. Chemical shifts for ^{1}H and ^{13}C were measured relative to TMS. In ^{1}H NMR spectra, the assignment of signals in the Cp^{Py} fragment was made on the evidence of double resonance and NOE experiments. Chemical shifts for ^{15}N were measured relative to liquid ammonia. UV-Vis spectra were recorded with a Hewlett-Packard 8452A diode array spectrophotometer. C, H microanalyses were done using a CHN-O-Rapid analyzer (Heracus).

All quantum-chemical calculations were carried out using the semiempirical ZINDO/1 method[26] implemented in the program package HyperChem Release 6.01.[27] Geometry optimization (RHF) for the ground states of all studied complexes in a vacuum was performed using the Polak–Ribiere algorithm down to a gradient value of 0.01 kcal mol^{-1}. The computations were performed with an IBM PC AT compatible workstation.

Preparations

Detailed characterization data are available as ESI.†

1-(Trimethylsilyl)-1*H*-cyclopenta[*b*]pyridine (1). Freshly distilled Me_3SiCl (14.9 ml, 12.75 g, 117.5 mmol) in 110 ml of THF was added to a solution of 2.89 g (23.5 mmol) of $Cp^{Py}Li$ in 70 ml of THF at rt. The resulting dark red mixture was stirred for 30 min and then evaporated to dryness *in vacuo*. Hexane (200 ml) was added, and this solution was filtered though a glass frit (G4). The filtrate was evaporated and the residue dried *in vacuo* to yield 4.18 g (94%) of a dark red oil. On the evidence of NMR spectroscopy, this sample included at least 95% of compound **1**.

Reaction of 1 with MeLi. To a solution of 4.17 g (22.0 mmol) of **1** in 40 ml of ether, 60 ml of a 0.36 M solution of MeLi in ether (21.6 mmol) was added dropwise over 2 h at −78 °C. A yellow precipitate formed and the slurry was stirred at rt for 20 h. The precipitate was filtered off (G4), washed with 10 ml of cold ether, and dried *in vacuo*. Yield 2.25 g (85%) of $Cp^{Py}Li$.

Cp^*ZrCl_3. Toluene (150 ml) was added to a mixture of 21.5 g (92.0 mmol) of freshly sublimed $ZrCl_4$ and 11.9 g (84.0 mmol) of Cp*Li. The slurry was refluxed and stirred for 2 days. A pale yellow precipitate was the filtered off (G4 glass frit) and washed with toluene (50 ml). The crude product was treated with hot decane (3 × 100 ml) using a special thick wall filtering (G4 frit) funnel equipped with a thermostatted (165–170 °C) oil jacket. A yellowish precipitate was formed as soon as the filtrate was cooled to room temperature. This precipitate was filtered off (G4), washed with pentane (3 × 50 ml) and dried *in vacuo* for 3 h. Yield 20.5 g (73%).

$Cp^{Py}Cp^*ZrCl_2$ (2). Toluene (200 ml) was added to a mixture of 2.88 g (23.0 mmol) of $Cp^{Py}Li$ and 7.65 g (23.0 mmol) of Cp^*ZrCl_3. The slurry was refluxed and stirred for 24 h, then filtered using a thick wall funnel equipped with a glass frit (G4) and a hot (90–95 °C) water jacket. The crystals which precipitated from the filtrate at −30 °C were separated, washed with a minimal amount of cold toluene and dried *in vacuo*. Yield 3.05 g (32%) of white needles of compound **2**.

$Cp^{Py}Zr(NMe_2)_3(NHMe_2)$ (3). A solution of 1.06 g (9.0 mmol) of freshly distilled cyclopenta[*b*]pyridine in 5 ml of toluene was added to a stirred solution of 2.50 g (9.3 mmol) of $Zr(NMe_2)_4$ in 100 ml of toluene. The dark red suspension was stirred for 1.5 h at rt, and filtered (G4 glass frit). The resulting pink precipitate was washed with cold hexane (2 × 50 ml) and dried *in vacuo*. Yield 2.40 g (70%) of compound **3**.

X-Ray diffraction study of complex 2

Crystals of **2** are unstable in air at room temperature and require use of the oil method under a nitrogen atmosphere. Crystal data, data collection, structure solution and refinement parameters for **2** are listed in Table 3. All hydrogen atoms were found objectively from a difference Fourier synthesis. However, in further calculations, they were placed in calculated positions and refined using a riding model. Only one of two possible positions of the nitrogen atom [the second one is instead of the C(18)–H(18A) group] in the pyridine ring is found with certainty as indicated by both the absence of an electron density peak corresponding to hydrogen in the vicinity of the N(1) atom and normal values of anisotropic thermal parameters of N(1) and C(18) as well as their abnormal values when we changed the positions of these atoms. Rather high values of R_σ together with the not very high accuracy of the structure discussed are due to the fact that the crystal was too small in two dimensions and, therefore, weakly reflected (mean *I*/*s* = 5.09). Although the absorption coefficient is rather low (0.922 mm^{-1}), we attempted to introduce absorption correction using both the SADABS procedure[31] and empirical *y*-scans. However, in both cases no improvement was achieved. Nevertheless, final structural results are good enough for discussion.

Table 3 Crystal data, data collection, structure solution and refinement parameters for **2**

Empirical formula	$C_{18}H_{21}Cl_2NZr$
Formula weight	413.48
Color, habit	White, oblong plate
Crystal size/mm	0.45 × 0.09 × 0.03
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	13.546(2)
b/Å	8.766(1)
c/Å	14.989(2)
β/°	97.552(7)
Volume/Å^3	1764.4(4)
Z	4
Absorption coefficient/mm^{-1}	0.922
F(000)	840
Diffractometer	Siemens SMART CCD[28]
Temperature/K	120.0(2)
Radiation (λ/Å)	Graphite monochromatized Mo-Kα (0.71073)
Reflections collected	11395
Independent reflections	3479 [R(int) = 0.3251]
Absorption correction	ψ-scan
Decay correction	None
Solution method	Direct methods (SHELX-86)[29]
Refinement method	Full-matrix least-squares on F^2 (SHELXL-93)[30]
Data/restraints/parameters	2948/0/206
Goodness-of-fit on F^2	1.001
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0933$, $wR_2 = 0.2161$
R indices (all data)	$R_1 = 0.1745$, $wR_2 = 0.2837$

CCDC reference number 179863.

See http://www.rsc.org/suppdata/dt/b2/b201829b/ for crystallographic data in CIF or other electronic format.

Olefin polymerization study

Polymerizations were conducted in a 500 ml stainless steal Zipperclave reactor equipped with a paddle stirrer, a temperature controller, an on demand supply of ethylene regulated to maintain a constant reactor pressure, and a supply of dry high pressure nitrogen to maintain an inert atmosphere. Monomers and solvents directly plumbed into the reactor were passed through drying columns prior to entering the reactor.

A typical reaction to produce polyethylene consisted of adding 180 ml of dry toluene and 3 ml of 10 wt% methylaluminoxane in toluene (Albemarle) to the reactor. After addition, the reactor was vented to reduce excess nitrogen pressure. The reactor was heated to the desired reaction temperature and charged with the desired differential pressure of ethylene. 1 mg of compound **2** was dissolved in 1 ml of dry toluene contained in a catalyst addition tube and was flushed into the reactor using approximately 20 ml of dry toluene under nitrogen pressure. The reaction was run for a period of 15 minutes at which time the ethylene flow was discontinued, and the reactor was quickly cooled and vented. The contents of the reactor were precipitated in methanol. The polymer was initially dried under a flow of nitrogen and then dried overnight in a vacuum oven at 90–100 °C under a slight nitrogen purge.

A typical reaction to produce an ethylene-1-hexene copolymer followed the above procedure except that 155 ml of dry toluene, 2.4 ml of 10 wt% methylaluminoxane and 25 ml of dry 1-hexene were added to the reactor. Additionally, 2 mg of pre-catalyst dissolved in 2 ml of dry toluene were used in the reaction.

A typical reaction to produce an ethylene–propylene copolymer followed the above procedure except that 230 ml of dry hexane and 2.4 ml of 10 wt% methylaluminoxane were added to the reactor. After heating the reactor to 115 °C, liquid propylene was added to the reactor until the equilibrated reactor pressure reached 103 psi. Ethylene (251 psi) was then added to the reactor. The precatalyst solution of 2 mg dissolved in 2 ml of dry toluene was flushed into the reactor using approximately 20 ml of dry hexane. The reaction was run for a period of 30 minutes. Work up of the polymer was as above except for drying the polymer overnight in a vacuum oven at 100–110 °C under a slight purge of nitrogen.

Molecular weights [weight average molecular weight (M_w) and number average molecular weight (M_n)] were measured by Gel Permeation Chromatography using a Waters 150 Gel Permeation Chromatograph equipped with a differential refractive index detector and calibrated using polystyrene standards. Samples were run in 1,2,4-trichlorobenzene (145 °C) using three Shodex GPC AT-80 M/S columns in series. No column spreading corrections were employed but data on generally accepted standards, *e.g.* National Bureau of Standards Polyethylene 1475, demonstrated a precision of 0.1 units for M_w/M_n, which was calculated from elution times. Numerical analyses were performed using Expert Ease® software available from the Waters Corporation.

Polymer comonomer incorporation was determined by ^{1}H NMR using a Varian Unity+ 400 MHz instrument run with a single 30° flip angle RF pulse. A total of 120 pulses with a delay of 8 seconds between pulses were signal averaged. The polymer sample was dissolved in heated tetrachloroethane-d_2 and signal collection took place at 120 °C. Complete polymerization results are summarized in Table 2.

Acknowledgements

Financial support from the Russian Foundation for Basic Research (Grant nos. 01-03-32699a and 01-03-32474a), President of the Russian Federation (Grant no. 98-15-96061), International Science and Technology Center (Grant. no. 1036/99) and ExxonMobil Chemical Company is gratefully acknowledged. We thank the Royal Society and the EPSRC for a Senior Research Fellowship (J. A. K. H.). We also thank Prof. Irina P. Beletskaya.

References and notes

1 *Metallocenes: Synthesis, Reactivity, Applications*, eds. A. Togni and R. L. Halterman, Wiley-VCH, New York, 1998.

2 J. M. Tanski and G. Parkin, *Organometallics*, 2002, **21**, 587.

3 (*a*) C. Janiak, U. Versteeg, K. C. H. Lange, R. Weimann and E. Hahn, *J. Organomet. Chem.*, 1995, **501**, 219; (*b*) C. Janiak, K. C. H. Lange, U. Versteeg, D. Lentz and P. Budzelaar, *Chem. Ber.*, 1996, **129**, 1517; (*c*) S. J. Brown, X. Gao, D. G. Harrison, L. V. H. Koch, R. E. Spense and G. P. A. Yap, *Organometallics*, 1998, **17**, 5445.

4 A. J. Ashe, III, X. Fang and J. W. Kampf, *Organometallics*, 1999, **18**, 1821.

5 (*a*) J. M. Dysard and T. D. Tilley, *J. Am. Chem. Soc.*, 2000, **122**, 3097; (*b*) J. M. Dysard and T. D. Tilley, *Organometallics*, 2000, **19**, 2671.

6 (*a*) A. J. Ashe, III, S. Al-Ahmad and J. W. Kampf, *Organometallics*, 1999, **18**, 4234; (*b*) G. E. Herberich, U. Englert, A. Fischer, J. Ni and A. Schmitz, *Organometallics*, 1999, **18**, 5496.

7 (*a*) J. A. Ewen, R. L. Jones, M. J. Elder, A. L. Rheingold and L. M. Liable-Sands, *J. Am. Chem. Soc.*, 1998, **120**, 10786; (*b*) J. A. Ewen, M. J. Elder, R. L. Jones, A. L. Rheingold, L. M. Liable-Sands and R. D. Sommer, *J. Am. Chem. Soc.*, 2001, **123**, 4763.

8 M. M. Robison, *J. Am. Chem. Soc.*, 1958, **80**, 6254.

9 Compound **I**. ^{1}H NMR ($CDCl_3$): δ 8.30 (dd, J = 5.05, 1.56 Hz, 1H, 2-H), 7.51 (dd, J = 7.42, 1.56 Hz, 1H, 4-H), 6.89 (dt, J = 5.74, 1.97 Hz, 1H, 5-H), 6.88 (dd, J = 7.42, 5.05 Hz, 1H, 3-H), 6.72 (dt, J = 5.74, 2.00 Hz, 1H, 6-H), 3.20 (dt, J = 2.00, 1.97 Hz, 1H, 7-H). ^{13}C NMR ($CDCl_3$): δ 163.7, 147.2, 138.8, 136.1, 133.3, 130.3, 118.8, 36.7.

Compound **II**. ^{1}H NMR ($CDCl_3$): δ 8.20 (dd, J = 5.06, 1.54 Hz, 1H, 2-H), 7.44 (dd, J = 7.56, 0.75 Hz, 1H, 4-H), 6.96 (dd, J = 7.56, 0.60 Hz, 1H, 3-H), 6.69 (dt, J = 5.90, 1.94 Hz, 1H, 7-H), 6.46 (dt, J = 5.90, 2.00 Hz, 1H, 6-H), 3.31 (dt, J = 2.00, 1.94 Hz, 1H, 5-H). ^{13}C NMR ($CDCl_3$): δ 165.0, 144.8, 137.1, 133.9, 130.0, 127.3, 120.8, 40.2.

10 C. B. Reese, *J. Am. Chem. Soc.*, 1962, **84**, 3979.

11 (*a*) J. C. Ruble and G. C. Fu, *J. Org. Chem.*, 1996, **61**, 7230; (*b*) C. E. Garett and G. C. Fu, *J. Am. Chem. Soc.*, 1998, **120**, 7479; (*c*) L.-N. Ji, D. L. Kershner, M. E. Rerek and F. Basolo, *J. Organomet. Chem.*, 1985, **296**, 83.

12 ^{1}H NMR (CD_2Cl_2): δ 9.60 (dd, J = 5.28, 1.47 Hz, 1H), 9.16 (dd, J = 5.86, 1.18 Hz, 1H), 8.63 (dt, J = 8.49, 1.17 Hz, 1H), 8.09 (dd, J = 7.57, 1.15 Hz, 1H), 7.54 (dd, J = 8.50, 5.27 Hz, 1H), 7.46 (dd, J = 7.62, 5.87 Hz, 1H), 6.63 (ddd, J = 9.96, 1.47, 0.88 Hz, 1H), 6.48 (dt, J = 9.97, 1.03 Hz, 1H), 6.07–6.13 (m, 4H).

13 This solution possesses characteristic absorption bands at 461, 488, and 510 nm.

14 (*a*) *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, 1982; (*b*) *Comprehensive Organometallic Chemistry (II). A Review of the Literature 1982–1994*, eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Exeter, 1995.

15 While this work was in progress, authors of the following patent studied the dimethyl derivative of **2** *i.e.* $Cp^{Py}Cp^*ZrMe_2$: R. A. Fischer and R. B. Temme, WO Patent Application 9837106 to Exxon.

16 (*a*) G. M. Diamond, R. F. Jordan and J. L. Petersen, *Organometallics*, 1996, **15**, 4030; (*b*) J. N. Christopher, G. M. Diamond, R. F. Jordan and J. L. Petersen, *Organometallics*, 1996, **15**, 4038; (*c*) D. W. Carpenetti, L. Kloppenburg, J. T. Kupec and J. L. Petersen, *Organometallics*, 1996, **15**, 1572; (*d*) J. N. Christopher, R. F. Jordan, J. L. Petersen and V. G. Young, Jr., *Organometallics*, 1997, **16**, 3044.

17 G. M. Diamond, R. F. Jordan and J. L. Petersen, *Organometallics*, 1996, **15**, 4045.

18 G. M. Diamond, R. F. Jordan and J. L. Petersen, *J. Am. Chem. Soc.*, 1996, **118**, 8024.

19 A. Vogel, T. Priermeier and W. A. Herrmann, *J. Organomet. Chem.*, 1997, **527**, 297.

20 (*a*) B. I. Ionin, B. A. Ershov and A. I. Koltsov, *NMR Spectroscopy in Organic Chemistry*, Khimiya, Leningrad, 1983; (*b*) V. W. von Philipsborn and R. Müller, *Angew. Chem.*, 1988, **98**, 381.

21 M. H. Chisholm, C. E. Hammond and J. C. Huffman, *Polyhedron*, 1988, **7**, 2515.

22 "High active catalyst" as it was rated by Gibson *et al.* in G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.

23 H. G. Alt and A. Köppl, *Chem. Rev.*, 2000, **100**, 1205.

24 K. R. Squire in *Proceedings of the 222nd American Chemical Society Meeting*, Chicago, USA, 2001.

25 *Synthetic Methods of Organometallic and Inorganic Chemistry*, ed. W. A. Herrmann, Thieme, Stuttgart, 1996 vol. 1.

26 (*a*) A. D. Bacon and M. C. Zerner, *Theor. Chim. Acta*, 1979, **53**, 21; (*b*) W. P. Anderson, W. D. Edwards and M. C. Zerner, *Inorg. Chem.*, 1986, **25**, 2728.

27 HyperChem Release 6.01 for Windows, Hypercube, Inc., Gainesville, USA, 2000.

28 SMART Version 4.050, Siemens Analytical X-Ray Instruments Inc., Madison, Wisconsin, USA, 1995.

29 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

30 G. M. Sheldrick, SHELXL-93. Program for the refinement of crystal structures, University of Göttingen, Germany, 1993.

31 G. M. Sheldrick, SADABS. Program for empirical absorption correction of area detector data, University of Göttingen, Germany, 1996.