ELSEVIER

Journal of Organometallic Chemistry 541 (1997) 249–260

Journal of Organometallic Chemistry

Mixed-membered-bisfulvalene dimetal-complexes via metallocene-substituted norbornenyl alcohols [1]

H. Schottenberger [a,*], M. Buchmeiser [b], C. Rieker [a], P. Jaitner [a], K. Wurst [a]

[a] *Institut für Allgemeine, Anorganische und Theoretische Chemie, Leopold Franzens Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria*

[b] *Institut für Analytische Chemie und Radiochemie, Leopold Franzens Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria*

Received 27 December 1996; accepted 9 January 1997

Abstract

A proven synthetic method for mixed-metal [0.0] bimetallocenophanes containing Fe, Ru and Co is presented in detail. Utilising norbonenyl alcohol precursors, doubly lithiated ruthenocene or ferrocene were reacted with bicyclo[2.2.1]-hept-2-en-7-one (norborn-2-en-7-one) to yield a mixture of stereoisomeric alcohols, or respectively spiro-ethers, which can be separated by means of chromatography. The initially formed alcoholates were further reacted with diethylchlorophosphate to yield the respective chloro-substituted derivatives. Subsequent reductive cleavage of the chlorine–carbon bonds by lithium-powder in DME afforded the metallocene-substituted norbornenyl carbanions, which eliminated ethylene at ambient temperature to form dilithium metallocenylenebis(cyclopentadienylides). In a final step, reaction with cobalt dichloride produced the mixed-metal bimetallocenophanes 1,1′-(1,1′-cobaltocenediyl)-ferrocene and 1,1′-(1,1′-cobaltocenediyl)-ruthenocene respectively.

Target-compounds isolated as monocationic hexafluorophosphate salts as well as isolable intermediate products were characterized mainly by NMR-, IR- and MS-techniques. The X-ray structures of 1,1′-(1,1′-cobaltoceniumdiyl)-ruthenocene PF_6^- and selected norbornenols are presented. *anti-,anti*-Bisnorbornenol **1b** exhibits significant sandwich plane distortions induced by hydrogen bridges. The dimers formed in the solid state resemble covalent ansa-type conformations. Furthermore, the synthetic route of reacting mono- and dilithiometallocenes with norbornenone was applied to the lithium and dilithium acetylides of ethynyl and 1,1′-diethynylferrocene.

The attempted extension of the described synthetic concept to mono- and dinorbornenol-substituted ferrocenylethynes for the final conversion to ferrocene-1,1′-bis(ethynylcyclopentadienides) did not allow the preparation of the desired ethyne-spacered bimetallocenophane species. © 1997 Elsevier Science S.A.

Keywords: Mixed–metal bimetallocenophanes; Reductive cleavage

1. Introduction

The electronically intriguing class of [0.0] metallocenophanes (or bimetallocenylenes) is attracting continuous interest [1], but has long been limited to the homonuclear members, of which the Fe-, Co-, Ni-, Cr-, V-, and Mo-containing species have been the first representatives [2,3]. Successful efforts on heteronuclear members containing fulvalene subunits have been mainly focused on half-sandwich complexes [4].

Earlier, we described the synthesis of the first heteronuclear [0.0] metallocenophane containing Fe and Co as the central metals [5]. The synthesis followed a well established route starting from fulvalene dianion, but, however, suffered from the statistical formation of the desired compounds. We now wish to report in detail the synthetic approach, which already proved to be successful for the synthesis of heteronuclear termetallocenes [6] as well as [0.0] metallocenophanes [7] (Scheme 1). The above-mentioned concept avoids statistically formed homonuclear products by the appropriate substitution of an already preformed metallocene starting unit.

2. Synthesis

Dilithiated metallocenes, namely 1,1′-dilithioferrocene and 1,1′-dilithioruthenocene, reacted smoothly with bicyclo[2.2.1]hept-2-en-7-one (norbornenone) to give

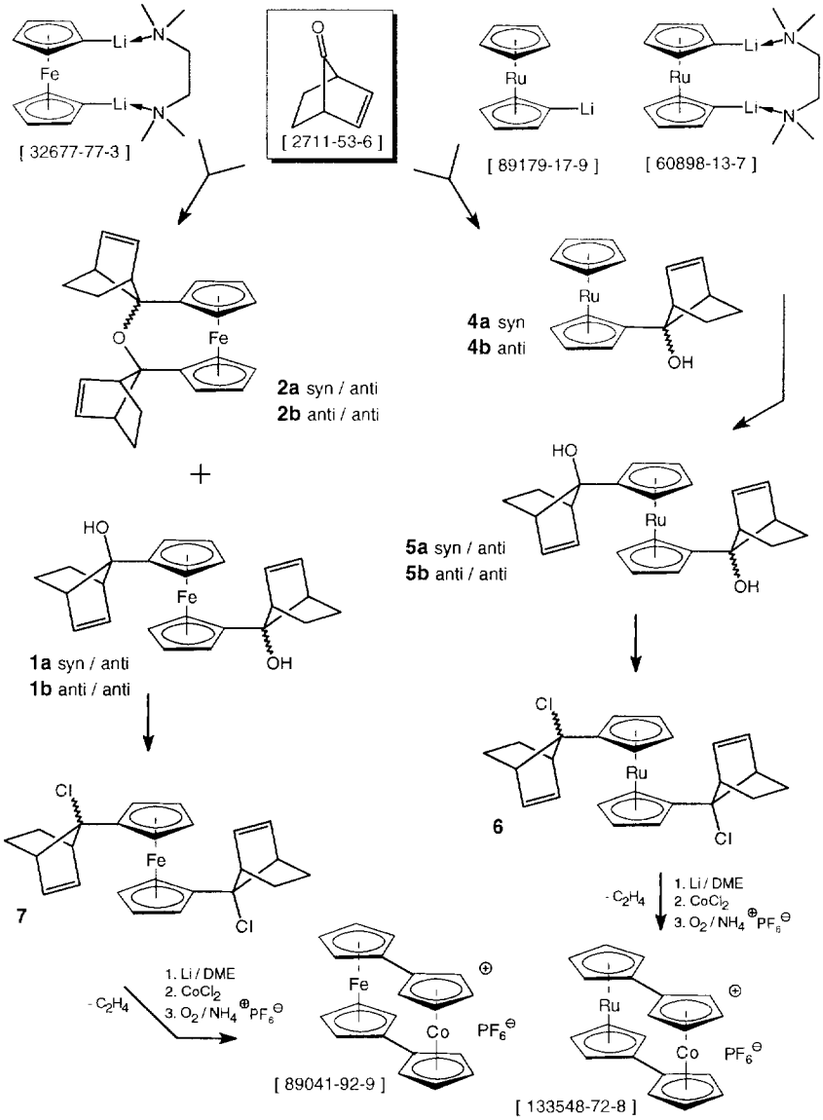
* Corresponding author. E-mail: herwig.schottenberger@uibk.ac.at.

[1] Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.

PII S0022-328X(97)00068-5

mixtures of stereoisomeric alcoholates. After conventional aqueous work-up the corresponding alcohols can easily be separated chromatographically on silica. In both series, only two of the three possible stereoisomers were detected, namely the anti–syn and the anti–anti isomers. The prefixes syn- and anti- in this context refer to the relative positions of the hydroxyl group and the double-bond in the bicyclic ring system.

In the case of ruthenocene as the starting metallocene, also both monosubstituted alcohols, the syn- and the anti-derivative, were isolated as minor products, due to the fact that the direct lithiation of ruthenocene by buthyllithium–TMEDA always yields mixtures of mono-, di- and traces of trilithiated products [8]. The initially formed alcoholates were further reacted with diethylchlorophosphate to produce the chloro-derivatives. This is in agreement with our findings for the corresponding monosubstituted isomeric ferrocenyl compounds [6], and may be explained by a nucleophilic SN1 substitution of the initially formed diethylphosphate by chloride ion under the reaction conditions. The ease of this reaction may be rationalized by the highly stabilizing effect that a ferrocenyl or ruthenocenyl substituent exerts on positive α-carbon atoms [9] and by the good leaving group ability of the phosphate ester [10]. Efforts to separate the isomeric chloro derivatives failed due to their sensitivity towards hydrolysis. However, in the ferrocenyl series, a stable by-product of this reaction, an oxa[3]ferrocenophane was isolated. This novel cyclic spiro-ether is evidently formed by nucleophilic attack of one not yet reacted alcoholate on the second already reacted functionality in the same



Scheme 1. Synthesis of directly linked metallocenylnorbornenes.

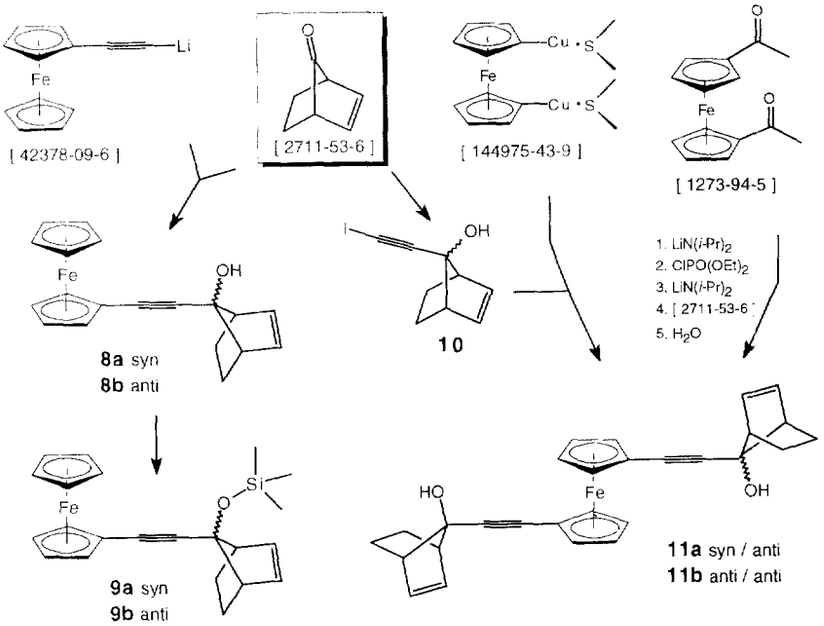
molecule. For sterical reasons, also an SN1 mechanism involving a carbocation as the intramolecular electrophile seems most likely. A similar reaction was observed when *p*-toluene sulfonic acid chloride was used as a chlorinating agent. However, by-products were more predominant, therefore diethylchlorophosphate is the preferable chlorination reactant.

The chloro-derivatives as well as the cyclic ethers are cleanly cleaved by powdered elemental lithium in DME without over-reduction of the metallocene moieties, which in related cases provides access to free substituted cyclopentadienides from the corresponding ferrocenes [11].

The initially formed metallocenediylbis(norbornenylcarbanions), by a retro Diels Alder reaction, spontaneously eliminate ethene to form the desired metallocenylenebis(cyclopentadienylides) which may be further reacted in situ. Attempts to isolate the 1,1′-bis(cyclopentadienyl)metallocenes failed due to the high intramolecular dimerization and intermolecular polymerization tendency of the neutral dimeric cyclopentadienes [10,11]. In addition, the extension of the synthetic concept to the attempted formation of ethyne-spacered metallocenes and [2.2] metallocenophanes was investigated.

Lithiated ethynylferrocene [12], as well as lithioferrocenes and the lithioruthenocenes represent readily available compounds [8]. They can be transformed into the two isomeric alcohols, *syn*- and *anti*-(7-hydroxybicyclo[2.2.1]hept-2-en-yl)ethynylferrocene, by a one pot reaction consisting of the deprotonation and subsequent reaction of ethynylferrocene with norbornenone (see Scheme 2). In contrast, the dilithiosalt of 1,1′-diethynylferrocene is less accessible [13]. Therefore, in order to develop a convenient synthesis, alternative synthetic routes have been evaluated. Two starting candidates, 1,1′-bis(3-hydroxy-3-methylbut-1-yn-1-yl)ferrocene and 1,1′-diacetylferrocene, can both be prepared in an easy and high yielding synthesis and may serve as precursors of 1,1′-diethynylferrocene, which is only stable in its deprotonated form [13]. One of the possible educts, the acetone-based Nef-adduct, 1,1′-bis(3-hydroxy-3-methylbut-1-yn-1-yl)ferrocene, represents thus a 1-hydroxy-1-methylethyl protected species [13] of diethynylferroceneone and is easily transformed to the dipotassium salt by deprotection of the starting material with 4 mequiv. of potassium hydride at elevated temperature. 1,1′-Diacetylferrocene may be transformed into the dilithiosalt of 1,1′diethynylferrocene [14] by a four-step synthesis, which was developed by Negishi et al. [15]. Deprotonation of the starting compound with 2 mequiv. of $LiN(i\text{-}Pr)_2$ and subsequent transformation into the corresponding diphosphate is followed by elimination of 2 mequiv. of diethylphosphate yielding the desired dilithiated diethynylferrocene. Reaction of the intermediate acetylides with 2 mequiv. of norbornenone at ambient temperature yields in both cases a mixture of three of the four possible stereoisomeric alcohols, which also can be separated on silica by means of middle pressure chromatography. As found for the directly linked metallocenylnorbornenols, again only the syn/anti- and the anti/anti-derivatives could be detected.

The stereochemical assignment of norbornenols is possible by means of the infrared O–H-stretching vibrations and is in accordance with literature data [16]. For unequivocal confirmation, already X-rayed single crys-



Scheme 2. Synthesis of ethyne-linked metallocenylnorbornenes.

tals have been compared with authentic samples by TLC.

The lack of formation of syn–syn-isomers is also the case for a third synthetic variant, an inverse Stephens Castro coupling [17] of dicupriated ferrocene with the norbornenyl-substituted iodoethyne **10**.

The attempted analogous preparation of ethynylcyclopentadienides was unsuccessful. This approach was also impossible by reduction of the corresponding Nicholas cations, formed from **11** via ethyne dicobalthexacarbonyl complexes. The failure of such preparations may be attributed to a possible carbene formation, due to the moderate leaving group ability of acetylide under the strongly reducing conditions during the final step of the cyclopentadienide formation.

3. Discussion

*3.1. X-ray structures of **1a**, **1b**, **2a**, **9b**, and [133548-72-8]*

3.1.1. Alcohols

As expected, the crystal packing of the stereoisomers of the intermediate norbornenols is mainly governed by hydrogen bonding, resulting in bridged dimers exhibiting varied chromatographical and solubility behavior on a macroscopic scale.

In the syn–anti conformation of **1a**, (see Fig. 1), half a molecule is in the asymmetric unit and the Fe atom lies in a symmetry center. Therefore the two Cp-rings have an exactly staggered arrangement, forced by hydrogen bridges as depicted.

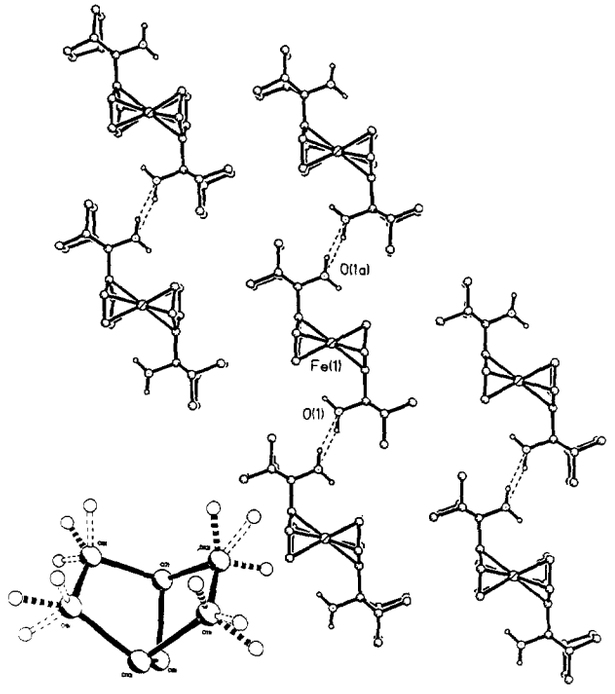


Fig. 1. Lattice structure and hydrogen bonding pattern of **1a** with disordered positions for the hydrogen atom of the hydroxyl group.

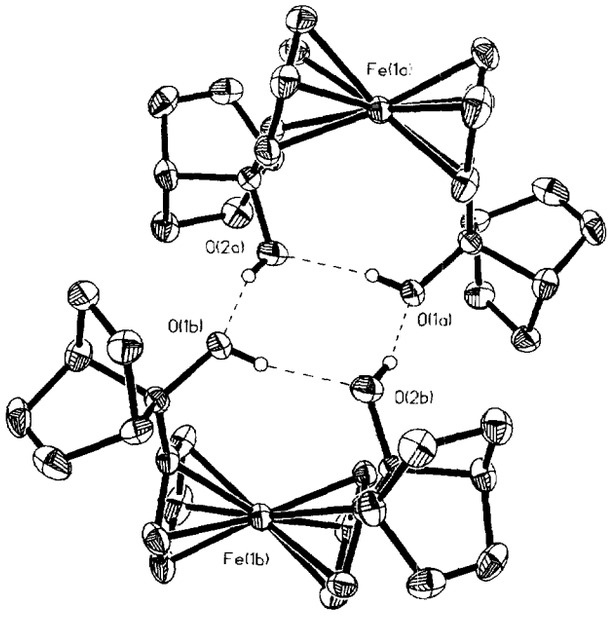


Fig. 2. Molecular structure of **1b**. Hydrogen bonding pattern of dimeric **1b**.

Fig. 1 shows the part of a sheet with infinitely linear chains of hydrogen-bonded molecules, which are connected row by row by van der Waals forces. The crystal is disordered in a ratio of 1:1. The disorder leads to two positions of the hydrogen atom bonded to the hydroxyl group and some of the hydrogen atoms on the norbornenyl group. This is also illustrated in Fig. 1 for one norbornenyl group. The distances between C(8)–C(9) and C(11)–C(12) are 1.428(6) and 1.436(6) Å, the averaged values between a single and double carbon–carbon bond.

On the crystal of the anti–anti stereoisomer **1b** there is no disorder and the lengths of the single bonds and the olefinic bonds on the two norbornenyl groups are 1.545(5), 1.556(5) Å and 1.321(5), 1.332(5) Å. The two Cp-rings in the ferrocenyl unit are unusually tilted. The dihedral angle is 9.5(1)° and the inclination results from the formation of a dimer, linked by hydrogen bonds. Fig. 2 shows the hydrogen bonding scheme of two molecules, which are related by a symmetry center and form a nearly planar ring of four hydrogen bonds with intramolecular O...O distances of 2.654(3) Å and intermolecular O...O distances of 2.677(3) Å. The crystal structure of pentaerythritol [18] has a similar eight-membered ring of hydrogen bonds. While in $C(CH_2OH)_4$ the O–H...O links are linear, the O–H...O angles in **1b** are 168° (intramolecular) and 163° (intermolecular) and the angle from the oxygen atom to

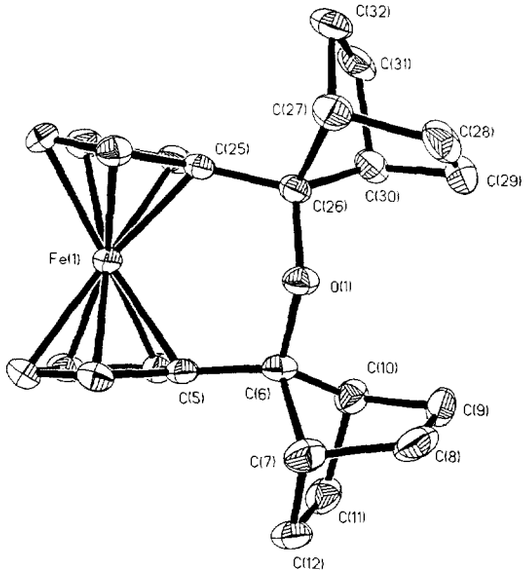


Fig. 3. Molecular structure of **2a**.

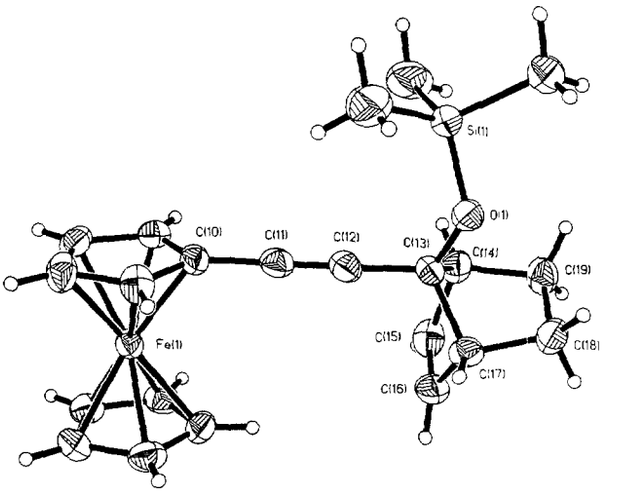


Fig. 4. Molecular structure of **9a**.

the hydrogen atoms is 98.6° at O(1) and 104.9° at O(2). In a synergistic mode, the hydrogen bridges force the metallocene plane to an unprecedented 'non-covalent ansa-ferrocene'; the above-mentioned tilt angle of 9.5° represents a value within the ranges reported for covalently strained ansa-ferrocenes [19].

This remarkable feature of this specific stereoisomer explains also the extreme solubility differences in comparison with the syn/anti isomer **1a**, which can be cleanly separated by extraction with hexane from **1b**, a stable dimer, almost insoluble in aliphatic hydrocarbons.

The crystal of **2a** (Fig. 3) has the same disorder as **1a**, with averaged values of the single and double bond lengths in the range of 1.429(5) to 1.441(5) Å. The dihedral angle of the two Cp-rings is 12.0(2)°, resulting from the bridging oxygen atom. The angle C(6)–O(1)–C(26) is elongated to 124.2(2)°.

The crystal structure of the anti stereoisomer ethyne derivative **9b** (Fig. 4) is well ordered and the bond lengths of the acetylenic unit are quite normal [25] with distances C(10)–C(11)–C(12)–C(13) of 143.6(4)–119.7(4)–147.7(4) Å and angles C(10)–C(11)–C(12) and C(11)–C(12)–C(13) of 178.9(3)° and 178.1(3)° respectively. The norbornenyl group has bond lengths of 1.553(4) and 1.316(5) Å, analogous to **1b** for the previously discussed single and double bonds.

For the bis(fulvalene) Co–Ru complex [**133548-72-8**], only electrochemical data have been published so far [21]. In its cationic form this unique compound exhibits diamagnetism, which is in contrast to the homologue iron compound. The ^{1}H NMR shows two groups of signals separated by 2 ppm. Such a far separation is characteristic for diamagnetic bis(fulvalene) dimetal complexes. As expected, each group of resonances consists of two pseudo-triplets. The more downfield-shifted triplet of each group can be assigned to the cobaltocenium part due to the positive charge on this part of the molecule. In analogy to ruthenocenylcobaltocenium [6], this assignment is also supported by the somewhat smaller coupling-constants of 1.8 Hz for the corresponding more upfield-shifted triplets (ruthenocenyl-part) in comparison to 2.1 Hz for the more downfield-shifted ones (cobaltocenyl-part). The IR-spectrum of the Ru–Co-compound is almost identical to the spectrum of the Fe–Co analogue [5], thus providing an additional proof of identity.

The molecular and crystal structures of the isomorphous and isostructural compounds bis(fulvalene)Co–Ru and bis(fulvalene)Co–Fe as its monocationic hexafluorophosphates reveal strikingly similar lattices. Details for the Fe–Co complex have already been discussed [3] and are also valid for the Ru–Co structure reported in the present paper (Fig. 5). When comparing the metal–metal distance of Fe–Co and Ru–Co an increase from 3.879(1) to 3.889(1) is observed. The central C–C bond of the fulvalene bridge reflects this trend to increase as well: 1.458(4) (Fe–Co) and 1.465(6) (Ru–Co). Severe distortions of the ligand frame are noteworthy: the dihedral angle C1–C5 to C6–C10 is 20.1(2), the torsion angle C2–1–6–7 is −158.2(4)° and of C2–1–6–10:

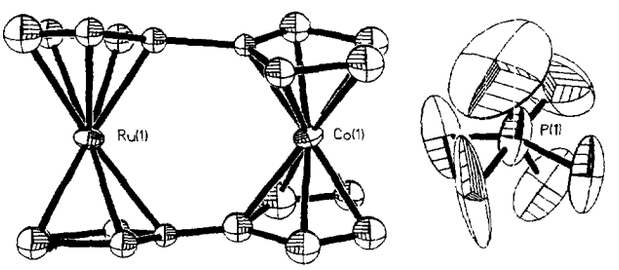


Fig. 5. Molecular structure of [**133548-72-8**].

19.8(4)°. The distances from the metal atom to the Cp-plane are 1.815(2) Å for Ru and 1.647(2) Å for Co. The two pairs of Cp-ligands of each metallocene unit deviate from coplanarity: the dihedral angle C1–5 to C1a–5a is 4.8(3)° and C6–10 to C6a–10a is 3.0(2)°. The anion hexafluorophosphate is disordered.

4. Experimental section

4.1. General comments

All the reactions were carried out in the absence of air using standard Schlenk techniques and vacuum-line manipulations. Solvents were deoxygenated, purified and dried prior to use. Instrumentation: Bruker AC 200 (^{1}H and ^{13}C NMR); Nicolet 510 FT-IR (IR); Bruins Instruments Omega 20 (UV–vis); Varian CH-7, Finnigan MAT 95 (MS); Siemens P4 (X-ray). Melting points were determined on a Kofler hot plate apparatus. Microanalyses were obtained from the Department for Microanalysis, University of Vienna, Austria, and from the Analytical Department of Lenzing AG, Lenzing, Austria, and are in accord with the calculated values.

4.2. X-ray structure determinations

Crystals of compound **1a**, **1b**, **2a**, **[133548-72-8]**, and **9b** were examined by similar procedures. The crystal was fixed to a glass fiber and measured on a Siemens P4 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were determined and refined from 21 to 25 randomly selected reflections in the 2Θ range of 10.5 to 25.0°, obtained by P4 automatic routines. Data were measured via ω-scans and corrected for Lorentz and polarization effects. An empirical absorption correction [20] based on a series of ψ-scans was applied for compounds **1a**, **1b**, **2a** and **[133548-72-8]**. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the International Tables for Crystallography [22]. Structures were solved by direct methods (SHELXS-86) [23] and refined by full matrix least squares against F^2 (SHELXL-93) [24]. The function minimized was $\Sigma[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ with $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. The fluorine atoms of **6** are disordered and were refined with the multiplicity of 0.5. All hydrogen atoms were successfully located by difference Fourier methods. They were included in idealized positions at the cyclopentadienyl rings and were refined isotropically at the norbornenyl group for compound **1b**, **9b** and the hydroxyl groups of **1b**. The norbornenyl group of **1a** and **2a** is disordered, as shown in Fig. 1, and the hydrogen atoms were calculated, except the olefinic hydrogen atoms which were refined isotropically with the multiplicity of 0.5. The hydrogen atom on the oxygen atom of **1a** is also disordered and was refined isotropically on two positions, each with a multiplicity of 0.5. All molecular structure drawings show the ellipsoids of the non-hydrogen atoms at the 50% probability level.

4.3. Preparative section

4.3.1. 1-[anti-7-Hydroxybicyclo[2.2.1]hept-2-ene-7-yl]-1'-(syn-7-hydroxybicyclo[2.2.1]hept-2-ene-7yl]ferrocene (**1a**) and 1,1'-bis[anti-7-hydroxybicyclo[2.2.1]hept-2-ene-7-yl]ferrocene (**1b**)

Dilithioferrocene · TMEDA (0.710 g, 2.58 mmol) was suspended in 100 ml THF, cooled to −80 °C. Norbornenone [7], (0.60 ml, 0.586 g, 5.42 mmol, 2.1 mol equiv.) was added and the mixture was warmed to 0 °C. In order to obtain the isomeric alcohols, the solution was diluted with 100 ml diethyl ether and ice water (50 ml) was added. The organic layer was washed with water (3 × 50 ml), and dried over $MgSO_4$. The solvent was evaporated and the alcohols were obtained out of the crude mixture by means of middle pressure chromatography (5 × 60 cm, silica G-60, 220–440 mesh, Fluka, hexane:diethyl ether = 80:20). After minor amounts of ferrocene and mono alcohols, the anti,anti- and finally the syn,anti-isomers are obtained. Both dialcohols were recrystallized from hexane.

It is also possible to conduct this reaction by a heterogenic protocol: when a suspension of the dilithioferrocene · TMEDA adduct is reacted in hexane for 24 h, the alcoholates separate quantitatively; under these conditions the formation of **1b** is favored over **1a**.

4.3.2. 1-(anti-7-Hydroxybicyclo[2.2.1]-hept-2-ene-7-yl]-1'-[syn-7-hydroxybicyclo[2.2.1]hept-2-ene-7-yl]ferrocene (**1a**)

0.343 g (33%), m.p.: 143–144 °C (hexane). IR (KBr): 3518, 3464 (*n* OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) *d* 0.8 (m_c, 2H, $H_{5'',6''endo}$), 0.95 (m_c, 2H, $H_{5''',6'''endo}$), 1.60 (m_c, 2H, $H_{5'',6''exo}$), 2.15 (m_c, 2H, $H_{5''',6'''exo}$), 2.50 (m_c, 2H, $H_{1'',4''}$), 2.68 (m_c, 2H, $H_{1''',4'''}$), 3.23 (bs, 1H, OH''), 4.48 (bs, 1H, OH'''), 4.11, (t, *J* = 1.9, 2H, $H_{3,4}$), 4.15 (t, *J* = 1.9, 2H, $H_{3',4'}$), 4.20 (t, *J* = 1.9, 2H, $H_{2,5}$), 4.32 (t, *J* = 1.9, 2H, $H_{2',5'}$), 5.82 (t, *J* = 2.0, 2H, $H_{2'',3''}$), 6.08 (t, *J* = 2.0, 2H, $H_{2''',3'''}$); HRMS calcd. for $C_{17}H_{18}FeO$: 402.315. LRMS found (70 eV): 402 (100%) [$M^{+\cdot}$].

4.3.3. 1,1'-Bis[anti-7-hydroxybicyclo[2.2.1]hept-2-ene-7-yl]ferrocene (**1b**)

0.623 g (60%), m.p.: 183–184 °C (hexane); IR (KBr): 3524, 3440 (*n* OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) *d* 0.80 (m_c, 4H, $H_{5'',5''',6'',6'''endo}$), 1.60 ($m_c$, 4H, $H_{5'',5''',6'',6'''exo}$), 2.68 (m_c, 4H, $H_{1'',1''',4'',4'''}$), 3.71, (bs, 2H, O*H*''), 4.15, (t,

$J = 1.9$, 4H, $H_{3,3',4,4'}$), 4.32, (t, $J = 1.9$, 4H, $H_{2,2',5,5'}$), 6.08, (t, $J = 2.0$, 4H, $H_{2'',2''',3'',3'''}$); HRMS calcd. for $C_{17}H_{18}FeO$: 402.315. LRMS found (70 eV): 402 (100%) [$M^{+\cdot}$].

4.3.4. *1,1'-Bis[7-chlorobicyclo[2.2.1]hept-2-ene-7-yl]ferrocene and isomeric 1,1'-(oxybis[bicyclo(2.2.1]hept-2-ene-7-ylidene]ferrocenes (7 mixture)*

It is of advantage to synthesize the chloro compounds by reacting the crude mixture of the lithium dialcoholates with diethyl chlorophosphate (0.80 ml, 0.944 g, 5.42 mmol, 2.1 mequiv., Merck, distilled under argon) rather than starting from the alcohols. The reaction mixture as described for **1a,b** was warmed to 50 °C and stirred for 2 h. The solvent was evaporated and the crude product dissolved in hexane. Filtration through Celite removes polar by-products. The hexane was removed in vacuo leaving an oily residue. It consists mainly of the dichloro-derivatives, which were identified by mass spectroscopy ($m/e = 438$). Any effort to separate the corresponding chloro compounds by means of chromatography (silica G-60, hexane:diethyl ether = 85:15) resulted in complete hydrolysis. Besides minor amounts of the alcohols, one fraction contains the isomeric cyclic ethers, which may be separated by crystallization from hexane.

4.3.5. *syn,anti-1,1'-Oxybis[bicyclo[2.2.1]hept-2-ene-7-ylidene]ferrocene (**2a**)*

^{1}H NMR ($CDCl_3$) *d* 0.83 (bm_c, 2H, $H_{5'',6''endo}$), 0.98 (bm_c, 2H, $H_{5''',6'''endo}$), 1.62 (bm_c, 2H, $H_{5''',6'''exo}$), 2.14 (bm_c, 2H, $H_{5'',6''exo}$), 2.72 (bm_c, 2H, $H_{1''',4'''}$) 2.82 (mb_c, 2 H, $H_{1'',4''}$), 3.99 (bs, 2 H, $H_{3,4}$), 4.05 (bs, 2 H, $H_{3',4'}$), 4.10 (bs, 2 H, $H_{2,5}$), 4.19 (bs, 2H, $H_{2',5'}$) 5.91 (bs, 2 H, $H_{2'',3''}$), 6.09 (bs, 2H, $H_{2''',3'''}$); ^{13}C NMR ($CDCl_3$) *d* 23.44 (t, $C_{5''',6'''}$), 23.55 (t, $C_{5'',6''}$), 49.90 (d, $C_{1''',4'''}$), 50.10 (d, $C_{1'',4''}$), 68.30 (d, $C_{3,4}$), 68.70 (d, $C_{3',4'}$), 68.90 (d, $C_{2,5}$), 69.91 (d, $C_{2',5''}$), 87.97 (s, $C_{7''}$), 90.36 (s, $C_{7'''}$), 91.19 (s, C_1), 92.60 (s, $C_{1'}$), 131.74 (d, $C_{2'',3''}$), 135.17 (d, $C_{2''',3'''}$); HRMS calcd. for $C_{24}H_{24}FeO$: 384.300. LRMS found (70 eV): 384 (100%) [$M^{+\cdot}$].

4.3.6. *anti,anti-1,1'-Oxybis[bicyclo[2.2.1]hept-2-ene-7-ylidene]ferrocene (**2b**)*

IR (KBr) $> 3200\,cm^{-1}$ (no absorbance); ^{1}H NMR ($CDCl_3$) *d* 1.08 (m_c, 4H, $H_{5'',5''',6'',6'''endo}$), 2.28 ($m_c$, 4H, $H_{5'',5''',6'',6'''exo}$), 2.89, (m_c, 4H, $H_{1'',1''',4'',4'''}$), 4.13, (d, $J = 1.9$, 4H, $H_{3,3',4,4'}$), 4.22, (t, $J = 1.9$, 4H, $H_{2,2',5,5'}$), 5.95 (t, $J = 2.0$, 4H, $H_{2'',2''',3'',3'''}$); ^{13}C NMR ($CDCl_3$) *d* 24.83 (t, $C_{5'',5''',6'',6'''}$), 53.47 (d, $C_{1'',1''',4'',4'''}$), 68.91 (d, $C_{3,3',4,4'}$) 71.85 (d, $C_{2,2',5,5'}$), 87.18 (s, $C_{7'',7'''}$), 91.32 (s, $C_{1,1'}$), 134.12 (d, $C_{2'',2''',3'',3'''}$); HRMS calcd. for $C_{24}H_{24}FeO$: 384.300. LRMS found (70 eV): 384(100%) [$M^{+\cdot}$].

4.3.7. *1,1'-(1,1'-Cobaltoceniumdiyl)-ruthenocene hexafluorophosphate **[5]**, [89041-92-9]*

The above described mixture of the chloro-derivatives was dissolved in 100 ml DME and lithium powder (0.770 mg, 11 mmol) was added under vigorous stirring. Though the formation of ethylene ceases after 2 h, the actual end of the reaction was determined by TLC (Polygram SIL UV_{257}, Macherey and Nagel; hexane; diethyl ether = 85:15). After completion of the reaction, excess lithium and all inorganic salts were removed by filtration through Celite. A deep orange solution was obtained, which was diluted to 250 ml of hexane prior to further use. Cobalt chloride (anhydrous, 0.40 mequiv.) was added to the above preformed solution of ferrocenediylyl-bis(cyclopentadienylide) dilithium. The reaction mixture was stirred overnight at 60 °C. The solution was cooled to room temperature, filtered and an equal volume of aqueous hexafluorophosphoric acid (5%) was added. Under vigorous stirring air was passed through the solution for 4 h. The desired product precipitates as a brown solid; this was filtered off and washed with diethyl ether until the washings were colorless. The solid was extracted with methylene chloride. The methylene chloride was evaporated and the residue was purified by recrystallization from acetonitrile–diethyl ether. Analytical data are identical with those previously found.

4.3.8. *Reaction of norbornenone with lithioruthenocenes · xTMEDA*

Ruthenocene (0.693 g, 3.0 mmol), was suspended in 100 ml of hexane and under vigorous stirring, TMEDA (0.90 ml, 0.70 g, 6.02 mmol, 2 mol equiv.) and *n*-butyllithium (3.75 ml, 6.0 mmol, 1.6 M in hexane) were added at room temperature. The reaction mixture was ultrasonicated for 45 min at 4 °C (Sonorex Bandulin). The slightly yellow-colored suspension, which consists of monolithio-, 1,1'-dilithio- and 1,1',3-trilithioruthenocene · *x*TMEDA was stirred for a further 15 min at room temperature. Finally, it was filtered off and extensively washed with hexane. After drying in vacuo, a slightly yellow, highly reactive solid was left. It was suspended in 80 ml of DME, cooled to −50 °C, and norbornenone (0.66 ml, 0.65 g, 6 mmol, 2.0 molequ.) was added. The cooling bath was removed and the reaction mixture was warmed to room temperature. In order to isolate the diastereomeric mono- and dialcohols, ice water (80 ml) and hydrochloric acid (2 N in water) were added. The pH should not drop below 6. Subsequently the mixture was extracted with chloroform (3 × 50 ml), the combined organic extracts were washed with water (3 × 50 ml) and finally dried over $MgSO_4$.

After removing the solvent in vacuo, the alcohols were separated from the crude mixture by means of middle pressure chromatography. (5 × 60 cm, silica,

220–440 mesh, Merck, chloroform:hexane:diethyl ether = 50:40:10). After a minimum amount of ruthenocene the desired alcohols are obtained (order: **4b**, **4a**, **5b**, **5a**) (*syn*-7-hydroxybicyclo[2.2.1]hept-2-ene-7-yl)ruthenocene (**4a**), (*anti*-hydroxybicyclo[2.2.1]hept-2-ene-7-yl)ruthenocene (**4b**), *anti,syn*-1,1′-bis(7-hydroxybicyclo[2.2.1]hept-2-ene-7-yl)ruthenocene (**5a**) and finally *anti,anti*-1,1′-bis(7-hydroxybicyclo[2.2.1]hept-2-ene-7-yl)ruthenocene (**5b**).

4.3.9. *(syn-7-Hydroxybicyclo[2.2.1]hept-2-ene-7-yl)ruthenocene (**4a**)*

Yield: 60 mg (6%). IR (KBr): 3460 (*n* OH) cm^{-1}; ^1H NMR ($CDCl_3$) *d* 0.98 (m_c, 2H, $H_{5'',6''endo}$), 1.99, (m_c, 2H, $H_{5'',6''exo}$), 2.04 (bs, 1H, OH), 2.41 (m_c, 2H, $H_{1'',4''}$), 4.40 (t, $J = 1.7$, 2H, $H_{3,4}$), 4.52 (s, 5H, $H_{1'-5'}$), 4.58 (t, $J = 1.7$, 2H, $H_{2,5}$) 5.89 (t, $J = 2.0$, 2H, $H_{2'',3''}$); ^{13}C NMR ($CDCl_3$) *d* 23.92 (t, $C_{5'',6''}$), 49.89 (d, $C_{1'',4''}$), 69.70 (d, $C_{3,4}$) 70.39 (d, $C_{1'-5'}$), 71.39 (d, $C_{2,5}$), 88.31 (s, $C_{7''}$), 99.22 (s, C_1) 134.05 (d, $C_{2'',3''}$); HRMS calcd. for $C_{24}H_{24}FeO$: 339.399. LRMS found (70 eV): 340 (80%) [$M^{+\cdot}$], 322(20%) [$M^{+\cdot} - H_2O$], 259(100%) [$RucCO^{+\cdot}$].

4.3.10. *(anti-7-Hydroxybicyclo[2.2.1]hept-2-ene-7-yl)ruthenocene (**4b**)*

Yield: 91 mg (9%); IR (KBr): 3460 (*n* OH) cm^{-1}; ^1H NMR ($CDCl_3$) *d* 0.86 (m_c, 2H, $H_{5''',6'''endo}$), 1.69 (m_c, 2H, $H_{5'',6''endo}$), 2.58 (bs, 1H, OH), 2.62 (m_c, 2H, $H_{1'',4''}$), 4.49 (t, $J = 1.7$, 2H, $H_{3,4}$), 4.54 (s, 5 H, $H_{1'-5'}$), 4.72 (t, $J = 1.7$, 2H, $H_{2,5}$), 6.09 (t, $J = 2.0$, 2H, $H_{2'',3''}$); ^{13}C NMR ($CDCl_3$) *d* 23.22 (t, $C_{5'',6''}$), 50.45 (d, $C_{1'',4''}$), 69.91 (d, $C_{3,4}$), 70.65 (d, $C_{1'-5'}$), 72.98 (d, $C_{2,5}$), 87.93 (s, $C_{7''}$), 99.98 (s, C_1), 135.00 (d, $C_{2'',3''}$); HRMS calcd. for $C_{24}H_{24}FeO$: 339.399. LRMS found (70 eV): 340 (70%) [$M^{+\cdot}$], 322 (18%) [$M^{+\cdot} - H_2O$], 259 (100%) [$RucCO^{+\cdot}$].

4.3.11. *(anti,syn)-1,1′-Bis(7-hydroxybicyclo[2.2.1]hept-2-ene-7-yl)ruthenocene (**5a**)*

Yield: (0.332 g (25%); IR (KBr): 3480, 3438 (*n* OH) cm^{-1}; ^1H NMR ($CDCl_3$) *d* 0.86 (m_c, 2H, $H_{5''',6'''endo}$), 0.98 (m_c, 2H, $H_{5'',6''endo}$), 1.69 (m_c, 2H, $H_{5''',6'''exo}$), 1.99 (m_c, 2H, $H_{5'',6''exo}$), 2.16 (bs, 1 H, OH″), 2.41 (m_c, 2H, $H_{1'',4''}$), 2.58 (bs, 1H, OH‴), 2.62 (m_c, 2H, $H_{1''',4'''}$) 4.40 (t, $J = 1.7$, 2H, $H_{3,4}$), 4.49 (t, $J = 1.7$, 2H, $H_{3',4'}$), 4.58 (t, $J = 1.7$, 2H, $H_{2,5}$), 4.72 (t, $J = 1.7$, 2H, $H_{2',5'}$,) 5.89 (t, $J = 2.0$, 2H, $H_{2'',3''}$), 6.09 (t, $J = 2.0$, 2H, $H_{2''',3'''}$); ^{13}C NMR ($CDCl_3$) *d* 23.12 (t, $C_{5''',6'''}$), 23.95 (t, $C_{5'',6''}$), 50.36 (d, $C_{1'',4''}$), 50.55 (d, $C_{1''',4'''}$), 69.72 (d, $C_{3,4}$), 69.91 (d, $C_{3',4'}$), 70.98 (d, $C_{2,5}$), 72.98 (d, $C_{2',5'}$), 87.93 (s, $C_{7'''}$), 88.47 (s, $C_{7''}$), 99,22 (s, C_1), 99.98 (s, $C_{1'}$), 134.05 (d, $C_{2''3''}$), 134.86 (d, $C_{2''',3'''}$); HRMS calcd. for $C_{24}H_{26}O_2Ru$: 447.538 LRMS found (70 eV): 448 (85%) [$M^{+\cdot}$].

4.3.12. *(anti,anti)-1,1′-Bis(7-hydroxybicyclo[2.2.1]hept-2-ene-7-yl)ruthenocene (**5b**)*

Yield: 0.685 g (51%); IR (KBr): 3440 (*n* OH) cm^{-1}; ^1H NMR ($CDCl_3$) *d* 0.83 (m_c, 4H, $H_{5'',5''',6'',6'''endo}$), 1.63 ($m_c$, 4H, $H_{5'',5''',6'',6'''exo}$), 2.30 (bs, 2H, $OH'' + OH'''$), 2.60 (m_c, 4H, $H_{1'',1''',4'',4'''}$), 4.50 (t, $J = 1.7$, 4H, $H_{3,3',4,4'}$), 4.73 (t, $J = 1.7$, 4H, $H_{2,2',5,5'}$), 6.09 (t, $J = 2.0$, 4H, $H_{2'',2''',3'',3'''}$); ^{13}C NMR ($CDCl_3$) *d* 23.15 (t, $C_{5'',5''',6'',6'''}$), 50.37 (d, $C_{1'',1''',4''4'''}$), 70.01 (d, $C_{3,3'4,4'}$), 71.39 (d, $C_{2,2'5,5'}$), 88.27 (s, $C_{7'',7'''}$), 100.12 (s, $C_{1,1'}$), 133.80 (d, $C_{2'',2''',3'',3'''}$); HRMS calcd. for $C_{24}H_{26}O_2Ru$: 447.538. LRMS found (70 eV): 448 (70%) [$M^{+\cdot}$].

4.3.13. *1,1′-Ruthenocenylene-1″,1‴-cobaltocenylenium hexafluorophosphate [133548-72-8]*

In general, a pre-separation of the alcohols is not necessary. To the crude mixture of lithium ruthenocenyl norbornenolates was added diethylchlorophosphate (0.88 ml, 1.035 g, 6.0 mmol, 2.0 molequ., Merck, distilled under argon). The reaction was warmed to ca. 50 °C and stirred for 2 h. All the volatiles were removed in vacuo and the mixture, which mainly consists of the desired stereoisomer bis(7-chloronorbornenyl)ruthenocenes **6**, was dissolved in 150 ml of diethyl ether. Filtration through Celite removes all polar by-products. The solvent was removed again and the residue was dissolved in 80 ml of DME. Lithium powder (0.840 g, 12 mmol) was added and the mixture was stirred vigorously for 15 h. The ethene formed was allowed to escape through a mercury bubbler. The mixture was finally filtered through Celite, and diluted with ca. 120 ml of DME. Cobalt chloride (0.350 g, 2.7 mmol, 0.9 molequ.) was added and the solution was stirred at 50 °C overnight. The solvent was removed and the residue was dissolved in 100 ml of ethanol (96%). Air was passed through the reaction mixture for 30 min. A precipitate formed, which was filtered off and washed with ethanol (4 × 20 ml). The combined extracts were treated with a solution of NH_4PF_6 (0.490 g, 3 mmol, 1 mequiv.) in 40 ml water and stirred at room temperature for 30 minutes. After evaporation of the solvent, the crude product was washed with water, dried, and then treated with diethyl ether. Final purification was achieved by middle pressure chromatography (5 × 60 cm, aluminium oxide basic, Activity III, acetone: diethyl ether = 80:20). The desired compound was determined by TLC: reaction with iodine results in the formation of the characteristic red-violet color. Finally the compound was recrystallized from acetone:diethyl ether. Yield: 0.110 g (6.5%); m.p.: > 300 °C (decomp.); IR (KBr): 3121m, 3107m, 1530m, 1418m, 1385m, 1267w, 1193w, 1122w, 1054m, 1033m, 1020m, 1005m, 860s, 846s, 829vs, 558s, 482m, 456m, 444w, 400w, 375w cm^{-1}; ^1H NMR (CD_3CN) *d* 4.59 (t, $J = 1.8$, 4H, $H_{3,3',4,4'}$), 5.09 (t, $J = 2.1$, 4H, $H_{3'',3''',4'',4'''}$), 6.57 (t,

J = 1.8, 4H, $H_{2,2',5,5'}$), 7.12 (t, J = 2.1, 4H, $H_{2'',2''',5'',5'''}$); ^{13}C NMR (CD_3CN) d 73.05 (d), 76.84 (d), 79.28 (d), 81.97 (d), 92.52 (s). HRMS calcd. for $C_{20}H_{16}RuCo^+$: 416.350. LRMS found: (70 eV): 417 (100%) [$M^{+\cdot}$], 208.5 (18%) [$M^{2+\cdot}$]; cyclic voltammetry: ($E_{1/2}$(DE_p) vs. Ag/AgCl, 0.1 M TBAH (10^{-3} mol l^{-1} in acetonitrile, 10 mV s^{-1}). E_{pa} = +1400 mV [Ru–Co]$^{2+}$/[Ru–Co]$^+$. $E_{1/2}$(DE_p) = −766(61) mV [Ru–Co]$^+$/[Ru–Co]^0. $E_{1/2}$(DE_p) = −1746(56) mV [Ru–Co]^0/[Ru–Co]$^-$.

*4.3.14. syn- (**8a**) and anti-(7-hydroxybicyclo[2.2.1]hept-2-ene-7-yl) ethynylferrocene (**8b**)*

Ethynylferrocene (0.95 mg, 4.53 mmol) was dissolved in DME, the solution was cooled to 0 °C and methyl lithium (1.6 M in diethyl ether, 2.8 ml, 4.5 mmol) was added. After 1 min, norbornenone (0.30 ml, 490 mg, 4.53 mmol) was added. The solution was allowed to warm to room temperature and after 10 min ice water (50 ml) was added. The mixture was extracted with diethyl ether (2 × 25 ml), the combined organic layers were washed with water (3 × 100 ml), dried over sodium sulfate and the solvent was removed in vacuo. The crude mixture (1.40 g, 97%) was purified by means of middle pressure chromatography (4 × 60 cm, silica G-60, Fluka, hexane:diethyl ether = 66:33). Two fractions were obtained.

(1) *syn*-(7-Hydroxybicyclo[2.2.1]hept-2-ene-7-yl)ethynylferrocene (**8a**). Yield: 0.9 g (62.5%); m.p.: 117–118 °C; IR (KBr): 3220bs, 3080w, 2980m, 2940m, 2879w, 2230m, 1575m, 1455m, 1410m, 1390m, 1320m, 1290m, 1255s, 1165s, 1145s, 1110vs, 1100s, 1070m, 820b,vs, 490b,vs cm^{-1}; ^1H NMR ($CDCl_3$) d 1.01 (dxd, 2H, J_1 = 7.7, J_2 = 1.8, $H_{5'',6''exo}$), 2.14 (dxd, 2 H, J_1 = 7.6, J_2 = 1.8, $H_{5''',6'''endo}$), 2,55 (s, 1H, O*H*), 2.85 (t, 2H, J = 2, $H_{4'',4''}$), 4.16 (t, 2H, J = 1.8, $H_{3,4}$), 4.19 (s, 5H, $H_{1'-5'}$), 4.40 (t, 2H, J = 1.8, $H_{2,5}$), 6.12 (m, 2H, $H_{1'',2''}$); ^{13}C NMR ($CDCl_3$) d 23.1 ($C_{5',6'}$), 52.40 ($C_{1'4'}$), 64.8 (C_q), 68.5 ($C_{3,5}$), 69.7 ($C_{1'-5'}$), 71.4 ($C_{2,5}$), 84.5 (C_q), 84.8 (C_q), 86.4 (C_q), 132.7 ($C_{2',3'}$); HRMS calcd. for $C_{19}H_{18}FeO$: 318.198. LRMS found (EI, 70 eV): 318(100%) [$M^{+\cdot}$].

(2) *anti*-(7-Hydroxybicyclo[2.2.1]hept-2-ene-7-yl)ethynylferrocene (**8b**). Yield: 0.5 g (35%); m.p.: 120-121 °C; IR (KBr): 3560s, 3400b,m, 3080w, 2980s, 2940s, 2230m, 1460m, 1410m 1325m, 1265s, 1250s, 1105vs, 1045s, 1030s, 1015s, 1000m, 820vs, 720vs, 680s, 490b,vs cm^{-1}; ^1H NMR ($CDCl_3$) d 1.05 (dxd, 2 H, J_1 = 7.7, J_2 = 1.8, $H_{5'',6''exo}$), 1.95 (dxd, 2 H, J_1 = 7.6, J_2 = 1.8, $H_{5''',6'''endo}$), 2,2 (s, 1H, O*H*), 2.77 (t, 2H, J = 2, $H_{4'',4''}$), 4.12 (t, 2H, J = 1.8, $H_{3,4}$), 4.17 (s, 5H, $H_{1'-5'}$), 4.36 (t, 2H, J = 1.8, $H_{2,5}$), 6.11 (m, 2H, $H_{1'',2''}$), assignment based on NOESY; ^{13}C NMR ($CDCl_3$) d 22.7 ($C_{5',6'}$), 51.60 ($C_{1',4'}$), 65.1 (C_q), 68.4 ($C_{3,4}$), 71.4 ($C_{1'-5'}$), 71.6 ($C_{2,5}$), 88.5 (C_q), 84.5 (C_q), 88.1 (C_q), 135.5 ($C_{2'3'}$); HRMS calcd. for $C_{19}H_{18}FeO$: 318.198. LRMS found (EI, 70 eV): 318(100%) [$M^{+\cdot}$].

*4.3.15. 7-Trimethyl-7-(ferrocenylethynyl)norbornenes (**9**)*

A mixture of *syn*- and *anti*-7-ferrocenylethynylnorbornen-7-ols **8** (255 mg, 0.80 mmol) was dissolved in 20 ml diethyl ether, the solution was cooled to 80 °C and a solution of *n*-butyllithium in pentane (2.0 M, 0.40 ml, 0.80 mmol) was added. After 10 min, trimethylsilylchloride (0.15 ml, 0.80 mmol) was added. The solution was warmed to room temperature and the solvent was evaporated. Chromatography (4 × 20 cm, silica-G 60, Fluka, 220–440 mesh, *n*-hexane) yields the product as a deep red oil, which only contains traces of bistrimethylsilyl ether. The latter was removed in vacuo, resulting in slow crystallization of the anti-isomer **9b**. Total yield of **9**: 248 mg (90%); IR (KBr): 3311m, 3066m, 2956s, 2900s, 2867s, 1457m, 1439w, 1407w, 1333m, 1302m, 1252vs, 1211m, 1187vs, 1125vs, 1092vs, 1075vs, 1025s, 969m, 901vs, 876vs, 803s, 787s, 7575, 716vs, 679s, 629s, 527m, 455w cm^{-1}; ^1H NMR ($CDCl_3$) d 0.18 (s, 9H, SiMe_3), 0.94 (dxd, 2H, J_1 = 7.6, J_2 = 1.8, $H_{5'',6''exo}$), 1.89 (dxd, 2H, J_1 = 7.6, J_2 = 1.8, $H_{5''',6'''endo}$), 2.70 (t, 2H, J = 2, $H_{4'',4''}$), 4.12 (t, 2H, J = 1.8, $H_{3,4}$), 4.14 (s, 5H, $H_{1'-5'}$), 4.34 (t, 2H, J = 1.8, $H_{2,5}$), 5.97–6.03 (m, 2H, $H_{1'',2''}$); ^{13}C NMR ($CDCl_3$) d 1.30 (SiMe_3), 22.8 ($C_{5'6'}$), 52.2 ($C_{1'4'}$), 68.12 ($C_{3,4}$), 69.56 ($C_{1'-5'}$), 70.95 ($C_{2,5}$), 134.50 ($C_{2',3'}$). HRMS calcd. for $C_{22}H_{26}FeOSi$: 390.110. LRMS found (EI, 70 eV): 390 (100%) [$M^{+\cdot}$], 317 (21%) [$M^{+\cdot}$ − 73 (trimethylsilyl)].

*4.3.16. (syn,anti)- (**11a**) and (anti,anti)-1,1'-bis((7-hydroxy norbornene-7-yl)ethynyl)ferrocene (**11b**)*

1,1'-Diacetylferrocene (2.18 g, 8.074 mmol) was dissolved in 50 ml THF and added over a period of 45 min to a stirred solution of lithiumdiisopropylamide in THF (2.0 M, 8.50 ml, 17.0 mmol). During the addition, the temperature was maintained at −80 °C. The solution was stirred at room temperature for an additional hour. Diethylchlorophosphate (2.5 ml, 17.3 mmol) was added and the reaction mixture was warmed to room temperature over a period of 2.5 h. Lithiumdiisopropylamide (0.66 M in THF, 54.6 ml, 36.4 mmol) was added dropwise at −80 °C over a period of 1 h. The mixture was again warmed to room temperature, chilled to −60 °C, and norbornenone (4.0 ml, 37.0 mmol) was added. Finally, the solution was warmed to room temperature, stirred for 18 h and carefully quenched with water. The solvent was reduced in vacuo, the residue poured on water and the suspension extracted with diethyl ether until the extracts appeared colorless. The combined organic layers were subsequently washed with 1 N HCl, water, sat. $NaHCO_3$-solution and finally water and dried over sodium sulfate. The solvent was removed in vacuo

and the oily residue was exposed to high vacuum in order to remove unreacted norbornenone. The crude product was passed over a column of silica (4 × 20 cm, 220–440 mesh, Fluka; diethyl ether). The mixture of diastereomers was separated by means of middle pressure chromatography (silica, 220–440 mesh; Fluka, column: 80 × 4 cm, diethyl ether: *n*-hexane = 80:20, flow rate 30 ml min^{-1}).

(*syn,anti*)-1,1′-Bis((7-hydroxybicyclo[2.2.1]hept-2-ene-7-yl)ethynyl)ferrocene (**11a**). The compound was obtained as a yellow solid. Recrystallization yielded 330 mg (9.1%); IR (KBr): 3540m, 3414b,s, 3103w, 3058w, 2960s, 2941s, 2906w, 2869m, 2234s, 1644b,m, 1567m, 1459s, 1341s, 1326s, 1266s, 1243s, 1169s, 1110vs, 1100vs, 1081vs, 1059vs, 1044vs, 1028s, 913m, 859s, 824s, 783s, 681s, 571s, 546s, 534s, 525s, 509vs, 500vs, 488vs, 475vs, 446s, 417m, 401s cm^{-1}; ^1H NMR ($CDCl_3$) *d* 1.0, (dxd, $J_1 = 6$, $J_2 = 3$, 2H), 1.1, (dxd, $J_1 = 6$, $J_2 = 3$, 2H), 1.95, (dxd, $J_1 = 6$, $J_2 = 3$, 2H), 2.10, (dxd, $J_1 = 6$, $J_2 = 3$, 2), 2.8, (''t'', 2H), 2.85, (''t'', 2H), 2.9, (s, 2H), 4.10, (m, 4H), 4.4, (m, 4H), 6.1, (m, 2H), 6.15, (m, 2H); ^{13}C NMR ($CDCl_3$) *d* 22.7, 23.1, 51.6, 52.4, 66.5, 67.1, 69.9, 70.1, 73.1, 84.3, 132.9, 135.3; HRMS calcd. for $C_{28}H_{26}FeO_2$: 450.359. LRMS found (EI, 70 eV): 450 (100%) [M^+], 404 (5%), 229 (20%).

(*anti,anti*)-1,1′-Bis((7-hydroxynorbornene-7-yl)ethynyl)ferrocene (**11b**). The compound was obtained as an orange solid. Recrystallization diethyl ether hexane yielded 250 mg (7%); IR (KBr): 3533m, 3408b,s, 3091w, 9062w, 2973m, 2941m, 2869w, 2233m, 1640b,s, 1550m, 1459s, 1349s, 1224s, 1258s, 1162vs, 1135vs, 1110vs, 1096vs, 1079vs, 1050vs, 1027vs, 971m, 861m, 820m, 793m, 714vs, 683m, 525m, 507m, 486m cm^{-1}; ^1H NMR ($CDCl_3$) *d* 0.93, (dxd, $J_1 = 6$, $J_2 = 3$, 4H, $H_{5'',5''',6'',6'''endo}$), 2.05, (dxd, $J_1 = 6$, $J_2 = 3$, 4H, $HH_{5'',5''',6'',6'''exo}$), 2.78, (s, 2H, O*H*), 2.83, (m, 4H, H, $H_{1'',1''',4'',4'''}$), 4.14, (''t'', $J = 1.8$, 4H, $H_{3,3',4,4'}$), 4.32, (''t'', $J = 1.8$, 4H, $H_{2,2',5,5'}$), 6.03, (m, 4H, $H_{2'',2''',3'',3'''}$); ^{13}C NMR ($CDCl_3$): *d* 23.07, 52.24, 66.43, 70.27, 73.01, 83.57, 85.50, 86.26, 132.63 (*C*=*C*); HRMS calcd. for $C_{28}H_{26}FeO_2$: 450.359. LRMS found (EI, 70 eV). 450 (100%) [M^+], 404 (5%), 229 (20%).

4.3.17. *syn- and anti-7-hydroxy-7-ethynylbicyclo[2.2.1]hept-2-ene (**10**)*

Norbornenone (5 ml, 46 mmol) was dissolved in 50 ml THF and a solution of ethynylmagnesiumbromide in THF (0.5 M, 101 ml, 50.5 mmol) was added at 0 °C over a period of 15 min. After 10 min, the solution was warmed to 40 °C and stirred for a further 60 min. The mixture was poured on a sat. aqueous solution of ammonium chloride, extracted with diethyl ether (3 × 100 ml), the combined organic extracts were washed with water (2 × 100 ml), and the washings were again extracted with diethyl ether (50 ml). The combined organic layers were dried over sodium sulfate. The solvent was removed in vacuo to give 5.24 g (85%) crude reaction mixture. The diastereomers were separated by means of middle pressure chromatography: column: 5 × 20 cm, silica G-60, 220–440 mesh, Fluka, *n*-hexane:diethyl ether = 15:85.

syn-7-Hydroxy-7-ethynylbicyclo[2.2.1]hept-2-ene (**10a**). The compound was obtained from the first fraction as a colorless, waxy solid. Yield: 3.4 g (55.1%); IR (KBr): 3430b,vs, 3390w,b, 3030w, 2923s, 2852s, 1669w, 1470m, 1280vs, 1185s, 1110vs, 1050vs, 1035s, 960m, 880m, 805b,vs, 710vs cm^{-1}; ^1H NMR ($CDCl_3$) *d* 1.00 (dxd, 2H, $J_1 = 7$, $J_2 = 3.5$, $H_{5,6endo}$), 1.94 (dxd, 2H, $J_1 = 10$, $J_2 = 3.5$, $H_{5,6exo}$), 2.71 (m, 2 H, $H_{1,4}$), 3.01 (s, 2 H, CC*H* + O*H*, 6.04, m,(2 H, *H*C–C*H*); ^{13}C NMR ($CDCl_3$) *d* 22.4 (CH_2), 51.1 ($C_{1,4}$), 65.0 ($C_{3,2}$), 83.4, 84.5, 86.4, 135.0 ($C_{2,3}$); HRMS calcd. for $C_9H_{10}O$: 134.177. LRMS found (EI, 70 eV): 134 (100%) [M^+].

anti-7-Hydroxy-7-ethynylbicyclo[2.2.1]hept-2-ene (**10b**). The compound was obtained from the second fraction as a colorless oil. Yield: 1.7 g (27.6%); IR (l-film): 4370b,vs, 3309vs, 3066m, 2948b,vs, 2873vs, 2107w, 1459m, 1366m, 1329m, 1297m, 1270s, 1212m, 1169s, 1136s, 1115vs, 1092s, 1055vs, 969m, 893s, 876s, 861s, 785m, 714s, 641m, 531w, 486w, 455w cm^{-1}; ^1H NMR ($CDCl_3$) *d* 1.00 (dxd, 2H, $J_1 = 7$, $J_2 = 3.5$, $H_{5,6endo}$), 1.91 (dxd, 2H, $J_1 = 10$, $J_2 = 3.5$, $H_{5,6exo}$), 2.66, (''t'', 2H, $J = 2$, $H_{1,4}$), 6.01 (m, 2H); ^{13}C NMR ($CDCl_3$) *d* 22.3 (CH_2), 51.0, 51.9, 135.0 ($C_{2,3}$); HRMS calcd. for $C_9H_{10}O$: 134.177. LRMS found (EI, 70 eV):134 (100%) [M^+].

4.3.18. *syn- and anti-7-(iodethynyl)-7-hydroxybicyclo[2.2.1]hept-2-ene (**10c,d**)*

4.3.18.1. By phase transfer catalysis. The diastereomeric mixture of 7-ethynylnorbornene-7-ols was converted into the corresponding terminal iodoacetylenes without further purification or separation. The oily mixture was dissolved in 25 ml DMF and sodium carbonate (10 g, 94.3 mmol), tetrabutylammonium bromide (4.5 g, 14.0 mmol) as well as copper(I) iodide (0.5 g 2.6 mmol) were added. A solution of iodine (11.5 g, 45.3 mmol) in 30 ml DMF was added under vigorous stirring over a period of 6 h. After the addition was complete, the mixture was stirred for further 14 h, poured on water and the mixture was extracted with diethyl ether (3 × 100 ml). The combined organic extracts were dried over sodium sulfate and the solvent was evaporated in vacuo). The compound is left behind as a yellow oil, which solidifies around 0 °C and appears to be very sensitive towards light, resulting in rapid decomposition. In this case a red color appears (free iodine), which may be removed by dissolving the residue in a minimum of

diethyl ether and extraction with a few milliliters of sodium thiosulfate solution (1 M).

4.3.18.2. By direct iodination. A diastereomeric mixture of 7-ethynylnorbornene-7-ol (2.68 g, 20 mmol) was dissolved in i-pentane and carefully dried over sodium sulfate. The solution was cooled to −60 °C and *n*-butyllithium (20 ml, 2.0 M in hexane, 40 mmol) was added. A solution of iodine (5 g, 19.7 mmol) in 30 ml THF was added, until a slight yellow brown color remained. The solution obtained contains lithium iodoethynylnorbornenolate in THF–i-pentane (ca. 0.2 M) and may be used as obtained for further syntheses. In any case, extensive exposure to light must be avoided in order to prevent decomposition, resulting in the formation of iodine and dimers.

HRMS calcd. for C_9H_9IO: 260.074. LRMS found (EI, 70 eV): 260 (20%) [$M^{+\cdot}$].

*4.3.19. (syn,anti)- (**11a**) and (anti,anti)-1,1′-bis((7-hydroxybicyclo[2.2.1]hept-2-ene-7-yl)ethynyl)ferrocene (**11b**)*

By copper mediated coupling. Dilithioferrocene · TMEDA (1.128 g, 3.6 mmol) was suspended in 50 ml THF, cooled to −30 °C and copper(I)bromide · dimethylsulfide (1.62 g, 7.90 mmol) was added. The mixture was warmed to room temperature, stirred for a further 90 min and a solution of 7-iodoethynyl-7-hydroxybicyclo[2.2.1]hept-2-ene in THF–i-pentane (36 ml, 0.2 M, 7.2 mmol) was added. The reaction mixture was poured on a saturated aqueous solution of ammonium chloride, extracted with diethyl ether and finally passed over a short column (4 × 20 cm, silica G-60, Fluka, *n*-hexane:diethyl ether = 33:66). After this pre-purification, the mixture of diastereomeric mono- and bis(7-hydroxynorbornene-7-yl)ferrocenes was separated by means of middle pressure chromatography. (4 × 80 cm, silica G-60 (Fluka), *n*-hexane:diethyl ether = 70:30, flow rate: 25 ml min^{-1}). The following compounds were separated from the crude mixture:

syn- and *anti*-(7-hydroxybicyclo[2.2.1]hept-2-ene7-yl) ethynylferrocene (**8a,b**) 420 mg (36.8%), based on dilithioferrocene;

(*syn,anti*)- and (*anti,anti*)-1,1′-bis(7-hydroxybicyclo(2.2.1]-hept-2-ene7-yl)ethynyl)ferrocene (**11a,b**) 1.01 g (62.5%). For analytical data see above.

5. Supporting information

Tables of crystal data, and structure refinement details, anisotropic thermal parameters, fractional atomic coordinates, and isotropic thermal parameters for the non-hydrogen atoms, all bond lengths and angles, and fractional atomic coordinates for the hydrogen atoms for **7**, **10a**, **10b** and **11** are available on request from the authors. The authors have deposited atomic coordinates for structures **7**, **10a**, **10b** and **11** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge, CB2 1EW, UK.

Acknowledgements

This work was supported by FWF, Wien under project P 10182 MOB.

References

[1] (a) P. Scott, P.B. Hitchcock, J. Organomet. Chem. 497 (1995) C1. (b) P. Scott, U. Rief, J. Diebold, H.H. Brintzinger, Organometallics 12 (1993) 3094.
[2] M.L.H. Green, V.S.B. Mtewa, A. Sella, A.N. Chernega, J. Chem. Soc. Dalton Trans. 2 (1994) 207 and references cited therin.
[3] P. Brueggeller, P. Jaitner, H. Schottenberger, K.E. Schwarzhans, J. Organomet. Chem. 417 (1991) C53 and references cited therein.
[4] (a) M. Tilset, K.P.C. Vollhardt, R. Boese, Organometallics 13 (1994) 3146. (b) S. Wan, M.J. Begley, P. Mountford, J. Organomet. Chem. 489 (1995) C28. (c) R.C. Kerber, B. Waldbaum, Organometallics 14 (1995) 4742. M.J. Begley, P. Mountford, P.J. Stewart, D. Swallow, S. Wan, J. Chem. Soc. Dalton Trans. (1996) 1323.
[5] K.E. Schwarzhans, H. Schottenberger, Z. Naturforsch. Teil B: 38 (1983) 1493 and references cited therein.
[6] (a) P. Jaitner, H. Schottenberger, S. Gamper, D. Obendorf, J. Organomet. Chem. 475 (1994) 113 and references cited therein.
[7] H. Schottenberger, G. Ingram, D. Obendorf, R. Tessadri, Synlett 12 (1991) 905.
[8] R. Sanders, U.T. Mueller-Westerhoff, J. Organomet. Chem. 512 (1996) 219.
[9] J. Lukasser, H. Angleitner, H. Schottenberger, H. Kopacka, M. Schweiger, B. Bildstein, K.-H. Ongania, K. Wurst, Organometallics 14 (1995) 5566.
[10] C. Rieker, G. Ingram, P. Jaitner, H. Schottenberger, K.E. Schwarzhans, J. Organomet. Chem. 381 (1990) 127 and references cited therein.
[11] M.E. Huttenloch, J. Diebold, U. Rief, H.H. Brintzinger, Organometallics 14 (1992) 3600.
[12] (a) J. Polin, H. Schottenberger, Org. Synth. 73 (1996) 262. (b) K. Wurst, O. Elsner, H. Schottenberger, Synlett 8 (1995) 833.
[13] (a) M. Buchmeiser, H. Schottenberger, J. Organomet. Chem. 441 (1992) 457. (b) J.K. Pudelski, M.R. Callstrom, Organometallics 13 (1994) 3095.
[14] G. Doisneau, G. Balavoine, T. Fillebeen-Khan, J. Organomet. Chem. 425 (1992) 223.
[15] E. Negishi, A.O. King, J.M. Tour, Org. Synth. 64 (1986) 44.
[16] F.R.S. Clark, J. Warkentin, Can. J. Chem. 49 (1971) 2223.
[17] M. Buchmeiser, H. Schottenberger, J. Organomet. Chem. 436 (1992) 223.
[18] M.F.C. Ladd, Acta Crystallogr. Sect. B: 35 (1979) 2375.
[19] M. Herberhold, Angew. Chem. Int. Ed. Engl. 34 (1995) 1837.

[20] A.C.T. North, D. Phillips, F.S. Mathews, Acta Crystallogr. Sect. A: 24 (1968) 351.
[21] D. Obendorf, H. Schottenberger, C. Rieker, Organometallics 10 (1991) 1293.
[22] International Tables for Crystallography, vol. C, Kluwer, Dordrecht, 1992.
[23] G.M. Sheldrick SHELXS-86: Program for Crystal Structure Solutions, Göttingen, 1986.
[24] G.M. Sheldrick, SHELXL-93: Program for the Refinement of Crystal Structures, Göttingen, 1993.
[25] H.B. Bürgi, J.D. Dunitz, Structure Correlation, VCH, Weinheim, 1994.