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Synthesis of ring-substituted bis-η^5-cyclopentadienyl derivatives of the Group IV elements containing the bicyclic ligands η^5-$C_5H_3(1,2\text{-}CH_2-)_n$, $n = 4$, 5, or 6

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Abstract

The synthesis of unsubstituted and substituted bicyclic η^5-cyclopentadienyl ligands and their Group IV metal complexes $[M\{\eta^5\text{-}C_5H_3(1,2\text{-}CH_2-)_n\}_2Cl_2]$, where $n = 4$, 5, 6 and M = Ti, Zr, Hf, is reported. An example of an *ansa*-bridged zirconium analogue is also described. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Zirconium; Hafnium; Metallocenes; Tetrahydroindenes; *ansa*-Metallocenes

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1. Introduction

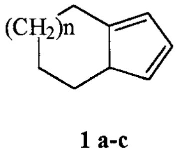
Metallocene complexes of Group IV metals having *ansa*-bridged ligands of the bis-indenyl, bis-fluorenyl type, or mixed ligands systems, such as fluorenyl-cyclopentadienyl ligands [1] are well established as highly active co-catalysts for the homo- and co-polymerisation of α-olefins. Tetrahydroindenyl derivatives can be more effective co-catalysts than the parent unsaturated derivatives, particularly for the incorporation of co- and ter-monomers [2].

The unsubstituted indenyl and fluorenyl ligands are directly available, whilst the normal route to tetrahydroindenyl ligands is via the catalytic hydrogenation of the corresponding unsaturated η^5-indenyl metallocenes [3]. Moreover, it appears that the hydrogenation modifies the steric and electronic properties of these metallocenes leading to a greater resistance to hydrolysis [4].

We were interested in developing more versatile and flexible routes to tetrahydroindenyl systems and also to related ligands containing seven- and eight-membered saturated ring systems attached to the cyclopentadienyl ring, as illustrated by the structure shown in Fig. 1.

The synthesis of tetrahydroindenyl-type ligands prior to their attachment to the transition metal has been explored by others [5] and elegant synthetic routes have been found. However the overall yields were often low or the method used was of limited applicability.

We report here a new and general synthetic pathway to construct fused cyclopentadienyl bicyclic ligands starting from readily available cycloalkanones.



a, n=1
b, n=2
c, n=3

1 a-c

Fig. 1. General formula of bicyclic ligands.

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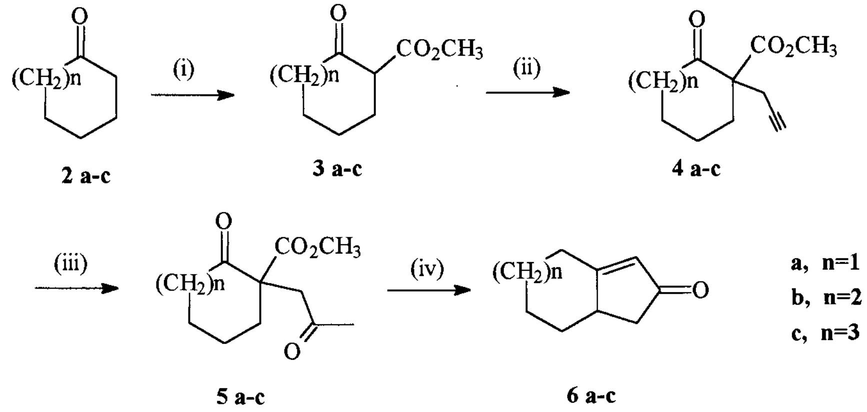


Scheme 1. (i) Dimethylcarbonate, NaH, benzene, 90°C; (ii) K_2CO_3, propargyl bromide, acetone, 80°C; (iii) HgO red, $BF_3{\cdot}Et_2O$, CH_3OH, trichloroacetic acid, 40°C; (iv) 10% KOH, 120°C.

2. Results and discussion

2.1. Synthesis and metalation of the ligands

The synthetic approach is outlined in Scheme 1. The starting materials are the cheap and commercially available cyclic ketones **2a**, **2b** and **2c**. They were converted into the corresponding *β*-ketoesters **3a**, **3b** and **3c**, respectively, by treatment with dimethylcarbonate and sodium hydride [6]: the larger the ring size, the higher the yield of this reaction. The *β*-ketoesters **3a** and **3b** are also commercially available while the substituted analogues of **3a** and **3b** are not available but may be prepared from the appropriate cyclic ketone.

These *β*-ketoesters **3a**, **3b** and **3c** were then alkylated with propargyl bromide in the presence of a large excess of potassium carbonate [7] to give the desired alkynes **4a**, **4b** and **4c** in a good yield and without any trace of *O*-alkylation. The use of harder bases gave decreased yields.

The enones **6a**, **6b** and **6c** were obtained in two steps, according to Islam and Raphael's [8] procedure, by hydration of the alkyne and intramolecular aldol condensation with dilute potassium hydroxide solution with simultaneous hydrolysis and decarboxylation of the ester group.

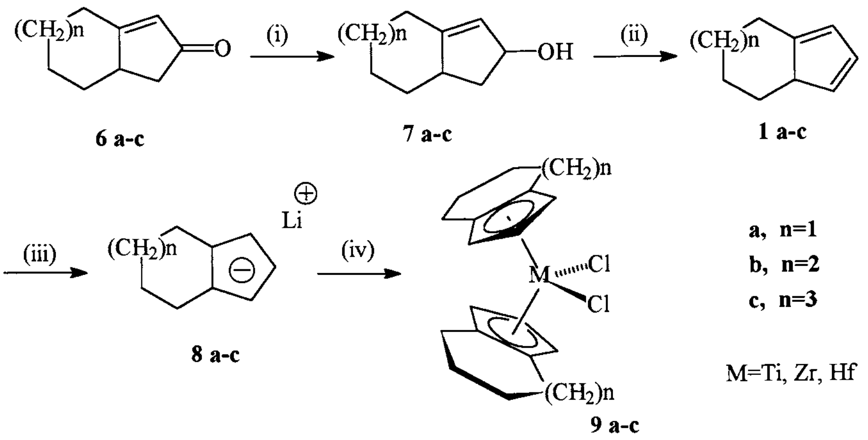
The first time the synthesis was performed, care was taken to isolate and purify all the intermediates in order to obtain a clean NMR spectra. Subsequently, the entire sequence of reactions was performed without any purification until the enone **6** stage was reached. In this way the reaction sequence was cheaper and faster, and no problems due to the impurities were found; the unavoidable losses due to chromatographic purification were minimised. As a result the overall yields increased, ranging from 61 to 83% over four steps (average yield per step from 88 to 96%).

The enones **6a**, **6b** and **6c** are the key-intermediates of the entire synthetic procedure, since it is possible to obtain from them either simple saturated fused bicyclic (Scheme 2) or 2-alkyl substituted cyclopentadienes, which can then be converted into *ansa*-bridged ligands.

Reduction of the enones **6a**, **6b** and **6c** with $LiAlH_4$ in diethyl ether at 0°C gave, respectively, the allylic alcohols **7a**, **7b** and **7c**, which were dehydrated under very mild conditions by treatment with Amberlyst 15, a strongly acidic ion-exchange resin. Since the resulting dienes **1a**, **1b** and **1c** (obtained as mixtures of isomers) undergo rapid polymerisation, it is crucial to reduce the work-up time of the dehydration step in order to improve the reaction yields. The yields of this reaction increased considerably with use of the ion-exchange resin compared to the usual acid work-up, since it can be easily and rapidly removed from the reaction medium by simple filtration. The filtered solution of each series of diene isomers was quickly degassed, cooled to -40°C and treated with a slight excess of *n*-butyllithium to give the corresponding lithium salts **8a**, **8b** and **8c** with an overall yield over the last three steps ranging from 71 to 88% (average yield per step ranging from 89 to 96%). The second purification step of the entire synthetic sequence occurs at this stage, because the lithium salt simply precipitates from the pentane solution as a white powder leaving any impurities in the supernatant liquor.

Treatment of the lithium salts 8 with MCl_4 (M = Ti, Zr, Hf) in 2.5:1 M ratio in THF at -78°C resulted in the formation of the corresponding metallocenes **9** with yields ranging from 48 to 68%.

The 2-alkyl substituted derivatives can be easily obtained in three steps from the enone derivatives. As a typical example, we describe here the synthesis for the six-membered ring system (Scheme 3). The reaction of **6a** with a lithium alkyl, such as methyllithium, gave the 2-alkyl allyl alcohol **10**, which was converted into the dienes **11** as previously described. The lithium salt **12** can be either converted into 2-alkyl substituted metallocenes or into *ansa*-metallocene ligands. The substitu-

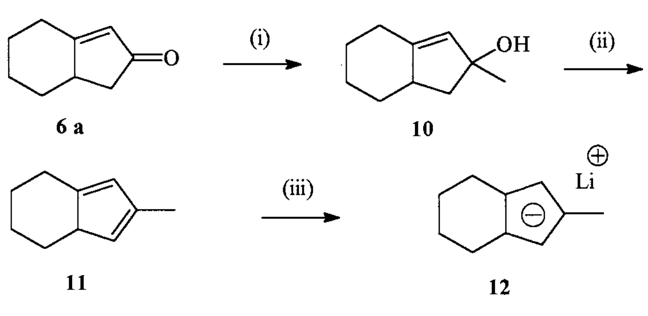


Scheme 2. (i) $LiAlH_4$, Et_2O, 0°C; (ii) Amberlyst 15, pentane; (iii) *n*-BuLi, pentane, −40°C; (iv) $ZrCl_4$, THF, −78°C.

tion in position 2 is particularly important since the corresponding *ansa*-bridged derivatives of zirconium are known to polymerise propene with high isotacticity [9].

Whilst the commonly reported salt elimination route (Scheme 4) yielded the corresponding 2-alkyl metallocenes **13a** and **13b**, this route was not feasible for the synthesis of the *ansa*-bridged analogues; however, the amine elimination route reported by Jordan et al. [10] proved to be successful (Scheme 5) and the ^{1}H-NMR analysis showed only the peaks corresponding to the *rac*-isomer of **15**.

In conclusion, the above synthetic pathway has proved successful for a 'tuned' synthesis of a variety of bicyclic cyclopentadienyl ligands and their corresponding organometallic compounds, in good yields, with only minor purification steps necessary, and reproducible in large-scale quantities. With this method it is possible to introduce as many structural modifications as desired in both rings and also to open the way to the corresponding *ansa*-bridged complexes.

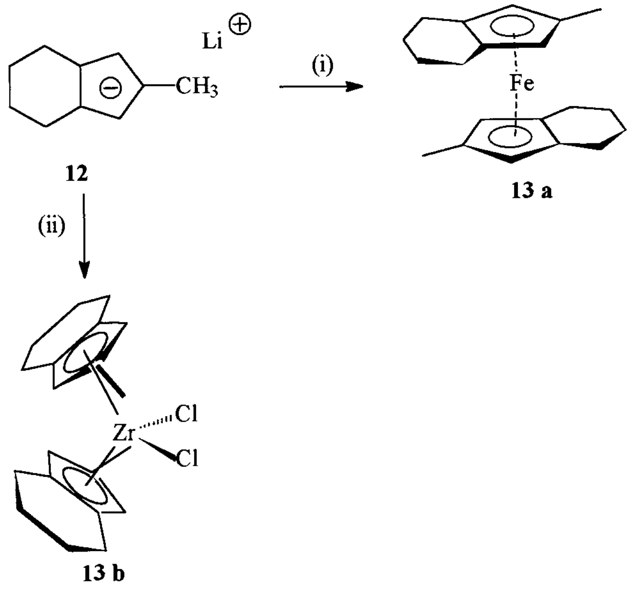


Scheme 3. (i) CH_3Li, Et_2O, 0°C; (ii) Amberlyst 15, pentane; (iii) *n*-BuLi, pentane, −40°C.

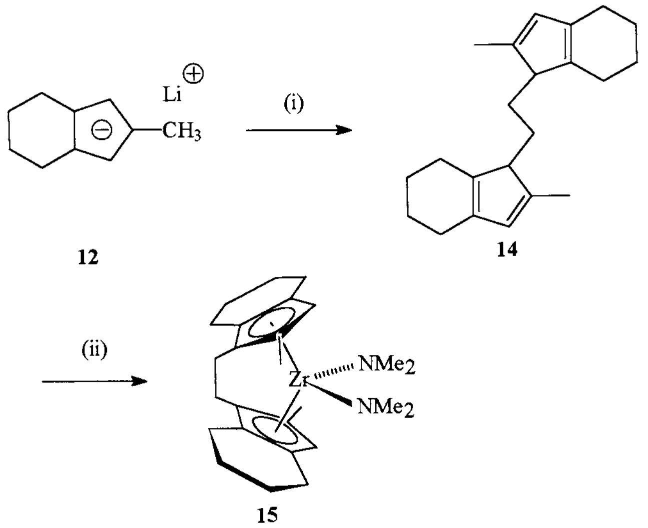
3. Experimental section

3.1. General procedures

All manipulations of air- and/or moisture-sensitive materials were carried out under inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques or in a dry-box under an atmosphere of nitrogen (< 10 ppm oxygen, < 20 ppm water). Nitrogen gas was purified by passage through a column containing BTS catalyst and 4 Å molecular sieves. Solvents and solutions were transferred, using a positive pressure of nitrogen, through stainless-steel cannulae (diameter 0.5–2.0 mm) and mixtures were filtered in a similar way using modified cannulae which could be fitted with glass-fibre filter disks (Whatman GFC). Unless otherwise specified, all reagents were purchased from commercial suppliers (Aldrich and Fluka) and used without



Scheme 4. (i) $FeCl_2$, THF, −78°C; (ii) $ZrCl_4$, toluene.



Scheme 5. (i) 1,2-Dibromoethane, THF, −78°C; (ii) $Zr(NMe_2)_4$, toluene, reflux.

further purification. $Zr(NMe_2)_4$ was prepared as described in the literature [10].

Reaction courses and product mixtures were routinely monitored by thin-layer chromatography (TLC) on silica gel pre-coated F_{254} plates. Preparative flash-chromatography was carried out with silica gel 60 Å (230–400 mesh ASTM). Anhydrous magnesium sulphate was used in drying operations.

All solvents to be used under inert atmosphere were thoroughly deoxygenated and dehydrated before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen and stored under nitrogen in Young's ampoules. The following drying agents were used: molten potassium for toluene, sodium for benzene, Na/K alloy for petroleum ether (b.p. 40–60°C) and pentane; sodium and benzophenone or Na/K alloy for diethyl ether and THF; CaH_2 for dichloromethane; 4 Å molecular sieves for methanol.

Deuterated chloroform and pyridine for use in NMR experiments of air sensitive compounds were, respectively distilled over CaH_2 and KOH and stored under nitrogen in Young's ampoules over 4 Å molecular sieves.

FTIR spectra were recorded as fluid films between NaCl plates using a Bruker IFS88 spectrometer.

NMR spectra were recorded on the following instruments: ^1H, 200.13 MHz, Bruker AC-200 and 300 MHz, Bruker AM-300; ^{13}C, 50.32 MHz, Bruker AC-200. Spectra were referenced internally using the residual protio solvent resonance relative to TMS ($\delta = 0$). All chemical shifts are quoted in δ(ppm) and coupling constants are given in Hz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), multiplet (m).

Elemental analyses were obtained by the Microanalytical Laboratory of the Inorganic Chemistry Laboratory, Oxford.

3.2. *β-Ketoesters* **3**

3.2.1. *General procedure*

Sodium hydride (9.51 g, 238 mmol, 60% dispersion in mineral oil) was weighed under nitrogen in a 250-ml three-necked round-bottomed flask and washed three times with dry pentane to remove the mineral oil. Each time the solution was separated by decantation after the sodium hydride was allowed to settle. The flask was then warmed to 90°C to evaporate the residual pentane. Dried benzene (130 ml) was added, followed by 14.65 g (161 mmol) of dimethylcarbonate. When the solvent started to reflux, 82 mmol of ketone **2** (pre-dried over anhydrous sodium sulphate, if necessary), dissolved in 25 ml of dry benzene, were added dropwise over a period of 30 min. After the addition was complete, the mixture was allowed to reflux until TLC analysis (diethyl ether/petroleum ether 1:2) showed traces of the starting ketone (about 4 h). The reaction mixture was cooled to 0°C. Then glacial acetic acid (16 ml) was added in small portions, causing the precipitation of a pasty solid. Ice-cold water (about 60 ml) was added dropwise and the stirring was continued until complete dissolution of the solid material. The benzene layer was separated and the aqueous phase was extracted three times with benzene. The combined organic fractions were washed with distilled water, dried and the solvent was eliminated at reduced pressure. The raw β-ketoester **3** was used in the next step without purification. IR (film): 1745, 1725, 1655, 1620 cm^{-1}.

3.2.2. *Methyl 2-oxo-1-cyclohexanecarboxylate* ***3a***

^1H-NMR ($CDCl_3$): δ 1.50–1.95 (m, 4H), 2.10–2.50 (m, 4H), 3.30–3.43 (m, 1H), 3.68 (s, 3H) ppm.

3.2.3. *Methyl 2-oxo-1-cycloheptanecarboxylate* ***3b***

^1H-NMR ($CDCl_3$): δ 1.40–2.20 (m, 7H), 2.35–2.67 (m, 3H), 3.50–3.62 (m, 1H), 3.72 (s, 3H) ppm.

3.2.4. *Methyl 2-oxo-1-cyclooctanecarboxylate* ***3c***

^1H-NMR ($CDCl_3$): δ 1.31–2.62 (m, 12H), 3.54–3.65 (m, 1H), 3.75 (s, 3H) ppm.

3.3. *Alkynes* **4**

3.3.1. *General procedure*

Propargyl bromide (17.8 ml, 80% solution w/w in toluene, 160 mmol) was added dropwise to a well stirred suspension of 76 mmol of the raw β-ketoester **3** and 42.30 g (305 mmol) of potassium carbonate in 450 ml of acetone. The mixture was refluxed until the ferric chloride test for enols was positive. After about 6 h, it was cooled to room temperature (r.t.) and filtered to remove most of the potassium carbonate. The acetone was evaporated under reduced pressure, the residue diluted with water, extracted three times with ether, dried and the solvent was evaporated under vacuum. The resulting oil was used without further purification. IR (film): 3325, 2130 cm^{-1}.

*3.3.2. Methyl 2-oxo-1-(2-propynyl)-1-cyclohexanecarboxylate **4a***

^{1}H-NMR (CDCl$_3$): δ 1.45–1.91 (m, 4H), 2.03 (t, $J = 2.7$ Hz, 1H), 2.14–2.85 (m, 4H), 2.70 (d, $J = 2.7$ Hz, 2H), 3.71 (s, 3H) ppm.

*3.3.3. Methyl 2-oxo-1-(2-propynyl)-1-cycloheptanecarboxylate **4b***

^{1}H-NMR (CDCl$_3$): δ 1.46–1.90 (m, 6H), 2.01 (t, $J = 2.6$ Hz, 1H), 2.03–2.38 (m, 2H), 2.40–2.58 (m, 2H), 2.63–2.78 (m, 1H), 2.88–3.02 (m, 1H), 3.75 (s, 3H) ppm.

*3.3.4. Methyl 2-oxo-1-(2-propynyl)-1-cyclooctanecarboxylate **4c***

^{1}H-NMR (CDCl$_3$): δ 1.20–1.95 (m, 9H), 2.00 (t, $J = 2.7$ Hz, 1H), 2.18–2.90 (m, 4H), 2.99–3.18 (m, 1H), 3.73 (s, 3H) ppm.

*3.4. Methylketones **5***

3.4.1. General procedure

A solution of the alkyne **4** (76.25 mmol) in 35 ml of dry methanol was added dropwise to a catalyst solution prepared by warming together at 45°C, 1.09 g (5.03 mmol) of red mercuric oxide, 0.2 ml (48% solution, 2.77 mmol) of boron trifluoride–diethyl ether complex, 20 mg of trichloroacetic acid and 4 ml of dry methanol in a three-necked flask equipped with a refluxing condenser and a CaCl$_2$ guard tube. After the initial exothermic reaction was over, the mixture was stirred for 2 h at 45°C (TLC: diethyl ether/petroleum ether 1:2), cooled to r.t. and poured into cold dilute sulphuric acid. Extraction with diethyl ether, drying and evaporation gave the required diketone **5**, which was used in the following reaction without further purification. IR (film): 1710 cm^{-1}.

*3.4.2. Methyl 2-oxo-1-(2-oxopropyl)-1-cyclohexanecarboxylate **5a***

^{1}H-NMR (CDCl$_3$): δ 1.68–1.80 (m, 4H), 1.95–2.40 (m, 1H), 2.20 (s, 3H), 2.32–2.55 (m, 2H), 2.70–2.90 (m, 1H), 2.85 (s, 2H), 3.68 (s, 3H) ppm.

*3.4.3. Methyl 2-oxo-1-(2-oxopropyl)-1-cycloheptanecarboxylate **5b***

^{1}H-NMR (CDCl$_3$): δ 1.40–2.24 (m, 8H), 2.21 (s, 3H), 2.42–2.59 (m, 1H), 2.63–2.82 (m, 2H), 3.10–3.22 (m, 1H), 3.72 (s, 3H) ppm.

*3.4.4. Methyl 2-oxo-1-(2-oxopropyl)-1-cyclooctanecarboxylate **5c***

^{1}H-NMR (CDCl$_3$): δ 1.98–2.40 (m, 10H), 2.22 (s, 3H), 2.54–2.68 (m, 2H), 2.89–3.18 (m, 1H), 3.18–3.35 (m, 1H), 3.68 (s, 3H) ppm.

*3.5. Enones **6***

3.5.1. General procedure

The diketone **5** (76.23 mmol) and 450 ml of a 10% aqueous solution of potassium hydroxide were heated at 120°C for 2 h under a slow stream of nitrogen (TLC: diethyl ether/petroleum ether 2:1). After cooling to r.t. the mixture was acidified with diluted sulphuric acid and the enone extracted with diethyl ether. The collected organic fractions were dried and the solvent evaporated under reduced pressure. The raw enone **6** was purified by flash-chromatography (same eluent as for the TLC). IR (film): 1705, 1615 cm^{-1}.

*3.5.2. Bicyclo[4:3:0] non-6-en-8-one **6a***

Yield over four steps: 61%; average yield per step 88%. Anal. Found: C, 79.1; H, 8.3%. C$_9$H$_{12}$O (136.19) Calc.: C, 79.4; H, 8.9%. ^{1}H-NMR (CDCl$_3$): δ 0.95–1.65 (m, 3H), 1.82–2.10 (m, 3H), 2.10–2.39 (m, 2H), 2.44–2.72 (m, 2H), 2.72–2.91 (m, 1H), 5.84 (s, 1H) ppm; ^{13}C-NMR (CDCl$_3$): δ 25.2, 27.0, 30.9, 34.9, 41.7, 42.3, 126.6, 184.9, 209.1 ppm.

*3.5.3. Bicyclo [5:3:0] dec-7-en-9-one **6b***

Yield over four steps: 83%; average yield per step 96%. Anal. Found: C, 79.7; H, 9.1%. C$_{10}$H$_{14}$O (150.22) Calc.: C, 80.0; H, 9.4%. ^{1}H-NMR (CDCl$_3$): δ 1.38–2.10 (m, 10H), 2.59–2.78 (m 2H), 2.86–3.02 (m, 1H), 5.84–5.91 (m, 1H) ppm; ^{13}C-NMR (CDCl$_3$): δ 26.3, 28.5, 30.3, 32.7, 34.2, 44.3, 44.5, 129.6, 188.3, 209.3 ppm.

*3.5.4. Bicyclo [6:3:0] undec-8-en-10-one **6c***

Yield over four steps: 71%; average yield per step 92%. Anal. Found: C, 80.1; H, 9.2%. C$_{11}$H$_{16}$O (164.25) Calc.: C, 80.4; H, 9.8%. ^{1}H-NMR (CDCl$_3$): δ 1.20–2.12 (m, 9H), 2.20–2.60 (m, 4H), 2.68–2.81 (m, 1H), 2.92–3.30 (m, 1H), 5.95 (s, 1H) ppm; ^{13}C-NMR (CDCl$_3$): δ 23.8, 25.5, 25.9, 27.5, 30.2, 30.8, 41.0, 43.4, 130.6, 189.2, 209.2 ppm.

*3.6. Allylic alcohols **7***

3.6.1. General procedure

The enone **6** (7.42 mmol) dissolved in 30 ml of anhydrous diethyl ether was added dropwise to a well stirred suspension of 0.30 g (7.90 mmol) of LiAlH$_4$ in 20 ml of anhydrous diethyl ether at 0°C. After 1 h at that temperature, the reaction, monitored by TLC, was complete (diethyl ether/petroleum ether 2.5:1). The excess of reducing agent was decomposed by careful addition of water, allowing the separation of the organic layer from the inorganic salts, which were washed with chloroform (5 × 50 ml) and then decanted. The combined organic extracts were dried and evaporated in vacuo to give the allylic alcohol **7** in quantitative yield. IR (film): 3355, 1670 cm $^{-1}$.

3.6.2. Bicyclo[4:3:0] non-6-en-8-ol **7a**

^{1}H-NMR ($CDCl_3$): δ 0.92–1.45 (m, 4H), 1.56 (m, 1H, exchanged on D_2O addition), 1.55–2.10 (m, 4H), 2.20–2.40 (m, 1H), 2.40–2.63 (m, 2H), 4.65–4.90 (m, 1H), 5.33 (m, 1H) ppm.

3.6.3. Bicyclo[5:3:0] dec-7-en-9-ol **7b**

^{1}H-NMR ($CDCl_3$): δ 1.15–1.80 (m, 11H), 2.20–2.60 (m, 3H), 4.62–4.70 (m, 1H), 5.40 (t, $J = 1.4$ Hz, 1H) ppm.

3.6.4. Bicyclo [6:3:0] undec-8-en-10-ol **7c**

^{1}H-NMR ($CDCl_3$): δ 1.30–2.12 (m, 13H), 2.35–2.67 (m, 3H), 4.61–4.80 (m, 1H), 5.44 (s br, 1H) ppm.

3.7. Lithium salts **8**

3.7.1. General procedure

The allylic alcohol **7** (2.89 mmol) in 20 ml of pentane was stirred together with 0.72 g of Amberlyst 15 at 0°C. After 30 min the reaction was complete (TLC: diethyl ether/petroleum ether 2:1), magnesium sulphate was added and, after stirring for a further 5 min, the suspension was directly filtered into a Schlenk flask, quickly degassed and cooled to − 40°C. *n*-Butyllithium (4.1 ml of 1 M solution in hexanes, 4.1 mmol) was added dropwise, the solution was allowed to reach r.t. and stirred overnight. The lithium salt **8** separated from the solution as a white dusty solid, which was filtered via a cannula and washed twice with petroleum ether. The residual solvent was pumped off leaving the lithium salt as a white pyrophoric powder.

3.7.2. Lithium bicyclo [4:3:0] non-6,8-dienyl **8a**

Yield over three steps: 81%; average yield per step 89%.

3.7.3. Lithium bicyclo [5:3:0] dec-7,9-dienyl **8b**

Yield over three steps: 86%; average yield per step 93%.

3.7.4. Lithium bicyclo [6:3:0] undec-8,10-dienyl **8c**

Yield over three steps: 88%; average yield per step 94%.

3.8. Metallocene dichlorides **9**

3.8.1. General procedure

The lithium salt **8** (4.452 mmol) in 100 ml of THF at − 78°C was slowly added to a stirred slurry of 1.486 mmol of metal tetrachloride in 30 ml of THF at − 78°C. The cooling bath was then removed and the suspension allowed to stir at r.t. overnight. The solvent was evaporated under reduced pressure to give a solid, which was dissolved in toluene leaving a precipitate of LiCl. The extract was then filtered through a cannula and the volume was reduced by about 80%. Cooling to − 20°C overnight gave a powder, which was filtered, washed with toluene at 0°C and dried in vacuo.

3.8.2. Bis (η^5-tetrahydroindenyl) titanium dichloride **9a′**

Red solid. Yield, 59%. Anal. Found: C, 60.5; H, 6.2; Cl, 19.85. $C_{18}H_{22}Cl_2Ti$ (357.16) Calc.: C, 61.2; H, 6.2; Cl, 19.7%. ^{1}H-NMR ($CDCl_3$): δ 1.50–1.62 (m, 4H), 1.77–1.90 (m, 4H), 2.47–2.56 (m, 4H), 2.83–2.93 (m, 4H), 5.75 (d, $J = 3.0$ Hz, 4H), 6.28 (t, $J = 3.0$ Hz, 2H) ppm; ^{13}C-NMR ($CDCl_3$): δ 21.9, 25.3, 109.8, 113.9, 137.2 ppm.

3.8.3. Bis (η^5-tetrahydroindenyl) zirconium dichloride **9a″**

White solid. Yield, 56%. Anal. Found: C, 53.8; H, 5.5; Cl, 17.6. $C_{18}H_{22}Cl_2Zr$ (400.50) Calc.: C, 54.0; H, 5.5; Cl, 17.7%. ^{1}H-NMR ($CDCl_3$): δ 1.51–1.75 (m, 4H), 1.75–1.94 (m, 4H), 2.45–2.65 (m, 4H), 2.78–2.98 (m, 4H), 5.80 (d, $J = 3.0$ Hz, 4H), 6.30 (t, $J = 3.0$ Hz, 2H) ppm; ^{13}C-NMR ($CDCl_3$): δ 22.3, 24.5, 109.6, 111.1, 132.1 ppm.

3.8.4. Bis (η^5-tetrahydroindenyl) hafnium dichloride **9a‴**

Off-white solid. Yield, 49%. Anal. Found: C, 44.9; H, 4.5; Cl, 14.5. $C_{18}H_{22}Cl_2Hf$ (487.77) Calc.: C, 44.3; H, 4.55; Cl, 14.5%. ^{1}H-NMR ($CDCl_3$): δ 1.51–1.72 (m, 4H), 1.75–1.90 (m, 4H), 2.50–2.65 (m, 4H), 2.65–3.05 (m, 4H), 5.69 (d, $J = 2.8$ Hz, 4H), 6.18 (t, $J = 2.8$ Hz, 4H) ppm; ^{13}C-NMR ($CDCl_3$): δ 22.3, 24.3, 108.0, 110.4, 130.2 ppm.

3.8.5. Bis (η^5-bicyclo [5:3:0] dec-7,9-dienyl) titanium dichloride **9b′**

Red solid. Yield, 48.5%. Anal. Found: C, 62.3; H, 6.7; Cl, 18.4. $C_{20}H_{26}Cl_2Ti$ (385.23) Calc.: C, 62.4 H, 6.8; Cl, 18.4%. ^{1}H-NMR ($CDCl_3$): δ 1.84–2.10 (m, 8H), 2.51–2.80 (m, 12H), 5.85–6.01 (m, 6H) ppm.

3.8.6. Bis (η^5-bicyclo [5:3:0] dec-7,9-dienyl) zirconium dichloride **9b″**

White solid. Yield, 61%. Anal. Found: C, 55.75; H, 6.1; Cl, 16.6. $C_{20}H_{26}Cl_2Zr$ (428.55) Calc.: C, 56.05; H, 6.1; Cl, 16.55%. ^{1}H-NMR ($CDCl_3$): δ 1.84–2.10 (m, 8H), 2.51–2.80 (m, 12H), 5.98–6.04 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$): δ 28.3, 30.5, 32.1, 106.68, 115.2, 135.1 ppm.

3.8.7. Bis (η^5-bicyclo [5:3:0] dec-7,9-dienyl) hafnium dichloride **9b‴**

Off-white solid. Yield, 55%. Anal. Found: C, 46.6; H, 5.2; Cl, 13.4. $C_{20}H_{26}Cl_2Hf$ (515.82) Calc.: C, 46.6; H, 5.1; Cl, 13.75%. ^{1}H-NMR ($CDCl_3$): δ 1.80–2.12 (m, 8H), 2.50–2.81 (m, 12H), 5.87–5.95 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$): δ 28.3, 30.3, 32.2, 105.2, 114.0, 133.0 ppm.

3.8.8. Bis (η^5-bicyclo [6:3:0] undec-8,10-dienyl) titanium dichloride **9c′**

Red solid. Yield, 45%. Anal. Found: C, 63.5; H, 7.15; Cl, 17.2. $C_{22}H_{30}Cl_2Ti$ (413.28) Calc.: C, 63.9; H, 7.3; Cl, 17.2%. ^{1}H-NMR ($CDCl_3$): δ 1.10–1.55 (m, 12H), 1.72–1.98 (m, 4H), 2.48–2.70 (m, 8H), 5.99 (d, $J = 3.0$ Hz, 4H), 6.14 (t, $J = 3.0$ Hz, 2H) ppm.

3.8.9. Bis (η^5-bicyclo [6:3:0] undec-8,10-dienyl) zirconium dichloride **9c″**

White solid. Yield, 63%. Anal. Found: C, 57.7; H, 6.95; Cl, 15.7. $C_{22}H_{30}Cl_2Zr$ (456.61) Calc.: C, 57.9; H, 6.6; Cl, 15.5%. ^{1}H-NMR ($CDCl_3$): δ 1.10–1.55 (m, 12H), 1.72–1.98 (m, 4H), 2.48–2.70 (m, 8H), 6.03 (d, $J = 3.0$ Hz, 4H), 6.17 (t, $J = 3.0$ Hz, 2H) ppm; ^{13}C-NMR ($CDCl_3$): δ 25.8, 27.2, 31.9, 108.3, 113.9, 133.2 ppm.

3.8.10. Bis (η^5-bicyclo [6:3:0] undec-8,10-dienyl) hafnium dichloride **9c‴**

Off-white solid. Yield, 53%. Anal. Found: C, 47.7; H, 5.6; Cl, 13.1. $C_{22}H_{30}Cl_2Hf$ (543.88) Calc.: C, 48.6; H, 5.6; Cl, 13.0%. ^{1}H-NMR ($CDCl_3$): δ 1.10–1.50 (m, 12H), 1.72–1.90 (m, 4H), 2.48–2.62 (m, 8H), 5.93 (d, $J = 3.0$ Hz, 4H), 6.07 (t, $J = 3.0$ Hz, 2H) ppm; ^{13}C-NMR ($CDCl_3$): δ 25.8, 27.0, 32.0, 106.9, 112.5, 131.1 ppm.

3.9. 10-Methyl bicyclo [4:3:0] non-6-en-8-ol **10**

The enone **6a** (9.88 mmol) in 20 ml of anhydrous diethyl ether was cooled to 0°C under nitrogen. When methyl lithium (7.9 ml, 11.85 mmol, 1.5 M in ether) was slowly added the yellow solution became orange. The mixture was stirred 30 min at 0°C and 30 min at r.t. (TLC, diethyl ether/petroleum ether 2:1). The reaction mixture was then cooled again to 0°C, the excess of alkylating agent was decomposed by careful addition of iced water and the separated organic phase was washed several times with diethyl ether. The collected organic fractions were dried and the solvent evaporated under reduced pressure. In total 8.30 mmol of the raw alcohol **10** was obtained as a mixture of two diastereoisomers (Yield: 84%). IR (film): 3355, 1670 cm^{-1}.

Major isomer. ^{1}H-NMR ($CDCl_3$): δ 0.85–1.55 (m, 5H), 1.27 (s, 3H), 1.63 (s, 1H, exchanged on D_2O addition), 1.65–2.10 (m, 4H), 2.15–2.50 (m, 2H), 5.25 (m, 1H) ppm.

Minor isomer. ^{1}H-NMR ($CDCl_3$): δ 0.85–1.55 (m, 5H), 1.37 (s, 3H), 1.60 (s, 1H, exchanged on D_2O addition), 1.65–2.10 (m, 4H), 2.15–2.50 (m, 2H), 5.31 (m, 1H) ppm.

3.10. Lithium 10-methyl bicyclo [5:3:0] dec-7,9-dienyl **12**

The allylic alcohol **10** (6.57 mmol) in 30 ml of pentane was stirred together with 0.72 g of Amberlyst 15 at 0°C. After 30 min the reaction was complete (TLC: diethyl ether/petroleum ether 2:1), magnesium sulphate was added and, after stirring for a further 5 min, the suspension was directly filtered into a Schlenk flask, quickly degassed and cooled to −40°C. a total of 5 ml of *n*-butyllithium (2.5 M solution in hexanes, 12.5 mmol) was added dropwise, the solution was allowed to reach r.t. and stirred overnight. The lithium salt **12** separated from the solution as a white dusty solid, which was filtered via a cannula and washed twice with petroleum ether. The residual solvent was pumped off leaving 0.6 g of the lithium salt as a white pyrophoric powder.

Yield over three steps: 60%; average yield per step 84%.

^{1}H-NMR (Pyridine-d_5): 1.87 (br, s, 4H), 2.29 (s, 3H), 2.90 (br, s, 4H), 5.78 (s, 2H) ppm.

3.11. Bis (10-methyl bicyclo [5:3:0] dec-7,9 dienyl) iron **13a**

Anhydrous $FeCl_2$ (63.4 mg, 0.5 mmol) dissolved in THF was added to a solution of the lithium salt **10** (140 mg, 1 mmol) dissolved in 20 ml of THF and cooled to −78°C. The solution turned orange while warming to r.t. The solvent was then removed under vacuum, the residue extracted with pentane, filtered and dried under vacuum yielding a red/orange oil in near quantitative yield.

Anal. Found: C, 74.8; H, 8.5. $C_{20}H_{26}Fe$ (322.265) Calc.: C, 74.5; H, 8.2%. ^{1}H-NMR ($CDCl_3$): δ 1.56–1.64 (m, 4H), 1.84–1.92 (m, 4H), 1.94 (s, 6H), 2.18–2.26 (m, 4H), 2.48–2.56 (m, 4H), 3.46 (s, 4H) ppm; ^{13}C-NMR ($CDCl_3$): δ 14.2, 23.1, 23.6, 69.8, 81.3, 83.6 ppm.

3.12. Bis (10-methyl bicyclo [5:3:0] dec-7,9 dienyl) zirconium dichloride **13b**

A Schlenk tube was charged with the lithium salt **12** (130 mg, 0.95 mmol) and $ZrCl_4$ (110 mg, 0.47 mmol). Toluene was added and the resulting suspension was stirred at r.t. for 24 h, filtered, concentrated and layered with pentane. After a further 24 h, a light coloured dusty solid precipitated. It was isolated by filtration and washing with pentane. Yield: 60%.

Anal. Found: C, 56.8; H, 6.6; Cl, 16.2. $C_{20}H_{26}Cl_2Zr$ (428.55) Calc.: C, 56.1; H, 6.1; Cl, 16.6%. ^{1}H-NMR ($CDCl_3$): δ 1.50–1.80 (m, 8H), 2.15 (s, 6H), 2.50–2.70 (m, 4H), 2.70–2.90 (m, 4H), 6.90 (s, 4H) ppm; ^{13}C-NMR ($CDCl_3$): δ 16.2, 22.5, 24.7, 114.6, 129.4, 139.5 ppm.

3.13. Ethylene-bis(10-methyl bicyclo [5:3:0] dec-7,9 diene) ***14***

A solution of 1,2 dibromoethane (181 µl, 2.1 mmol, dried over anhydrous $CaCl_2$) dissolved in THF and cooled to 0°C, was slowly added via a thin cannula to a solution of the organolithium compound **12** (600 mg, 4.3 mmol) dissolved in 20 ml of THF and cooled to − 78°C. The resulting pale yellow solution was allowed to warm to r.t. and stirred for 24 h. Saturated ammonium chloride solution was added to quench the reaction. Extraction with diethyl ether, drying and evaporation gave 543 mg of the bis-diene **14** (yield: 85%) which was used in the following reaction without further purification.

3.14. Ethylene-bis(η^5-10-methyl bicyclo [5:3:0] dec-7,9 dienyl) zirconium bis(dimethyl amide) ***15***

The bis-diene **14** (0.543 g, 1.83 mmol) was dissolved in toluene and added to a suspension of zirconium tetrakis(dimethylamide) (505 mg, 1.87 mmol) in toluene. The resulting cloudy solution was refluxed for 18 h, allowed to cool, and filtered. A total of 0.365 g of a cream coloured solid were obtained (unoptimised yield: 42%). An aliquot was removed and analysed by ^{1}H-NMR analysis which showed only the peaks corresponding to the *rac*-isomer of **15**.

Anal. Found: C, 67.0; H, 8.9; N, 5.7. $C_{26}H_{40}N_2Zr$ (471.83) Calc.: C, 66.2; H, 8.5; N, 5.9%. ^{1}H-NMR ($CDCl_3$): δ 1.72–1.78 (m, 4H), 2.12 (s, 6H), 2.30–2.35 (m, 8H), 2.50 (s, 12H), 2.71 (s, 4H), 2.80–2.85 (m, 4H), 5.90 (s, 2H) ppm; ^{13}C-NMR ($CDCl_3$): δ 16.1, 23.1, 23.4, 24.4, 25.2, 28.7, 46.8, 126.8, 128.2, 129.2, 131.4, 139.9 ppm.

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