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New 1,3-disubstituted side-chain functionalized indenyl ligands and zirconium complexes derived from them

D. P. Krut´ko,[a]★ **S. A. Belov,**[a] **R. S. Kirsanov,**[a] **D. A. Lemenovskii,**[a] **and A. V. Churakov**[b]

[a]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (495) 932 8846. E-mail: kdp@org.chem.msu.ru
[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 954 1279

New functionalized indenyl ligands $Ind^X = 1,3\text{-}C_9H_5(Pr^i)(CH_2CH_2X)$ (X = OMe or NMe_2) and $1,3\text{-}C_9H_5(Pr^i)[CMe_2CH_2(2'\text{-py})]$ and the zirconium sandwich complexes $(Ind^X)Cp^*ZrCl_2$ (Cp* is pentamethylcyclopentadienyl) were synthesized. The photochemical behavior and the reduction reactions of zirconocene dichlorides were investigated. The properties of these compounds are determined mainly by the high lability of Zr—Ind bonds. The reduction of $(Ind^X)Cp^*ZrCl_2$ (X = NMe_2) selectively affords the complex $Cp^*[\eta^5:\eta^2\text{-}(C,N)\text{-}C_9H_5(Pr^i)CH_2CH_2N(Me)CH_2]ZrH$ as the intramolecular NCH_2—H bond activation product. The molecular structures of the complex $(Ind^X)Cp^*ZrCl_2$ (X = OMe) and its photochemical decomposition product $[Cp^*ZrCl_2(OMe)]_2$ were established by X-ray diffraction.

Key words: functionalized indenyl ligands, zirconium, photochemical decomposition, reduction, C—H-activation, X-ray diffraction study.

In recent years, it has been shown[1—4] that, due to the unusual η^9 coordination, indenyl ligands containing bulky substituents ($SiMe_2R$ or Pr^i) at positions 1 and 3 can stabilize the Zr^{II} center in zirconium sandwich complexes without loss of high reactivity. In continuation of our studies on the chemistry of functionalized cyclopentadienyl derivatives of Group IV metals, we synthesized and characterized the complexes $[1,3\text{-}C_9H_5(Pr^i)(CR_2CH_2X)]Cp^*ZrCl_2$ (R = H or Me) containing the heteroatomic functional group (X = OMe, NMe_2, or 2-py) in one of the substituents of the five-membered ring of the indenyl ligand. Investigations of the reduction of zirconocene dichlorides and a comparison of these data with the results of our previous research on their tetramethylcyclopentadienyl analogs[5—8] are of particular interest.

Results and Discussion

Synthesis of ligands and Zr^{IV} complexes

Disubstituted indenes $1,3\text{-}C_9H_6(Pr^i)(CH_2CH_2X)$ (X = OMe (**1**) or NMe_2 (**2**)) were synthesized by the reaction of lithium 3-isopropylindenide with $ClCH_2CH_2X$ without the isolation of intermediates (Scheme 1). To synthesize metal complexes, the resulting oily compounds were transformed into the corresponding lithium indenides (Li-**1**) and (Li-**2**).

Analogously, the addition of α-picolyllithium at the *exo* position of 1-isopropyl-3-(isopropylidene)indene afforded the pyridine-containing ligand $1,3\text{-}C_9H_5(Pr^i)[CMe_2CH_2(2'\text{-py})]$ (**3**) in good yield (Scheme 2). The lithium salt of the ligand (Li-**3**) was isolated and characterized after the reaction of **3** with Bu^nLi as an adduct with one Et_2O molecule.

All three indenes **1—3** are mixtures consisting of two isomers (**A** and **B**) with respect to the double bond in the five-membered ring in different ratios. The assignment of the signals of the isomers in the ^{13}C NMR spectra (see the Experimental section) was made taking into account their relative intensities measured in the ^1H NMR spectra.

An interesting feature of the NMR spectra of indenide Li-**3** is that (as opposed to MeO- and Me_2N-functionalized indenyl salts) the signals for the protons of the bridging CH_2 and $C(CH_3)_2$ groups in the ^1H NMR spectrum and the signals of $C(\underline{C}H_3)_2$ in the ^{13}C NMR spectrum at 27 °C are substantially broadened. Although detailed studies by dynamic NMR spectroscopy were not carried out, it can be suggested that this broadening is associated with the reversible intramolecular coordination of the lithium cation simultaneously by the indenyl ring and the nitrogen atom of the pyridine substituent giving the seven-membered metallacycle. In this case, the substituents in the bridging group should become nonequivalent. This process is consistent with the higher coordination ability

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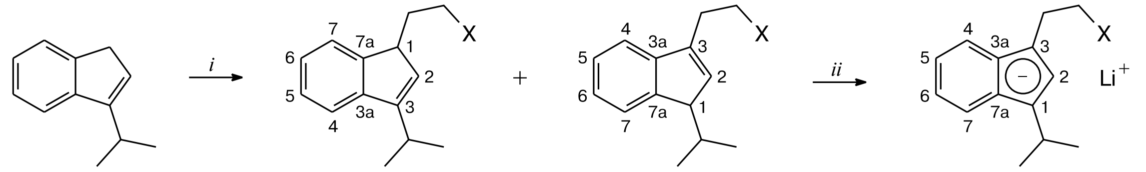
Scheme 1



A **B**

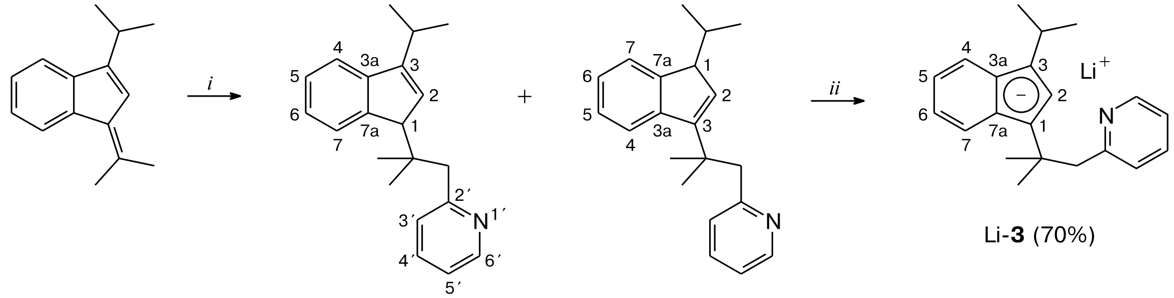
1 (76%), **2** (81%)

Li-**1** (72%), Li-**2** (92%)

X = OMe (**1**, Li-**1**), NMe (**2**, Li-**2**)

i. 1) Bu^nLi, THF; 2) $Cl(CH_2)_2X$; 3) H_2O. *ii*. Bu^nLi, Et_2O.

Scheme 2



A **B**

3 (89%)

Li-**3** (70%)

i. 1) $Bu^nLi + 2\text{-}MeC_5H_4N$, THF; 2) H_2O. *ii*. Bu^nLi, Et_2O.

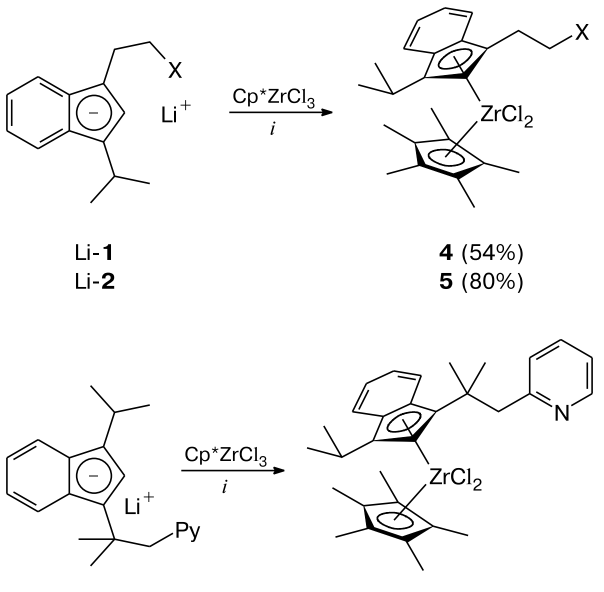
of the pyridine substituent to the Li cation compared to that of the MeO and Me_2N groups.

The mixed-ligand sandwich complexes $(Ind^X)Cp^*ZrCl_2$ ($Ind^X = 1,3\text{-}C_9H_5(Pr^i)(CH_2CH_2X)$, where X = OMe (**4**) or NMe_2 (**5**), or $1,3\text{-}C_9H_5(Pr^i)[CMe_2CH_2(2'\text{-py})]$ (**6**); Cp* is pentamethylcyclopentadienyl) were synthesized by the reactions of the corresponding lithium indenides Li-**1**—Li-**3** with Cp^*ZrCl_3 with prolonged heating in toluene (Scheme 3). In this case, the elimination of the indenyl ligand from the starting half-sandwich complex as the side reaction, which we have observed[9] in the synthesis of $[1,3\text{-}C_9H_5(SiMe_3)_2](C_5Me_4CH_2CH_2NMe_2)ZrCl_2$ (**7**) starting from $[1,3\text{-}C_9H_5(SiMe_3)_2]ZrCl_3$ and $(C_5Me_4CH_2CH_2NMe_2)^-Li^+$, is impossible and, in spite of the drastic conditions, the reaction is sufficiently selective.

It should be noted that sandwiches **4**—**6** are readily soluble not only in ethereal (THF, Et_2O) but also in hydrocarbon (toluene, hexane) solvents.

Although the heteroatomic group in sandwich complexes **4**—**6** is not coordinated to the metal atom, it has an effect on the properties of these compounds. Thus, nitrogen-containing complexes **5** and **6**, unlike the unfunctionalized derivatives, proved to be very sensitive to moisture. This fact is attributed to the presence of the group, which has basic properties and, hence, accelerates the

Scheme 3



Li-**1**
Li-**2**

4 (54%)
5 (80%)

Li-**3**

6 (37%)

X = OMe (**4**), NMe_2 (**5**)

i. Toluene, 100 °C, 16 h.

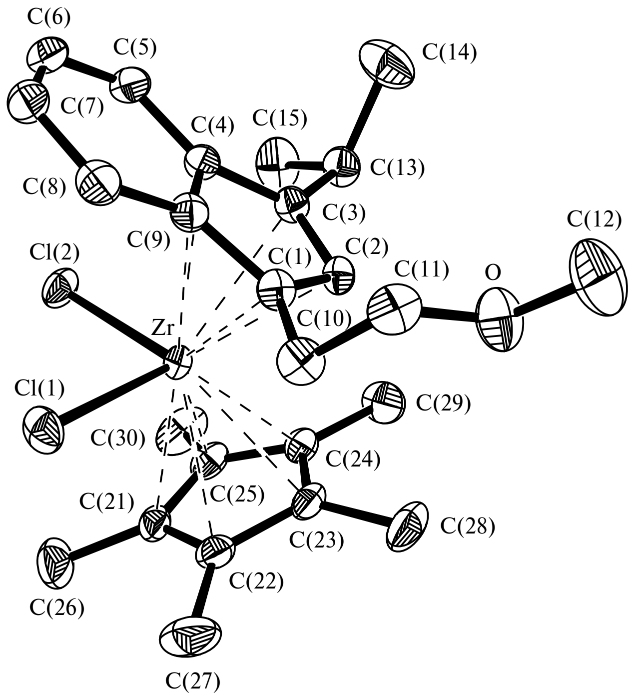


Fig. 1. Molecular structure of complex **4**. Hydrogen atoms are omitted.

hydrolysis,[10] in the coordination environment of the Zr atom. The Me_2N-substituted complex **7** exhibits similar properties; the hydrolysis of this complex occurs in an unusual fashion and is accompanied by the elimination of the indenyl ligand.[9]

The molecular structure of complex **4** (Fig. 1) is similar to that of the unfunctionalized complexes [1,3-$C_9H_5(SiMe_3)_2$]Cp*$ZrCl_2$ (**8**),[9] (1,3-$C_9H_5Ph_2$)Cp*$ZrCl_2$ (**9**), and (1,3-$C_9H_5Ph_2)_2ZrCl_2$ (**10**).[11] The only substantial difference is that the Zr—C(1) distance is the shortest Zr—C_{Ind} distance in **4** (Table 1), whereas the Zr—C(2) distance to the unsubstituted position of the ring in the shortest distance in **8**—**10** (2.521(2) Å for **8**, 2.500(3) Å for **9**, 2.500(4) Å and 2.486(3) Å for **10**). Nevertheless, the Zr—C(1—3) distances in all these compounds are shorter than the Zr—C(4) and Zr—C(9) distances (see Fig. 1).

Table 1. Selected bond lengths and bond angles in the structure of compound **4**

Bond	d/Å	Parameter	Value
Zr—Cl(2)	2.4338(3)	Bond	d/Å
Zr—C(1)	2.4816(13)	Zr—C(21)	2.5152(13)
Zr—C(2)	2.4907(13)	Zr—C(23)	2.5420(13)
Zr—C(9)	2.6206(13)	Zr—C(25)	2.5316(13)
Zr—C(22)	2.5435(14)	Zr—Pl(2)*	2.2273(6)
Zr—C(24)	2.5292(13)		
Zr—Pl(1)*	2.2507(6)	Angle	ω/deg
Zr—Cl(1)	2.4502(3)	Cl(2)—Zr—Cl(1)	95.659(13)
Zr—C(3)	2.5635(13)	Pl(1)—Pl(2)*	55.14(4)
Zr—C(4)	2.6695(13)		

* Pl(1) and Pl(2) are the mean planes of the five-membered cyclopentadienyl and indenyl rings, respectively.

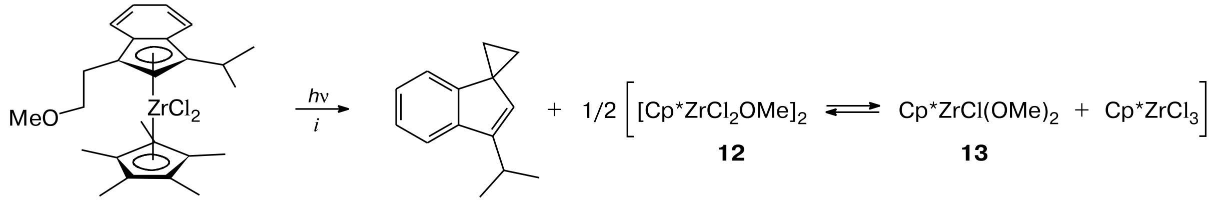
This fact reflects the known tendency of Zr^{IV} to be η^3-coordinated by the indenyl ligand.[12]

Photochemical behavior of complexes 4—6

A rather unusual property of complexes **4**—**6** is that they are photochemically unstable. It appeared that solutions of all three compounds in ethereal solvents (Et_2O, THF) are unstable to even diffuse daylight and are decomposed under direct daylight during 8 h. At the same time, solutions of **4**—**6** are stable in the dark during several months and are not decomposed even upon heating (THF, 65 °C, 8 h). Solutions of **4**—**6** in benzene or hexane are also stable.

The decomposition of a solution of **4** in THF under direct daylight for 16 h afforded spiro compound **11** and the half-sandwich complexes [Cp*$ZrCl_2$(OMe)]$_2$ (**12**), Cp*ZrCl$(OMe)_2$ (**13**), and Cp*$ZrCl_3$ (Scheme 4) in virtually quantitative yields (NMR spectroscopic data). The simultaneous formation of three complexes is apparently attributed to the mutual exchange of the ligands Cl^- and OMe^- in solution. Being the least soluble, compound **13** precipitated and was isolated in the individual state.

Scheme 4



4 **11**

i. THF, 25 °C.

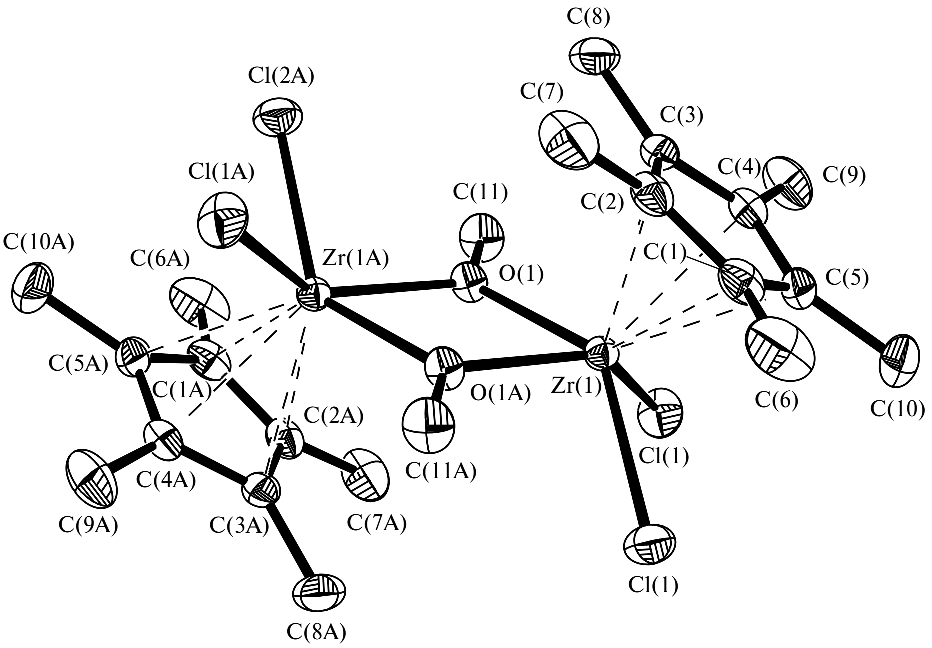


Fig. 2. Molecular structure of complex **12**. Hydrogen atoms are omitted.

Table 2. Selected bond lengths and bond angles in the structure of compound **12**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Zr(1)—O(1)	2.1508(12)	Zr(1)—Cl(2)	2.4444(5)	O(1)—Zr(1)—O(1A)	69.82(5)
Zr(1)—O(1A)	2.1477(12)	Zr(1)—Zr(1A)	3.5250(4)	Cl(1)—Zr(1)—Cl(2)	87.491(19)
Zr(1)—Cl(1)	2.4391(5)	Zr—Pl*	2.1944(8)	Zr(1)—O(1)—Zr(1A)	110.18(5)

* Pl is the mean plane of the cyclopentadienyl ring.

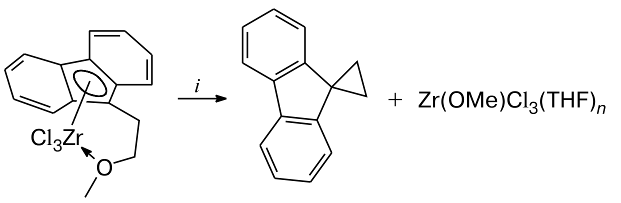
The slower decomposition of **4** gave single crystals of **12**, which were studied by X-ray diffraction.

Compound **12** is a centrosymmetric dimer (Fig. 2, Table 2) with the transoid arrangement of the pentamethylcyclopentadienyl ligands and the planar central fragment $Zr_2(\mu_2\text{-}OMe)_2$. The Zr atom in the molecule is in a square-pyramidal coordination environment (by assuming that the Cp* ligand occupies the vertex of the pyramid). On the whole, the geometric parameters of molecule **12** are similar to those found previously[13] for the related complex $[Cp^*Zr(OMe)_2]_2(\mu_2\text{-}OMe)_2$.

It should be noted that the analogous elimination of the methoxy group from functionalized fluorenyl half-sandwich complex **14** giving the corresponding fluorenyl spiro compound (Scheme 5) has been observed previously.[14] However, this reaction occurs upon heating.

The photochemical decomposition of complexes **5** and **6** is also accompanied by the Zr—Ind bond cleavage. In this case, the elimination of the functional substituent does not occur. Apparently, the initially formed indenyl radical abstracts a proton from the solvent molecule to form indenes **2** and **3**, which are the major reaction products.

Scheme 5



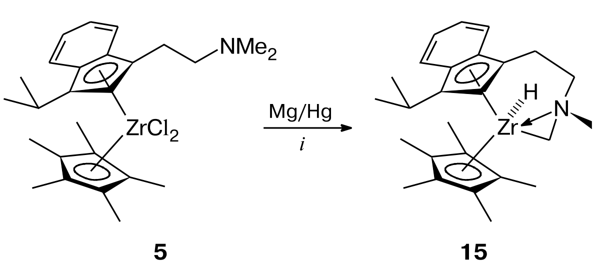
14

i. THF, 60 °C, 30 min.

Reduction of complexes 4—6

Functionalized sandwich complexes **4—6** were reduced in two ways: with the use of magnesium amalgam in THF or with sodium amalgam in benzene at 25 °C. The reaction of **5** with Mg/Hg in THF leads to the intramolecular C—H activation of one of the NCH_2—H bonds and the virtually quantitative formation of the product $Cp^*[\eta^5{:}\eta^2\text{-}(C,N)\text{-}C_9H_5(Pr^i)CH_2CH_2N(Me)CH_2]ZrH$ (**15**) (Scheme 6).

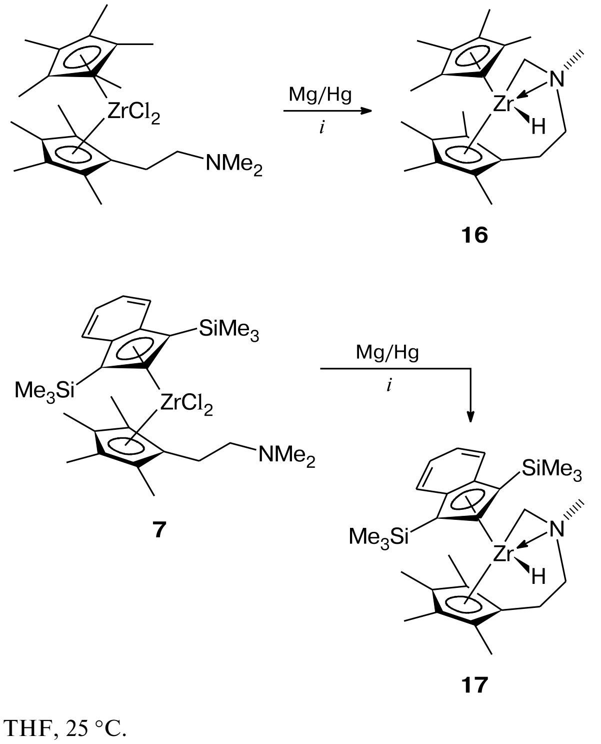
Scheme 6



i. THF, 25 °C.

The structure of complex **15** was determined by NMR spectroscopy. This complex is structurally similar to the reduction products Cp*[η^5:η^2-(*C*,*N*)-$C_5Me_4CH_2CH_2N$-(Me)CH_2]ZrH (**16**)[6] and [η^5-$C_9H_5(SiMe_3)_2$][η^5:η^2-(*C*,*N*)-$C_5Me_4CH_2CH_2N(Me)CH_2$]ZrH (**17**),[9] which we have prepared previously starting from Cp*($C_5Me_4CH_2CH_2NMe_2$)$ZrCl_2$ and complex **7** (Scheme 7). Evidently, all three reactions occur in a similar way.

Scheme 7



i. THF, 25 °C.

In the ^{1}H NMR spectrum of complex **15**, the chemical shift δ (^{1}H) of the signal of NMe (2.21 ppm) is similar to that of this group in **16** (δ 2.24), as opposed to the abnormally low value (1.17 ppm) in **17**, in which the NMe group is in the shielding cone of the six-membered ring of the indenyl ligand. Hence, the NMe group in compound **15** is directed away from the phenylene fragment. At the same time, the signal of the hydride ligand in **15** (3.23 ppm) is shifted downfield compared to the signals of **16** and **17** (2.81 and 2.77 ppm, respectively), which is indicative of its deshielding by the phenylene fragment. Other parameters of the ^{1}H and ^{13}C NMR spectra for the corresponding fragments of three hydride complexes **15**—**17** are very similar. This is evidence for the similar configuration of the atoms (with the central arrangement of the nitrogen atom) in the bisecting plane of these compounds. This configuration was unambiguously established by X-ray diffraction and a series of homonuclear NOE experiments for complex **16** (see Ref. 6) and is apparently thermodynamically favorable.[8]

The reduction of methoxy-substituted complex **4** with Mg/Hg in THF in the dark is accompanied by the degradation of the sandwich structure. Like the photochemical decomposition of this complex, the reduction affords spiro compound **11** (see Scheme 4). The elimination of the indenyl ligand occurs most likely in the intermediate step of the formation of the Zr^{III} complex. In the case under consideration, the oxidative addition of the Zr^{II} center at the O—CH_3 bond is not observed, as opposed to the reduction of Cp*($C_5Me_4CH_2CH_2OMe$)$ZrCl_2$ under the same conditions.[5]

The reduction of pyridine-containing sandwich complex **6** with both Mg/Hg in THF and Na/Hg in C_6H_6 afforded mixtures of unidentified products. We have observed[7] the same situation in the reduction of the complex Cp*[$C_5Me_4CH_2$(2-py)]$ZrCl_2$ containing a single-unit bridge with Mg/Hg in THF. An increase in the length of the bridging fragment did not lead to the formation of the *ortho*-C—H-activation product Cp*$_2$Zr(H)[η^2-(*C*,*N*)-2-C_5H_4N], which is generated by the reduction of Cp*$_2ZrCl_2$ in pyridine.[8]

The reduction of **4** and **5** with Na/Hg in benzene is also nonselective. Apparently, the Zr—Ind bond cleavage is the prevailing process in this case as well.

To conclude, let us note that the photochemical instability of complexes **4**—**6** and their reductive behavior are indicative of the relatively weak Zr—Ind bond in these compounds. This is consistent with the results of the reduction of Cp*(1,3-$C_9H_5Ph_2$)$ZrCl_2$ and [1,3-$C_9H_5Ph_2$]$_2$-$ZrCl_2$, resulting in the elimination of the indenide anion,[11] as well as with the synthesis and hydrolysis of sandwich complex **7** accompanied by the loss of the indenyl ligand.[9] Hence, it can be concluded that the lability of 1,3-disubstituted indenyl ligands is a key factor determining the chemical behavior of the complexes under consideration.

Experimental

All operations, including the preparation of samples for NMR spectroscopy, were carried out under an inert atmosphere or in sealed evacuated Schlenk-type glassware. All solvents, including deuterated solvents, were purified according to standard procedures, degassed, and recondensed under high vacuum (10^{-3} Torr) directly into a reaction vessel or an NMR tube. Magnesium amalgam,[5] isopropylindene,[15] 1-isopropyl-3-(isopropylidene)indene,[15] and $\mathrm{Cp^*ZrCl_3}$[16] were synthesized according to procedures described in the literature.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 and 100 MHz, respectively) at 27 °C using the chemical shifts of the signals of the corresponding deuterated solvents as the internal standard (7.24 and 77.0 ppm for $\mathrm{CDCl_3}$, 7.15 and 128.0 ppm for $\mathrm{C_6D_6}$, and 1.73 and 25.3 ppm for THF-d_8, respectively). The atomic numbering scheme for indenes, lithium indenides, and the zirconium complexes corresponds to those shown in Schemes 1 and 2. The elemental analysis was carried out on an automated Carlo-Erba analyzer.

1-(2-Methoxyethyl)-3-(isopropyl)indene (1) (major isomer **A** (~90%)). A 2.14 *M* $\mathrm{Bu^nLi}$ solution in hexane (22 mL, 0.047 mol) was added dropwise to a solution of isopropylindene (7.4 g, 0.047 mol) in THF (100 mL) at 0 °C, and the reaction mixture was stirred at 20 °C for 4 h. The reaction solution was cooled to 0 °C, and a solution of $\mathrm{CH_3OCH_2CH_2Cl}$ (4.7 g, 0.05 mol) in THF (10 mL) was added dropwise. Then the reaction mixture was stirred at 20 °C for 5 h and quenched with water (30 mL). The organic layer was separated, washed three times with water, and dried over $\mathrm{Na_2SO_4}$. The solvent was distilled off *in vacuo*. The red oily product was obtained in a yield of 7.7 g (0.036 mol, 76%). ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 1.26 and 1.27 (both d, 3 H, $\mathrm{CH\underline{Me}_2}$, $^3J_{\mathrm{H,H}} = 6.8$ Hz); 1.71 and 2.16 (both m, 1 H, $\mathrm{C\underline{H}_2CH_2O}$); 2.90 (sept, 1 H, $\mathrm{C\underline{H}Me_2}$, $^3J_{\mathrm{H,H}} = 6.8$ Hz); 3.36 (s, 3 H, OMe); 3.48 (m, 3 H, $\mathrm{CH_2O}$, H(1)); 6.19 (s, 1 H, H(2)); 7.19 (t, 1 H, $^3J_{\mathrm{H,H}} = 7.3$ Hz); 7.28 (t, 1 H, $^3J_{\mathrm{H,H}} = 7.9$ Hz) (H(5), H(6)); 7.36 (d, 1 H, $^3J_{\mathrm{H,H}} = 7.6$ Hz); 7.41 (d, 1 H, $^3J_{\mathrm{H,H}} = 7.5$ Hz) (H(4), H(7)).

Lithium 1-isopropyl-3-(2-methoxyethyl)indenide (Li-1). A 2.14 *M* $\mathrm{Bu^nLi}$ solution in hexane (17 mL, 0.036 mol) was added to a solution of **1** (7.7 g, 0.036 mol) in $\mathrm{Et_2O}$ (50 mL), and the reaction mixture was stirred at 20 °C for 24 h. Then the solvent was evaporated to dryness. The residue was washed three times with hexane and dried under high vacuum. The pale-yellow product was obtained in a yield of 5.8 g (0.026 mol, 72%). ^{1}H NMR (THF-d_8), δ: 1.33 (d, 6 H, $\mathrm{CH\underline{Me}_2}$, $^3J_{\mathrm{H,H}} = 6.9$ Hz); 3.13 (t, 2 H, $\mathrm{C\underline{H}_2CH_2O}$, $^3J_{\mathrm{H,H}} = 6.2$ Hz); 3.21 (s, 3 H, OMe); 3.29 (sept, 1 H, $\mathrm{C\underline{H}Me_2}$, $^3J_{\mathrm{H,H}} = 6.9$ Hz); 3.78 (t, 2 H, $\mathrm{CH_2O}$, $^3J_{\mathrm{H,H}} = 6.2$ Hz); 6.23 (s, 1 H, H(2)); 6.40 (m, 2 H, H(5), H(6)); 7.25 and 7.32 (both m, 1 H, H(4), H(7)). ^{13}C NMR, δ: 25.61 (q, $\mathrm{CH\underline{Me}_2}$, $^1J_{\mathrm{C,H}} = 124$ Hz); 28.62 (d, $\mathrm{\underline{C}HMe_2}$, $^1J_{\mathrm{C,H}} = 123$ Hz); 29.78 (t, $\mathrm{\underline{C}H_2CH_2O}$, $^1J_{\mathrm{C,H}} = 124$ Hz); 58.39 (q, OMe, $^1J_{\mathrm{C,H}} = 141$ Hz); 74.94 (t, $\mathrm{CH_2O}$, $^1J_{\mathrm{C,H}} = 141$ Hz); 94.91, 113.65, 127.22, and 127.64 (all s, C(1), C(3), C(3a), C(7a)); 112.42 (d, C(2)H, $^1J_{\mathrm{C,H}} = 150$ Hz); 112.89, 113.34, 117.24, and 118.27 (all d, C(4)H, C(5)H, C(6)H, C(7)H, $^1J_{\mathrm{C,H}} = 153$ Hz).

(2-Dimethylaminoethyl)(isopropyl)indene (2) (a mixture of isomers **A** and **B** (~4 : 6)). A 2.14 *M* $\mathrm{Bu^nLi}$ solution in hexane (20 mL, 0.043 mol) was added dropwise to a solution of isopropylindene (6.7 g, 0.042 mol) in THF (50 mL) at 0 °C, and the reaction mixture was stirred at 20 °C for 2 h. The solution was cooled to 0 °C, and a solution of $\mathrm{Me_2NCH_2CH_2Cl}$ (4.6 g, 0.043 mol) in THF (10 mL) was added dropwise. Then the reaction mixture was stirred at 20 °C for 5 h, quenched with water (30 mL), and extracted with pentane. The organic layer was separated, dried over $\mathrm{Na_2SO_4}$, and concentrated *in vacuo*. After the distillation *in vacuo* (100—120 °C, (1—5)$\cdot10^{-2}$ Torr), the pale-brown oily product was obtained in a yield of 7.8 g (0.034 mol, 81%). ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 0.60 and 1.10 (both d, $\mathrm{CH\underline{Me}_2}$(B), $^3J_{\mathrm{H,H}} = 6.8$ Hz); 1.26 and 1.27 (both d, $\mathrm{CH\underline{Me}_2}$(A), $^3J_{\mathrm{H,H}} = 6.8$ Hz); 1.65 and 2.07 (both m, $\mathrm{C\underline{H}_2CH_2N}$ (A)); 2.24 (s, $\mathrm{NMe_2}$ (A)); 2.29 and 2.41 (both m, $\mathrm{CH_2N}$ (A)); 2.30 (m, $\mathrm{C\underline{H}Me_2}$ (B)); 2.33 (s, $\mathrm{NMe_2}$ (B)); 2.61 and 2.73 (both m, $\mathrm{C\underline{H}_2C\underline{H}_2N}$ (B)); 2.90 (sept, $\mathrm{C\underline{H}Me_2}$ (A), $^3J_{\mathrm{H,H}} = 6.8$ Hz); 3.35 (m, H(1) (B)); 3.43 (m, H(1) (A)); 6.17 (br.s, H(2) (A)); 6.18 (br.s, H(2) (B)); 7.16—7.41 (set of m, H(4), H(5), H(6), H(7) (A, B)). ^{13}C{^{1}H} NMR, δ: 17.68, 21.55 ($\mathrm{CH\underline{Me}_2}$ (B)); 21.82, 21.90 ($\mathrm{CH\underline{Me}_2}$ (A)); 26.17 ($\mathrm{\underline{C}H_2CH_2N}$ (B)); 26.81 ($\mathrm{\underline{C}HMe_2}$ (A)); 29.74 ($\mathrm{\underline{C}H_2CH_2N}$ (A)); 30.06 ($\mathrm{\underline{C}HMe_2}$ (B)); 45.40 ($\mathrm{NMe_2}$ (A)); 45.48 ($\mathrm{NMe_2}$ (B)); 46.82 (CH(1) (A)); 55.52 (C(1)H (B)); 57.55 ($\mathrm{CH_2N}$ (A)); 58.55 ($\mathrm{CH_2N}$ (B)); 118.69, 123.00, 124.57, 126.18 (C(4)H, C(5)H, C(6)H, C(7)H) (B)); 119.41, 122.88, 124.57, 126.18 (C(4)H, C(5)H, C(6)H, C(7)H) (A)); 142.08, 145.39, 147.50 (C(3), C(3a), C(7a) (B)); 144.43, 148.60, 150.11 (C(3), C(3a), C(7a) (A)).

Lithium 1-isopropyl-3-(2-dimethylaminoethyl)indenide (Li-2). A 2.14 *M* $\mathrm{Bu^nLi}$ solution in hexane (10 mL, 0.021 mol) was added to a solution of **2** (4.0 g, 0.017 mol) in $\mathrm{Et_2O}$ (50 mL), and the reaction mixture was stirred at 20 °C for 24 h. Then the reaction solution was concentrated and cooled to 0 °C. The yellow crystalline precipitate that formed was separated, washed with $\mathrm{Et_2O}$ in the cold, and dried under high vacuum. The pale-yellow crystalline product was obtained in a yield of 2.5 g. The remaining solution was concentrated, and hexane was added. The precipitate that formed was washed with the solvent and dried *in vacuo*. The total yield was 3.7 g (0.016 mol, 92%). ^{1}H NMR (THF-d_8), δ: 1.36 (d, 6 H, $\mathrm{CH\underline{Me}_2}$, $^3J_{\mathrm{H,H}} = 6.9$ Hz); 2.13 (s, 6 H, $\mathrm{NMe_2}$); 2.62 (t, 2 H, $\mathrm{CH_2N}$, $^3J_{\mathrm{H,H}} = 6.3$ Hz); 3.00 (t, 2 H, $\mathrm{C\underline{H}_2CH_2N}$, $^3J_{\mathrm{H,H}} = 6.3$ Hz); 3.30 (sept, 1 H, $\mathrm{C\underline{H}Me_2}$, $^3J_{\mathrm{H,H}} = 6.9$ Hz); 6.27 (s, 1 H, H(2)); 6.43 (m, 2 H, H(5), H(6)); 7.26 and 7.34 (both d, 1 H, H(4), H(7), $^3J_{\mathrm{H,H}} = 7.9$ Hz). ^{13}C NMR, δ: 25.57 (q, $\mathrm{CH\underline{Me}_2}$, $^1J_{\mathrm{C,H}} = 124$ Hz); 26.55 (t, $\mathrm{\underline{C}H_2CH_2N}$, $^1J_{\mathrm{C,H}} = 124$ Hz); 28.97 (d, $\mathrm{\underline{C}HMe_2}$, $^1J_{\mathrm{C,H}} = 123$ Hz); 45.93 (q, $\mathrm{NMe_2}$, $^1J_{\mathrm{C,H}} = 133$ Hz); 63.45 (t, $\mathrm{CH_2N}$, $^1J_{\mathrm{C,H}} = 132$ Hz); 97.15, 114.17, 126.73, and 126.96 (all s, C(1), C(3), C(3a), C(7a)); 111.57 (d, C(2)H, $^1J_{\mathrm{C,H}} = 150$); 112.92, 113.61, 117.41, and 118.63 (all d, C(4)H, C(5)H, C(6)H, C(7)H, $^1J_{\mathrm{C,H}} = 153$ Hz).

2-[2-(Isopropylindenyl)-2-methylpropyl]pyridine (3) (a mixture of isomers **A** and **B** (~1 : 2)). A 2.45 *M* $\mathrm{Bu^nLi}$ solution in hexane (8 mL, 0.020 mol) was added to a solution of α-picoline (1.86 g, 0.020 mol) in THF (10 mL) at −15 °C, and the reaction mixture was stirred at 20 °C for 1 h. Then a solution of 1-isopropyl-3-(isopropylidene)indene ((3.89 g, 0.020 mol) in THF (5 mL) was added. The reaction mixture was stirred at 20 °C for 14 h and quenched with a 15% HCl solution (60 mL). The organic layer was separated, and the aqueous layer was twice extracted with $\mathrm{CHCl_3}$. After the neutralization of the aqueous layer with a KOH solution, the resulting new organic layer was separated, and the aqueous layer was extracted three times with $\mathrm{CHCl_3}$. The combined extracts were dried over $\mathrm{MgSO_4}$, and the solvent was removed *in vacuo*. The orange oily product was obtained in a yield of 5.38 g (0.018 mol, 89%). ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 0.47 and 1.05 (both d, $\mathrm{CH\underline{Me}_2}$ (B), $^3J_{\mathrm{H,H}} = 6.8$ Hz); 1.00 and 1.07 (both s, $\mathrm{CMe_2}$ (A)); 1.27 and 1.30 (both d, $\mathrm{CH\underline{Me}_2}$ (A), $^3J_{\mathrm{H,H}} = 6.8$ Hz); 1.38 (s, $\mathrm{CMe_2}$ (B)); 2.30 (m, $\mathrm{C\underline{H}Me_2}$ (B)); 2.76 and 2.84 (AB system, $\mathrm{CH_2}$ (A), $^2J_{\mathrm{H,H}} = 12.8$ Hz); 2.91 (sept, $\mathrm{C\underline{H}Me_2}$ (A),

$^3J_{H,H}$ = 6.8 Hz); 3.21 and 3.36 (AB system, CH_2 (B), $^2J_{H,H}$ = 12.8 Hz); 3.25 (m, H(1) (B)); 3.36 (s, H(1) (A)); 6.00 (d, H(2) (B), $^3J_{H,H}$ = 2.0 Hz); 6.31 (s, H(2) (A)); 6.70—7.74 (set of m, H(4), H(5), H(6), H(7), H(3´), H(4´), H(5´) (py) (A, B)); 8.49 (d, H(6´) (py) (B), $^3J_{H,H}$ = 4.8 Hz); 8.54 (d, H(6´) (py) (A), $^3J_{H,H}$ = 4.6 Hz).

Lithium salt of 2-[2-(3-isopropylinden-1-yl)-2-methylpropyl]pyridine (adduct with one Et_2O molecule) (Li-3). A 2.45 *M* Bu^nLi solution in hexane (13 mL, 0.032 mol) was added to a solution of **3** (9.1 g, 0.032 mol) in Et_2O (50 mL), and the reaction mixture was stirred at 20 °C for 24 h. Then the solvent was evaporated to dryness. The residue was washed three times with hexane and dried under high vacuum. The red-brick crystalline product (the adduct with one Et_2O molecule) was obtained in a yield of 7.6 g (0.022 mol, 70%). ^1H NMR (THF-d_8), δ (signals of Et_2O are not given): 1.32 (d, 6 H, $CH\underline{Me}_2$, $^3J_{H,H}$ = 6.8 Hz); 1.41 (br.s, 6 H, CMe_2); 3.28 (br, 2 H, CH_2); 3.38 (sept, 1 H, $C\underline{H}Me_2$, $^3J_{H,H}$ = 6.8 Hz); 6.13 (s, 1 H, H(2)); 6.53 (m, 2 H, H(5), H(6)); 7.03 (t, 1 H, H(5´) (py), $^3J_{H,H}$ = 6.2 Hz); 7.25 (d, 1 H, H(3´) (py), $^3J_{H,H}$ = 7.8 Hz); 7.44 (d, 1 H, H(4) or H(7), $^3J_{H,H}$ = 7.8 Hz); 7.59 (m, 2 H, H(4´) (py), H(7) or H(4)); 7.87 (d, 1 H, H(6´) (py), $^3J_{H,H}$ = 4.7 Hz). ^{13}C NMR, δ: 25.83 (q, $CH\underline{Me}_2$, $^1J_{C,H}$ = 125 Hz); 27.77 (d, $\underline{C}HMe_2$, $^1J_{C,H}$ = 123 Hz); 30.86 (br.q, $C\underline{Me}_2$, $^1J_{C,H}$ = 125 Hz); 37.88 (s, $\underline{C}Me_2$); 51.57 (t, CH_2, $^1J_{C,H}$ = 127 Hz); 108.86, 112.44, 121.45, and 126.09 (all s, C(1), C(3), C(3a), C(7a)); 111.31 (d, $^1J_{C,H}$ = 153 Hz), 114.04 and 114.40 (both d, $^1J_{C,H}$ = 154 Hz), 119.07 and 120.42 (both d, $^1J_{C,H}$ = 150 Hz) (C(2)H, C(4)H—C(7)H); 122.04 (d, $^1J_{C,H}$ = 165), 127.21 and 137.88 (both d, $^1J_{C,H}$ = 163 Hz) (C(3´)H, C(4´)H, C(5´)H (py)); 148.17 (d, C(6´)H (py), $^1J_{C,H}$ = 177 Hz); 162.63 (s, C(2´) (py)).

[1-Isopropyl-3-(2-methoxyethyl)indenyl](pentamethylcyclopentadienyl)dichlorozirconium, [1,3-$C_9H_5(Pr^i)(CH_2CH_2OMe)$]-($C_5Me_5$)$ZrCl_2$ (4). A suspension of lithium indenide Li-**1** (894 mg, 4.0 mmol) and Cp^*ZrCl_3 (1.176 g, 3.5 mmol) in toluene (60 mL) was heated at 100 °C for 16 h. The solvent was removed *in vacuo*, the substance was extracted with hexane, the solution was concentrated, and the precipitate that formed was washed with cold hexane (2×5 mL) and dried under high vacuum. The yellow crystalline product was obtained in a yield of 976 mg (1.9 mmol, 54%). Found (%): C, 58.12; H, 6.56. $C_{25}H_{34}Cl_2OZr$. Calculated (%): C, 58.57; H, 6.68. ^1H NMR (THF-d_8), δ: 1.28 (d, 3 H, $^3J_{H,H}$ = 6.8 Hz), 1.31 (d, 3 H, $^3J_{H,H}$ = 7.0 Hz) ($CH\underline{Me}_2$); 1.95 (s, 15 H, C_5Me_5); 2.83 and 3.11 (both m, 1 H, $C\underline{H}_2CH_2O$); 3.24 (s, 3 H, OMe); 3.40 and 3.52 (both m, 1 H, $C\underline{H}_2O$); 3.42 (sept, 1 H, $C\underline{H}Me_2$, $^3J_{H,H}$ = 6.9 Hz); 6.35 (s, 1 H, H(2)); 7.14 (m, 2 H, H(5), H(6)); 7.58 and 7.62 (both m, 1 H, H(4), H(7)). ^{13}C NMR, δ: 12.50 (q, $C_5\underline{Me}_5$, $^1J_{C,H}$ = 127 Hz); 23.45 and 24.19 (both q, $CH\underline{Me}_2$, $^1J_{C,H}$ = 126 Hz); 28.86 (t, $\underline{C}H_2CH_2O$, $^1J_{C,H}$ = 128 Hz); 29.10 (d, $\underline{C}HMe_2$, $^1J_{C,H}$ = 128 Hz); 58.65 (q, OMe, $^1J_{C,H}$ = 140 Hz); 73.96 (t, $\underline{C}H_2O$, $^1J_{C,H}$ = 141 Hz); 111.68, 125.79, 128.04, and 130.12 (all s, C(1), C(3), C(3a), C(7a)); 121.05 (d, C(2)H, $^1J_{C,H}$ = 168 Hz); 125.20, 125.30, 125.37, and 125.43 (all d, C(4)H, C(5)H, C(6)H, C(7)H, $^1J_{C,H}$ = 159—160 Hz); 125.22 (s, $\underline{C}_5Me_5$). ^1H NMR (C_6D_6), δ: 1.25 and 1.26 (both d, 3 H, $CH\underline{Me}_2$, $^3J_{H,H}$ = 6.9 Hz); 1.79 (s, 15 H, C_5Me_5); 2.84 and 3.14 (both m, 1 H, $C\underline{H}_2CH_2O$); 3.03 (s, 3 H, OMe); 3.21—3.38 (set m, 3 H, $C\underline{H}_2O$, $C\underline{H}Me_2$); 6.16 (s, 1 H, H(2)); 7.01 (m, 2 H, H(5), H(6)); 7.51 and 7.61 (both m, 1 H, H(4), H(7)).

Single crystals suitable for X-ray diffraction were obtained by the crystallization from Et_2O.

[1-(2-Dimethylaminoethyl)-3-isopropylindenyl](pentamethylcyclopentadienyl)dichlorozirconium, [1,3-$C_9H_5(Pr^i)$-($CH_2CH_2NMe_2$)](C_5Me_5)$ZrCl_2$ (5) was synthesized analogously to complex **4** from lithium indenide Li-**2** (808 mg, 3.44 mmol) and Cp^*ZrCl_3 (1.14 g, 3.43 mmol). The yellow crystalline product was obtained in a yield of 1.45 g (2.76 mmol, 80%). The elemental analysis data were unsatisfactory because complex **5** is highly prone to hydrolysis. ^1H NMR (C_6D_6), δ: 1.26 and 1.28 (both d, 3 H, $CH\underline{Me}_2$, $^3J_{H,H}$ = 6.8 Hz); 1.83 (s, 15 H, C_5Me_5); 2.15 (s, 6 H, NMe_2); 2.42 (m, 2 H, CH_2N); 2.85 and 3.12 (both m, 1 H, $C\underline{H}_2CH_2N$); 3.35 (sept, 1 H, $C\underline{H}Me_2$, $^3J_{H,H}$ = 6.8 Hz); 6.18 (s, 1 H, H(2)); 7.03 (m, 2 H, H(5), H(6)); 7.56 and 7.61 (both d, 1 H, H(4), H(7), $^3J_{H,H}$ = 8.4 Hz). $^{13}C\{^1H\}$ NMR, δ: 12.43 ($C_5\underline{Me}_5$); 23.06, 24.13 ($CH\underline{Me}_2$); 26.11 ($\underline{C}H_2CH_2N$); 28.45 ($\underline{C}HMe_2$); 43.36 (NMe_2); 60.92 (CH_2N); 111.59, 125.44, 127.19, 129.23 (C(1), C(3), C(3a), C(7a)); 119.95 (C(2)H); 124.77 ($\underline{C}_5Me_5$); 124.77, 124.98, 125.07, 125.23 (C(4)H, C(5)H, C(6), C(7)H).

{1-[1,1-Dimethyl-2-(2-pyridyl)]ethyl-3-isopropylindenyl}-(pentamethylcyclopentadienyl)dichlorozirconium, [1,3-$C_9H_5(Pr^i)$-($CMe_2CH_2(2\text{-}C_5H_4N)$)]($C_5Me_5$)$ZrCl_2$ (6). A suspension of lithium indenide Li-**3** (512 mg, 1.38 mmol) and Cp^*ZrCl_3 (382 mg, 1.15 mmol) in toluene (30 mL) was heated at 100 °C for 16 h. The solvent was removed *in vacuo*. The precipitate that formed was washed with cold hexane (3×5 mL) and extracted with toluene (20 mL). After the removal of the solvent and drying under high vacuum, the yellow crystalline product was obtained in a yield of 250 mg (0.43 mmol, 37%). The elemental analysis data were unsatisfactory because complex **6** is highly prone to hydrolysis. ^1H NMR (THF-d_8), δ: 1.20 and 1.22 (both d, 3 H, $CH\underline{Me}_2$, $^3J_{H,H}$ = 6.8 Hz); 1.60 and 1.80 (both s, 3 H, CMe_2); 1.83 (s, 15 H, C_5Me_5); 2.89 and 3.15 (AB system, 2 H, CH_2, $^2J_{H,H}$ = 12.3 Hz); 3.41 (sept, 1 H, $C\underline{H}Me_2$, $^3J_{H,H}$ = 6.8 Hz); 6.01 (d, 1 H, H(3´) (py), $^3J_{H,H}$ = 7.8 Hz); 6.53 (s, 1 H, H(2)); 6.87 (dd, 1 H, H(5´) (py), $^3J_{H,H}$ = 4.8 Hz, $^3J_{H,H}$ = 7.5 Hz); 7.00—7.15 (set of m, 3 H, H(5), H(6), H(4´) (py)); 7.61 (d, 1 H, $^3J_{H,H}$ = 8.6 Hz), 7.79 (d, 1 H, $^3J_{H,H}$ = 8.8 Hz) (H(4), H(7)); 8.28 (d, 1 H, H(6´) (py), $^3J_{H,H}$ = = 4.9 Hz). $^{13}C\{^1H\}$ NMR, δ: 12.42 ($C_5\underline{Me}_5$); 22.43, 24.78 ($CH\underline{Me}_2$); 27.88 ($\underline{C}HMe_2$); 29.20, 29.53 ($C\underline{Me}_2$); 41.42 ($\underline{C}Me_2$); 54.68 (CH_2); 121.35, 124.55, 124.70, 124.78, 125.05, 125.37, 127.09, 135.44 (C(2)H, C(3)H, C(4)H, C(5)H, C(6)H, C(7)H, C(3´)H, C(4´)H, C(5´)H (py)); 122.29, 127.50, 127.64, 129.65 (C(1), C(3), C(3a), C(7a)); 149.23 (C(6´)H (py)); 160.21 (C(2´) (py)).

Photochemical decomposition of complex 4. A solution of complex **4** (130 mg) in THF (30 mL) was subjected to direct solar radiation. After the irradiation for 16 h, the yellow solution became colorless, and complex **13** precipitated as a white solid. The precipitate was filtered off, washed with a small amount of THF, and dried *in vacuo*. The slow (14 days) decomposition of **4** in THF-d_8 in a sealed NMR tube under diffuse daylight resulted in the precipitation of single crystals of **12** studied by X-ray diffraction, whereas virtually pure spiro compound **11** remained in the solution.

1,1-(1,2-Ethanediyl)-3-(isopropyl)indene, (Pr^i)$C_9H_5(CH_2)_2$ (11). ^1H NMR (THF-d_8), δ: 1.29 (d, 6 H, $CH\underline{Me}_2$, $^3J_{H,H}$ = 6.9 Hz); 1.48 and 1.54 (both m, 2 H, CH_2CH_2); 2.97 (sept.d, 1 H, $C\underline{H}Me_2$, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 1.2 Hz); 5.87 (d, 1 H, H(2), $^4J_{H,H}$ = 1.2 Hz); 6.93 and 7.37 (both d, 1 H, H(4), H(7), $^3J_{H,H}$ = 7.5 Hz); 7.07 and 7.17 (both t, 1 H, H(5), H(6), $^3J_{H,H}$ = 7.5 Hz). ^{13}C NMR, δ: 14.35 (t, CH_2CH_2, $^1J_{C,H}$ = 164 Hz); 22.49

Table 3. Crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for compounds **4** and **12**

Compound	**4**	**12**
Molecular formula	$C_{25}H_{34}Cl_2O_1Zr_1$	$C_{22}H_{36}Cl_4O_2Zr_2$
M	512.64	656.75
Crystal dimensions/mm	0.40×0.20×0.20	0.30×0.20×0.20
Crystal system	Tetragonal	Monoclinic
Space group	$I4_1/a$	$P2_1/c$
a/Å	32.7758(5)	8.3422(6)
b/Å	32.7758(5)	20.4791(14)
c/Å	9.1283(3)	8.5510(6)
β/deg	90	115.392(1)
V/Å^3	9806.1(4)	1319.73(16)
Z 16	2	
d_{calc}/g cm^{-3}	1.389	1.653
μ/mm^{-1}	0.680	1.211
F(000)	4256	664
Number of reflections		
measured	35226	14434
independent	6513	3511
R_{int}	0.0209	0.0227
with $I > 2\sigma(I)$	5876	3210
Number of refined parameters	270	142
R_1 [$I > 2\sigma(I)$]	0.0232	0.0247
wR_2 (based on all reflections)	0.0610	0.0661
Goodness-of-fit on F^2	1.044	1.037
Residual electron density (max/min)/e Å^{-3}	0.350/–0.289	0.763/–0.400

(q, $CH\underline{Me}_2$, $^1J_{C,H}$ = 126 Hz); 27.90 (d, $\underline{C}HMe_2$, $^1J_{C,H}$ = 126 Hz); 32.32 (s, C(1)); 118.10 (d, $^1J_{C,H}$ = 157 Hz), 120.10 (d, $^1J_{C,H}$ = = 155 Hz), 124.77 (d, $^1J_{C,H}$ = 159 Hz), 125.69 (d, $^1J_{C,H}$ = 160 Hz), 132.89 (d, $^1J_{C,H}$ = 162 Hz) (C(2)H, C(4)H, C(5)H, C(6)H, C(7)H); 144.59, 148.60, and 150.05 (all s, C(3), C(3a), C(7a)).

(Pentamethylcyclopentadienyl)(dimethoxy)chlorozirconium, $(C_5Me_5)ZrCl(OMe)_2$ (13). ^{1}H NMR (THF-d_8), δ: 2.01 (s, 15 H, C_5Me_5); 3.29 (s, 6 H, OMe).

Reduction of complexes 4—6 with Mg/Hg or Na/Hg (general procedure). A solution of the complex (80—100 mg) in THF-d_8 (0.6 mL) was stirred with magnesium amalgam (~50 mg, ~10 equiv.) at 20 °C for 2—7 days. The solution (as a rule, dark-brown) was separated from the precipitate and quantitatively transferred into an NMR tube. The reduction with sodium amalgam in C_6D_6 was carried out analogously with the use of Na/Hg (~8 g, ~10 equiv.) containing 0.5% Na (w/w).

Hydrido({*N*-[2-(η^5-3-isopropylinden-1-yl)ethyl]-*N*-methylamino}methyl-κ*N*)(η^5-pentamethylcyclopentadienyl)zirconium, $(C_5Me_5)[\eta^5{:}\eta^2\text{-}(C,N)\text{-}C_9H_5(Pr^i)CH_2CH_2N(Me)CH_2]ZrH$ (15). ^{1}H NMR (THF-d_8), δ: –0.15 and 1.51 (both d, 1 H, $ZrCH_2N$, $^2J_{H,H}$ = 8.7 Hz); 1.09 and 1.50 (both d, 3 H, $CH\underline{Me}_2$, $^3J_{H,H}$ = = 6.7 Hz); 1.58 (s, 15 H, C_5Me_5); 2.16 and 2,54 (both m, 1 H, $C\underline{H}_2CH_2N$); 2.21 (s, 3 H, NMe); 3.05 and 3.35 (both m, 1 H, $CH_2C\underline{H}_2N$); 3.13 (sept, 1 H, $C\underline{H}Me_2$, $^3J_{H,H}$ = 6.7 Hz); 3.23 (s, 1 H, ZrH); 6.46 (s, 1 H, H(2)); 6.83 and 6.94 (both t, 1 H, H(5), H(6), $^3J_{H,H}$ = 7.5 Hz); 7.34 and 7.39 (both d, 1 H, H(4), H(7), $^3J_{H,H}$ = 8.6 Hz). ^{13}C NMR, δ: 11.93 (q, $C_5\underline{Me}_5$, $^1J_{C,H}$ = = 126 Hz); 21.11 and 25.95 (both q, $CH\underline{Me}_2$, $^1J_{C,H}$ = 126 Hz); 21.71 (t, $\underline{C}H_2CH_2N$, $^1J_{C,H}$ = 128 Hz); 26.25 (d, $\underline{C}HMe_2$, $^1J_{C,H}$ = 126 Hz); 45.91 (t, $ZrCH_2N$, $^1J_{C,H}$ = 141 Hz); 52.18 (q, NMe, $^1J_{C,H}$ = 136 Hz); 68.29 (t, CH_2N, $^1J_{C,H}$ = 136 Hz); 104.30 (d, C(2)H, $^1J_{C,H}$ = 168 Hz); 108.91, 113.87, 115.43, and 119.62 (all s, C(1), C(3), C(3a), C(7a)); 113.50 (s, $\underline{C}_5Me_5$); 120.90, 122.03, 122.19, and 122.85 (all d, C(4)H, C(5)H, C(6)H, C(7)H, $^1J_{C,H}$ = 158—159 Hz).

X-ray diffraction study of complexes 4 and 12. The X-ray diffraction data sets were collected on an automated Bruker SMART APEX II diffractometer (Mo*K*α radiation, λ = 0.71073 Å, graphite monochromator) at 170 K. Both structures were solved by direct methods (SHELX-86).[17] All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method based on F^2 (SHELXL-97).[18] All hydrogen atoms were positioned geometrically and refined using a riding model. The X-ray diffraction data collection and refinement statistics are given in Table 3.

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