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Bulky peralkylated cyclopentadienes by extension of Jutzi's pentamethylcyclopentadiene procedure☆

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Abstract

In alkaline solution pentanone-3 undergoes a condensation reaction with isobutyraldehyde to form *trans*-4,6-dimethylhept-5-en-3-one (**1**) and 3,5-diisopropyl-2,6-dimethyl-2,3,5,6-tetrahydro-γ-pyrone (**2**) upon addition of isobutyraldehyde to **1**. Treatment of **2** with *p*-toluenesulfonic acid under mild conditions gives 2,5-dimethyl-3,4-diisopropylcyclopent-2-en-1-one (**3**) with concomitant loss of water. With methyl- or isopropylmagnesium chloride **3** can be converted to tautomeric mixtures of the respective 1,2,3,4,5-pentaalkylated cyclopentadienes $HC_5Me_2(CHMe_2)_3$ (**4**) or $HC_5Me_3(CHMe_2)_2$ (**5**), which on deprotonation with sodium amide yield the sodium salts NaC_5Me_2-3,5-$(CHMe_2)_3$-1,2,4 (**6**) or NaC_5Me_3-3,4,5-$(CHMe_2)_2$-1,2 (**7**). From **6** or **7** and $MnCl_2$ or $[FeBr_2(DME)]$ the novel metallocenes $[\{C_5Me_3(CHMe_2)_2\}_2Mn]$ (**8**), $[\{C_5Me_3(CHMe_2)_2\}_2Fe]$ (**9**), and $[\{C_5Me_2(CHMe_2)_3\}_2Fe]$ (**10**) have been prepared and investigated by spectroscopic and analytical methods. Complex **8** as well as octaisopropylferrocene (**11**) could also be characterized by X-ray crystal structure determination. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Peralkylated cyclopentadienes; Manganese; X-ray crystal structure

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1. Introduction

When, in 1962, the pentamethylcyclopentadienyl ligand attracted the attention of organometallic chemists by its unexpected emergence from titanium tetrachloride and a mixture of olefins at 300°C under high pressure [1], a research program was started immediately and led to a first review on pentamethylcyclopentadienyl complexes a few years later [2]. Progress was severely hampered, however, by the tedious and expensive five-step procedure of deVries, which was the only way to make free pentamethylcyclopentadiene these days ([3], Scheme 1). Anticipated to be 'the type of completely substituted π-cyclopentadienyl derivative for study' [2], C_5Me_5 set out to overcome the prototype stage and develop into a working horse for organometallic chemists, while an ongoing search for more convenient methods of pentamethylcyclopentadiene preparation produced promising results. The procedure of deVries was optimized [4] and in the group of Whitesides two new synthetic approaches were developed (Scheme 1). Another two synthetic routes had been invented just before by Burger, Delay, and Mazenod, who were interested in the unusual behaviour of the keto function of 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene ([5], Scheme 1). One of these starts with rather expensive hexamethyl (Dewar benzene), the second uses the very cheap starting materials pentanone-3 and acetaldehyde to produce 1,2,4,5-tetramethyl-tetrahydro-γ-pyrone, which can be dehydrated to tetramethylcyclopent-2-en-1-one (Scheme 1). The yield of only 8% pentamethylcyclopentadiene after four steps rendered this method unattractive. A major

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☆ Dedicated to Professor P. Jutzi on the occasion of his 60th birthday.

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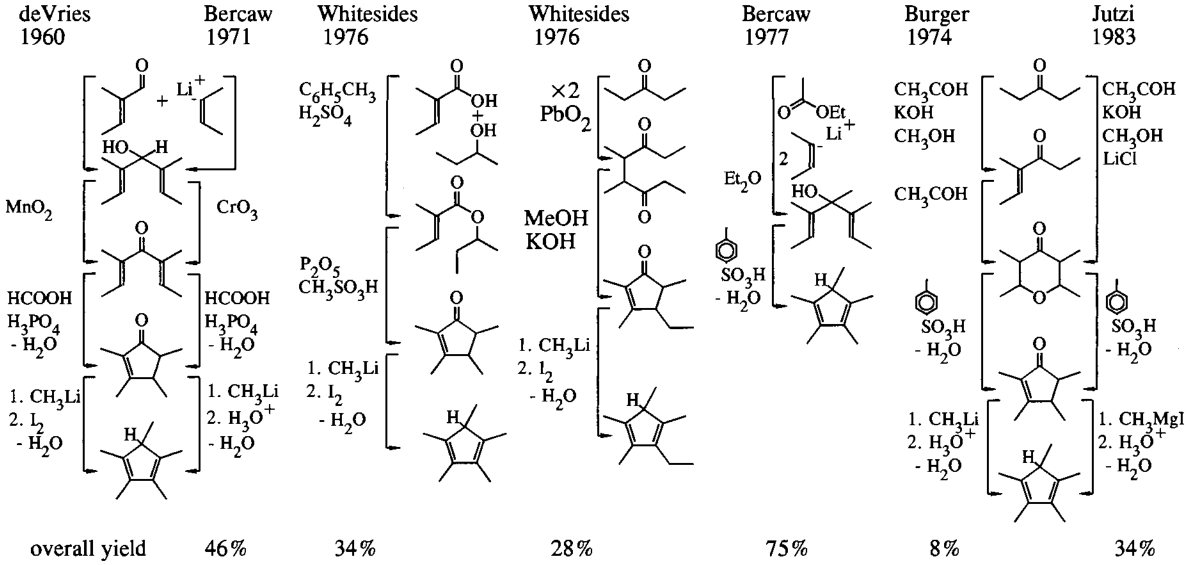


Scheme 1. Milestones of 1,2,3,4,5-pentaalkylcyclopentadiene synthesis.

breakthrough was achieved in 1977 by Bercaw [6], who used ethyl acetate and two equivalents of 2-lithio-2-butene in a convenient two-step synthesis (Scheme 1) with an overall yield of 75%. This method quickly became the absolutely dominating way to make pentamethylcyclopentadiene.

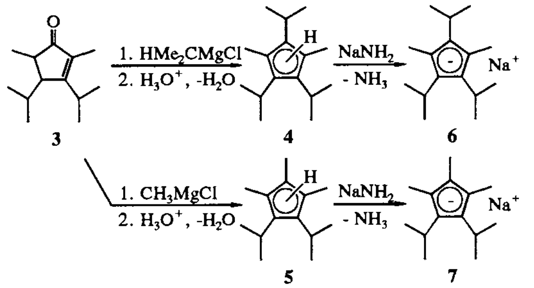
The possibility to employ ethyl propionate, butyrate, valerate, benzoate [6] and other alkyl or alkenyl groups has been used mainly to prepare tetramethylethylcyclopentadiene for the sometimes superior crystallinity of the respective complexes [7] and more recently also for introduction of side chains with functional groups [8].

Although Bercaw's procedure was a great help for almost every worker in the field, there was one group of researchers entering C_5Me_5 chemistry in Würzburg and continuing in Bielefeld who obviously did not share this feeling of satisfaction. The bulk of work done between 1975 and 1990 ([9] lists some relevant review articles) and the experimental part of some of the publications of Jutzi in the field of main group element compounds with pentamethylcyclopentadienyl ligands [10] gives us an idea of the possible reason for this attitude. The consumption of pentamethylcyclopentadiene documented there probably raised the idea of producing it more cheaply and …'since the author reported' (this refers to Ref. [5]) 'that he made no attempts to improve this synthesis, we have done so' [11]. The result turned out to be a contraction to three instead of four steps and an overall yield of 34% instead of 8% (Scheme 1). Cheap starting materials make this procedure the most economic way to produce pentamethylcyclopentadiene as well as all other HC_5Me_4R derivatives available from tetramethylcyclopent-2-en-1-one [12]. Although convenience still favours Bercaw's procedure for small amounts, in larger scale preparations Jutzi's method is far ahead not only for using cheap starting compounds: The base-catalyzed reaction of pentanone-3 with acetaldehyde in methanol solution at little more than ambient temperature can be done easily in a 6 l flask, whereas for the same net result 16 mol of lithium metal in 16 l of diethyl ether need to be reacted with 1081 g of 2-bromo-2-butene as a first step of Bercaw's procedure.

During our own work on the synthesis of peralkylated cyclopentadienes with substituents bulkier than methyl we tested the potential of Jutzi's condensation reaction for the synthesis of pentaethyl- and pentaisopropylcyclopentadiene. It turned out quickly that neither heptanone-4 nor diisobutylketone nor even acetone with appropriate aldehydes under the conditions given by Jutzi gave the desired tetrahydro-γ-pyrone derivatives in our hands. Only pentanone-3 seemed to combine proper acidity and steric accessibility with a desirable lack of self-reactivity in the strongly alkaline solution. The promising combination of pentanone-3 with isobutyraldehyde had to be postponed until the pentaethylcyclopentadiene [13] and the pentaisopropylcyclopentadienide problem [14] had been solved and until the magnetic behaviour of manganocenes with bulky alkyl substituents called for more subtle variations of the substituent pattern [15].

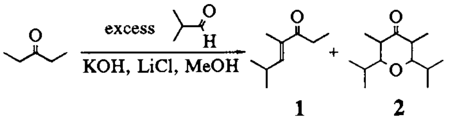
2. Results and discussion

A solution of pentanone-3 and potassium hydroxide in methanol in the presence of lithium chloride reacts at 60–70°C smoothly with isobutyraldehyde to afford an orange–yellow mixture. Aqueous workup and subse-



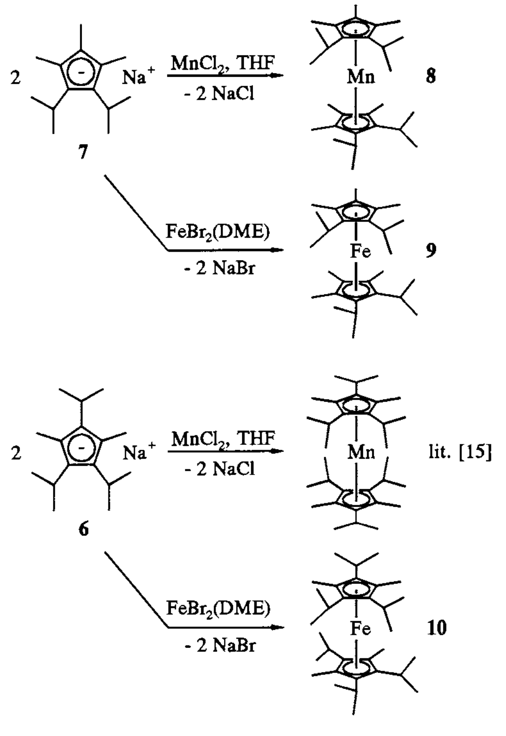
Scheme 2. 1,2,3,4,5-Pentaalkylcyclopentadienes from cyclopentenone **3**.

quent distillation gave the monocondensation product **1** in 53% yield and the tetrahydro-γ-pyrone derivative **2** as a mixture of diastereomers in 41% yield together with only small amounts of an oily mixture with high boiling point, which was not characterized (Eq. (1), condensation of pentanone-3 with isobutyraldehyde).



(1)

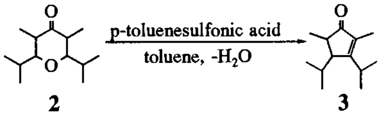
For **1** only one isomer was observed, which most probably exhibits trans geometry. The tetrahydropyrone derivative **2** is a mixture of stereoisomers. We expect two diastereomers with a symmetry plane besides four pairs of enantiomers and indeed the gas chromatogram shows six peaks grouped closely together. NMR spectra are straightforward for **1**, which possesses a characteristic olefinic proton. Complex **2** was characterized by mass spectra and elemental analysis; assignment of NMR signals for the mixture of isomers has not been attempted.



Scheme 3. Synthesis of the decaalkylmanganocenes and -ferrocenes **8**–**10**.

In comparison with acetaldehyde isobutyraldehyde is less reactive and needs higher temperatures for complete reaction. At the same time the formation of aldehyde condensation products without ketone involvement is greatly reduced which results in a very light colour compared to the typical dark red–brown solutions obtained with acetaldehyde. The reduced aldehyde reactivity also accounts for a large fraction of monocondensation product **1**.

Dehydration of **2** with toluenesulfonic acid in boiling toluene using a water separator proceeded with formation of substantial amounts of higher boiling byproducts. Since water elimination is not reversible in this reaction, mild conditions can be employed without removal of water formed during the elimination step and give a good yield of 3,4-diisopropyl-2,5-dimethylcyclopent-2-en-1-one 3 (77%, see Section 3; Eq. (2), formation of cyclopentenone **3** by water elimination).



(2)

Introduction of an isopropyl or methyl group in 1-position using the respective Grignard reagents and spontaneous elimination of water during workup under acidic conditions gives triisopropyl-dimethyl-cyclopentadiene (**4**) or diisopropyltrimethylcyclopentadiene (**5**) as a mixture of tautomers (Scheme 2). Because of a very complex spectral pattern for these mixtures, NMR spectra have not been investigated in detail. They show, however, the absence of olefinic protons as expected.

Salt formation with sodium amide in refluxing tetrahydrofuran gives sodium 1,2,4-triisopropyl-3,5-dimethylcyclopentadienide **6** or 1,2-diisopropyl-3,4,5-trimethylcyclopentadienide **7** (Scheme 2). $^{13}C\{^1H\}$-NMR spectra of a solution of **6** in tetrahydrofuran reveal three singlets for ring carbon atoms in the expected range.

Both sodium salts were used for ferrocene and manganocene synthesis (Scheme 3). Reactions with the appropriate metal halides in tetrahydrofuran gave 1,1′,2,2′-tetraisopropyl-3,3′,4,4′,5,5′-hexamethylmanganocene (**8**).

The orange–red colour of **8** already suggested low spin behaviour at r.t. which could be confirmed by magnetic susceptibility measurements from 2 to 300 K exhibiting paramagnetic behaviour with an effective magnetic moment of 2.18 μ_B. This compares very well to 2.16 μ_B found for the decamethyl derivative [16]. Alkylated manganocenes with a high spin configuration

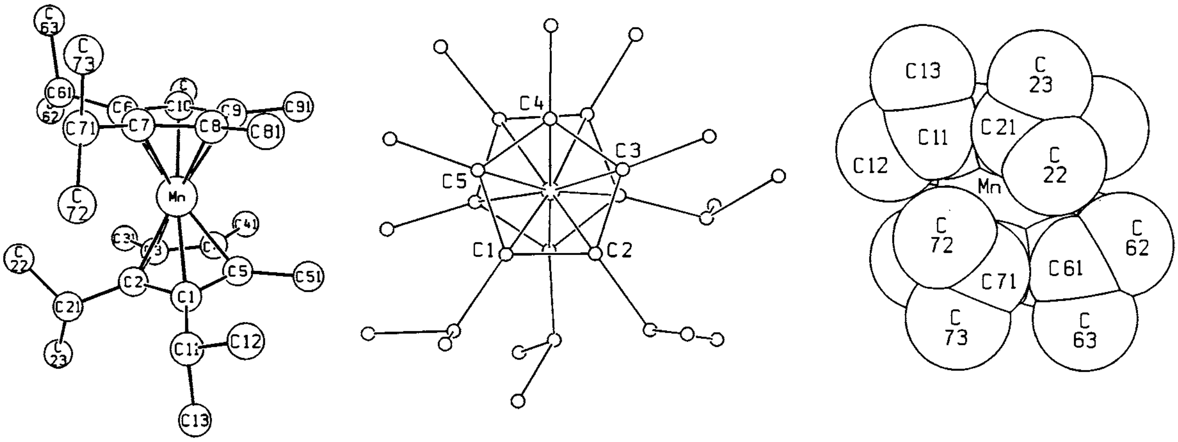


Fig. 1. Crystal and molecular structure of tetraisopropyl-hexamethylmanganocene **8**. Selected distances (Å) and angles (°) for **8**: Mn–C1 2.170(2), Mn–C2 2.164(2), Mn–C3 2.144(2), Mn–C4 2.128(2), Mn–C5 2.143(2), Mn–C6 2.182(2), Mn–C7 2.174(2), Mn–C8 2.144(2), Mn–C9 2.121(2), Mn–C10 2.139(2), largest deviation of a ring atom from the least squares plane 0.0054, distance Mn–ring plane 1.772 (ring C1–C5), 1.775 (ring C6–C10), angle between the ring normals 9.7°, angles between ring normals and Mn–Cp_{cent} 1.1° (ring C1–C5), 1.6° (ring C6–C10). For details regarding the projection on one ring plane (C1 to C5) and the isopropyl conformation see text.

at r.t. like 1,1′,2,2′,4,4′-hexa(*tert*-butyl)manganocene, octaisopropylmanganocene or 1,1′,2,2′,4,4′-hexaisopropyl-3,3′,5,5′-tetramethylmanganocene all show a light yellow colour [15]. Complex **8** gave single crystals from petroleum ether suitable for X-ray diffraction (Fig. 1) [17]. The most interesting feature of the molecular structure of **8** is the close proximity of all four isopropyl groups resulting in a bent metallocene structure with an interplanar angle of 9.7°. Unexpected at first and seeming to support the hypothesis of van der Waals attraction contributing to the driving force for metallocene bending in main group derivatives [18], a close look on the data revealed, that this conformation has nothing to do with van der Waals attraction for two reasons.

1. There are 11 non-bonding carbon–carbon distances from 3.694 to 3.954 Å well below the 4.1 Å found as closest inter-ligand contact for bent decamethylmetallocenes of magnesium, calcium, and ytterbium in the gas phase [19]. Two isopropyl methine carbon atoms (C11 and C61) show out of plane bending by 0.256 and 0.297 Å corresponding to angles of 9.6 and 11.1° between the respective mean plane (both rings are essentially planar) and the ring C–$CHMe_2$ bond. Pronounced bending as well as short non-bonding distances are strongly indicative of severe contraction.

2. Isopropyl groups are particularly suited to minimize steric interaction by adopting a proper orientation. Therefore the closest inter ligand contacts in crystalline **8** (3.694 and 3.708 Å) do not occur between pairs of isopropyl groups, but between two pairs of ring methyl substituents (C51...C91 and C41...C11), the next closest interaction is 3.733 Å between isopropyl methyl C72 and one isopropyl methine carbon of the other ring (C11). If the two pairs of isopropyl substituents had tried to evade each other by adopting a centrosymmetric conformation of the molecule, there would have been repulsion between methyl and isopropyl substituents [20]. Furthermore, there would have been no possibility to relief steric strain by metallocene bending.

The structure is a demonstration of the steric bulk that can be tolerated by alkylated manganocenes taking into accout severe distortion without switching to the much larger manganese–carbon distances coming along with a high spin configuration (cf. 2.050 Å Mn–Cp_{cent} for 1,1′-bis(trimethylsilyl)manganocene [21] and 2.05 Å for the high spin isomer of 1,1′-dimethylmanganocene [22]). In **8** the Mn-ring center distances are 1.772 and 1.775 Å and compare very well with the 1.73 Å value for the low spin isomer of 1,1′-dimethylmanganocene [22]. In the more heavily substituted 1,1′,2,2′,4,4′-hexaisopropyl-3,3′,5,5′-tetramethylmanganocene the steric bulk is just a bit larger. This derivative has a low spin configuration at very low temperatures and abruptly switches to high spin behaviour on warming above 167 K [15]. The four methyl groups obviously make a significant contribution to the overall steric bulk. If these are omitted, a slow gradual increase of the effective magnetic moment has recently been observed for 1,1′,2,2′,4,4′-hexaisopropylmanganocene on warming up from 200 K (2.32 μ_B) to 348 K (still mostly low spin with 3.25 μ_B) [23]. A comparison of hexa- and octaisopropylmanganocene structures given in the same paper [23] confirms the conclusions drawn from the magnetic properties [15,23] of low spin- and high spin-manganocenes. The metal–ring center distances are 1.755 Å for hexaisopropylmanganocene and 2.06 Å for octaisopropylmanganocene [23] and compare well with the structural data mentioned above for other low spin- and high spin-manganocenes, respectively.

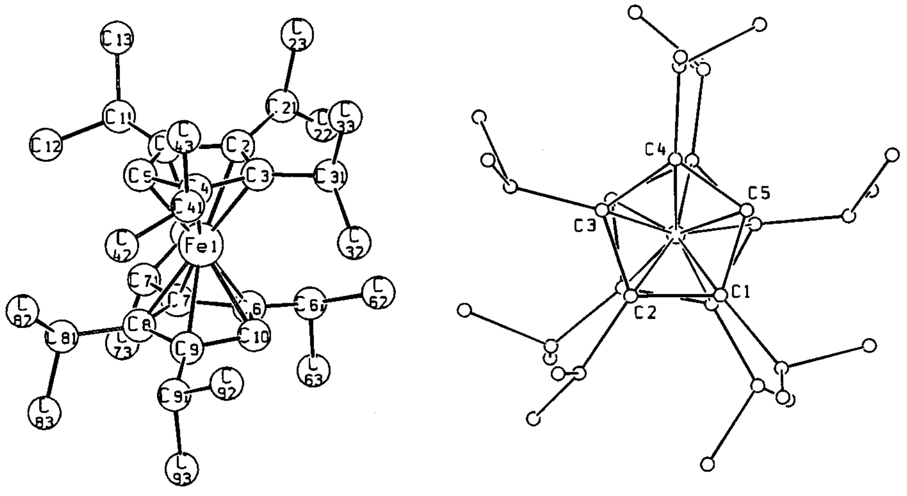


Fig. 2. Crystal and molecular structure of octaisopropylferrocene **11**. Selected distances (Å) and angles (°) for **11**: Fe–C1 2.098(4), Fe–C2 2.103(4), Fe–C3 2.100(4), Fe–C4 2.107(3), Fe–C5 2.068(3), Fe–C6 2.108(3), Fe–C7 2.100(3), Fe–C8 2.099(3), Fe–C9 2.114(3), Fe–C10 2.070(3), largest deviation of a ring atom from the least squares plane 0.0135 (C10), distance Fe–ring plane 1.707 (ring C1–C5), 1.708 (ring C6–C10), angle between the ring normals 178.9°, angles between ring normals and Fe–Cp_{cent} 0.5° (ring C1–C5), 0.3° (ring C6–C10).

In order to study NMR spectra of the ferrocene related to **8**, $FeBr_2(DME)$ was reacted with sodium 1,2-diisopropyl-3,4,5-trimethylcyclopentadienide **7**. The ensuing 1,1′,2,2′-tetraisopropyl-3,3′,4,4′,5,5′-hexamethylferrocene **9** nicely shows the expected signal pattern in ^{1}H-NMR spectra consisting of two singlets for ring methyl groups in a 2:1 ratio, one septet for two methine protons, and two doublets for isopropyl methyl groups. This is similar to the spectra of tetraisopropylferrocene shown in Ref. [24] (although this is the 1,1′,3,3′-isomer), only the ring proton signals reported there are replaced with ring methyl singlets of threefold intensity in the proper spectral region. Crystallization of **9** by sublimation or from solutions gave no single crystals suitable for X-ray diffraction in our hands.

The 1,2,4-triisopropyl-3,5-dimethylcyclopentadienyl ligand has been used first to fine tune the magnetic properties of alkylated manganocenes. Comparison of octaisopropylmanganocene and 1,1′,2,2′,4,4′-hexaisopropyl-3,3′,5,5′-tetramethylmanganocene shows the somewhat greater steric impact of the tetraisopropylcyclopentadienyl ligand [15]. In order to compare the respective ferrocenes as well, 1,1′,2,2′,4,4′-hexaisopropyl-3,3′,5,5′-tetramethylferrocene **10** has been obtained similarly from sodium triisopropyl-dimethyl-cyclopentadienide **6** and $FeBr_2(DME)$. Whereas octaisopropylferrocene **11** displays broad ^{1}H-NMR signals (200 MHz) at r.t. and shows signal coalescence at 288 K, the proton NMR signals of **10** even at 400 MHz are sharp at r.t. and begin to broaden below. Two out of three doublets together with the septet of higher intensity broaden first on cooling and are therefore assigned to the vicinal isopropyl groups in 1-, and 2-position. Coalescence of isopropyl signals is observed at 218 K. The spectral pattern observed below that temperature is rather complicated and the signals could not be resolved at still lower temperatures down to 183 K. This is presumably due to the presence of stereoisomers, which probably form different rotamers each. If isopropyl group rotation is frozen on the timescale of the NMR experiment, the two vicinal isopropyl groups are most likely to be locked in a position turned away from each other as we have seen in the crystal structure of manganocene **8**. For the third isopropyl group located between two methyl groups, only an orientation with one methyl above and one below the ring plane makes sense. Therefore the methine H–C vector of this substituent, viewed from the position of the central atom, points right or left giving rise to local chirality. Two such rings on one central atom can then form a racemic mixture or the meso diastereomer. Rotamers arising from slowed rotation of the ligands about the metal–ring axis provide additional signal splitting. Crystallization of **10** by sublimation or from solution in our hands did not afford single crystals suitable for X-ray diffraction (Fig. 2).

By sublimation of octaisopropylferrocene **11** well-shaped single crystals suitable for X-ray diffraction could be obtained [25]. The molecule shows no crystallographically imposed symmetry. The conformation of the molecule is closer to an ecliptic than to a staggered arrangement (torsion angle 10.1°) of the two five-membered rings. Three interlocking isopropyl neighbours of one ring point into one direction, the fourth one has its methyl groups above and below the ring plane directed towards the only ring proton. In the other ring, the isopropyl group attached to C2 is disordered such, that to about 50% a similar 3:1 orientation and to another 50% a 2:2 orientation is populated with two pairs of isopropyl groups being oriented in opposite directions. Although the isopropyl groups of one ring try to evade contacts with those of the other ring by pointing in opposite directions, several non bonding C...C distances around and below 3.6 Å are found and the distances Fe–ring plane are both 1.71 Å, which is rather long for a ferrocene and surpassed only by 1.72 Å in decaphenylferrocene [26]. For decamethylferrocene an interplanar distance of 3.31 Å has been observed [27]. Steric strain also causes out of plane bending of isopropyl methine carbon atoms by values up to 13.9° corresponding to a position 0.34 Å above the ring plane (C91). With an interplanar angle of only 1.1°, **11** exhibits an almost undistorted FeC_{10} sandwich framework with ten Fe–C distances in a narrow range from 2.068(3) to 2.114(3) Å. With respect to the 9.3° interplanar angle found for the octaisopropylferrocenium cation [28], the absence of such distortion in the neutral counterpart **11** shows, that in addition to steric bulk the possibility of a Jahn–Teller contribution might have considerable influence on the distortion of the 17 VE octaisopropylferrocenium cation.

3. Experimental

The condensation reaction was carried out in a 20 l flask with two pressure-equalized dropping funnels, a double-walled reflux condenser, a mechanical stirrer and a quickfit neck closed with a screw cap during the reaction. The flask was placed in a pan filled with Styropor® flakes to keep the temperature above 60°C during the reaction. No inert gas atmosphere was applied.

To a solution of 573.4 g (19.22 mol) potassium hydroxide and 87.7 g (2.04 mol) lithium chloride in 3.8 l of methanol 2.641 kg (30.66 mol) of pentanone-3 were added with stirring via dropping funnel within ca. 15–20 min. During ketone addition some solids are precipitated giving the mixture a somewhat cloudy appearance. At 30°C dropwise addition of 6.636 kg (92.03 mol) isobutyraldehyde was started such that the whole amount of 8.4 l was introduced within 12 h. After 2 h the suspension was orange–yellow and reached a temperature of 60°C. The temperature was then maintained between 60 and 70°C during the aldehyde addition. Stirring was continued for another 12 h, then 2 l of water were introduced and the contents of the flask were neutralized with 10% hydrochloric acid. The aqueous phase containing methanol was pumped out through a glass tube inserted into the quickfit neck down to the bottom of the flask by careful admission of nitrogen through the outlet of one addition funnel while the second outlet was closed. In the same way the organic phase was stirred with two 1 l portions of water and one portion of brine, then pumped out and collected. In a 6 l distillation apparatus equipped with a vigreux column (length 30 cm) low boiling components like methanol and small amounts of starting compounds are removed at atmospheric pressure up to a boiling point of 85°C. The total volume of about 10 l is processed in three batches. The residual organic phase is treated likewise under water aspirator vacuum in two batches, where 2.279 kg of the monocondensation product (**1**) containing small amounts of the higher boiling main product **2** is collected in a boiling point range from 68 to 90°C at 20 mbar (16.25 mol, 53%). Only one isomer of **1** was found by GC-MS: $m/z = 140$ (M^+, 57%). The distillation was continued at a pressure of ca. 0.1 mbar and gave as a main fraction 2.672 kg (12.6 mol, 41%) of the tetraalkyl-tetrahydro-pyrone isomeric mixture **2** within a boiling range from 65 to 89°C. Elemental analysis of $C_{13}H_{24}O_2$ (**2**), (M = 212.33): Anal. Calc.: C 73.54, H 11.39; Found: C 73.67, H 11.73; GC-MS: $m/z = 212$ (M^+, 3 and 5%) for two out of six peaks grouped closely together in the gaschromatogram.

The preparation can be linearly scaled down and has been carried out with a 1 mol amount of pentanone-3. For such smaller scale preparations external heat should be applied to reach a temperature range of 60–70°C during the aldehyde addition. If the temperature is too low, more monocondensation product **1** and a reduced yield of the tetraalkyl-tetrahydro-pyrone isomeric mixture **2** are obtained.

3.1. *3,4-Diisopropyl-2,5-dimethylcyclopent-2-en-1-one (3)*

In a 4 l flask, a solution of 684.3 g (3.22 mol) 2,3,5,6-tetrahydro-2,6-diisopropyl-3,5-dimethyl-pyrone **1**, 1.8 l of toluene, and 60 g (0.315 mol) toluenesulfonic acid monohydrate (isomeric mixture) was stirred at r.t. for 48 h. The black–brown solution was washed with 300 ml of water, then stirred with 300 ml of a saturated sodium carbonate solution, washed with two 250 ml portions of water and separated from the aqueous solutions. In aspirator vacuum (20 mbar) a mixture of toluene and water was collected in a boiling range from 30 to 42°C. From ca. 60 to 95°C (20 mbar) a small amount of the monocondensation product **1**, then 480.5 g (2.47 mol, 77%) of light yellow **3** was distilled off at a pressure of 0.1 mbar in a boiling range from 67 to 93°C. A higher boiling fraction contained only negligible amounts of the desired cyclopentenone and was discarded.

1: ^{1}H-NMR (δ, C6D6): 6.33 (d, $^3J_{H-H} = 9.3$ Hz, 1H, C3–*H*), 2.62 (sep, $^3J_{H-H} = 6.8$ Hz, 1H, C2–*H*), 2.54 (q, $^3J_{H-H} = 7.6$ Hz, 2H, C6–*H*), 1.75 (s, 3H, C9–*H*), 1.02 (t, $J_{H-H} = 7.2$ Hz, 3H, C7–*H*), 0.98 (d, $J_{H-H} = 6.8$ Hz, 6H, C1,8–*H*). ^{13}C-NMR (δ, C_6D_6): 201.3 (s, 1C, C5), 148.0 (dsep, $^1J_{C-H} = 150.3$ Hz, $^3J_{C-H} = 6.5$ Hz, 1C, C3), 135.0 (s, broad because of long range coupling, 1C, C2), 30.2 (tq, $^{1}J_{C-H} = 125.8$ Hz, $^{3}J_{C-H} = 4.1$ Hz, 1C, C8), 28.5 (d, $^{1}J_{C-H} = 128.3$ Hz, 1C, C4), 22.0 (q, $^{1}J_{C-H} = 126.2$ Hz, 1C, C9), 18.9 (qd, $^{1}J_{C-H} = 127.5$ Hz, $^{3}J_{C-H} = 8.5$ Hz, 2C, C1, C8), 8.9 (q, $^{1}J_{C-H} = 127.5$ Hz, 1C, C7).

2: ^{1}H- and ^{13}C-NMR spectra show a mixture of isomers. The signals could not be assigned. MS (EI, 70 eV): 212 (M^{+}, 4%), 169 (M^{+} $-CHMe_2$, 11%), 140 (M^{+} $-HMe_2CC(O)H$ = **1**$^{+}$, 8%), 111 (**1**$^{+}$ $-C_2H_5$, 100%), 43 ($CHMe_2^{+}$, 12%), 41 ($C_3H_5^{+}$, 12%). Anal. Calc. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.67; H, 11.73.

3: ^{1}H-NMR (δ, without solvent, external C_6D_6 reference): 3.10 (sep, $^{3}J_{H-H} = 7.1$ Hz, 1H, C3–C*H*Me$_2$), 2.63 (s, broadened due to long range coupling, not resolved, 1H, C2–*H*), 2.54 (sepd, $^{3}J_{H-H} = 6.6$ Hz, $^{4}J_{H-H} = 2.9$ Hz, 1H, C4–CHMe$_2$), 2.23 (q, 1H, $^{3}J_{H-H} = 7.3$ Hz, C5–*H*), 1.93 (s, broadened due to long range coupling, not resolved, 3H, C2–C*H*$_3$), 1.48 (d, $^{3}J_{H-H} = 7.3$ Hz, 6H, C4–CHC*H*$_3$), 1.42 (d, $^{3}J_{H-H} = 7.3$ Hz, 6H, C4–CHC*H*$_3$), 1.29 (d, $^{3}J_{H-H} = 7.1$ Hz, 6H, C3–CHC*H*$_3$), 1.28 (d, $^{3}J_{H-H} = 7.5$ Hz, 6H, C3–CHC*H*$_3$), 0.85 (d, $^{3}J_{H-H} = 6.9$ Hz, 3H, C5–C*H*$_3$). ^{13}C-NMR (δ, without solvent, external C_6D_6 reference): 209.5 (s, 1C, C1), 172.6 (s, 1C, C3), 134.8 (s, 1C, C2), 56.4 (d, $^{1}J_{C-H} = 130$ Hz, 1C, C4), 39.9 (d, $^{1}J_{C-H} = 129$ Hz, 1C, C5), 30.2 (d, $^{1}J_{C-H} = 122$ Hz, 1C, C3–*C*HMe$_2$), 29.1 (d, $^{1}J_{C-H} = 120$ Hz, 1C, C4–*C*HMe$_2$), 22.3 (q, $^{1}J_{C-H} = 127$ Hz, 1C, *C*H$_3$), 21.3 (q, $^{1}J_{C-H} = 127$ Hz, 1C, *C*H$_3$), 19.8 (q, $^{1}J_{C-H} = 127$ Hz, 1C, *C*H$_3$), 19.0 (q, $^{1}J_{C-H} = 127$ Hz, 1C, *C*H$_3$), 15.9 (q, $^{1}J_{C-H} = 124$ Hz, 1C, *C*H$_3$), 8.8 (q, $^{1}J_{C-H} = 126$ Hz, 1C, C5–*C*H$_3$). Anal. Calc. for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 79.96; H, 11.63. MS (EI, 70 eV): 194 (M^{+}, 17%), 151 (M^{+} $-CHMe_2$, 25%), 140 (M^{+} $-C_4H_{10}$, 100%), 111 (**1**$^{+}$ $-C_2H_5$, 100%), 43 ($CHMe_2^{+}$, 12%), 41 ($C_3H_5^{+}$, 12%). Anal. Calc. for $C_{13}H_{22}O_2$: C, 80.35; H, 11.41. Found: C, 80.33; H, 11.53.

3.2. *Triisopropyldimethylcyclopentadiene, mixture of tautomers (**4**)*

To a 5% excess of isopropylmagnesium chloride in 50 ml of diethyl ether a solution of 24.79 g (128 mmol) of **3** in 35 ml diethyl ether are added dropwise. After complete addition the reddish–brown solution is warmed to reflux for 2 h and stirred at r.t. for another 12 h. The solution is then cooled in an ice bath and ca. 250 ml of diluted hydrochlorid acid (5%) are added slowly with stirring. The phases are separated, the water phase is extracted with 30 ml diethyl ether and the combined organic phases are washed with 100 ml of water, 100 ml of a sodium hydrogencarbonate solution and with two 15 ml portions of water. After stirring with anhydrous sodium sulfate the resulting solution is filtered over a medium porosity glass frit and the sodium sulfate residue washed with diethyl ether. The combined ethereal solutions are evaporated and from the residual oil (48 g) after a small forerun 20.17 g (91.5 mmol, 72%) of **4** were distilled over a vigreux column with a boiling range between 45 and 65°C as a mixture of tautomers. NMR spectra show a complex pattern as expected, which was not investigated in detail. Anal. Calc. for $C_{16}H_{28}$: C, 87.19; H, 12.80. Found: C, 86.28; H, 12.85.

3.3. *Diisopropyltrimethylcyclopentadiene, mixture of tautomers (**5**)*

A total of 29.15 g (150 mmol) of complex **3** was added dropwise to a magnetically stirred suspension of 22.50 g (149 mmol) of methylmagnesium chloride diethylether adduct in 100 ml of diethylether at a rate to maintain gentle reflux. After complete addition, the solution is kept under reflux for 2 h, then allowed to cool to r.t. Addition of ice and addition of 6% hydrochloric acid until the precipitated solids are completely dissolved is followed by phase separation and extraction of the aqueous solution with 50 ml of diethyl ether. The combined organic phases are washed with 100 ml saturated sodium hydrogencarbonate solution and with 100 ml water, then dried over sodium sulfate. Distillation over a vigreux column yielded 24.58 g (127.8 mmol, 85%) **7** as a yellow oil in a boiling range from 42–55°C at 0.1 mbar.

3.4. *Sodium 1,2,4-triisopropyl-3,5-dimethylcyclopentadienide (**6**)*

A total of 13.00 g (59.0 mmol) of complex **4** (tautomeric mixture) was added to a suspension of 3.46 g (89 mmol) sodium amide in 125 ml of tetrahydrofuran and heated to gentle reflux for 4 h. After centrifugation the light brown–yellow solution was evaporated to dryness and the yellowish solid washed with two 25 ml portions of petroleum ether to give 7.197 g (29.7 mmol, 50%) **6** as a white powder. ^{13}C{^{1}H}-NMR (C_4H_8O, δ): 119.7 (s, 1C, ring *C*CHMe$_2$), 117.2 (s, 2C, ring *C*CHMe$_2$), 103.2 (q, 2C, ring *C*CH$_3$, $^{2}J_{CH} = 5.4$ Hz), 28.1 (2C, *C*HMe$_2$[1]), 27.8 (1C, *C*HMe$_2$[1]), 25.8 (4C, CH(*C*H$_3$)$_2$[1]), 25.4 (2C, CH(*C*H$_3$)$_2$[1]), 14.5 (q, 2C, *C*H$_3$, $^{1}J_{CH} = 122$ Hz).

3.5. *Sodium 1,2,-diisopropyl-3,4,5-trimethylcyclopentadienide (**7**)*

A total of 23.97 g (124.6 mmol) of complex **5** (tautomeric mixture) was added to a suspension of 4.84 g

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[1] Coupling constant not determined due to signal superimposition.

(124.0 mmol) sodium amide in 150 ml of tetrahydrofuran and heated to gentle reflux for 12 h. After centrifugation the brown–orange solution was removed from the colourless precipitate of **7**. Washing with two 25 ml portions of petroleum ether gave 9.26 g (43.2 mmol, 35%) **7** as a white powder.

3.6. *1,1′,2,2′-tetraisopropyl-3,3′,4,4′,5,5′-hexamethyl-manganocene (**8**)*

To a suspension of 0.50 g (4.0 mmol) of anhydrous manganese(II)chloride in 5 ml of tetrahydrofuran a solution of 1.72 g (8.0 mmol) sodium 1,2-diisopropyl-3,4,5-trimethylcyclopentadienide in 10 ml of tetrahydrofuran was added via addition funnel at -70°C. The resulting brown–yellow suspension was allowed to warm up and was stirred at r.t. for another 5 h. After evaporation of the solvent the brown residue was extracted with ca. 50 ml of petroleum ether and the extract subjected to centrifugation. Evaporation to dryness gave 0.22 g (0.50 mmol, 25%) of orange–red **8** as a microcrystalline solid. Analytical samples were obtained by recrystallization from petroleum ether at -78°C. Anal. Calc. for $C_{28}H_{46}Mn$: C, 76.85; H, 10.60. Found: C, 75.47; H, 10.38. $\mu_{eff} = 2.14$ B. M.

3.7. *1,1′,2,2′-Tetraisopropyl-3,3′,4,4′,5,5′-hexamethyl-ferrocene (**9**)*

A total of 0.61 g (2.0 mmol) [$FeBr_2$(DME)] and 0.86 g (4.0 mmol) NaC_5R_2-1,2-Me_3-3,4,5 (R = $CHMe_2$) were suspended and partially dissolved in 40 ml of THF and stirred for 1 h under reflux. The solvent was then removed in vacuo and the orange–brown residue was extracted with 30 ml of petroleum ether. After centrifugation and evaporation of the solution **9** was obtained as a crude, brown solid. Recrystallization from petroleum ether at -78°C yielded 0.275 g (0.63 mmol, 31%) of brown–yellow **9**, which sublimes on heating above 100°C/10^{-5} mbar. ^{1}H-NMR (δ, C_6D_6): 2.74 (sep, 2H, CHMe$_2$), 1.75 (s, 6H, CCH_3), 1.64 (s, 3H, CCH_3), 1.32 (d, $J_{H-H} = 7.2$ Hz, 6H, CHMe$_2$), 1.23 (d, $J_{H-H} = 6.8$ Hz, 6H, CHMe$_2$). ^{13}C-NMR (δ, C_6D_6): 90.6 (2C, ring CCHMe$_2$), 81.2 (1C, ring C4), 77.2 (2C, ring C3,C5), 26.5 (d, 2C, CHMe$_2$, $^1J_{C-H} = 125$ Hz), 24.0 (q, 4C, CH(CH$_3$)$_2$, $^1J_{C-H} = 125$ Hz), 11.8 (q, 2C, C3–CH$_3$, C5–CH$_3$, $^1J_{C-H} = 125$ Hz), 10.3 (q, 1C, C4–CH$_3$, $^1J_{C-H} = 125$ Hz). MS (EI, 70 eV): 438 (M$^+$, 100%), 149 ($C_5Me_3HR^+$, 50%, R = $CHMe_2$), 43 ($CHMe_2^+$, 47%). Anal. Calc. for $C_{28}H_{46}Fe$: C, 76.69; H, 10.57. Found: C, 75.07; H, 10.83.

3.8. *1,1′,2,2′,4,4′-Hexaisopropyl-3,3′,5,5′-tetramethyl-ferrocene (**10**)*

A total of 1.52 g (5.0 mmol) [$FeBr_2$(DME)] and 2.40 g (10.0 mmol) NaC_5R_3-1,2,4-Me_2-3,5 (R = $CHMe_2$) were suspended and partially dissolved in 50 ml THF and stirred for 1 h under reflux. The solvent was then removed in vacuo and the orange–brown residue was extracted with 30 ml of petroleum ether. After centrifugation and evaporation of the solution **10** was obtained together with oily byproducts which were removed almost completely by warming to 50–60°C at 10^{-4} mbar. Recrystallization from petroleum ether at -78°C yielded 1.59 g (3.21 mmol, 64%) of **10**. Analytical samples were obtained by sublimation at 120°C/10^{-5} mbar as orange–red crystals. ^{1}H-NMR (δ, C_7D_8, 293 K): 2.81 (sep, $^3J_{H-H} = 7.0$ Hz, 4H, CHMe$_2$), 2.75 (sep, $^3J_{H-H} = 7.0$ Hz, 2H, CHMe$_2$) , 1.76 (s, 12H, CCH_3), 1.30 (d, $^3J_{H-H} = 7.0$ Hz, 12H, CH(CH_3)$_2$), 1.24 (d, $^3J_{H-H} = 7.0$ Hz, 12H, CH(CH_3)$_2$), 1.20 (d, $^3J_{H-H} = 7.0$ Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H}-NMR (δ, C_7D_8, 298 K): 91.6 (1C, ring CCHM$_2$), 90.8 (2C, ring CCHMe$_2$), 75.4 (2C, ring CMe), 27.1 (d, 1C, CHMe$_2$, $^1J_{C-H} = 123$ Hz), 26.9 (d, 1C, CHMe$_2$, $^1J_{C-H} = 126$ Hz), 24.3 (q, 2C, CH(CH$_3$)$_2$, $^1J_{C-H} = 125$ Hz), 24.0 (q, 2C, CH(CH$_3$)$_2$, $^1J_{C-H} = 126$ Hz), 23.5 (q, 2C, CH(CH$_3$)$_2$, $^1J_{C-H} = 125$ Hz), 12.5 (q, 2C, ring CCH$_3$, $^1J_{C-H} = 125$ Hz). Anal. Calc. for $C_{32}H_{54}Fe$: C, 77.10; H, 11.69. Found: C, 77.34; H, 10.88.

4. Supplementary material

Listings of anisotropic temperature factors and atomic coordinates with equivalent isotropic displacement parameters, hydrogen atom parameters, and complete bond distances and angles of complexes **8** and **11** can be obtained from the authors on request.

5. Conclusions

The possibility to synthesize 2,5-diisopropyl-3,4-dimethylcyclopentenone from cheap bulk chemicals makes a range of previously unknown cyclopentadienyl ligands with considerable steric bulk accessible for the first time. It also shows that condensation reactions like the economic procedure developed by Jutzi 15 years ago still bear interesting synthetic potential.

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[25] Crystal structure determination of octaisopropylferrocene $FeC_{34}H_{58}$ (**11**): Siemens P4 four circle diffractometer, Mo–K_α radiation, $\lambda = 71.073$ pm, $2\Theta_{max} = 55.0°$, $T = 293(2)$ K, crystal dimensions $0.45 \times 0.30 \times 0.12$ mm^3, monoclinic, space group $P2_1/n$, lattice parameters (293 K): $a = 10.657(5)$, $b = 17.548(5)$, $c = 16.792(5)$ Å, $\beta = 95.721(5)°$, $V = 3125(2)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.111$ g cm^{-1}, μ(Mo–K_α) = 5.01 cm^{-1}, empirical absorption correction (ψ scans), transmission factors 0.81734–0.73196, structure solution: direct methods (SIR97), full-matrix least-squares refinement based on F_o^2 (SHELXL-97), 9151 reflections, 7181 unique reflections, 349 parameters, 55 restraints, $R_1(F_o > 2\sigma(F_o)) = 0.0597$, $wR_2 = 0.1281$, R_1(all data) = 0.1294, $wR_2 = 0.1577$, residual electron density +0.723 to −0.571 e Å^{-1}. Hydrogen atoms have been localized using the riding model provided with SHELXL-97.

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