Formation of Quaternary Stereogenic Centers by Wagner-Meerwein Rearrangement – Synthesis of Optically Active Cyclopentadienyl Complexes from Borneol and Fenchol

Christian Färber[a], Gotthelf Wolmershäuser[b], and Helmut Sitzmann[b]

[a] FB 18 der Universität, Mönchebergstraße 19, D-34109 Kassel, Germany
[b] FB Chemie der TU, Erwin-Schrödinger-Straße 54, D-67663 Kaiserslautern, Germany

Reprint requests to Prof. Dr. Helmut Sitzmann. Fax: +49-631-205-4676.
E-mail: sitzmann@chemie.uni-kl.de

Z. Naturforsch. **2009**, *64b,* 25 – 40; received September 24, 2008

Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

The development of optically active cyclopentadienyl complexes as enantioselective catalysts calls for simple synthetic procedures for cyclopentadienes with optically active alkyl substituents. While *exo*-bornyl chloride and *exo*-fenchyl bromide do not react or exclusively eliminate hydrogen halide with cyclopentadienylmetal compounds in ether solvents or ammonia, they undergo Wagner-Meerwein rearrangement and substitution with cyclopentadienylmagnesium chloride in toluene. The bornyl cation yields racemic *exo*-bornylcyclopentadiene and partially racemized isocamphylcyclopentadiene, but for the fenchyl cation no racemization pathway is available, and the main diastereomer among the lithium salts of the ensuing substituted cyclopentadienes can be isolated in 95 % diastereomeric purity by solvent extraction. This material with the IUPAC name lithium (2*R*)-2,5,5-trimethylbicyclo[2.2.1]hept-2-ylcyclopentadienide carries an alkyl substituent having no trivial name so far. *Exo*-norbornylcyclopentadiene could be synthesized in high yield with a similar procedure. The same protocol works with 1-bromoadamantane. The novel alkylcyclopentadienes have been converted to ferrocenes and molybdenum complexes of the type $[Cp^RMo(CO)_3CH_3]$. (2*R*)-2,5,5-Trimethylbicyclo[2.2.1]hept-2-ylcyclopentadiene with an optical purity of 78 % *ee* (the optical purity of the starting material fenchol) was converted into an optically active titanocene dichloride and tested in the catalytic hydrogenation of 2-phenyl-1-butene. The hydrogenation product was obtained with 31 % *ee*, which compares favorably with results obtained with other group 4 metallocene dichlorides with one optically active alkyl substituent on each ring ligand. Facile procedures for the synthesis of the starting compounds *exo*-bornyl chloride and *exo*-fenchyl bromide based on the tosylate method have been developed with a tosylate melt or with toluene serving as solvents.

Key words: Bornyl Chloride, Fenchyl Bromide, Optical Activity, Enantioselective Hydrogenation, Titanocene Dichloride

Introduction

Catalytically active cyclopentadienyl complexes of early and late transition metals as well as lanthanides are available for a broad variety of synthetic reactions in organic chemistry. Examples are hydrogenation [1, 2], hydroboration, hydrosilylation, intramolecular hydroamination/cyclization [3], hydrophosphination, Diels-Alder cycloaddition reactions [4, 5], di- [6], oligo- [7] and polymerization [8, 9] of olefins [10], carboalumination [11], and other transformations. There are many cyclopentadienyl ligands with optically active substituents known in the literature [12]. Nevertheless, the design of optically active cyclopentadienyl and linked bis(cyclopentadienyl) ligands for catalytic applications is often related to the work of Kagan on menthyl- or neomenthylcyclopentadienide. The success of this seminal paper is owed to the ease of the synthetic procedure, which converts readily available menthyl tosylate to neomenthylcyclopentadiene by nucleophilic substitution with sodium cyclopentadienide in 24 % yield [13].

Some odors of commercial interest like the camphoraceous odor [14] or the odor of sandalwood [15] are associated with terpene derivatives, which have been synthesized in considerable variety without employing reactions of nucleophiles with terpene alcohol derivatives. Chiral pool alcohols such as borneol

or fenchol have been the object of mechanistic studies and analytic work, but have not been used for the introduction of optically active alkyl groups by nucleophilic substitution on a preparative scale. We were attracted by the perspective of optically active cyclopentadienyl ligand syntheses offered by terpene cages. When starting this work, we certainly anticipated experimental problems related to Wagner-Meerwein rearrangements, but hoped to find a way to generate novel cyclopentadienyl ligands with optically active substituents comparable in yield and number of steps to the procedure of Kagan [13].

Results and Discussion

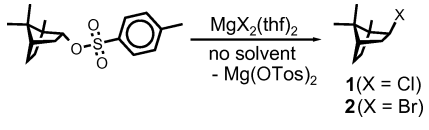
Initial attempts at a nucleophilic substitution in bornyl tosylate with sodium cyclopentadienide failed to yield any detectable amount of substitution product in tetrahydrofuran, diethyl ether, dimethoxyethane, or liquid ammonia. There was either no reaction, or (at elevated temperatures) only elimination products could be detected by GC-MS. Similar observations were made when potassium or lithium cyclopentadienide or cyclopentadienylmagnesium chloride were employed under similar conditions in ethereal solvents, respectively.

As alternative starting compounds *endo*-bornyl chloride, available by addition of hydrogen chloride to β-pinene in chloroform or petroleum ether [16–18], albeit with significant fenchyl chloride contamination [19], and *exo*-bornyl chloride were taken into consideration. The most facile procedure given in the literature for the *exo* derivative is the selenium dioxide-catalyzed conversion of borneol with chlorotrimethylsilane [20], but in our hands only the silyl ether of borneol could be distilled from the reaction mixture in almost quantitative yield. The procedure given by Marinetti [21] allowed us to prepare the desired *exo*-bornyl chloride from *endo*-borneol with two equivalents of triphenylphosphane oxide in boiling tetrachloromethane. The bornene by-product could be removed almost completely by repeated product sublimation.

Experiments with cyclopentadienyllithium, -sodium or -magnesium compounds were all unsuccessful. Only with cyclopentadienylmagnesium chloride in toluene *exo*-bornyl chloride gave a trace of a product with the GC retention time and mass expected for a substitution product. The desired substitution reaction in our hands works reproducibly when cyclopentadienylmagnesium chloride and *exo*-bornyl chloride are reacted in toluene suspension at rather high concentrations of at least 1 mol/L around r. t. Use of cyclopentadienylmagnesium bromide leads to chloride/bromide exchange, followed by elimination. Under similar conditions *endo*-bornyl tosylate or *endo*-bornyl chloride react with cyclopentadienylmagnesium chloride to substitution products as well, albeit very slowly.

A more efficient procedure for the synthesis of *exo*-bornyl chloride appeared highly desirable, because we were unable to reproduce the 65 % yield given in lit. [21], and scale-up turned out unsuccessful in our hands as well. Since procedures involving hydrogen chloride formation would likely cause Wagner-Meerwein rearrangement reactions, we directed our attention towards the so-called "tosylate method" [22], which should allow for conversion of *endo*-bornyl tosylate with alkali chlorides or magnesium chloride in acetone or ethereal solvents to the desired product by an S_N2 mechanism with inversion. We were unable to find examples for the preparation of bicyclic alkyl halides like bornyl halides *via* the tosylate method in the literature, and experiments with different salts in acetone, dimethoxyethane or tetrahydrofuran failed to accomplish the exchange of tosylate for chloride or bromide.

Magnesium dichloride tetrahydrofuran adduct (1 : 2) could be used for the conversion of molten *endo*-bornyl tosylate to *exo*-bornyl chloride (**1**) in the absence of solvent:



The *exo*-bornyl chloride obtained showed the same optical purity as the material prepared according to the literature procedure ($[\alpha]^{20}$ = 41.02°; c = 17.3; Et_2O [21]).

The same method is also useful for the synthesis of *exo*-bornyl bromide (**2**), if the bis(tetrahydrofuran) adduct of magnesium bromide is used. The bromide obtained in 40 % yield is accompanied by elimination products. The literature method uses borneol, bromomethane, triphenylphosphane, and 1,2,4-triazolidine-3,5-dione and promises a 75 % yield [23]. Subsequent test reactions with **2** regarding nucleophilic substitution with cyclopentadienylmagnesium bromide led to extensive elimination without formation of the desired substitution products.

Table 1. Crystal structure determination of complexes **3**-Mo, **4**-Mo, **7**-Fe, and **11**-Fe.

	3-Mo	**4**-Mo	**7**-Fe	**11**-Fe
Formula	$C_{19}H_{24}MoO_3$	$C_{19}H_{24}MoO_3$	$C_{30}H_{38}Fe$	$C_{30}H_{42}Fe$
M_r, g mol^{-1}	396.32	396.32	454.45	458.49
Crystal size, mm^3	$0.60 \times 0.40 \times 0.20$	$0.50 \times 0.50 \times 0.42$	$0.52 \times 0.10 \times 0.02$	$0.44 \times 0.16 \times 0.08$
Space group	*Pbca*	$P2_12_12_1$	$P\bar{1}$	$P2_1$
a, Å	14.2276(8)	10.1324(8)	7.2385(18)	7.3302(6)
b, Å	12.6474(11)	11.7235(7)	11.127(3)	10.5777(8)
c, Å	20.1795(12)	15.2964(9)	13.992(4)	15.5927(16)
α, deg	90	90	84.75(4)	90
β, deg	90	90	89.48(3)	98.646(11)
γ, deg	90	90	86.60(3)	90
V, Å^3	3631.1(4)	1817.0(2)	1120.2(5)	1195.27(18)
Z	8	4	2	2
T, K	293(2)	293(2)	193(2)	293(2)
$D_{calc.}$, g cm^{-3}	1.450	1.449	1.347	1.274
μ, cm^{-1}	7.34	7.33	6.89	6.46
Transmission factors	0.684 – 0.817	0.6645 – 0.8167	0.7158 – 0.9864	0.7642 – 0.9501
θ range, deg	2.47 – 27.10	2.66 – 27.10	2.82 – 26.02	2.55 – 28.05
hkl range	±17, ±16, ±25	±12, ±15, ±19	±8, ±13, ±17	±8, ±13, ±20
Refl. measured	55798	29322	11285	14546
Refl. unique	3977	3954	4114	5359
R_{int}	0.0623	0.0810	0.2594	0.0961
Program used	SIR-97	SIR-97	SIR-97	SHELXS-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Data/restraints/param. ref.	3977/36/241	3954/95/287	4114/0/280	5359/1/286
$R1$ $[I \geq 2\sigma(I)]$[a]	0.0369	0.0294	0.0583	0.0420
$wR2$ (all data)[b]	0.1099	0.0725	0.1812	0.0788
x(Flack)	–	0.01(5)	–	−0.009(18)
GooF (all data)[c]	1.044	1.008	0.521	0.765
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	−0.538/0.502	−0.274/0.567	−0.564/0.436	−0.253/0.326

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 2.7067P]$ with $P = (F_o^2 + 2F_c^2)/3$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; [c] GooF $= \{\Sigma[w(F_o^2 - F_c^2)]/(n-p)\}^{1/2}$; n = number of reflections, p = number of ref. parameters.

The substitution reaction of **1** and cyclopentadienylmagnesium chloride was followed by metalation with *n*-butyllithium in diethyl ether to give a mixture of lithium salts of the monosubstituted cyclopentadiene diastereomers in 34 % yield [2 : 3 ratio of *exo*-bornylcyclopentadienyl lithium (**3**-Li, about 40 %) and isocamphylcyclopentadienyl lithium (**4**-Li, about 60 %)]. Crystallization for diastereomer separation was not successful for the lithium salt mixture. A somewhat better result was obtained by recrystallization of the potassium salt from a dimethoxyethane/petroleum ether mixture (1 : 1), but produced only very small amounts of pure salt of **4**-K. The most effective enrichment of diastereomers was accomplished with diethyl ether, which extracted isocamphylcyclopentadienyl lithium (**4**-Li) in more than 92 % diastereomeric purity and left an enriched sample of *exo*-bornylcyclopentadienyl lithium (**3**-Li) undissolved after several extraction steps, whose diastereomeric purity never exceeded 80 %, however.

Gas chromatography of *exo*-bornylcyclopentadiene (**3**-H) and isocamphylcyclopentadiene (**4**-H) allowed for peak separation of the enantiomers only for isocamphylcyclopentadiene. According to the measured intensities, the enantiomeric purity of this material is only 50 % *ee*, which is significantly lower than that of the starting material *exo*-bornyl chloride (78 % *ee*). This finding indicates partial racemization during the substitution reaction.

3-Li and **4**-Li were converted to ferrocenes in order to confirm the conclusions drawn from gas chromatography and to obtain more information about the optical purity of the *exo*-bornylcyclopentadienyl system **3**. ^{13}C NMR spectra of the corresponding ferrocene, **3**-Fe, show 15 main signals as expected for one isomer. Closer inspection of the spectra reveals two signals, which are split in two resonances of equal intensity each corresponding to *meso*-**3**-Fe and *rac*-**3**-Fe.

For **4**-Fe, each signal has a partner of about half the intensity of the main signal, which confirms the assignment of 50 % *ee* to the ligand **4**-H.

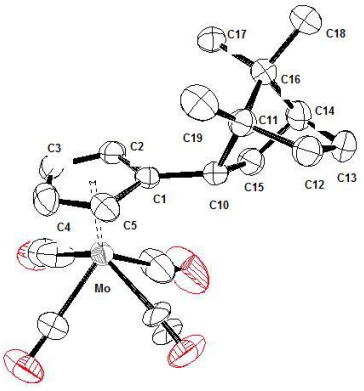


Fig. 1. Molecular structure of **3**-Mo in the crystal (the methyl group at the Mo atom and the CO ligand in *trans* position are disordered; displacement ellipsoids at the 50 % probability level). Bond lengths (Å) and angles (deg): Mo-C1 2.346(3), Mo-C2 2.323(3), Mo-C3 2.338(3), Mo-C4 2.322(3), Mo-C5 2.327(3), Mo-ring plane 2.002, C1-C2 1.422(5), C2-C3 1.379(6), C3-C4 1.386(7), C4-C5 1.414(5), C5-C1 1.419(5), C1-C10 1.508(4), C10-C15 1.536(4), C11-C19 1.493(5), C11-C12 1.532(5), C11-C16 1.550(5), C12-C13 1.527(7), C13-C14 1.525(6), C14-C15 1.538(5), C14-C16 1.522(5), C16-C17 1.529(5), C16-C18 1.539(5); angle between ring plane and line C1-C10 2.3°.

Molybdenum complexes of the type $[Cp^RMo(CO)_3CH_3]$ (Cp^R = substituted cyclopentadienyl ligand) were prepared for the ligand systems **3** and **4**.

EI mass spectra of **3**-Mo and **4**-Mo show the molecular ions with correct isotope patterns as well as carbon monoxide elimination products.

^{1}H NMR spectra of **3**-Mo show 11 signals, of which one multiplet is a superposition of three signals, and three resonances are superpositions of two signals each. The signals at lowest field, a pseudo-doublet and a pseudo-triplet of equal intensity, correspond to the four cyclopentadienyl protons, multiplets at 2.38, (1 H), 1.75 (3 H), 1.60 (2 H), and 1.19 ppm (2 H) are observed for the eight protons of the bicyclic cage, and four singlets are due to three methyl groups of the bornyl part and to the Mo-C*H*$_3$ group at highest field (0.32 ppm). ^{13}C NMR spectra show one signal for each carbon atom of **3**-Mo, three signals at low field (240.6, 227.4, and 227.3 ppm) for three carbonyl ligands, five signals for the ring carbon atoms, the alkyl-substituted carbon atom at 118.6 ppm, the four remaining ring C signals between 96.3 and 88.8 ppm, ten signals for the $C_{10}H_{17}$ bornyl cage between 50.0 and 14.1 ppm, and one signal at −20.6 ppm for the methyl carbon connected to the molybdenum atom.

Crystals of **3**-Mo suitable for X-ray diffraction were grown from diethyl ether solution. The structure shows

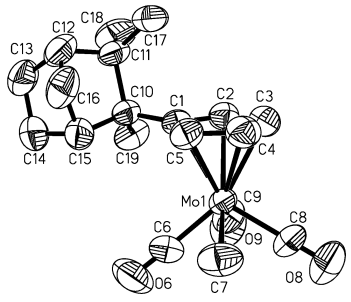


Fig. 2. Molecular structure of **4**-Mo in the crystal (the methyl group at the Mo atom and the CO ligand in *trans* position are disordered). Bond lengths (Å) and angles (deg): Mo-C1 2.382(4), Mo-C2 2.353(8), Mo-C3 2.331(6), Mo-C4 2.304(7), Mo-C5 2.294(9), Mo-ring plane 2.003; angle between ring plane and line C1-C10 7.6°.

a four-legged piano stool fragment with one *exo*-bornyl substituent. Fig. 1 shows the (1*S*)-(−) enantiomer. Both enantiomers are present in the unit cell and symmetry-related by an inversion center of space group *Pbca*. For selected bond lengths and angles see caption of Fig. 1.

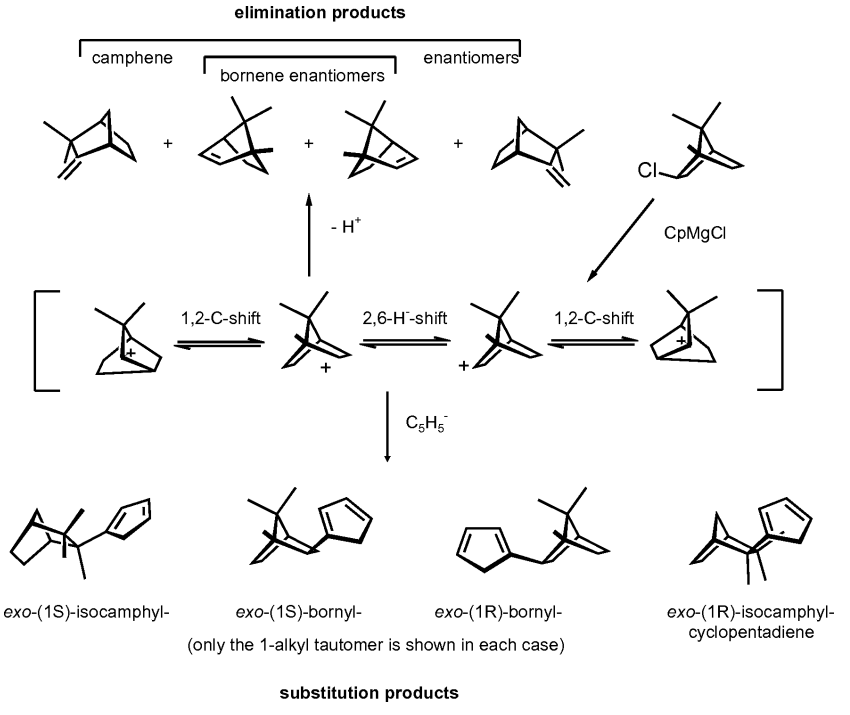
^{1}H NMR spectra of **4**-Mo indicate a tertiary alkyl substituent connected to the five-membered ring, because a signal in the allylic region comparable to the 2.38 ppm signal of **3**-Mo is missing here. Apart from four well-separated signals for the cyclopentadienyl protons between 4.7 and 4.3 ppm, the signal at lowest field is observed at 1.92 ppm.

^{13}C NMR spectra of **4**-Mo are very similar to those of **3**-Mo in their overall appearance, but the low-field signal among the five ring carbon resonances is observed at 128.1 ppm, which is 9.5 ppm lower than the corresponding signal of **3**-Mo as expected for a ring carbon atom connected to a tertiary alkyl substituent.

Crystals of **4**-Mo suitable for X-ray diffraction were obtained from diethyl ether solution. The crystal selected for structure determination belonged to the non-centrosymmetric space group $P2_12_12_1$ and consisted of the main enantiomer tricarbonyl-methyl-*exo*-[(1*R*)-2,3,3-trimethyl-bicyclo[2.2.1]hept-2-yl]-cyclopentadienyl-molybdenum(II), whose piano-stool fragment carries an isocamphyl substituent (Fig. 2).

Mechanistic considerations

The evidence presented in the preceding section calls for an explanation of the complete racemization for the *exo*-bornylcyclopentadiene and the partial racemization for the isocamphylcyclopentadiene formed in the substitution reaction of *exo*-bornyl chlo-



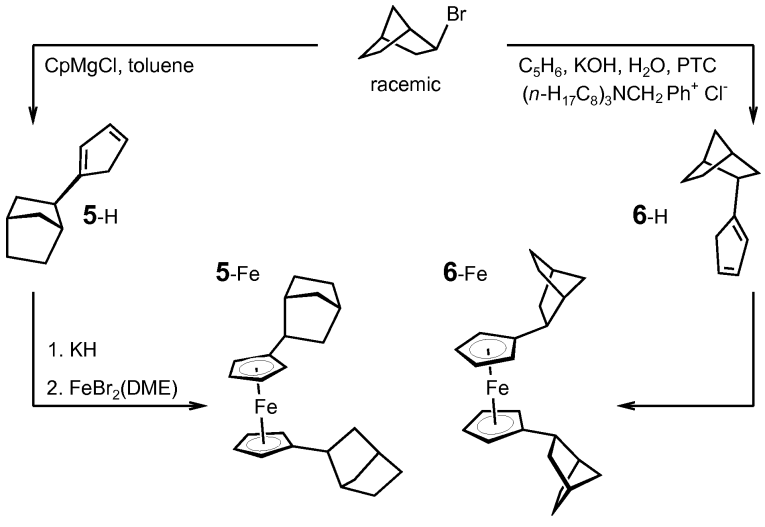
Scheme 1. Carbocations from *exo*-bornyl chloride, and their rearrangement leading to product formation by elimination or substitution.

ride (**1**) with cyclopentadienylmagnesium chloride. Early research work in this area was conducted by Meerwein [24, 25] who investigated rearrangement reactions of terpene derivatives first observed by his mentor Wagner about 20 years earlier. The so-called Wagner-Meerwein rearrangement was explained in terms of hydrogen migration and alkyl shift reactions of hypothetic carbenium ions and was investigated in more detail and largely confirmed by Bartlett and Pöckel [26, 27]. The observation of exclusive *exo* attack of nucleophiles at localized carbenium ions led to the formulation of a delocalized carbonium ion, which resembles both the bornyl and the camphyl cation [28]. The underlying concept was further elaborated, *e. g.* by Winstein [29] and by Ingold [30], and later the equivalence of C1, C2 and C6 of the norbornyl cation at −156 °C on the NMR time scale could be inferred from ^{13}C NMR spectra by Olah [31]. Acid-catalyzed racemization of camphene was explained as a consequence of hydride shifts by Hückel and Vogt [32].

The reactivity observed in our case is following these principles of rearrangement. Under the reaction conditions employed only the magnesium cation as a Lewis acid is well suited to induce carbocation reactivity. Because the toluene solvent does not favor formation of free ions, contact ion pairs are most likely present as intermediates.

Scheme 1 accounts for substitution products as well as for the elimination products observed, whose major constituent camphene has been identified by comparison of the gas chromatograms of reaction solutions without and with addition of pure camphene.

Lewis acid attack of Mg^{2+} at the chloro substituent of **1** generates a secondary bornyl cation prone to rearrangement reactions. If the bornyl cation initially formed has a significant lifetime, its substitution product can not be completely racemic. We have to assume that this "classical", secondary cation instantaneously rearranges either to the tertiary camphyl cation *via* a 1,2-alkyl shift, or to a nonclassical, hydride-bridged carbocation, which results in complete racemization of elimination or substitution products originating from this intermediate. Among those initially formed secondary bornyl cations, which end up in substitution products (34 % of the starting compound **1**), 62 % rearrange to the symmetric and hence racemic, non-classical bornyl carbocation, and 38 % undergo 1,2-C shift to form the optically active part of the camphyl cation. The latter is trapped by C-C bond formation with the cyclopentadienyl anion *via* the *exo* face as optically active **4**-H. The symmetrical carbonium



Scheme 2. Synthesis of *exo*- and *endo*-norbornylcyclopentadiene (only the 1-alkyl tautomer shown) and of the ferrocenes **5**-Fe and **6**-Fe derived thereof (PTC: Phase Transfer Catalysis).

ion (62 %) is trapped by the cyclopentadienyl anion to form racemic *exo*-bornylcyclopentadiene **3**-H (40 %) or undergoes a 1,2-alkyl shift (22 %) to be trapped as the racemic part of **4**-H.

Substitution reactions with exo-norbornyl bromide and adamantyl bromide

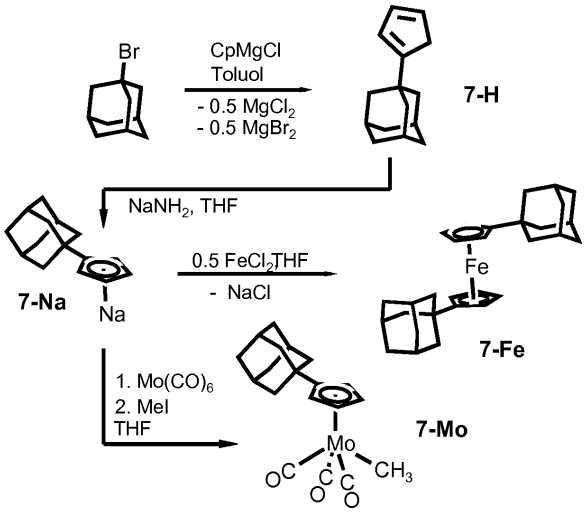
The synthetic methods developed for the conversion of borneol to cyclopentadiene derivatives were extended to *exo*-norbornyl bromide and adamantyl bromide.

Commercially available *exo*-norbornyl bromide could not be converted to norbornylcyclopentadienes in test reactions with cyclopentadienides of different metals in tetrahydrofuran at room or elevated temperatures. When *exo*-norbornyl bromide was added to a suspension of one equivalent of cyclopentadienylmagnesium chloride in toluene, the onset of a slow substitution reaction at r. t. could be detected by gas chromatography after a few hours of stirring. At 60 °C the reaction was almost complete within 2 h. The GC peak corresponding to the substitution product (**5**-H) had 90 % intensity, and a peak with 3 % intensity could be assigned to the elimination product. A tetrahydrofuran solution of the product was metalated with potassium hydride to furnish an 85 % yield of potassium *exo*-norbornylcyclopentadienide (**5**-K), which was converted to a ferrocene derivative (**5**-Fe) with iron(II) bromide for further characterization.

The needles of **5**-Fe crystallized from pentane solution appeared to be suitable for X-ray diffraction, but the data obtained could not be refined because the structure turned out to be incommensurable. The melting point of **5**-Fe was found at 80 – 82 °C, very close to the literature value given for 1,1′-bis(*exo*-norbornylcyclopentadienyl)iron(II) (81 – 83 °C [33]). For comparison, the *endo* isomer of norbornylcyclopentadiene (**6**-H) was synthesized in low yield *via* a phase transfer-catalyzed substitution reaction of *exo*-norbornyl bromide and cyclopentadiene in aqueous potassium hydroxide solution with a phase transfer catalyst. Potassium *endo*-norbornylcyclopentadienide (**6**-K) was obtained in 10 % yield and converted to bis(*endo*-norbornylcyclopentadienyl)iron(II) (**6**-Fe), which had a melting range of 98 – 99 °C (lit.: 96 – 98 °C [33]). In Scheme 2 the synthesis of *exo*- and *endo*-norbornylcyclopentadiene and of the ferrocenes **5**-Fe and **6**-Fe are outlined.

The substitution reaction of *exo*-norbornyl bromide with cyclopentadienylmagnesium chloride in toluene resembles the reaction of *exo*-bornyl chloride in producing only *exo* products. We assume, that a norbornyl cation is generated by Mg^{2+} attack and trapped by the cyclopentadienyl anion exclusively in *exo* position.

Adamantylcyclopentadiene (**7**-H) was previously synthesized in 97 % yield *via* reaction of 1-bromoadamantane with nickelocene and triphenylphosphane [34]. A substitution reaction of adamantyl halide with a cyclopentadienyl anion appears to be unknown. The reaction of 1-bromoadamantane with cyclopentadienylmagnesium chloride in toluene proceeds within 1 h at 100 °C. By GC-MS investigation of the reaction solution small amounts



Scheme 3. Synthesis of adamantylcyclopentadiene (**7**-H) and the complexes **7**-Fe and **7**-Mo.

of benzyladamantane were detected, which can be interpreted as an indication for radical intermediates. Traces of diadamantylcyclopentadiene (**8**) have also been detected. Workup and metalation with sodium amide furnished sodium 1-adamantylcyclopentadienide (**7**-Na) in 90 % isolated yield. Hydrolysis of a sample gave only one GC peak. The salt was used for the synthesis of 1,1′-bis(1-adamantylcyclopentadienyl)iron(II) (**7**-Fe) and (1-adamantylcyclopentadienyl)tricarbonyl-methyl-molybdenum(II) (**7**-Mo) (Scheme 3).

The ferrocene **7**-Fe was obtained in 90 % yield from **7**-Na and iron(II) chloride as an orange powder with a melting range of 185 – 187 °C. **7**-Fe is less soluble than the parent compound, which is unusual for 1,1′-dialkylferrocenes and demonstrates that the rigid adamantyl cage lowers the solubility. The ring protons appear as AA′BB′ spin system in ^{1}H NMR spectra taken in [D$_1$]chloroform, the adamantyl substituent exhibits four signals. Three equivalent CH_2 groups with equivalent pairs of protons give one signal at 1.72 ppm, the other set of three equivalent CH_2 groups with one axial and one equatorial proton each show up as one broadened doublet at 1.77 ppm. At 2.00 ppm the signal for three CH protons is observed. The material could not be sublimed, but crystallized from pentane as single crystals suitable for X-ray diffraction. The **7**-Fe sandwich shows a ring conformation intermediate between staggered and eclipsed, the metal-ring center distance of 1.66 Å is almost identical with the distance found for the parent compound. The C-C bond between

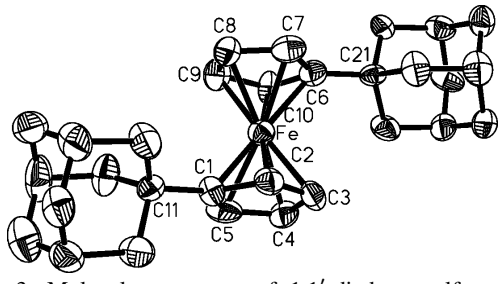


Fig. 3. Molecular structure of 1,1′-diadamantylferrocene (**7**-Fe) in the crystal (displacement ellipsoids 50 %). Bond lengths (Å) and angles (deg): Fe-C1 2.076(10), Fe-C2 2.047(11), Fe-C3 2.019(12), Fe-C4 2.041(11), Fe-C5 2.036(11), Fe-C6 2.066(11), Fe-C7 2.059(12), Fe-C8 2.052(12), Fe-C9 2.070(11), Fe-C10 2.029(11), Fe-ring plane 1.645 / 1.665; angle between ring plane and line C1-C11 6.2°, corresponding angle for line C6-C21 3.5°.

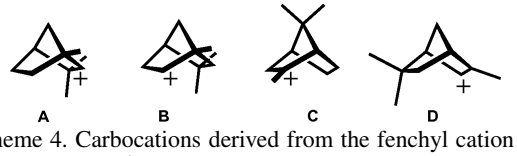
ring and substituent is bent out of the ring plane by 6.2° (Fig. 3).

(1-Adamantylcyclopentadienyl)tricarbonyl-methyl-molybdenum(II) **7**-Mo was obtained by the standard procedure (Scheme 3) as a light-brown powder, which could be sublimed at a pressure lower than 10^{-3} mbar at 95 °C without decomposition to form intensely yellow crystals. ^{13}C NMR spectra show the substituted ring C atom at 129.0 ppm, the ring-CH groups at 90.9 and 89.8 ppm, and the adamantyl carbon atoms at 44.6 (methyne, 3C), 36.7 (remote CH_2, 3C), 33.1 (*ipso*-C, 1C), and 29.0 ppm (CH_2 connected to C-*ipso*, 3C). The signal for the methyl ligand at molybdenum was observed at −21.0 ppm.

The fenchol approach

Fenchol was selected as another optically active starting material from the chiral pool. The secondary carbocation derived from fenchol should undergo Wagner-Meerwein rearrangement, but racemization should not occur (Scheme 4).

The cations **A** – **D** are all related to the fenchyl cation by hydride or alkyl shifts, but there is no symmetry relation between any two of them, all four are diastereomers. For this reason we may expect substitution products generated by *exo* attack of the cyclopen-



Scheme 4. Carbocations derived from the fenchyl cation by Wagner-Meerwein rearrangement.

tadienyl anion on fenchyl tosylate or halide to preserve the full optical activity of the starting compound fenchol.

A modified protocol for the synthesis of more than 100 g of fenchyl tosylate [35] free of unreacted fenchol in a 500 mL flask is described in the Experimental Section. This material together with cyclopentadienylmagnesium chloride was stirred in toluene at r. t. After 3 h a gas chromatogram showed mainly elimination products along with 26 % substitution products. Similar test runs at elevated temperatures resulted in more enhanced elimination.

A 29 % yield of a lithium salt mixture was obtained after workup of the substituted cyclopentadienes and metalation with *n*-butyllithium. The gas chromatogram of a hydrolyzed sample revealed four products with relative intensities 31 : 25 : 40 : 4. When metalation with *n*-butyllithium was carried out in hexane with 10 % tetrahydrofuran, a small amount of a colorless precipitate could be isolated by filtration. Gas chromatography after hydrolysis revealed that the precipitate was a lithium salt of the main component.

Turning to *exo*-fenchyl bromide, tosylate melt experiments with magnesium bromide tetrahydrofuran adduct gave more than 60 % yield of the desired *exo*-fenchyl bromide together with some elimination product contaminated with by-products. The tosylate method in toluene suspension, however, gave satisfactory results. The product **10** collected in high yield after fractional distillation was found to be 95 % diastereomerically pure, containing only traces of elimination products and fenchol.

In reactions of *exo*-fenchyl bromide (**10**) with cyclopentadienylmagnesium bromide in toluene it was demonstrated that **10** is the superior starting compound compared to the tosylate **9**. Not only the yield of the isolated lithium salt mixture after workup and metalation was above 30 %, the product selectivity was also increased.

The main product **11**-Li could be separated from the lithium salt mixture by diethyl ether extraction. Complexes **11**-Fe and **11**-Mo were prepared for its characterization.

^{1}H NMR spectra of the corresponding molybdenum complex $[(C_5H_4C_{10}H_{15})Mo(CO)_3CH_3]$ (**11**-Mo) prepared according to standard procedures revealed the absence of an allylic proton (no signal between 4.4 and 1.6 ppm), hence the alkyl substituent must be a tertiary alkyl group.

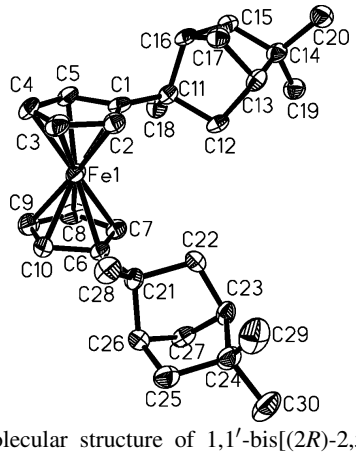
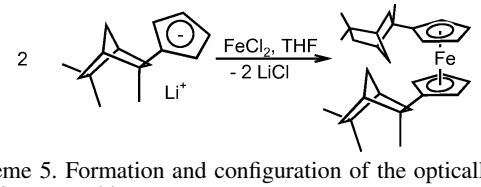


Fig. 4. Molecular structure of 1,1′-bis[(2*R*)-2,5,5-trimethylbicyclo[2.2.1]hept-2-yl]ferrocene (**11**-Fe) in the crystal. Bond lengths (Å) and angles (deg): Fe1-C1 2.068(4), Fe1-C2 2.042(4), Fe1-C3 2.040(4), Fe1-C4 2.050(4), Fe1-C5 2.062(4), Fe1-C6 2.071(4), Fe1-C7 2.046(4), Fe1-C8 2.032(4), Fe1-C9 2.053(4), Fe1-C10 2.047(4), Fe1-ring planes 1.659 / 1.659, C1-C11 1.521(6), C-C within the cyclopentadienyl unit between 1.386(7) and 1.440(6), within the C10 substituent between 1.517(6) and 1.570(5); angle at C1 bridge C16-C17-C13 94.0(3), C13-C14-C15 99.8(3), C15-C16-C17 99.6(3), angle between the two ring planes 1.6°.



Scheme 5. Formation and configuration of the optically active ferrocene **11**-Fe.

^{13}C NMR spectra of the crude ferrocene **11**-Fe show the dominant signals of the optically active compound and with low intensity the signals of the *meso* compound. Crystals suitable for X-ray diffraction were obtained from diethyl ether. The structural parameters are much like those of **7**-Fe except for the torsion angle of the two alkylcyclopentadienyl rings, which is 87.8° for **11**-Fe (Fig. 4). The space group is noncentrosymmetric ($P2_1$). Both rings carry the alkyl substituent in the same optically active configuration (Scheme 5).

The tertiary alkyl group seen in **11**-Fe has been observed in a few organic compounds, where it was called "β-fenchenhydro…", because this alkyl group to the best of our knowledge never received a name of its own. The corresponding tertiary alcohol, for example, was called "β-fenchene hydrate" [36].

The optical purity of the ligand could not be determined from the NMR spectra of **11**-Fe, but was assessed in the titanocene dichloride derivative with two (2*R*)-2,5,5-trimethylbicyclo[2.2.1]hept-2-yl substituents, $[(C_{10}H_{17}C_5H_4)_2TiCl_2]$ (**11**-Ti). In this case, a ^{1}H NMR signal at 2.28 ppm (doublet of doublets) shows a small satellite of the same type corresponding to the *meso* isomer of **11**-Ti. A crude sample showed an intensity ratio for both signals corresponding to an optical purity of the ligand of 78 % *ee*, whereas the optical purity was decreased in **11**-Ti "purified" by crystallization. Obviously the *meso* isomer is less soluble than the optically active component and is enriched by crystallization.

11-Ti was activated with *n*-butyllithium and tested as a catalyst for the hydrogenation of 2-phenyl-1-butene. For complete reaction a catalyst load of 1 mol-% was not sufficient similar to reports on other experiments with 5 [37] or even 10 mol-% of catalyst precursor. Analysis of the phenylbutane product showed a selectivity of 31 % *ee*. Taking into account the optical purity of the fenchol and the catalyst precursor **11**-Ti derived therefrom (78 % *ee*), the enantioselectivity of **11**-Ti in this hydrogenation experiment is higher than the 15 % *ee* value obtained with dichlorobis(methylcyclopentadienyl)-titanium [38] and comparable with that of dichlorobis-(phenylmenthylcyclopentadienyl)titanium [39], which showed the best performance among the titanocene derivatives with one optically active substituent per ring ligand in 2-phenylbutane hydrogenation so far (34 % *ee* [37]).

Conclusion

The tosylate method for conversion of alkyl tosylates to alkyl halides can be extended to the synthesis of *exo*-bornyl chloride and *exo*-fenchyl bromide using toluene as a solvent or the pure, molten tosylate without solvent. Substitution with cyclopentadienyl anions to give secondary or tertiary alkyl halides can be accomplished with cyclopentadienylmagnesium halides in toluene even in the case of *exo*-bornyl chloride, *exo*-fenchyl bromide, or adamantyl bromide, where with more common solvents or reagents such as lithium or sodium salts only elimination or no reaction take place. The substitution products obtained by cyclopentadienylmagnesium halide attack on secondary alkyl halides in toluene can be understood on the basis of carbocation reactivity and Wagner-Meerwein rearrangement. With adamantyl bromide under similar conditions, a contribution of radical processes must be concluded from the observation of traces of benzyladamantane besides the main product adamantylcyclopentadiene. The enantioselectivity in hydrogenation of 2-phenyl-1-butene with 1,1′-bis[(2*R*)-2,5,5-trimethylbicyclo[2.2.1]hept-2-yl]titanocene dichloride (**11**-Ti) as catalyst precursor (the optically active alkyl substituent was derived from *exo*-fenchyl bromide) compares favorably with similar results using other optically active substituents in the same class of catalysts and calls for further experiments with *ansa*-metallocene derivatives.

Experimental Section

All synthetic operations were performed under inert gas atmosphere in standard Schlenk apparatus. The separation of lithium cyclopentadienides by extraction with diethyl ether was carried out in a drybox from MBraun, Garching. Tetrahydrofuran and *n*-hexane were distilled from potassium metal, toluene from sodium metal. NMR spectra were taken on a Bruker DPX 400 NMR spectrometer. Chemical shifts are given in ppm and refer to the appropriate solvent signals. Mass spectra were taken on a Finnigan MAT 90 mass spectrometer.

*exo-Bornyl chloride (**1**)*

In a wide Schlenk tube under inert atmosphere, *endo*-bornyl tosylate (101 g, 327.5 mmol thoroughly ground, fine powder) and magnesium chloride tetrahydrofuran adduct (39.2 g, 163.8 mmol) are mixed carefully by shaking and rotating the vessel until the solids show uniform distribution. A stir bar is introduced, and the tube is closed with a ground glass joint cap equipped with stopcock and oil bubbler.

The Schlenk tube is immersed in a boiling water bath such that the outer water level is higher than that of the solids and the stopcock is opened to the oil bubbler for pressure equilibration. As soon as the mixture has melted, magnetic stirring is started.

After about ten minutes magnetic stirring may become impossible because of partial solidification of the melt. At this point a slow stream of inert gas is introduced into the Schlenk tube, the cap is removed and a mechanical stirrer is used in order to continue stirring for the last few minutes before the mixture turns solid. Heating is now switched off, but the vessel is left in the hot water bath for another 10 – 15 min for completion of the reaction.

The mixture is allowed to cool to r. t. and treated with ice and water (500 mL). The resulting suspension of organic material in a solution of magnesium salts is extracted with diethyl ether (1.2 L), and the ether extract is separated

and dried with magnesium sulfate. Complete evaporation of volatiles using a rotary evaporator operated at a pressure around 20 – 30 mbar without external heating gives an almost colorless, liquid residue, which is transferred to a 250 mL round-bottomed flask for sublimation. At *ca.* 0.1 mbar sublimation of the product proceeds between 60 and 80 °C water bath temperature. The residue in the sublimation flask shows no signs of decomposition and can be dissolved in pentane and cooled to 7 °C for recovery of pure bornyl tosylate (10.4 g, 33.7 mmol). *exo*-Bornyl chloride was obtained in a 43.7 g yield (253 mmol, 86.1 % with respect to bornyl tosylate consumption). – ^{1}H NMR ($CDCl_3$): δ = 3.95 (dd, J = 8.4 Hz, J = 4.7 Hz, 1H), 2.2 (m, 1H), 2.01 (m, AB, J = 13.8 Hz, J = 4.7 Hz, 1H), 1.78 (m, 1H), 1.71 (m, 1H), 1.68 (m, 1H), 1.1 (m, 2H), 1.09 (s, 3H), 0.99 (s, 3H), 0.85 (s, 3H). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 68.36 (1 C; *C*HCl), 49.78 (1 C), 47.40 (1 C), 46.07 (1 C), 42.42 (1 C), 36.26 (1 C), 26.95 (1 C), 20.46 (1 C), 20.11 (1 C), 13.42 (1 C). – Analysis for $C_{10}H_{17}Cl$ (172.69): calcd. C 69.55, H 9.92; found C 69.74, H 9.92. – Optical rotation: $[\alpha]_D^{20}$ = 41.02 °(c = 17.3; Et_2O).

*exo-Bornyl bromide (**2**)*

The same procedure as described for *exo*-bornyl chloride (**1**), using the tetrahydrofuran adduct of magnesium bromide instead of the chloride, gives pure *exo*-bornyl bromide, albeit in only 40 % yield. The sublimation residue is substantially larger than found for the chloride and does not consist of recoverable bornyl tosylate.

exo-Bornyl bromide is a colorless, waxy solid, which has a refreshing camphor-like smell and starts to turn brown as an indication of decomposition after a few days at r. t. in daylight. – ^{1}H NMR ($CDCl_3$): δ = 4.12 (dd, $^3J_{HH}$ = 8.66 Hz, $^3J_{HH}$ = 4.99 Hz, 1H), 2.37 (m, 1H), 2.08 (m, 1H), 1.75 (m, 3H), 1.14 (m, 2H), 1.1 (m, 2H), 1.13 (s, 3H), 1.02 (s, 3H), 0.85 (s, 3H). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 61.09 (1 C; *C*HBr), 49.28 (1 C), 47.72 (1 C), 46.63 (1 C), 42.87 (1 C), 36.45 (1 C), 26.91 (1 C), 20.46 (1 C), 20.07 (1 C), 15.37 (1 C). – Analysis for $C_{10}H_{17}Br$ (217.15): calcd. C 55.31, H 7.89; found C 54.64, H 7.81.

*(exo-Bornyl)cyclopentadiene (**3**-H), (exo-camphyl)cyclopentadiene (**4**-H), lithium(exo-bornyl)cyclopentadienide (**3**-Li) and lithium(exo-camphyl)cyclopentadienide (**4**-Li)*

To a mixture of cyclopentadienylmagnesium chloride diethyl ether adduct (35 g, 173 mmol) and toluene (70 mL) cooled in an ice bath, solid *exo*-bornyl chloride (30 g, 173 mmol) is added under inert gas. The reaction mixture is stirred for 1 h, then the ice bath is removed, and stirring is continued for several hours. The reaction is finished as soon as the *exo*-bornyl chloride has been consumed completely (GC control). Most of the toluene solvent is removed in a vacuum at r. t., and the remaining mixture is poured on ice water (250 mL) with an addition of 3 % hydrochloric acid (100 mL). Extraction with diethyl ether portions (700 mL in total), drying of the organic extracts with magnesium sulfate and evaporation of diethyl ether together with unsubstituted cyclopentadiene (resulting from hydrolysis of some unreacted cyclopentadienylmagnesium chloride) without external heating (this is important, because the monoalkylcyclopentadiene products could dimerize *via* Diels-Alder cycloaddition) gives a light-yellow oil, which is transferred to a Schlenk flask. By several cycles of evacuation and admission of inert gas traces of oxygen are removed, before dried and deoxygenated diethyl ether is introduced (120 mL). Metalation is accomplished by dropwise addition of *n*-butyllithium (1.6 mol/L in hexane, 50 mL, 80 mmol) with formation of a colorless precipitate. The mixture is stirred over night, and the solvent is completely removed *in vacuo*. The remaining solid is suspended in pentane (150 mL) and collected on a glass frit of medium porosity under inert gas. The almost colorless, sometimes ivory solid is washed with a small amount of pentane and dried *in vacuo* to give a mixture of monoalkylcyclopentadienyl lithium salts (12.2 g, 58.6 mmol, 33.9 %).

Four signals pertaining to four stereoisomers show up in the gas chromatogram of a hydrolyzed sample: t_R = 21.4 min (27.4 %), 22.0 min (59.5 %), 22.3 min (7.4 %) und 22.6 min (5.7 %).

Lithium (*exo*-camphyl)cyclopentadienide of more than 90 % diastereomeric purity can be separated in one step from the other diastereomers by diethyl ether extraction. Silicon grease should be avoided. The lithium salt mixture (1.8 g, 8.64 mmol) is suspended in dry diethyl ether (40 mL) and stirred for 10 min, then filtered through a medium porosity glass frit. The solution is evaporated to yield lithium (*exo*-camphyl)cyclopentadienide (0.55 g, 2.64 mmol, 30.6 %) of 92.3 % diastereomeric purity. In the solid residue on the filter (1.25 g, 6.00 mmol, 69.4 %) lithium (*exo*-bornyl)cyclopentadienide and lithium (*exo*-camphyl)cyclopentadienide are present in a 7 : 5 ratio. More extraction steps gave samples containing up to 76 % lithium (*exo*-bornyl)cyclopentadienide (52 % *de*), but failed to yield highly enriched material.

*Lithium (exo-camphyl)cyclopentadienide (**4**-Li)*

^{1}H NMR ([D_8]THF): δ = 5.59 (m, 4H, ring-C*H*), 2.51 (m, 1H), 1.85 – 1.70 (m, 3H), 1.40 – 1.12 (m, 3H), 1.27, 1.02, 0.60 (each: s, 3H, CH_3), 0.85 (m, 1H). – ^{13}C{^{1}H} NMR ([D_8]THF): δ = 129.10 (1C, ring-*C*-alkyl), 102.31 (2C, Cp ring-*C*), 100.34 (2C, Cp ring-*C*), 51.75, 49.96, 45.70, 43.87, 36.99, 30.50, 25.54, 24.96, 23.71, 22.56 (each: 1 C, alkyl cage).

*Lithium (exo-bornyl)cyclopentadienide (**3**-Li)*

^{1}H NMR ([D_8]-THF): δ = 5.63 – 5.56 (m, 4H, ring-C*H*), 2.89 – 2.85 (m, 1H, C*H*Cp), 2.29 – 2.24 (m, 1H), 1.78 – 1.55

(m, 4H), 1.27 (m, 2H), 1.03, 0.86, 0.84 (each: s, 3H, CH_3). – $^{13}C\{^1H\}$ NMR ([D_8]THF): δ = 122.03 (1C, ring-*C*-alkyl), 103.34 (2C, Cp ring-*C*), 101.38 (2C, Cp ring-*C*), 49.20, 48.81, 47.29, 46.57, 40.58, 37.39, 28.20, 21.52, 20.33, 14.64 (each: 1 C, alkyl cage).

*(exo-Norbornyl)cyclopentadiene (**5**-H) and potassium (exo-norbornyl)cyclopentadienide (**5**-K)*

To a magnetically stirred suspension of cyclopentadienylmagnesium chloride diethyl ether adduct (15.52 g, 78 mmol) in toluene (60 mL), *exo*-norbornyl bromide (13.63 g, 78 mmol) was added. The mixture was placed in an oil bath of 60 °C and stirring was continued for 2 h. Complete consumption of the bromide was indicated by GC. Most of the toluene was removed in a vacuum, the remaining mixture was poured on ice water (120 mL) containing hydrochloric acid (3 %, *ca.* 30 mL) and extracted with diethyl ether (200 mL). The combined organic phases were dried with magnesium sulfate, and most of the solvent was removed by rotary evaporation without external heating. The remaining oily liquid was transferred to a Schlenk flask, diluted with dry tetrahydrofuran (50 mL) and metalated by addition of potassium hydride in several portions (3.12 g, 78 mmol, addition of each portion was accompanied by vigorous gas evolution) with stirring at ambient temperature, which was continued for 2 h after complete hydride addition. The dark mixture was filtered, the filtrate evaporated to dryness and the residue washed several times with pentane. Drying *in vacuo* yielded potassium (*exo*-norbornyl)cyclopentadienide as a colorless powder (13.1 g, 66.3 mmol, 85 %).

*(endo-Norbornyl)cyclopentadiene (**6**-H) and potassium (endo-norbornyl)cyclopentadienide (**6**-K)*

A mixture of *exo*-norbornyl bromide (40.9 g, 234 mmol), freshly cracked cyclopentadiene (10.29 g, 156 mmol), water (70 mL), potassium hydroxide (46 g, 820 mmol), and the phase-transfer catalyst methyltrioctylammonium chloride (Adogen 464) (10 g, 24.7 mmol) was stirred mechanically at 60 – 80 °C for 1 h, and for another 30 min at 100 °C, and then allowed to cool to r. t.

Diethyl ether (150 mL) was added, the phases were separated, and the organic phase was washed with diluted hydrochloric acid (3 %, 100 mL) for neutralization, then dried with magnesium sulfate. Distillation of the dark material after evaporation of the solvent at 5 – 10 mbar gave a light-yellow liquid and left a dark, viscous material, which was discarded. The volatiles were subjected to fractional distillation at 5 mbar and gave a substantial forerun followed by a colorless liquid in a boiling range of 83 – 85 °C (2.82 g, 17.7 mmol, 11.3 %) at an oil bath temperature between 145 and 160 °C.

GC showed two closely spaced peaks in a 1 : 1 ratio typical for a pair of enantiomers, t = 17.0 and 17.2 min.

Metalation with potassium hydride (0.71 g, 17.7 mmol) in tetrahydrofuran (15 mL) proceeded with vigorous gas evolution. Work-up as described for the *exo* isomer produced potassium (*endo*-norbornyl)cyclopentadienide as a colorless powder (3.14 g, 15.8 mmol, 90 %).

*1-Adamantylcyclopentadiene (**7**-H)*

A mixture of 1-adamantyl bromide (8.47 g, 39.4 mmol), toluene (40 mL) and cyclopentadienylmagnesium chloride diethyl ether adduct (7.80 g, 39.4 mmol) was stirred at 60 °C oil bath temperature, and the reaction was monitored by GC until the bromide had been consumed, which took about 4 h. Most of the toluene was then evaporated in a vacuum at ambient temperature, the residue was diluted with diethyl ether (200 mL) and treated with diluted hydrochloric acid (3 %, 150 mL). The organic phase was dried with magnesium sulfate, reduced to *ca.* 100 mL volume and added dropwise to a boiling solution of isopropylmagnesium chloride freshly prepared from isopropyl chloride (3.59 mL, 40 mmol) and magnesium turnings (1.00 g, 41.1 mmol) in diethyl ether (50 mL). Addition of more diethyl ether (100 mL) was necessary to keep the product in solution, while stirring was continued over night at ambient temperature. Filtration in order to remove unreacted magnesium, evaporation of most of the solvent, addition of pentane (150 mL) for product precipitation and filtration over a glass frit of medium porosity gave adamantylcyclopentadienylmagnesium chloride diethyl ether adduct as a colorless powder (8.50 g, 27, mmol, 68.5 %) after drying *in vacuo*.

Remark: An excess of isopropylmagnesium chloride will not result in product contamination and can be removed by repeated washing with pentane containing 5 – 10 % diethyl ether.

*endo-Fenchyl tosylate (**9**)*

To a solution of fenchol (75 g, 486 mmol) in pyridine an excess of solid toluenesulfonyl chloride (104.86 g, 550 mmol) was added, and the mixture was stirred at 60 °C for 7 d, poured into a solution of concentrated hydrochloric acid (200 mL) in water (800 mL) and extracted with portions of diethyl ether (*ca.* 1.5 L). The combined organic extracts were treated with sodium hydrogencarbonate solution (500 mL) and with water (200 mL), then dried over magnesium sulfate. The solvent was removed to leave a colorless powder (141.5 g, 459 mmol, 94 %). – ^1H NMR ($CDCl_3$): δ = 7.90 (d, J = 8.3 Hz, 2H, aryl-H), 6.80 (d, J = 8.3 Hz, 2H, aryl-H), 4.29 (d, J = 1.9 Hz, 1H, C*H*OTs), 1.92 (s, 3H, aryl-CH_3), 1.90 – 1.82 (m, 1H), 1.74 – 1.68 (m, 1H), 1.57 (d, J = 3.8 Hz, 1H), 1.47 – 1.29 (m, 2H), 1.09 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 0.98 (d, J = 1.3 Hz, 2H), 0.97 (s, 3H, CH_3). –

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 144.34 (1C; aryl-C), 134.51 (1C; aryl-C), 129.56 (2C; aryl-C), 128.01 (2C; aryl-C), 94.11 (1C; CHOTs), 48.98 (1C), 48.08 (1 C), 41.14 (1C), 39.44 (1C), 29.36 (1C), 25.99 (1C), 25.69 (1C), 21.58 (1C), 20.99 (1C), 18.80 (1C). – Analysis for $C_{17}H_{24}O_3S$ (308.44): calcd. C 66.20, H 7.84; found C 66.22, H 7.74.

*exo-Fenchyl bromide (**10**)*

A three-necked flask was equipped with mechanical stirrer and inert gas inlet, immersed in an oil bath of 45 °C and charged with a suspension of magnesium bromide tetrahydrofuran adduct (53.22 g, 162.1 mmol) in toluene (250 mL). Solid fenchyl tosylate (100 g, 324.2 mmol) was added, and the mixture was stirred for 7 d. Complete conversion was confirmed by NMR spectroscopy. The mixture was poured onto ice water (600 mL), and the products were extracted with diethyl ether (250 mL). The combined organic extracts were dried over magnesium sulfate, and diethyl ether and toluene were removed at 40 °C. Vacuum distillation at 1.5 mbar using a Vigreux column (length 20 cm, inner diameter 15 mm) gave a main fraction in a boiling range from 47 to 49 °C, which solidified. According to the gas chromatogram the compound was 90 % pure and showed 95 % *de*. 59.17 g of the colorless liquid containing 50.59 g (233 mmol) product could be isolated. Fenchyl tosylate (6.0 g, 19.5 mmol) was recovered by recrystallization of the residue from pentane. – ^1H NMR (C_6D_6): δ = 3.57 (d, $^4J_{HH}$ = 2.4 Hz, 1H, C*H*Br), 1.83 – 1.78 (m (pdq), $^2J_{HH}$ 10.3 Hz, 1H), 1.55 (s (br), 1H), 1.45 – 1.30 (multiplets, 2H), 1.24 – 1.15(m, 2H), 1.24 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.00 – 0.91 (m, 1H), 0.88 (m (br), $^2J_{HH}$ = 10.3 Hz, 1H), 0.81 (s, 3H, CH_3). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 76.83 (1 C; *CH*Br), 50.61, 49.74, 44.23, 41.56, 35.74, 31.26, 26.24, 25.50, 21.82 (1 C each).

*Synthesis and metalation of substituted cyclopentadienes including **11**-H from fenchyl tosylate*

a) *Experiment 1 without ultrasound irradiation:* To a suspension of cyclopentadienylmagnesium chloride diethyl ether adduct (14.0 g, 70 mmol) in toluene (30 mL) fenchyl bromide was added in one portion (13.9 g, 90 % purity, 57.6 mmol), and the mixture was stirred over night at ambient temperature. The toluene was removed almost completely under vacuum without external heating, then diethyl ether (400 mL) and a mixture of ice water (200 mL) with concentrated hydrochloric acid (50 mL) was added. The phases were separated, the aqueous phase was extracted with diethyl ether (100 mL), and the combined organic extracts were dried over magnesium sulfate. By complete evaporation of the diethyl ether *in vacuo* any residual unsubstituted cyclopentadiene was removed, and the remainder was stirred with diethyl ether (75 mL) and degassed by brief exposition to a vacuum. Then the vessel was flushed with inert gas. Metalation with *n*-butyllithium (1.6 M, 20 mL, 32 mmol) gave a light-yellow suspension. Work-up as described above gave a colorless mixture of diastereomers containing 57.4 % lithium (2*R*)-2,5,5-trimethylbicyclo[2.2.1]-hept-2-ylcyclopentadienide **11**-Li, and two other diastereomers (16.3 % and 26.3 %); total yield of lithium salts 3.64 g (17.5 mmol, 30.4 %).

b) *Experiment 2 with ultrasound irradiation:* In a thick-walled Schlenk tube cyclopentadienylmagnesium chloride diethyl ether adduct (10.00 g, 50.16 mmol) was suspended in toluene (10 mL), and a solution of fenchyl bromide (9 mL, 11.0 g, 92.6 % purity containing 7.4 % elimination product, 47 mmol) in toluene (10 mL) was added at once. The magnetically stirred suspension was sonicated for 24 h while the temperature of the ultrasound bath was kept at 20 °C. After 24 h of sonication diluted hydrochloric acid (3 %, 50 mL) was added, and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were dried over magnesium sulfate, and the solvents were removed almost completely *in vacuo*. The remaining light-yellow liquid was dissolved in diethyl ether (100 mL), and a hexane solution of *n*-butyllithium (1.5 m, 25 mL, 37.5 mmol) was added at ambient temperature. The mixture was stirred magnetically over night, then the suspension was reduced in volume to 50 mL *in vacuo*, hexane was added (50 mL), and the product was collected on a medium porosity glass frit as a light-yellow powder, which was washed with pentane (50 mL) and dried *in vacuo*. Yield: 4.68 g (22.5 mmol, 45 %) consisting of **11**-Li (48 %) and two other diastereomers (24 % and 28 %).

*Diethyl ether extraction of **11**-Li*

The lithium salt mixture obtained from one of the procedures given above is placed on a medium porosity glass frit and extracted several times with portions of diethyl ether (10 mL per gram of lithium salt mixture). **11**-Li is sparingly soluble and remains on the frit, the other diastereomers are found in the extract. After about eight washings the diastereomeric purity of the remaining **11**-Li is better than 90 %. – ^1H NMR ([D_8]THF): δ = 5.6 (m ABCD spin system), 4H, ring-C*H*), 2.14 (m, 1H), 1.69 – 1.59 (m, 5H), 1.58 – 1.51 (m, 2H), 1.36 (s, 3H, CH_3) 1.15 (s, 6H, CH_3). – $^{13}C\{^1H\}$ NMR ([D_8]THF): δ = 133.02 (1C, ring-*C*-alkyl), 101.06, 100.77 (2C each, Cp ring *C*), 51.45, 41.32, 40.05, 38.23, 37.78, 37.20, 36.77, 32.15, 29.21, 25.54 (1 C each, cage *C* atom).

Ferrocene derivatives

The ferrocene derivatives have all been synthesized using the same experimental procedure: The alkali alkylcyclopentadienide was stirred with iron(II) chloride or bromide dimethoxyethane adduct in a 2 : 1 molar ratio in tetrahydrofuran at ambient temperature for 24 h. The solvent was then removed *in vacuo*, and the product was

extracted with pentane (*e. g.* two extraction steps with 2×20 mL pentane for 1 mmol of iron halide used). The evaporated pentane extracts gave orange-yellow oils or tarry solids, whose NMR spectra showed free ligand as the only detectable impurity. All crystallizations were carried out from diethyl ether solution between −30 and −70 °C.

*Bis(exo-bornylcyclopentadienyl)iron (**3**-Fe)*

From lithium *exo*-bornylcyclopentadienide (**3**-Li) (1.50 g, 7.2 mmol) and iron(II) bromide dimethoxyethane adduct (1.10 g, 3.6 mmol) in tetrahydrofuran (50 mL) an oily product was generated by the general method described before. Recrystallization from diethyl ether (7 mL) at −30 °C gave an orange-yellow, microcrystalline precipitate. Yield: 1.38 g (3.0 mmol, 83 %), melting range 101 – 102 °C. – ^{1}H NMR ($CDCl_3$): Broad signals due to superposition of signals of *rac* and *meso* diastereomers, δ = 4.03 – 3.92 (m, 8H, Cp-*H*), 2.79 – 2.70 (m, 2H), 2.05 – 1.95 (m, 2H), 1.86 – 1.72 (m, 4H), 1.62 – 1.54 (2H), 1.39 – 1.15 (m, 6H), 0.94 / 0.92 (s, 6H, C*H*$_3$), 0.80 / 0.79 (s, 12H, C*H*$_3$). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 91.05 (2 C; R*-*C*, Cp ring), 71.53 (2 C; ring *C*H), 68.53 (2 C; ring *C*H), 67.62 (2 C; ring *C*H), 67.40 (2 C; ring *C*H), 49.21 (2 C, cage C), 48.59 (2 C, cage C), 47.24 (2 C, cage C), 45.64 (2 C, cage C), 39.98 (2 C, cage C), 35.66 (2 C, cage C), 27.68 (2 C, cage C), 21.31 (2 C, cage C), 19.99 (2 C, cage C), 14.04 (2 C, cage C). – Analysis for $C_{30}H_{42}Fe$ (458.51): calcd. C 78.59, H 9.23; found C 78.21, H 9.32.

*Bis(exo-camphylcyclopentadienyl)iron (**4**-Fe)*

From lithium *exo*-camphylcyclopentadienide (**4**-Li) (373 mg, 1.8 mmol) and iron(II) bromide dimethoxyethane adduct (270 mg, 0.9 mmol) in tetrahydrofuran (20 mL) an oily product was generated by the general method described above. Recrystallization from saturated diethyl ether solution at −30 °C gave an orange-yellow, microcrystalline product, which melted at 144 – 145 °C and could be sublimed at 138 – 142 °C, 10^{-3} mbar. Yield: 321 mg (0.70 mmol, 78 %) mixture of rac and meso diastereomers (see Results and Discussion). – ^{1}H NMR (C_6D_6): δ = 4.12 (s(br), 1H, ring C*H*), 3.98 (s(br), 2H, ring C*H*), 3.76 (s(br), 1H, ring C*H*), 2.54 (s(br), 1H), 2.14 (d, J_{HH} = 8.8 Hz), 1.88 – 1.80 (m, 1H), 1.70 – 1.60 (m, 2H), 1.38 – 1.32 (m, 1H), 1.34 (1.31) (s, 3H, C*H*$_3$), 1.17 (m (2 lines), 1H), 0.90 (s, 3H, C*H*$_3$), 0.80 – 0.73 (m, 1H), 0.60 (0.59) (s, 3H, C*H*$_3$). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 99.34 (2 C; R*-*C*, Cp ring), 68.58 (2 C; ring *C*H), 67.73 (2 C; ring *C*H), 67.32 (2 C; ring *C*H), 67.30 (2 C; ring *C*H), 50.54 (2 C, cage C), 48.38 (2 C, cage C), 43.97 (2 C, cage C), 43.58 (2 C, cage C), 36.83 (2 C, cage C), 29.60 (2 C, cage C), 24.87 (2 C, cage C), 23.12 (2 C, cage C), 23.00 (2 C, cage C), 22.28 (2 C, cage C). – Analysis for $C_{30}H_{42}Fe$ (458.51): calcd. C 78.59, H 9.23; found C 78.69, H 9.49. – EI-MS: m/z = 458 (M^+, 100 %).

*Bis(exo-norbornylcyclopentadienyl)iron (**5**-Fe)*

From potassium *exo*-norbornylcyclopentadienide (**5**-K) (300 mg, 1.50 mmol) and iron dibromide dimethoxyethane adduct (231 mg, 0.76 mmol) in tetrahydrofuran (20 mL) an oily product was obtained according to the general procedure given before and recrystallized from saturated diethyl ether solution to give thin, light-yellow needles (183 mg, 0.50 mmol, 66.1 %) which melted at 80 – 82 °C. – ^{1}H NMR ($CDCl_3$): δ = 3.99 (m, 2H, ring C*H*), 3.91 (m, ring C*H*, 2H), 2.46 (m, 1H, Cp-C*H*), 2.27, 2.06, 1.6 – 1.45 (m, 4H), 1.45 – 1.13 (m, 4H). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 94.84 (1C, ring *C*-alkyl), 68.27, 68.06, 67.85, 67.70 (1C each, ring *C*-H), 44.70, 42.46, 39.03, 36.39, 35.83, 30.18, 29.02. – Analysis for $C_{24}H_{30}Fe$ (374.35): calcd. C 77.00, H 8.08; found C 77.01, H 8.06.

*Bis(endo-norbornylcyclopentadienyl)iron (**6**-Fe)*

The known compound was synthesized just like the *exo* derivative, using **6**-K for comparison of the two stereoisomers. M. p. 98 – 99 °C. – ^{1}H NMR ($CDCl_3$): δ = 3.98, 3.92 (both m, 2H, ring C*H*), 2.85, 2.20, 2,06, 1,86 (both m, 1 H), 1.50 – 1.35 (m, 7H). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 90.60 (1C, ring *C*-alkyl), 69.98, 68.73, 67.95, 66.91 (1C each, ring *C*H), 44.09, 41.55, 40.76, 37.81, 36.15, 30.35, 23.54.

*Bis(adamantylcyclopentadienyl)iron (**7**-Fe)*

From sodium adamantylcyclopentadienide (378 mg, 1.7 mmol) and iron dibromide dimethoxyethane adduct (259 mg, 0.85 mmol) in tetrahydrofuran (20 mL) an orange powder was obtained in 350 mg yield (0.77 mmol, 90 %) using the general procedure given above. Recrystallization from diethyl ether gave an analytically pure sample. Attempted sublimation in a vacuum better than 10^{-3} mbar at temperatures up to 180 °C failed. M. p. 185 – 187 °C. – ^{1}H NMR ($CDCl_3$): δ = 4.05 (AA′BB′,Cp ring-*H*, 4H), 2.00 (s (br), CpC(CH$_2$)$_3$(C*H*)$_3$(CH$_2$)$_3$, 3 H), 1.80 (s (br), Cp-C(CH$_2$)$_3$(CH)$_3$(C*H*H)$_3$, 3 H), 1.75 (s (br), Cp-C(CH$_2$)$_3$(C*H*)$_3$(CHH)$_3$, 3 H), 1.72 (s (br), Cp-C(C*H*$_2$)$_3$(C*H*)$_3$(CHH)$_3$, 6 H); (C_6D_6): δ = 4.08 (AA′BB′,Cp ring-*H*, 4H), 1.99 (s (br), CpC(CH$_2$)$_3$(C*H*)$_3$(CH$_2$)$_3$, 3 H), 1.87 (d, $^3J_{HH}$ = 2.06 Hz, Cp-C(C*H*$_2$)$_3$(C*H*)$_3$(CHH)$_3$, 6 H), 1.71 (s (br), Cp-C(CH$_2$)$_3$(C*H*)$_3$(C*HH*)$_3$, 6 H). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 119.41 (1 C, Cp ring-*C*-alkyl), 67.54 (2 C, Cp ring-*C*H), 64.77 (2 C, Cp-ring-*C*H), 44.56 (3 C, Cp-C(CH$_2$)$_3$(*C*H)$_3$(CHH)$_3$), 37.54 (3 C, CH$_2$, Cp-C(CH$_2$)$_3$(CH)$_3$(*C*HH)$_3$), 29.33 (3 C, CH, Cp-C(*C*H$_2$)$_3$(CH)$_3$(CHH)$_3$), 29.05 (1 C, Cp-*C*(CH$_2$)$_3$(CH)$_3$(CHH)$_3$). – Analysis for $C_{30}H_{38}Fe$ (454.23): calcd. C 79.28, H 8.43, found C 79.27, H 8.42.

*Bis[(2R)-2,5,5-trimethylbicyclo[2.2.1]hept-2-ylcyclopentadienyl]iron (**11**-Fe)*

The standard procedure with (**11**-Li) (199 mg, 0.96 mmol) and iron(II) bromide dimethoxyethane adduct (144 mg, 0.48 mmol) in tetrahydrofuran (15 mL) gave an oily material, which was recrystallized from diethyl ether to yield 160 mg (0.35 mmol, 73 %) of an orange-yellow solid. M. p. 135 – 136 °C. – ^{1}H NMR ($CDCl_3$): δ = 4.04 (m, 6 H, Cp-*H*), 3.99 (m, 2 H, Cp-*H*), 1.76 – 1.60 (multiplets, 10 H), 1.53 – 1.54 (m, 4H), 1.47 (s, 6 H, CH_3), 1.14 (m, 2 H), 1.09 (s, 6 H, CH_3), 0.98 (s, 6 H, CH_3). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 102.49 (2 C, alkyl-*C* Cp ring), 68.70 (2 C; *C*H Cp ring), 68.19 (2 C; *C*H Cp ring), 67.92 (2 C; *C*H Cp ring), 66.74 (2 C; *C*H Cp ring), 52.39 (2 C, cage), 49.47 (2 C, cage), 40.23 (2 C, cage), 39.59 (2 C, cage), 38.96 (2 C, cage), 37.04 (2 C, cage), 36.29 (2 C, cage), 32.41 (2 C, cage), 25.83 (2 C, cage), 25.72 (2 C, cage). – Analysis for $C_{30}H_{42}Fe$ (458.51): calcd. C 78.59, H 9.23; found C 78.35, H 9.15.

Molybdenum complexes

The corresponding molybdenum derivatives [Cp^{x}Mo-$(CO)_3CH_3$] were prepared by heating tetrahydrofuran solutions of equimolar amounts of molybdenum hexacarbonyl and the substituted alkali cyclopentadienide to reflux for four to six h. The solution was allowed to cool to ambient temperature. An equivalent amount of iodomethane was added, and the mixture was again heated to reflux for 1 h. The solvent was evaporated, the residue extracted with pentane, the organic phase was filtered and evaporated to yield an orange-yellow oil, which was then recrystallized from saturated diethyl ether solution between −30 and −70 °C.

*exo-Bornylcyclopentadienyl-tricarbonyl-methylmolybdenum (**3**-Mo)*

Lithium *exo*-bornylcyclopentadienide (**3**-Li) (500 mg, 2.40 mmol), hexacarbonylmolybdenum (633 mg, 2.40 mmol), and methyl iodide (148 μL, 338 mg, 2.39 mmol) in tetrahydrofuran (30 mL) gave 436 mg (1.10 mmol, 46 %) of red crystals. – ^{1}H NMR ($CDCl_3$): δ = 5.22 (m, 2H, ring-C*H*), 5.11 (m, 2H, ring-C*H*), 2.38 (m, 1H, C_5H_4-C(cage)*H*), 1.85 – 1.71 (m, 3H), 1.66 – 1.55 (m, 2H), 1.26 – 1.12 m, 2H), 0.87, 0.82, 0.76 (each: s, 3H, CH_3), 0.32 (s, 3H, Mo-CH_3). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 240.56, 227.39, 227.28 (1C each, CO), 118.58 (1C, ring *C*-alkyl), 96.29, 90.85, 90.66, 88.79 (1C each, ring *C*H), 50.00, 47.65, 47.25, 45.36, 39.77, 35.56, 27.19, 21.36, 19.95, 14.09 (each 1C of the alkyl cage), −20.58 (1C, Mo-*C*H_3). – Analysis for $C_{19}H_{24}MoO_3$ (398.08): calcd. C 57.58, H 6.10; found C 56.12, H 5.90.

*Isocamphylcyclopentadienyl-tricarbonyl-methylmolybdenum (**4**-Mo)*

Lithium isocamphylcyclopentadienide (635 mg, 3.05 mmol), hexacarbonylmolybdenum (805 mg, 3.05 mmol), and methyl iodide (190 μL, 433 mg, 3.05 mmol) in tetrahydrofuran (35 mL) gave 476 mg (1.20 mmol, 39 %) of red crystals. Sublimation at 95 – 98 °C oil bath temperature and 10^{-2} mbar gave an orange-yellow solid. – ^{1}H NMR ($CDCl_3$): δ = 4.66, 4.50, 4.45, 4.32 (each: m, 1H, ring-C*H*), 1.92 (m, 1H), 1.77 – 1.75 (m, 1H), 1.61 – 1.55 (m, 2H), 1.43 – 1.40 (m, 1H), 1.19 – 1.13 (m, 2H), 0.96 (m, 1H), 0.94, 0.73, 0.51 (each: s, 3H, CH_3), 0.48 (s, 3H, Mo-CH_3). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 241.04, 227.49, 227.41 (each: 1C, CO), 128.07 (1C, ring *C*-alkyl), 93.99, 91.84, 91.34, 88.86 (each: 1C, ring *C*H), 50.83, 48.48, 44.65, 44.28, 36.88, 30.18, 25.34, 24.75, 22.57, 22.22 (1C each, cage), −21.07 (1C, Mo-*C*H_3). – Analysis for $C_{19}H_{24}MoO_3$ (398.08): calcd. C 57.58, H 6.10; found C 57.24, H 6.05.

*Adamantylcyclopentadienyl-tricarbonyl-methylmolybdenum (**7**-Mo)*

From sodium adamantylcyclopentadienide (618 mg, 2.77 mmol), molybdenum hexacarbonyl (731 mg, 2.77 mmol) and methyl iodide (170 μL, 388 mg, 2.75 mmol), reacted in tetrahydrofuran (30 mL) as described above, a solid residue was obtained after tetrahydrofuran evaporation. Extraction had to be carried out with toluene, and evaporation of the filtered solution gave a light-brown, air-stable powder (650 mg, 1.09 mmol, 39 %), which could be sublimed at 95 – 98 °C oil bath temperature and 10^{-3} mbar pressure as intensely yellow microcrystals. – ^{1}H NMR ($CDCl_3$): δ = 4.51 (AA′BB′, (4 lines), Cp-ring, 4 H), 1.81 (s (br), 3H, CpC$(CH_2)_3$-(C*H*$)_3$(CHH$)_3$), 1.55 (s (br), 3H, Cp-C$(CH_2)_3$(CH$)_3$(C*H*H$)_3$), 1.52 (s (br), 3H, CpC$(CH_2)_3$-(C*H*$)_3$(CH*H*$)_3$), 1.48 (d, 6H, $^3J_{HH}$ = 2.4 Hz, CpC(C*H*$_2)_3$(C*H*$)_3$-(CHH$)_3$), 0.51 (s, 3H, Mo-CH_3). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 241.61 (1 C, *C*O), 228.02 (2 C, *C*O), 129.03 (1 C, Cp ring *C*-alkyl), 90.89 (2 C, Cp ring *C*H), 89.80 (2 C, Cp ring *C*H), 44.57 (3 C, CpC$(CH_2)_3$(*C*H$)_3$(CHH$)_3$), 36.66 (3 C, *C*H$_2$Cp-C$(CH_2)_3$-(CH$)_3$(*C*HH$)_3$), 33.06 (1 C, Cp-*C*$(CH_2)_3$(CH$)_3$(CHH$)_3$), 29.00 (3C, Cp-C(*C*H$_2)_3$(CH$)_3$(CHH$)_3$), −21.04 (1 C, Mo-CH_3). – Analysis for $C_{19}H_{22}MoO_3$ (396.06): calcd. C 57.57, H 5.60; found C 60.10, H 6.35. (For an impurity of 10 % adamantylcyclopentadiene 60.81 % C and 6.05 % H would be expected).

*(2R)-2,5,5-Trimethylbicyclo[2.2.1]hept-2-ylcyclopentadienyl-tricarbonyl-methyl-molybdenum (**11**-Mo)*

11-Li (150 mg, 0.72 mmol), hexacarbonylmolybdenum (190 mg, 0.72 mmol), and methyl iodide (45 μL, 103 mg,

0.73 mmol), reacted in tetrahydrofuran (10 mL) as described above, gave 139 mg (0.35 mmol, 48 %) red crystals. – ^{1}H NMR (C_6D_6): δ = 4.57 (m, 1 H, ring C*H*), 4.45 (m, 2 H, ring C*H*), 4.40 (m, 1 H, ring C*H*), 1.55 (m (four lines, like AB spin system), 2H), 1.48 (m (four lines, like AB spin system), 2H), 1.42 (s (br), 1H), 1.37 (AB, 1H, J_{HH}= 2.6 Hz, J_{HH} = 13.2 Hz), 1.24 (AB, 1H, J_{HH}= 4.7 Hz, J_{HH} = 13.5 Hz), 1.15 (s, 3H, CH_3), 1.03 (AB, 1H, J_{HH}= 4.7 Hz, J_{HH} = 13.2 Hz), 0.93, 0.90 (each: s, 3H, CH_3), 0.51 (s, 3H, Mo-CH_3). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 241.46, 228.05, 227.98 (each: 1C, CO), 129.74 (1C, ring *C*-alkyl), 93.40, 91.89, 91.67, 90.20 (1C each, ring *C*H), 52.09, 49.27, 40.04, 39.00, 37.00, 35.95, 32.21, 26.97, 25.34 (1C each, cage), −21.14 (1C, Mo-*C*H$_3$). – Analysis for $C_{19}H_{24}MoO_3$ (398.08): calcd. C 57.58, H 6.10; found C 56.16, H 6.16.

*Bis[(2R)-2,5,5-trimethylbicyclo[2.2.1]hept-2-ylcyclopentadienyl]dichlorotitanium(IV) (**11**-Ti)*

To a magnetically stirred solution of titanium tetrachloride (341 mg, 1.80 mmol, distilled prior to use) in benzene (15 mL) in a round-bottomed flask cooled in an ice bath was added a solution of **11**-Li (750 mg, 3.60 mmol) in tetrahydrofuran (15 mL). The reddish-brown suspension was allowed to warm to r. t., and stirring was continued for 1 d. Then ice water was added slowly (15 mL), and the solvents were evaporated from the organic phase *in vacuo*. The residue was extracted with chloroform (300 mL), the organic phase was washed with water several times and dried with magnesium sulfate. Evaporation of most of the solvent, heating of the residual mixture in order to dissolve most of the precipitate formed during evaporation, and hot filtration gave a solution, which was stored at 0 °C to yield a red microcrystalline product (523 mg, 1.0 mmol, 56 %), m. p. with decomp. 242 – 245 °C. – ^{1}H NMR ($CDCl_3$): δ = 6.55 ("q", 4H, ring C*H*), 6.49 ("t", 2H, ring C*H*), 6.28 ("d", 2H, ring C*H*), 2.28 (dd, $^3J_{HH}$ = 4.7 Hz, $^2J_{HH}$ = 14.1 Hz, 2H), 1.89 (d(br), 2H), 1.77 (d(br), 2H), 1.68 (dd, $^4J_{HH}$ = 2.4 Hz, $^2J_{HH}$ = 14.1 Hz, 2H), 1.58 (dd, $^4J_{HH}$ = 2.4 Hz, $^2J_{HH}$ = 13.2 Hz, 2H), 1.40 (m(br), 4H), 1.35 (s, 6H, CH_3), 1.17 (dd, $^3J_{HH}$ = 4.7 Hz, $^2J_{HH}$ = 13.2 Hz, 2H), 1.04, 0.96 (each: s, 6H, CH_3). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 152.84 (2 C, ring *C*-alkyl), 121.93 (2 C; R*Cp, ring *C*-H), 119.02 (2 C; R*Cp, ring *C*-H), 117.91 (2 C; R*Cp, ring *C*-H), 113.21 (2 C; R*Cp, ring *C*-H), 52.54 (2 C, cage), 49.77 (2 C, cage), 43.30 (2 C, cage), 39.43 (2 C, cage), 37.96 (2 C, cage), 36.97 (2 C, cage), 36.25 (2 C, cage), 31.97 (2 C, cage), 25.36 (2 C, cage), 24.35 (2 C, cage). – Analysis for $C_{30}H_{34}Cl_2Ti$ (513.39): calcd. C 69.10, H 8.12; found C 68.08, H 8.13.

Crystal structure determination

Crystal structure analyses have been carried out on a Stoe IPDS diffractometer. Information on the single crystals employed, cell parameters and details regarding data collection and refinement can be found in Table 1.

In complexes **3**-Mo and **4**-Mo the methyl group at the molybdenum atom and the carbonyl ligand in its *trans* position were found to be disordered. Restraints on displacement parameters have been used. For complex **4**-Mo, where the cyclopentadienyl ring is also affected by the disorder, geometrical restraints were also applied.

CCDC 703191 – 703194 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The authors thank the *Deutsche Forschungsgemeinschaft* for funding (DFG grant Nr. Si 366/9-1, 9-2) and Dr. G. Hornung for the acquisition of mass spectra. H. S. thanks his mentor Professor Scherer for his friendly support.

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