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Zirconium complexes bearing η^5-5′,6′,7′-trihydrospiro [cycloalkane-1,4′-indenyl] ligands

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ABSTRACT

Tetrahydroindenes including spiro-cyclopentyl and -cyclohexyl fragments were successfully synthesized either via base-catalyzed cyclization of the respective γ-diketone or via acid-catalyzed Nazarov cyclization of the corresponding divinylketones. These substituted cyclopentadienes were metallated with ^{n}BuLi. The following reaction of the lithium salts with Cp*$ZrCl_3$ gave three novel zirconocenes bearing spiro-cycloalkane fragments. One of these complexes, (η^5-5′,6′,7′-trihydrospiro[cyclohexane-1,4′-(2-methylindenyl)]) (η^5-pentamethyl-cyclopentadienyl)zirconium dichloride, has been characterized by X-ray crystal structure analysis.

1. Introduction

The group 4 metallocenes bearing η^5-4,5,6,7-tetrahydroindenyl ligands ($IndH_4$) are of particular importance for olefin polymerization catalysis, as the respective *ansa*-complexes are known to form catalysts for isotactic polypropylene (*i*PP) synthesis [1]. In 1982, Brintzinger et al. described synthesis of *rac*-$C_2H_4(IndH_4)_2TiCl_2$ via PdO_2-catalyzed hydrogenation of benzene rings fused to Cp in *rac*-C_2H_4(inden-1-yl)$_2TiCl_2$ [2a]. Later, *rac*-$C_2H_4(IndH_4)_2ZrCl_2$ was obtained in a similar manner [2b]. Hydrogenation of the catalyst component avoids formation of the respective undesirable *meso*-species, as *ansa*-metallocenes bearing $IndH_4$ ligands are less prone to the epimerization under the effect of light or heat [3]. Thus, the hydrogenated pre-catalyst is useful for producing high molecular weight isotactic polypropylene [4], that is of particular importance for possible industrial application of these catalysts. On the other hand, the hydrogenation of organometallic precursors seems not to be a practical method, and several attempts to carry out these reactions failed [5]. Therefore, the development of an alternative synthesis of the ligands is of importance. Only scarce examples of the successful synthetic approaches have been already described in the literature [6].

Here, we describe synthesis of novel zirconium complexes bearing the Me-substituted 5′,6′,7′-trihydrospiro[cycloalkane-1,4′-indenyl] ligands, i.e. the ligands including a quaternary carbon atom (spiro fragment) in α-position of the saturated ring of $IndH_4$. Obviously, these complexes cannot be obtained via the above-mentioned hydrogenation approach. Therefore, synthesis of the respective substituted cyclopentadienes has been developed and studied in detail. It should be noted, that, at this stage of the research, we did not aim to synthesize also the respective bridging ligands and *ansa*-zirconocenes, as this was found to be a separate difficult synthetic task deserving separate detailed description.

2. Results and discussion

2.1. Synthesis of 2′-methyl-1′,5′,6′,7′-tetrahydrospiro[cyclohexane-1,4′-indene] (7) via base-catalyzed cyclization of the respective γ-diketone

Synthesis of the substituted cyclopentadiene **7** was achieved as shown in the Scheme 1.

First, a large-scale synthesis of spiro[5.5]undecan-1-one (**1a**) was carried out via alkylation of cyclohexanone by 1,5-dibromopentane [7]. This reaction gave **1a** in as high as 85% yield in the presence of 2 eqv. of KO^{t}Bu in benzene for 5 h at reflux. α-Bromoketone **2** was obtained in almost quantitative yield via bromination of **1a** by Br_2 in ether was further used in reaction with an excess of sodium salt of ethyl acetoacetate to form ethyl 3-oxo-2-(1-oxospiro [5.5]undec-2-yl)butanoate (**3**). Actually, we did not try to obtain analytically pure **3**, so a mixture of **3** and ethyl acetoacetate was

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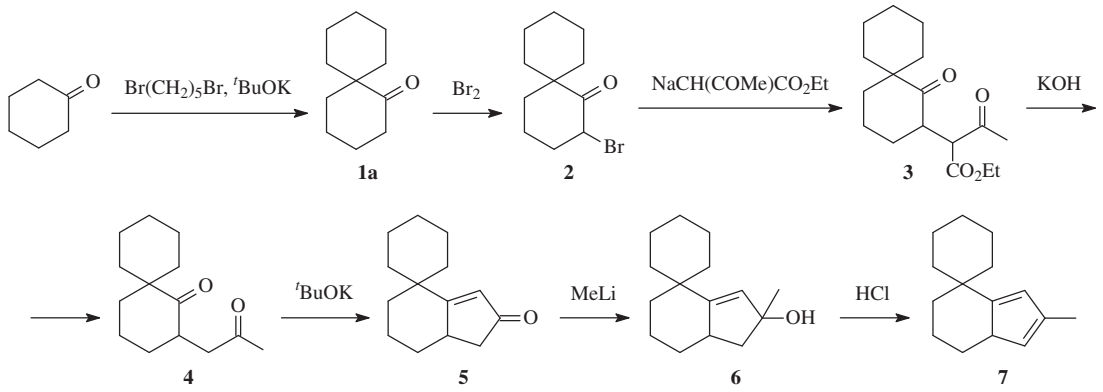


Scheme 1.

further decarboxylated in the presence of an excess of KOH in aqueous ethanol at reflux. The following work-up procedure gave 1,4-diketone **4** which was isolated in 42% overall yield (based on cyclohexanone). It should be noted that we did not observe the following intramolecular condensation of **4** to cyclopentenone **5** under the conditions used, as this reaction probably requires the use of a stronger base. In this way, **5** was formed from **4** in the presence of 1.2 eqv. of KO^{t}Bu in benzene at reflux. Thus, **5** was isolated by flash-chromatography on Silica Gel 60 in 72% yield as yellowish oil.

Further on, reaction of **5** with 1 eqv. of MeLi gave cyclopentanol **6** which was isolated and used without further purification. To obtain the desired cyclopentadiene **7** we used acid-free conditions for dehydration of **6**, i.e. carried out this reaction in the presence of 0.5 eqv. of molecular iodine in hexanes. However, in this case, **7** was found to be formed in as low as 38% yield on 40 min at room temperature.

*2.2. Synthesis of 2′-methyl-1′,5′,6′,7′-tetrahydrospiro[cyclohexane-1,4′-indene] (**7**), 2′,3′-dimethyl-1′,5′,6′,7′-tetrahydrospiro[cyclohexane-1,4′-indene] (**14a**) and 2′,3′-dimethyl-1′,5′,6′,7′-tetrahydrospiro [cyclopentane-1,4′-indene] (**14b**) via acid-catalyzed Nazarov reaction*

The substituted cyclopentadienes **14a** and **14b** bearing spiro fragments were obtained as shown in Scheme 2.

The key stage of this synthesis was the acid-catalyzed Nazarov cyclization of the respective divinylketones [8]. In this way, first, spiro[5.5]undecan-1-one (**1a**) reacted with 2,2,2-tribromo-1,3,2-benzodioxaphosphole in CH_2Cl_2 to form vinyl bromide **8a** in 88% yield [9]. The following reaction of the organolithium reagent, obtained via a slow addition of ^{t}BuLi to **8a** in THF–hexanes at −80 °C, with methyl vinyl ketone gave the desired divinyl carbinol **9c** in only 25% yield, as the major product of this reaction was found to be spiro[5.5]undec-1-ene (Scheme 3).

This by-product formed via deprotonation of methyl vinyl ketone by vinyllithium was isolated in 70% yield. Alternatively, the addition of the lithium reagent obtained from **8a** to acrolein gave divinyl carbinol **9a** in 84% yield. It was further selectively oxidized by activated MnO_2 in ether to form divinyl ketone **10a** in almost quantitative yield. Cyclopentenone **11a** was obtained via Nazarov cyclization of **10a** in the presence of $SnCl_4$ in dichloromethane and isolated in 96% yield using flash-chromatography on Silica Gel 60. It should be noted that saturated H_3PO_4 or H_2SO_4 were found to be less useful catalysts of the Nazarov reaction under the conditions used.

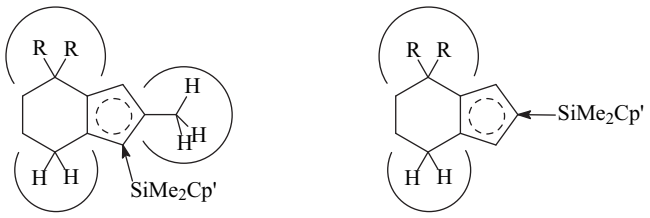
Deprotonation of **11a** by LDA at −80 °C followed by alkylation with MeI gave the Me-substituted cyclopentenone **12a** in 80% yield. Reaction of **12a** with 1 eqv. of MeLi resulted in the respective 1,2-addition product **13a** isolated and used without further purification. Finally, dehydration of the latter carbinol in biphase medium consisting of ether and saturated hydrochloric acid gave the desired cyclopentadiene **14a** in high yield. The overall yield of **14a** for this 7-stage synthesis from cyclohexanone was 40%.

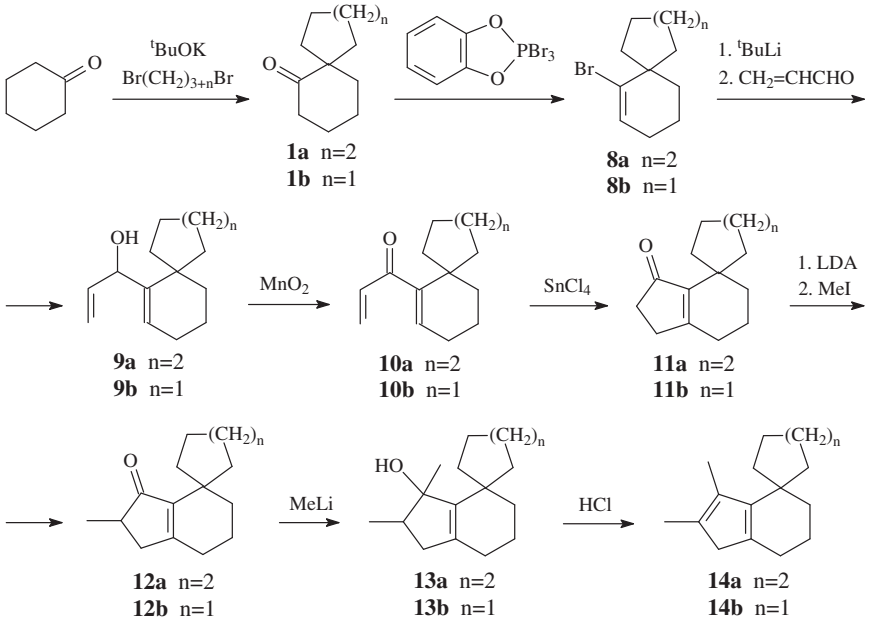
Analogously, the spiro ligand **14b** bearing cyclopentyl fragment was successfully synthesized via acid-catalyzed Nazarov reaction. In this case, the overall yield of the target material from cyclopentanone was shown to be 12%, that particularly results from ineffective reaction of spiro[4.5]decan-6-one (**1b**) with 2,2,2-tribromo-1,3,2-benzodioxaphosphole giving vinyl bromide **8b** in 40% yield.

In addition, we used the above-described approach for synthesizing cyclopentadiene **7**. It was obtained from cyclopentenone **12a** as shown in the Scheme 4.

The reduction of **12a** by LAH in ether followed by dehydration of the formed alcohol **13c** in biphase medium consisting of ether and saturated hydrochloric acid gave the target material in 47% yield.

The first attempts to obtain the respective *bis*(cyclopentadienyl) dimethylsilanes of importance for synthesizing *ansa*-complexes failed. For instance, a treatment of the lithium, sodium, or copper [10] salt of **7** by 0.5 eqv. of dichlorodimethylsilane in THF–hexane gave mixtures of unidentified compounds rather than the desired product. However, in the case of sodium salt, the desired ligand could be isolated from the reaction mixture in low (4%) yield. Low reactivity of cyclopentadienyl anions under study is likely to be accounted for by steric reasons. If a given $IndH_4$ ligand includes Me in position 2, the $SiMe_2$ bridge is to be introduced between two saturated hydrocarbon fragments, as shown in the left sketch below. Alternatively, if hydrogen is in position 2, the silylene bridge can occupy this position 2 (the right sketch below). However, *ansa*-metallocenes bearing the latter ligands and having C_s symmetry are of less interest for *i*PP synthesis. In the nearest future, we plan to develop an alternative protocol for synthesizing the target bridging





Scheme 2.

ligands bearing the silylene bridge in position 1 starting from the cyclopentadienes **7**, **14a**, and **14b**.

2.3. Synthesis of zirconium complexes *17a–c*

To obtain the zirconocenes bearing novel spiro ligands the above-described cyclopentadienes **7**, **14a**, and **14b** were deprotonated by 1 eqv. of ^{n}BuLi in toluene–hexanes, and to the formed lithium salts formed were treated by 1 eqv. of Cp*$ZrCl_3$ (Scheme 5).

The reaction mixtures were stirred at room temperature and then additionally overnight at 90 °C. The following work-up procedure (see Experimental Section below) and crystallization of the crude products from toluene gave analytically pure complexes **15a–c** in 67, 74, and 63% yields, respectively. According to ^{1}H NMR spectroscopy, the compounds include η^5-Cp* and η^5-5′,6′,7′-trihydrospiro[cycloalkane-1,4′-indenyl] ligands as shown in Scheme 5.

2.4. Study of molecular structure of *15a*

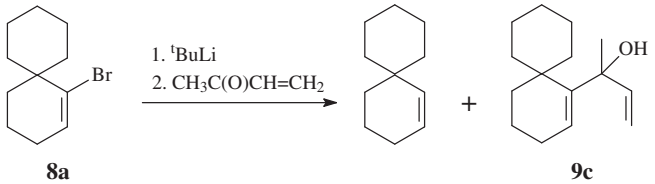
The solid-state structure of **15a** bearing η^5-2′-methyl-5′,6′,7′-trihydrospiro[cyclohexane-1,4′-indenyl] ligand was determined by X-ray diffraction analysis. An asymmetric unit cell of **1** is presented by two symmetrically independent molecules **15a** and **15a′**. General view of **1** is depicted in Fig. 1.

Two molecules differ by the geometry of permethylated Cp* ligand. It is disordered in both molecules, but in different ways: in **1**, the Cp* ligand is disordered over two positions with equal occupancies relative to the C1 atom while in **1′**, it is disordered approximately relative to Cp centroid (again over two positions with occupancies equal to 0.6:0.4). In both molecules, the zirconium atom adopts a typical pseudotetrahedral coordination with two substituted η^5-C_5R_5 and two σ-Cl ligands (see Table 1, for corresponding angles).

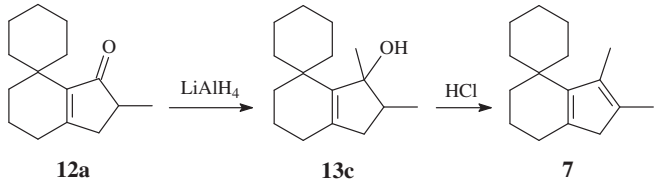
Due to the disorder we will not discuss geometry characteristics of permetylated Cp ligand in both molecules. For the other Cp ligands, the Zr–C bonds lengths distribution shows usually observed trends [11]: elongation of Zr–C distances from C11,C12 (C11′,C12′) atoms to C14(C14′) (see Table 1 and Fig. 1). This is reflected in the shift (Δx) of a projection of the zirconium atom on Cp cycle from its geometrical center towards C11(11′)–C12(12′) bond. In both molecules, cyclohexane adopts usual chair conformation while cyclohexene is characterized by half-chair conformation. The orientation of cyclohexene substituent can be described by torsion angle which is formed by bisector of Cl1(1′)–Zr1(1′)–Cl2(2′) angle, Zr1(1′)–Cp(centroid) line and by the line connected Cp(centroid) and the center of C13(13′)–C14(14′) bond. For **1** and **1′** these angles are found to be nearly the same: −65.1(5)° and −65.4(5)°, correspondingly.

3. Conclusion

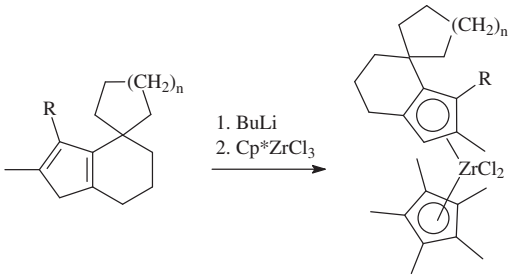
Thus, the first examples of metal complexes bearing η^5-5′,6′,7′-trihydrospirocyclo-lkane-1,4′-indenyl] ligands as well as the respective starting substituted cyclopentadienes were successfully synthesized and unambiguously characterized. In addition, solid-state structure of complex **15a** including η^5-2′-methyl-5′,6′,7′-trihydrospiro[cyclohexane-1,4′-indenyl] ligand was confirmed by X-ray



Scheme 3.



Scheme 4.



7 n=2 R=H
14a n=2 R=Me
14b n=1 R=Me

15a n=2 R=H
15b n=2 R=Me
15c n=1 R=Me

Scheme 5.

diffraction analysis. Synthesis of the respective *ansa*-complexes bearing spiro-functionalized $IndH_4$ fragments is underway.

4. Experimental

All starting materials were obtained from commercial suppliers and used without further purification. Ether, THF, hexanes, toluene, and benzene were distilled under Ar from sodium and benzophenone. All reactions involving air or moisture sensitive compounds were performed under argon or nitrogen atmospheres utilizing standard Schlenk line techniques and/or in a Vacuum Atmospheres Dry-Box (under nitrogen). All glassware was oven dried prior to use. Analytical liquid chromatography was performed using a Waters Delta 600 HPLC system including a 996 Photodiode Array Detector, Symmetry C18 (Waters, 60 Å, 5 μm, 4.6 × 250 mm) in a methanol–water mobile phase. ^1H and ^{13}C spectra were recorded with Avance 400 DPX spectrometers for 1–10% solutions in deuterated solvents. Chemical shifts for ^1H and ^{13}C were measured relatively to TMS. C, H microanalyses were done using a Carlo Erba 1106 analyzer.

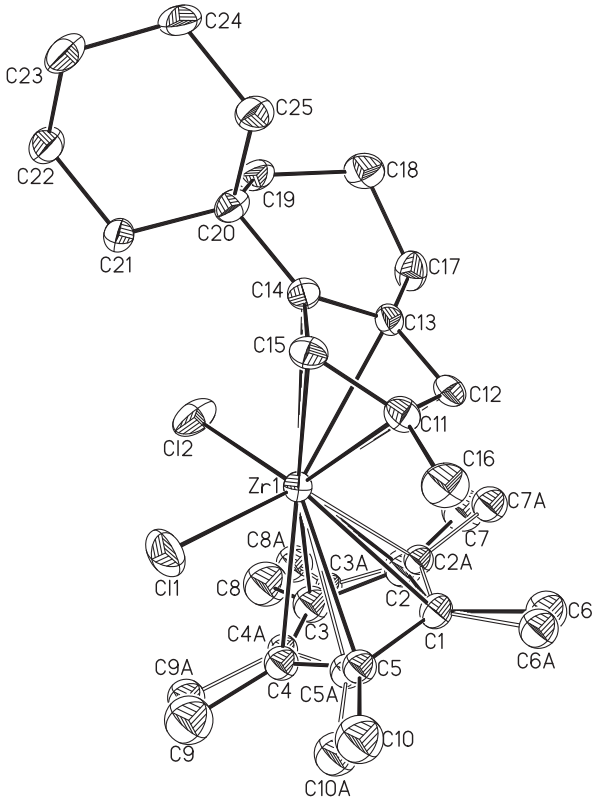


Fig. 1. ORTEP view of **15a**. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Bonding in second part of disordered Cp* ligand is shown by open lines and denoted with letter "A".

Table 1
Selected geometry characteristics of **15a** and **15a′**.

Bond, Å	**15a**	**15a′**	Distance, Å/Angle, °	**15a**	**15a′**
Zr–Cl(1)	2.445(2)	2.438(2)	Zr–Cp(c)	2.236(6)	2.228(6)
Zr–Cl(2)	2.436(2)	2.437(2)	Δ*x*	0.19(2)	0.19(2)
Zr–C(11)	2.487(6)	2.470(6)	Cl(1)–Zr–Cl(2)	99.96(7)	97.64(7)
Zr–C(12)	2.452(6)	2.459(6)	Cl(1)–Zr–Cp(c)	104.2(2)	105.1(2)
Zr–C(13)	2.544(6)	2.541(6)	Cl(2)–Zr–Cp(c)	106.3(2)	107.3(2)
Zr–C(14)	2.640(6)	2.622(6)			
Zr–C(15)	2.572(6)	2.566(6)			

4.1. Spiro[5.5]undecan-1-one (**1a**)

To a 1000 ml, two-neck round bottom flask equipped with reflux condenser and charged with cyclohexanone (39.2 g, 0.4 mol) and 1,5-dibromopentane (92.0 g, 0.4 mol) a small portion of ^{t}BuOK was added. When reaction mixture heated, dry benzene (500 ml) and ^{t}BuOK (89.6 g, 0.8 mol) were added at once. Further on, this mixture was refluxed for 5 h and then cooled to room temperature. To the solution ca. 350 ml of 0.5 M HCl was added. The organic layer was separated, and the aqueous layer was extracted with benzene (2 × 100 ml). The combined extract was washed by water (2 × 100 ml), dried over Na_2SO_4, and the solvent was removed in vacuum. The product was obtained by vacuum rectification, 72–78 °C/1 mm Hg. Yield 56.4 g (85%) of colorless oil. ^1H NMR ($CDCl_3$): δ 2.39 (t, J = 6.5 Hz, 2H), 1.92–1.79 (m, 4H), 1.75–1.65 (m, 4H), 1.53–1.44 (m, 4H), 1.44–1.29 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 216.90, 48.92, 38.57, 33.65, 28.17, 26.25, 21.98, 20.55. Anal. calc. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.40; H, 11.02%.

4.2. Spiro[4.5]decan-6-one (**1b**)

To a 2000 ml, two-neck round bottom flask equipped with reflux condenser and charged with cyclohexanone (78.4 g, 0.8 mol) and 1,5-dibromobutane (172.8 g, 0.8 mol) small portion of ^{t}BuOK was added. When reaction mixture heated, dry benzene (500 ml) and ^{t}BuOK (179.2 g, 1.6 moll) were added at once. After the mixture ceased to reflux on its own, the mixture was heated under reflux for 5 h. Then reaction was cooled to room temperature and 4 M HCl (ca. 350 ml) was added. The phases were separated and aqueous layer was extracted with benzene (2 × 100 ml). The combined organic portion was washed with water, dried over Na_2SO_4 and the solvent was removed by rotary evaporation. Spiro[4.5]decan-6-one was obtained by fractional distillation (106–110 °C/12 mm. Hg). Yield, 90.1 g (74%) of colorless oil. ^1H NMR ($CDCl_3$): δ 2.31 (t, J = 6.5 Hz, 2H), 2.01–1.92 (m, 2H), 1.77–1.70 (m, 2H), 1.65–1.60 (m, 4H), 1.54–1.45 (m, 4H), 1.35–1.26 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 214.32, 56.63, 39.76, 39.23, 35.24, 27.16, 25.05, 22.67. Anal. calc. for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.73; H, 10.61%.

4.3. 2-Bromospiro[5.5]undecan-1-one (**2**)

To spiro[5.5]undecan-1-one (30.4 g, 0.183 mol) in 200 ml of dry Et_2O was added dropwise bromine (9.3 ml, 0.183 mol) at 0 °C. An almost colorless solution was obtained. Diethyl ether was removed by rotary evaporation at 35 °C of water bath. To remove traces HBr and Et_2O, 100 ml of hexane was added and evaporated three times.

The product was used without further purification. ^{1}H NMR ($CDCl_3$): δ 4.95 (dd, J = 5.5, 12.5 Hz, 1H), 2.65–2.55 (m, 1H), 2.07 (dd, J = 4.0, 12.5 Hz, 1H), 2.05–1.83 (m, 4H), 1.78–1.64 (m, 2H), 1.62–1.33 (m, 6H), 1.32–1.17 (m, 2H). Anal. calc. for $C_{11}H_{17}BrO$: C, 53.89; H, 6.99. Found: C, 53.77; H, 6.92%.

4.4. Ethyl 3-oxo-2-(1-oxospiro[5.5]undec-2-yl)butanoate (**3**)

To small pieces of sodium (8.4 g, 0.365 mol) in dry benzene (250 ml) was added at room temperature ethyl acetoacetate (95.2 g, 0.732 mol). After the mixture ceased to reflux on its own, the mixture was heated under reflux to dissolve remaining sodium metal. 2-bromospiro[5.5]undecan-1-one (44.9 g, 0.183 mol) in dry benzene (120 ml) was added at once at room temperature and reaction mixture was heated to reflux for 2 h. Then reaction was cooled to room temperature and 200 ml of water was added. The phases were separated and aqueous layer was extracted with benzene (2 × 100 ml). The combined organic portion was washed with water, dried over Na_2SO_4 and the solvent was removed by rotary evaporation. The product (119.2 g) consisted of a mixture of ethyl acetoacetate and ethyl 3-oxo-2-(1-oxospiro[5.5]undec-2-yl) butanoate. This mixture was used without further purification for preparing 2-(2-oxopropyl)spiro[5.5]undecan-1-one.

4.5. 2-(2-Oxopropyl)spiro[5.5]undecan-1-one (**4**)

To a 2000 ml, two-neck round bottom flask equipped with a condenser and charged with obtained on the previous stage mixture (119.2 g) were added water solution of KOH (116 g KOH in 600 ml of water) and methanol (600 ml) under argon. The reaction mixture was heated to reflux for 6 h. Then reaction was cooled to room temperature and CH_2Cl_2 (200 ml) was added. The phases were separated and aqueous layer was extracted with CH_2Cl_2 (2 × 200 ml). The combined organic portion was washed with water (2 × 100 ml), dried over Na_2SO_4 and the solvent was removed by rotary evaporation. 1,4-diketone was purified by column chromatography on silica gel (40–63 μm, d 10 mm, l 1000 mm; eluent: hexane–ethyl acetate–CH_2Cl_2 2:1:1) and obtained as yellow oil (17.1 g, 42%). ^{1}H NMR ($CDCl_3$): δ 3.35–3.25 (m, 1H), 2.92 (dd, J = 8.5, 17.5 Hz, 1H), 2.20 (s, 3H), 2.10 (dd, J = 4.5, 17.5 Hz, 1H), 2.06–1.82 (m, 4H), 1.72–1.52 (m, 4H), 1.50–1.22 (m, 7H), 1.08–0.98 (m, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 215.98, 207.38, 48.96, 43.32, 41.97, 34.88, 33.99, 33.84, 30.28, 26.13, 22.08, 21.89, 20.42. Anal. calc. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.84; H, 10.13%.

4.6. 5′,6′,7′,7a′-Tetrahydrospiro[cyclohexane-1,4′-inden]-2′(1′H)-one (**5**)

To a 500 ml, two-neck round bottom flask equipped with a condenser and charged with a solution of 2-(2-oxopropyl)spiro [5.5]undecan-1-one (10.0 g, 0.045 mol) in dry benzene (250 ml) was added ^{t}BuOK (6.05 g, 0.054 mol) under argon. The reaction mixture was heated to reflux for 3.5 h. Then reaction was cooled to room temperature and water (100 ml) was added. The phases were separated and organic layer was washed with water (2 × 100 ml), dried over Na_2SO_4 and the solvent was removed by rotary evaporation. Spiro compound **5** was purified by column chromatography on silica gel (40–63 μm, d 10 mm, l 400 mm; eluent: hexane–ethyl acetate–CH_2Cl_2 4:1:1) and obtained as yellow oil (6.6 g, 72%). ^{1}H NMR ($CDCl_3$):signals of two isomers, δ 5.90 and 5.80 (s, 1H), 2.91–2.83 and 2.79–2.72 (m, 1H), 2.57 and 2.52 (d, J = 6.5 Hz, 1H), 2.35–2.1 (m, 3H), 2.00–0.80 (m, 14H). ^{13}C{^{1}H} NMR ($CDCl_3$): signals of two isomers, δ 209.69, 209.38, 183.06, 176.73, 127.24, 125.99, 52.66, 42.33, 38.30, 38.10, 36.83, 36.31, 36.19, 33.35, 31.41, 30.34, 26.34, 26.18, 24.19, 21.83, 21.70, 21.43, 21.23, 20.71, 20.59. Anal. calc. for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.78; H, 9.71%.

4.7. 2′-Methyl-1′,2′,5′,6′,7′,7a′-hexahydrospiro[cyclohexane-1,4′-inden]-2′-ol (**6**)

To a solution of 5′,6′,7′,7a′-tetrahydrospiro[cyclohexane-1,4′-inden]-2′(1′*H*)-one (6.4 g, 31.4 mmol) in dry THF (100 ml) at −80 °C was slowly added 0.9 M Et_2O solution of MeLi (39 ml, 35.1 mmol). Then the reaction was allowed gradually to come to room temperature and stirring was continued for additional 1 h. Water (100 ml) was added. The phases were separated and aqueous layer was extracted with Et_2O (3 × 50 ml). The combined organic portion was dried over Na_2SO_4 and the solvent was removed by rotary evaporation. The product was used without further purification.

4.7.1. 2′-Methyl-1′,5′,6′,7′-tetrahydrospiro[cyclohexane-1,4′-indene] (**7**)

The mixture of 2′-methyl-1′,2′,3′,5′,6′,7′-hexahydrospiro[cyclohexane-1,4′-inden]-2′-ol (2.0 g, 9.1 mmol), hexane (60 ml) and I_2 (1.2 g, 4.7 mmol) was stirred at room temperature during a period of 40 min. Spiro compound (**7**) was purified by flash-chromatography on silica gel (40–63 μm, d 20 mm, l 100 mm; eluent: hexane) and obtained as white solid (0.69 g, 38% yield). ^{1}H NMR ($CDCl_3$): several isomers, δ 6.18–6.14 (m), 5.97 (br s), 5.90 (q, J = 1.5 Hz), 5.84–5.82 (m), 5.39–5.34 (m), 2.78–2.71 (m), 2.67 (dt, J = 1.0, 2.5 Hz), 2.57–2.43 (m), 2.22–1.86 (m), 1.82–0.7 (m). Anal. calc. for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.73; H, 11.27%.

4.7.2. 2′-Methyl-1′,5′,6′,7′-tetrahydrospiro[cyclohexane-1,4′-indene] (**7**)

Concentrated HCl (30 ml) was added to a solution of 2′-methyl-1′,2′,3′,5′,6′,7′-hexahydrospiro[cyclohexane-1,4′-inden]-3′-ol (20.0 g, 90.9 mmol) in 400 ml of Et_2O. The mixture was stirred for ca. 30 min at room temperature and then water (200 ml) was added. The phases were separated and aqueous layer was extracted with Et_2O (2 × 50 ml). The combined organic portion was washed with 10% aqueous $NaHCO_3$, dried over Na_2SO_4 and concentrated by rotary evaporation. Spiro compound (**7**) was purified by flash-chromatography on silica gel (40–63 μm, d 20 mm, l 150 mm; eluent: hexane) and obtained as white solid (8.6 g, 47% yield). ^{1}H NMR ($CDCl_3$): several isomers, δ 6.18–6.14 (m), 5.97 (br s), 5.90 (q, J = 1.5 Hz), 5.84–5.82 (m), 5.39–5.34 (m), 2.78–2.71 (m), 2.67 (dt, J = 1.0, 2.5 Hz), 2.57–2.43 (m), 2.22–1.86 (m), 1.82–0.7 (m). Anal. calc. for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.73; H, 11.27%.

4.8. 1-Bromospiro[5.5]undec-1-ene (**8a**)

To a solution of 2-bromo-1,3,2-benzodioxaphosphole (32.2 g, 0.147 mol) in dry CH_2Cl_2 (100 ml) was added dropwise CH_2Cl_2 solution (50 ml) of Br_2 (6.9 ml, 0.134 mol) for ca. 30 min at 0 °C. The reaction mixture was stirred at 0 °C for an additional 30 min then spiro[5.5]undecan-1-one (22.2 g, 0.134 mol) was added at once and reaction was allowed gradually to come to room temperature. Stirring was continued for 2 h. The reaction was quenched with sat. aq. $NaHCO_3$. The phases were separated and organic layer was washed with water (2 × 100 ml), dried over Na_2SO_4 and the solvent was removed by rotary evaporation. Spiro compound (**8a**) was purified by flash-chromatography on silica gel (40–63 μm, d 20 mm, l 300 mm; eluent: hexane) and obtained as light-yellow oil (27 g, 88% yield). ^{1}H NMR ($CDCl_3$): δ 6.06 (t, J = 4.0 Hz, 1H), 2.02 (dt, J = 4.5, 6.0 Hz, 2H), 1.85–1.75 (m, 4H), 1.67–1.50 (m, 5H), 1.47–1.34 (m, 4H), 1.21–1.09 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.49, 130.16, 40.53, 34.83, 31.94, 28.41, 25.52,

21.22, 18.33. Anal. calc. for $C_{11}H_{17}Br$: C, 57.65; H, 7.48. Found: C, 57.75; H, 7.29%.

4.9. 6-Bromospiro[4.5]dec-6-ene (**8b**)

To a solution of 2-bromo-1,3,2-benzodioxaphosphole (139.5 g, 0.637 mol) in dry CH_2Cl_2 (450 ml) was added dropwise CH_2Cl_2 solution (150 ml) of Br_2 (29.7 ml, 0.579 mol) for ca. 30 min at 0 °C. The reaction mixture was stirred at 0 °C for an additional 30 min then spiro[4.5]decan-6-one (88.0 g, 0.579 mol) was added at once and reaction was allowed gradually to come to room temperature. Stirring was continued for 2 h. The reaction was quenched with sat. aq. $NaHCO_3$. The phases were separated and organic layer was washed with water (2 × 200 ml), dried over Na_2SO_4 and the solvent was removed by rotary evaporation. Spiro compound (**8b**) was purified by flash-chromatography on silica gel (40–63 μm, d 40 mm, l 800 mm; eluent: hexane) and obtained as light-yellow oil (49.8 g, 40% yield). ^{1}H NMR ($CDCl_3$): δ 6.02 (t, J = 4.0 Hz, 1H), 2.05–2.00 (m, 2H), 1.99–1.90 (m, 2H), 1.75–1.55 (m, 8H), 1.46–1.37 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 135.30, 129.63, 48.88, 38.88, 37.87, 28.01, 25.53, 19.79. Anal. calc. for $C_{10}H_{15}Br$: C, 55.83; H, 7.03. Found: C, 55.69; H, 6.81%.

4.10. 1-Spiro[5.5]undec-1-en-1-ylprop-2-en-1-ol (**9a**)

To a solution of 1-bromospiro[5.5]undec-1-ene (5.0 g, 21.8 mmol) in dry THF (100 ml) at −80 °C was slowly added 1.7 M hexane solution of ^{t}BuLi (25.7 ml, 43.6 mmol). The reaction mixture was stirred at −80 °C for an additional 1 h then THF solution (20 ml) of acrolein (3.7 g, 65.4 mmol) was added for ca. 5 min and reaction was allowed gradually to come to room temperature. Water (200 ml) was added. The phases were separated and aqueous layer was extracted with Et_2O (2 × 50 ml). The combined organic portion was dried over Na_2SO_4 and the solvent was removed by rotary evaporation. Spiro compound (**9a**) was purified by column chromatography on silica gel (40–63 μm, d 10 mm, l 400 mm; eluent: hexane–CH_2Cl_2 4:1) and obtained as light-yellow oil (3.8 g, 85% yield). ^{1}H NMR ($CDCl_3$): δ 5.92–5.82 (m, 2H), 5.30 (dt, J = 17.0, 1.5 Hz, 1H), 5.09 (dt, J = 10.5, 1.5 Hz, 1H), 4.76 (br s, 1H), 2.01 (dt, J = 4.0, 6.0 Hz, 2H), 1.76–1.59 (m, 4H), 1.57–1.40 (m, 9H), 1.33–1.25 (m, 1H), 1.20–1.07 (m, 1H). Anal. calc. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.28; H, 11.05%.

4.11. 1-Spiro[4.5]dec-6-en-6-ylprop-2-en-1-ol (**9b**)

To a solution of 6-bromospiro[4.5]dec-6-ene (41.8 g, 0.194 mol) in dry THF (400 ml) at −80 °C was slowly added 1.7 M hexane solution of ^{t}BuLi (229.0 ml, 0.389 mol). The reaction mixture was stirred at −80 °C for an additional 1 h then THF solution (100 ml) of acrolein (32.7 g, 0.584 mol) was added for ca. 30 min and reaction was allowed gradually to come to room temperature. Water (300 ml) was added. The phases were separated and aqueous layer was extracted with Et_2O (2 × 100 ml). The combined organic portion was dried over Na_2SO_4 and the solvent was removed by rotary evaporation. Spiro compound (**9b**) was purified by column chromatography on silica gel (40–63 μm, d 10 mm, l 800 mm; eluent: hexane–CH_2Cl_2 4:1) and obtained as yellow oil (29.0 g, 78% yield). ^{1}H NMR ($CDCl_3$): δ 5.93–5.81 (m, 2H), 5.29 (dt, J = 17.0, 1.5 Hz, 1H), 5.08 (dt, J = 10.5, 1.5 Hz, 1H), 4.75 (br s, 1H), 2.06–2.00 (m, 2H), 1.90–1.81 (m, 2H), 1.73–1.49 (m, 9H), 1.47–1.37 (m, 2H). Anal. calc. for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.51; H, 10.27%.

4.12. 2-Spiro[5.5]undec-1-en-1-ylbut-3-en-2-ol (**9c**)

To a solution of 1-bromospiro[5.5]undec-1-ene (5.8 g, 25.3 mmol) in dry THF (100 ml) at −80 °C was slowly added 1.7 M hexane solution of ^{t}BuLi (30 ml, 51.0 mmol). The reaction mixture was stirred at −80 °C for an additional 1 h then THF solution (50 ml) of methyl vinyl ketone (7.3 g, 105 mmol) was added at once and reaction was allowed gradually to come to room temperature. Water (200 ml) was added. The phases were separated and aqueous layer was extracted with Et_2O (2 × 50 ml). The combined organic portion was dried over Na_2SO_4 and the solvent was removed by rotary evaporation. Spiro compound (**9c**) was purified by column chromatography on silica gel (40–63 μm, d 10 mm, l 400 mm; eluent: hexane–CH_2Cl_2 4:1) (1.4 g, 25% yield). ^{1}H NMR ($CDCl_3$): δ 5.96 (dd, J = 10.5, 17.5 Hz, 1H), 5.60 (t, J = 4.0 Hz, 1H), 5.08 (dd, J = 1.0, 17.5 Hz, 1H), 4.89 (dd, J = 1.0, 10.5 Hz, 1H), 2.22–2.06 (m, 2H), 1.99–1.93 (m, 2H), 1.71–1.62 (m, 1H), 1.57–1.42 (m, 5H), 1.40 (s, 3H), 1.42–1.33 (m, 5H), 1.26 (br d, J = 12.0 Hz, 1H), 1.16–1.03 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.87, 147.56, 124.61, 110.17, 77.76, 38.03, 34.69, 34.58, 31.75, 31.40, 25.84, 25.78, 21.69, 21.64, 17.45. Anal. calc. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.73; H, 11.15%.

4.13. 1-Spiro[5.5]undec-1-en-1-ylprop-2-en-1-one (**10a**)

To a solution of 1-spiro[5.5]undec-1-en-1-ylprop-2-en-1-ol (1.6 g, 7.75 mmol) in dry hexane (30 ml) at −40 °C, was added by portions MnO_2 for 0.5 h (3.4 g, 38.8 mmol; MnO_2 had been previously stirred in vacuum during a period of 12 h at 140 °C). The reaction mixture was stirred at −40 °C for an additional 1 h then reaction was heated under reflux for 16 h. After heating, MnO_2 precipitate was removed by filtration. Solution was concentrated by rotary evaporation. Spiro compound (**10a**) was purified by flash-chromatography on silica gel (40–63 μm, d 20 mm, l 300 mm; eluent: hexane–CH_2Cl_2 4:1) and obtained as colorless oil (1.52 g, 96% yield). ^{1}H NMR ($CDCl_3$): δ 6.61 (dd, J = 10.5, 17.5 Hz, 1H), 6.37 (t, J = 4.0 Hz, 1H), 6.12 (dd, J = 1.5, 17.0 Hz, 1H), 5.75 (dd, J = 1.5, 10.5 Hz, 1H), 2.17 (dt, J = 4.0, 6.2 Hz, 2H), 2.07 (dt, J = 4.5, 12.5 Hz, 2H), 1.72–1.66 (m, 2H), 1.66–1.56 (m, 3H), 1.52–1.40 (m, 4H), 1.35 (br d, J = 14.0 Hz, 2H), 1.29–1.16 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 196.42, 147.26, 137.70, 136.67, 128.56, 37.07, 33.60, 30.28, 25.93, 25.59, 21.38, 17.47. Anal. calc. for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.99; H, 10.23%.

4.14. 1-Spiro[4.5]dec-6-en-6-ylprop-2-en-1-one (**10b**)

To a solution of 1-spiro[4.5]dec-6-en-6-ylprop-2-en-1-ol (28.7 g, 0.149 mol) in dry hexane (600 ml) at −40 °C, was added by portions MnO_2 for 0.5 h (64.8 g, 0.745 mol; MnO_2 had been previously stirred in vacuum during a period of 12 h at 140 °C). The reaction mixture was stirred at −40 °C for an additional 1 h then reaction was heated under reflux for 16 h. After heating, MnO_2 precipitate was removed by filtration. Solution was concentrated by rotary evaporation. Spiro compound (**10b**) was purified by column chromatography on silica gel (40–63 μm, d 10 mm, l 500 mm; eluent: hexane–CH_2Cl_2 4:1) and obtained as colorless oil (26.8 g, 95% yield). ^{1}H NMR ($CDCl_3$): δ 6.63 (dd, J = 10.5, 17.5 Hz, 1H), 6.35 (t, J = 4.0 Hz, 1H), 6.17 (dd, J = 1.5, 17.0 Hz, 1H), 5.79 (dd, J = 1.5, 10.5 Hz, 1H), 2.21–1.97 (m, 4H), 1.79–1.58 (m, 8H), 1.47–1.38 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 192.02, 142.31, 136.39, 133.56, 129.81, 42.48, 38.56, 36.61, 25.93, 25.17, 18.02. Anal. calc. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.14; H, 8.76%.

4.15. 1′,2′,6′,7′-Tetrahydrospiro[cyclohexane-1,4′-inden]-3′(5′H)-one (**11a**)

To a solution of 1-spiro[5.5]undec-1-en-1-ylprop-2-en-1-one (15.2 g, 74.5 mmol) in dry CH_2Cl_2 (150 ml) at −80 °C was added dropwise $SnCl_4$ (38.9 g, 149 mmol). The reaction was allowed gradually to come to room temperature and stirring was continued for 4 h. Ice water (200 ml) was added. The phases were separated and aqueous layer was extracted with CH_2Cl_2 (2 × 50 ml). The combined organic portion was washed with sat. aq. $NaHCO_3$ and dried over Na_2SO_4. Rotary evaporation of CH_2Cl_2 gave red oil. Spiro compound (**11a**) was purified by column chromatography on silica gel (40–63 μm, d 10 mm, l 400 mm; eluent: hexane–CH_2Cl_2 4:1) and obtained as yellow oil (14.0 g, 92% yield). ^{1}H NMR ($CDCl_3$): δ 2.73–2.63 (m, 2H), 2.07–2.04 (m, 2H), 1.87–1.80 (m, 4H), 1.74–1.68 (m, 1H), 1.65–1.57 (m, 4H), 1.56–1.42 (m, 5H), 2.38–2.28 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 206.57, 171.67, 144.69, 35.12, 35.03, 32.86, 31.36, 29.36, 29.09, 26.09, 21.85, 18.94. Anal. calc. for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.06; H, 9.62%.

4.16. 1′,2′,6′,7′-Tetrahydrospiro[cyclopentane-1,4′-inden]-3′(5′H)-one (**11b**)

To a solution of 1-spiro[4.5]dec-6-en-6-ylprop-2-en-1-one (20.2 g, 0.106 mol) in dry CH_2Cl_2 (150 ml) at −80 °C was added dropwise $SnCl_4$ (55.3 g, 0.212 mol). The reaction was allowed gradually to come to room temperature and stirring was continued for 4 h. Ice water (200 ml) was added. The phases were separated and aqueous layer was extracted with CH_2Cl_2 (2 × 50 ml). The combined organic portion was washed with sat. aq. $NaHCO_3$ and dried over Na_2SO_4. Rotary evaporation of CH_2Cl_2 gave red oil. Spiro compound (**11b**) was purified by column chromatography on silica gel (40–63 μm, d 10 mm, l 500 mm; eluent: hexane–CH_2Cl_2 4:1) and obtained as yellow oil (18.6 g, 92% yield). ^{1}H NMR ($CDCl_3$): 2.47–2.36 (m, 2H), 2.09–2.00 (m, 4H), 1.88–1.82 (m, 4H), 1.78–1.67 (m, 2H), 1.50–1.42 (m, 2H), 1.41–1.33 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 206.92, 171.66, 144.30, 42.64, 37.81, 37.58, 35.46, 29.68, 29.54, 26.44, 20.86. Anal. calc. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.01; H, 9.64%.

4.17. 2′-Methyl-1′,2′,6′,7′-tetrahydrospiro[cyclohexane-1,4′-inden]-3′(5′H)-one (**12a**)

To THF solution (250 ml) of diisopropylamide (8.1 g, 80 mmol) was added at once 2.5 M hexane solution of ^{n}BuLi (32 ml, 80.0 mmol) at −80 °C. The reaction mixture was stirred at −80 °C for an additional 30 min and THF solution (30 ml) of 1′,2′,6′,7′-tetrahydrospiro [cyclohexane-1,4′-inden]-3′(5′*H*)-one (15.6 g, 76.5 mmol) was added dropwise. The reaction was kept at this temperature during a period of 1 h. MeI (39.8 g, 0.28 mol) was added dropwise at −80 °C and reaction was allowed gradually to come to room temperature. Water (200 ml) was added. The phases were separated and aqueous layer was extracted with CH_2Cl_2 (2 × 50 ml). The combined organic portion was dried over Na_2SO_4 and concentrated by rotary evaporation. Spiro compound (**12a**) was purified by column chromatography on silica gel (40–63 μm, d 10 mm, l 300 mm; eluent: hexane–CH_2Cl_2 4:1) and obtained as yellow viscous oil (13.3 g, 80%). ^{1}H NMR ($CDCl_3$): δ 2.65 (dd, J = 7.0, 18.0 Hz, 1H), 2.32–2.11 (m, 5H), 2.00 (dt, J = 18.0, 1.5 Hz, 1H), 1.75–1.58 (m, 5H), 1.53–1.25 (m, 5H), 1.19 (br d, J = 14.0 Hz, 2H), 1.12 (d, J = 7.5, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 210.96, 171.53, 143.45, 40.14, 38.38, 34.45, 32.61, 32.36, 30.89, 29.40, 25.57, 21.30, 18.51, 16.56. Anal. calc. for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 83.07; H, 9.79%.

4.18. 2′-Methyl-1′,2′,6′,7′-tetrahydrospiro[cyclopentane-1,4′-inden]-3′(5′H)-one (**12b**)

To a THF solution (250 ml) of diisopropylamide (9.8 g, 97.4 mmol) was added at once 2.5 M hexane solution of ^{n}BuLi (39 ml, 97.4 mmol) at −80 °C. The reaction mixture was stirred at −80 °C for an additional 30 min and THF solution (40 ml) of 1′,2′,6′,7′-tetrahydrospiro[cyclopentane-1,4′-inden]-3′(5′*H*)-one (18.5 g, 97.4 mmol) was added dropwise. The reaction was kept at this temperature during a period of 1 h. MeI (27.6 g, 0.195 mol) was added dropwise at −80 °C and reaction was allowed gradually to come to room temperature. Water (200 ml) was added. The phases were separated and aqueous layer was extracted with CH_2Cl_2 (2 × 50 ml). The combined organic portion was dried over Na_2SO_4 and concentrated by rotary evaporation. Spiro compound (**12b**) was purified by column chromatography on silica gel (40–63 μm, d 10 mm, l 400 mm; eluent: hexane–CH_2Cl_2 4:1) and obtained as yellow viscous oil (13.8 g, 69%). ^{1}H NMR ($CDCl_3$): δ 2.47–2.33 (m, 2H), 2.21 (ddt, J = 7.0, 20.0, 1.0 Hz, 1H), 2.15–2.00 (m, 3H), 1.88 (t, J = 6.0 Hz, 2H), 1.78–1.68 (m, 2H), 1.68–1.61 (m, 1H), 1.52–1.44 (m, 2H), 1.43–1.35 (m, 4H), 1.14 (d, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 208.90, 169.27, 142.80, 42.05, 40.10, 38.35, 37.45, 37.40, 37.09, 28.94, 26.03, 25.95, 20.37, 16.64. Anal. calc. for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.57; H, 10.0%.

4.19. 2′,3′-Dimethyl-1′,2′,3′,5′,6′,7′-hexahydrospiro[cyclohexane-1,4′-inden]-3′-ol (**13a**)

To a solution of 2′-methyl-1′,2′,6′,7′-tetrahydrospiro[cyclohexane-1,4′-inden]-3′(5′*H*)-one (13.4 g, 61.3 mmol) in dry THF (200 ml) at −80 °C was slowly added 0.9 M Et_2O solution of MeLi (76 ml, 68.6 mmol). Then the reaction was allowed gradually to come to room temperature and stirring was continued for additional 1 h. Water (100 ml) was added. The phases were separated and aqueous layer was extracted with Et_2O (3 × 50 ml). The combined organic portion was dried over Na_2SO_4 and the solvent was removed by rotary evaporation. The product was used without further purification.

4.20. 2′,3′-Dimethyl-1′,2′,3′,5′,6′,7′-hexahydrospiro[cyclopentane-1,4′-inden]-3′-ol (**13b**)

To a solution of 2′-methyl-1′,2′,6′,7′-tetrahydrospiro[cyclopentane-1,4′-inden]-3′(5′*H*)-one (13.8 g, 67.5 mmol) in dry THF (200 ml) at −80 °C was slowly added 0.9 M Et_2O solution of MeLi (83 ml, 74.9 mmol). Then the reaction was allowed gradually to come to room temperature and stirring was continued for additional 1 h. Water (100 ml) was added. The phases were separated and aqueous layer was extracted with Et_2O (3 × 50 ml). The combined organic portion was dried over Na_2SO_4 and the solvent was removed by rotary evaporation. The product was used without further purification.

4.21. 2′-Methyl-1′,2′,3′,5′,6′,7′-hexahydrospiro[cyclohexane-1,4′-inden]-3′-ol (**13c**)

To a suspension of $LiAlH_4$ (8.0 g, 0.21 mol) in Et_2O (320 ml) at 0 °C, was added dropwise a solution of 2′-methyl-1′,2′,6′,7′-tetrahydrospiro[cyclohexane-1,4′-inden]-3′(5′*H*)-one (20.5 g, 0.094 mol) in Et_2O (100 ml). After heating for 4 h under reflux, ethyl acetate (20 ml) was added to the cooled suspension, followed by the addition water (200 ml). The phases were separated and aqueous layer was extracted with Et_2O (2 × 50 ml). The combined organic portion was dried over Na_2SO_4 and the solvent was removed by rotary evaporation. The product was used without further purification.

4.22. 2′,3′-Dimethyl-1′,5′,6′,7′-tetrahydrospiro[cyclohexane-1,4′-indene] (**14a**)

Concentrated HCl (15 ml) was added to a solution of 2′,3′-dimethyl-1′,2′,3′,5′,6′,7′-hexahydrospiro[cyclohexane-1,4′-inden]-3′-ol (13.2 g, 56.4 mmol) in 200 ml of Et_2O. The mixture was stirred for ca. 30 min at room temperature and then water (200 ml) was added. The phases were separated and aqueous layer was extracted with Et_2O (2 × 50 ml). The combined organic portion was washed with 10% aqueous $NaHCO_3$, dried over Na_2SO_4 and concentrated by rotary evaporation. Spiro compound (**14a**) was purified by flash-chromatography on silica gel (40–63 μm, d 20 mm, l 150 mm; eluent: hexane) and obtained as white solid (10.5 g, 86% yield). ^{1}H NMR ($CDCl_3$): several isomers, δ 5.97–5.93 (m), 5.87–5.85 (m), 2.8–2.67 (m), 2.55–2.40 (m), 2.20–0.8 (m). Anal. calc. for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.60; H, 11.40%.

4.23. 2′,3′-Dimethyl-1′,5′,6′,7′-tetrahydrospiro[cyclopentane-1,4′-indene] (**14b**)

Concentrated HCl (15 ml) was added to a solution of 2′,3′-dimethyl-1′,2′,3′,5′,6′,7′-hexahydrospiro[cyclopentane-1,4′-inden]-3′-ol (13.7 g, 62.2 mmol) in 200 ml of Et_2O. The mixture was stirred for ca. 30 min at room temperature and then water (200 ml) was added. The phases were separated and aqueous layer was extracted with Et_2O (2 × 50 ml). The combined organic portion was washed with 10% aqueous $NaHCO_3$, dried over Na_2SO_4 and concentrated by rotary evaporation. Spiro compound (**14b**) was purified by flash-chromatography on silica gel (40–63 μm, d 20 mm, l 200 mm; eluent: hexane) and obtained as white solid (10.8 g, 85% yield). ^{1}H NMR ($CDCl_3$): several isomers, δ 5.99–5.94 (m), 5.88–5.86 (m), 2.8–2.65 (m), 2.55–2.40 (m), 2.23–0.84 (m). Anal. calc. for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.89; H, 11.11%.

4.24. (η^5-5′,6′,7′-Trihydrospiro[cyclohexane-1,4′-(2-methylindenyl)]) (η^5-pentamethyl-cyclopentadienyl)zirconium dichloride (**15a**)

To a solution of **7** (1.67 g, 8.24 mmol) in dry toluene (80 ml) was added 2.5 M hexane solution of ^{n}BuLi (3.3 ml, 8.24 mmol) at room temperature. The reaction mixture was stirred during period of 30 h. Cp*$ZrCl_3$ (2.74 g, 8.24 mmol) was added at once at −20 °C. Then the reaction was allowed gradually to come to room temperature and stirring was continued for additional 48 h. The reaction was heated to 90 °C for 12 h. After cooling, the solution was passed through cellit. Cellit was washed with toluene (20 ml) and combined organic portion was evaporated in vacuum. The crude product was washed with hexane (40 ml) and crystallized from toluene (40 ml). Yield, 2.83 g (67%) of yellow crystals. ^{1}H NMR (CD_2Cl_2): δ 6.36 (d, J = 2.5 Hz, 1H), 5.65 (d, J = 2.5 Hz, 1H), 2.41 (br dd, J = 5.0, 15.0 Hz, 1H), 2.36–2.27 (m, 1H), 2.25–2.08 (m, 2H), 2.03 (s, 3H), 1.97 (s, 15H), 1.91 (dt, J = 13.5, 4.0 Hz, 1H), 1.82–1.67 (m, 2H), 1.65–1.53 (m, 4H), 1.50–1.37 (m, 3H), 1.28–1.19 (m, 1H), 1.17–1.08 (m, 1H). Anal. calc. for $C_{25}H_{36}Cl_2Zr$: C, 60.21; H, 7.28. Found: C, 59.80; H, 6.82%.

4.25. (η^5-5′,6′,7′-Trihydrospiro[cyclohexane-1,4′-(2,3-dimethylindenyl)]) (η^5-pentamethyl-cyclopentadienyl)zirconium dichloride (**15b**)

To a solution of **14a** (1.13 g, 5.24 mmol) in dry toluene (50 ml) was added 2.5 M hexane solution of ^{n}BuLi (2.1 ml, 5.24 mmol) at room temperature. The reaction mixture was stirred during period of 30 h. Cp*$ZrCl_3$ (1.74 g, 5.24 mmol) was added at once at −20 °C. Then the reaction was allowed gradually to come to room temperature and stirring was continued for additional 48 h. The reaction was heated to 90 °C for 12 h. After cooling, the solution was passed through cellit. Cellit was washed with toluene (20 ml) and combined organic portion was evaporated in vacuum. The crude product was washed with hexane (40 ml) and crystallized from toluene (40 ml). Yield, 1.99 g (74%) of yellow crystals. ^{1}H NMR (CD_2Cl_2): δ 5.62 (s, 1H), 2.43–2.36 (m, 2H), 2.24 (s, 3H), 2.20–2.05 (m, 4H), 1.98 (s, 15H), 1.78 (s, 3H), 1.69–1.60 (m, 2H), 1.56–1.38 (m, 7H), 1.28–1.15 (m, 1H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 140.97, 131.72, 123.73, 123.60, 119.03, 109.66, 37.84, 33.96, 32.87, 27.53, 26.07, 25.12, 21.96, 21.35, 19.98, 14.70, 12.22, 12.17. Anal. calc. for $C_{26}H_{38}Cl_2Zr$: C, 60.91; H, 7.47. Found: C, 60.53; H, 7.19%.

4.26. (η^5-5′,6′,7′-Trihydrospiro[cyclopentane-1,4′-(2,3-dimethylindenyl)]) (η^5-pentamethyl-cyclopentadienyl)zirconium dichloride (**15c**)

To a solution of **14b** (1.57 g, 7.74 mmol) in dry toluene (80 ml) was added 2.5 M hexane solution of ^{n}BuLi (3.1 ml, 7.74 mmol) at room temperature. The reaction mixture was stirred during period of 30 h. Cp*$ZrCl_3$ (2.57 g, 7.74 mmol) was added at once at −20 °C. Then the reaction was allowed gradually to come to room temperature and stirring was continued for additional 48 h. The reaction was heated to 90 °C for 12 h. After cooling, the solution was passed through cellit. Cellit was washed with toluene (20 ml) and combined organic portion was evaporated in vacuum. The crude product was washed with hexane (40 ml) and crystallized from toluene (40 ml). Yield, 2.43 g (63%) of yellow crystals. ^{1}H NMR (CD_2Cl_2): δ 5.63 (s, 1H), 1.50–1.42 (m, 1H), 2.39–2.30 (m, 1H), 2.11 (s, 3H), 2.05–1.90 (m, 2H), 2.00 (s, 15H), 1.76 (s, 3H), 1.78–1.65 (m, 4H), 1.64–1.40 (m, 6H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 142.97, 130.22, 123.56, 122.14, 119.38, 109.49, 45.00, 40.77, 38.53, 36.02, 26.26, 25.84, 24.93, 22.22, 13.63, 12.21, 12.14. Anal. calc. for $C_{25}H_{36}Cl_2Zr$: C, 60.21; H, 7.28. Found: C, 60.07; H, 6.92%.

4.27. Crystal structure of **15a**

The single crystals suitable for X-ray study were obtained by slow cooling the saturated solution of **15a** in hot toluene. It should be noted that in spite of all our attempts, the quality of single crystals was far from excellent. Single crystals are characterized by weak reflection ability which is in part related to the disorder.

At 120 K, $C_{25}H_{36}Cl_2Zr$ (**1**) is triclinic, space group P-1: a = 11.9474 (10) Å, b = 14.7230(12) Å, c = 15.2428(13) Å, α = 108.270(2)°, β = 95.257(2)°, γ = 111.096(2), V = 2311.3(3) Å^3, Z = 4, M = 498.7, d_{calc} = 1.433 g cm^{-3}, μ = 0.716 mm^{-1}. 21802 reflections were collected at SMART 1000 CCD difractometer (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scans, $2\theta < 54°$) at 120 K. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic/isotropic approximation: the disordered fragments were refined in isotropic approximation while all the other non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in geometrically calculated positions and refined within riding model. 9921 independent reflections [R_{int} = 0.0516] were used in the refinement procedure that was converged to wR_2 = 0.1838 calculated on F^2_{hkl} (GOF = 1.085, R_1 = 0.0680 calculated on F_{hkl} using 6237 reflections with $I > 2\sigma(I)$). For the analysis of data collected and crystal structures refinement we used SAINT Plus [12], SADABS [13] and SHELTL-97 [14] program packages.

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Appendix A. Supplementary material

CCDC 721089 contains the supplementary crystallographic data for **15a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.04.021.

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