Synthesis and Some Chemical Transformations of (*Z*)- and (*E*)-2-Acetyl-1-ferrocenyl-3-methylbuta-1,3-dienes − A New Type of Cationic Cycloaddition

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Dehydration of (*E*)- and (Z)-2-acetyl-1-ferrocenyl-3-methylbut-1-en-3-ols gave the corresponding (*E*)- and (Z)-2-acetyl-1-ferrocenyl-3-methylbuta-1,3-dienes, which have a cross-conjugated system of three double bonds. These heterotrienes readily afford the products of linear and cyclodimerization by following a cationic cyclodimerization mechanism; they also form Diels–Alder adducts with azodicarboxylic and maleic acid *N*-phenylimides. The spatial structures of (*E*)-2-acetyl-1-ferrocenyl-3-methylbuta-1,3-diene, (*E*,*E*)-1,5-diferrocenyl-2-isopropenyl-6-isopropylidene-3-methyl-1,3-octadiene-7-one, and 7-ferrocenyl-4-(ferrocenylmethylidene)-8-isopropylidene-1,3,5-trimethyl-9-oxabicyclo[3.3.1]non-2-ene were elucidated by X-ray diffraction analyses of single crystals.

Introduction

Recently, compounds comprising metallocene units (in particular, ferrocene) and ene, diene, and polyene fragments have garnered the interest of researchers.[1,2] Ferrocenyl-substituted 1,3-dienes gained prominence by virtue of their exciting structures, chemical reactivity, and potential use as molecular building blocks and, in the realm of supramolecular chemistry, as redox-switching receptors.[3−7]

The following methods are currently applied to access ferrocenylbuta-1,3-dienes having a terminal double bonds: (*i*) dehydration of ferrocenyl(methyl)allylic alcohols;[8−10] (*ii*) deprotonation of ferrocenyl(methyl)allylic cations,[8−13] and (*iii*) the Wittig reaction.[14] Ferrocenyl-, (aryl)ferrocenyl-, (alkyl)ferrocenyl-, (alkyl)diferrocenyl- and (aryl)diferrocenylbuta-1,3-dienes have been reported; their thermal and proton-induced cyclodimerization[9,11] and cationic cycloaddition[10,12] reactions occur with high diastereoselectivity. The reaction products comprise alkylaryl(ferrocenyl)-substituted six-membered carbocycles that are either free or fused to other carbo- or heterocyclic systems. Many of the compounds synthesized display high biological activity.[12,15] Stepwise, non-synchronous mechanisms have been proven experimentally[16,17] for the proton-induced cyclodimerization and cationic cycloaddition, which are essential from a theoretical point of view.

Ferrocenyl-substituted 1,3-dienes and linear cross-conjugated trienes that have terminal methylene groups and functionalized substituents remain virtually unexplored. At the same time, the prospects of their use for the solution of synthetic, practical, and theoretical problems seem fairly broad. In this connection, we became interested in investigating approaches to the synthesis of functionalized ferrocenylbuta-1,3-dienes and cross-conjugated trienes and to study their chemical behavior.

In this paper, we describe the synthesis of (*Z*)- and (*E*)-2-acetyl-1-ferrocenyl-3-methylbuta-1,3-dienes and 3-(ferrocenylmethylidene)-2,4-dimethylpenta-1,4-diene and report some of their reactions, such as [4+2] cycloaddition, protonation, and cationic dimerization.

Results and Discussion

Condensation of ferrocenecarbaldehyde with acetylacetone in benzene in the presence of pyridine and piperidine yields 3-(ferrocenylmethylidene)pentane-2,4-dione (**1**; Scheme 1), which served as our starting material for the preparation of acetyl(ferrocenyl)butadienes.

3-(Ferrocenylmethylidene)pentane-2,4-dione (**1**) was isolated in 71% yield; a side product, 6-ferrocenyl-3-(ferrocen-

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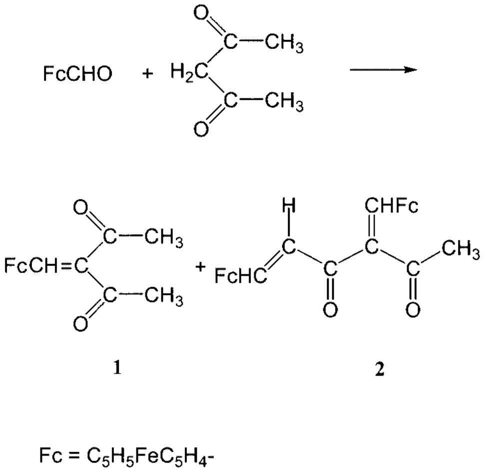
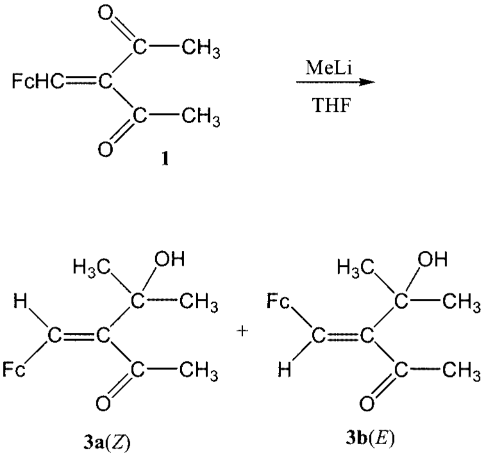


Scheme 1



Scheme 2

ylmethylidene)hex-5-ene-2,4-dione (**2**), was obatined in 12% yield.

We found that the reaction of the β-diketone **1** with even a fourfold molar excess of methyllithium in THF afforded preferentially the mono-addition products, with the ratio of isomeric β-hydroxy ketones **3a** and **3b** being ca.1:2 as determined from ^{1}H NMR spectroscopic data (Scheme 2).

The structures of the hydroxy ketones **3a** and **3b**, which were separated by chromatography on alumina, were established based on ^{1}H and ^{13}C NMR spectra and data from elemental analysis. The (*Z*) configuration was ascribed tentatively to the minor isomer **3a**, and an (*E*) configuration to compound **3b**.

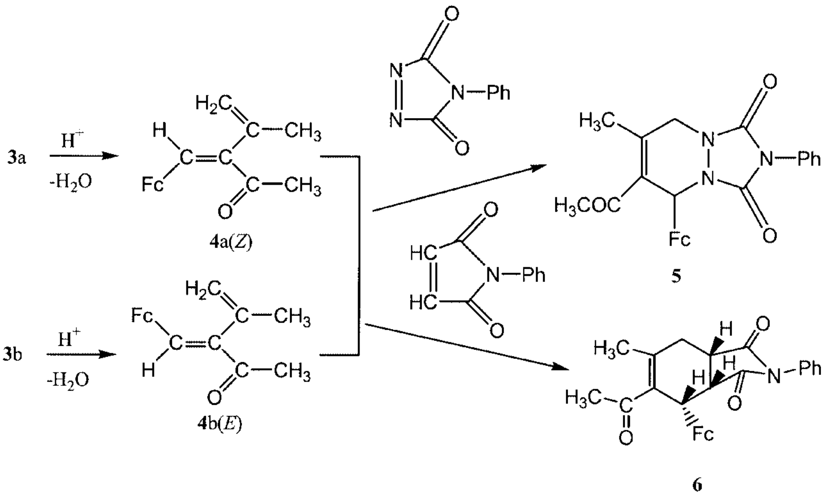
Both of the hydroxy ketones, **3a** and **3b**, dehydrated smoothly when heated in acetic acid, and the corresponding dienes, **4a** and **4b**, were isolated quantitatively as single isomers (Scheme 3).

The structures of compounds **4a** and **4b** were established based on their NMR spectra. The structure of one of these dienes, viz., compound **4b**, was confirmed by X-ray crystallographic analysis. A general view of molecule **4b** and its crystal packing are shown in Figure 1 (a and b), respectively, and require no special comment.

Data from X-ray diffraction analysis confirm unambiguously (*E*)-configuration of this compound and, correspondingly, of the hydroxy ketone **3b**.

The acetyl(ferrocenyl)methylbutadienes **4a** and **4b** are crystalline compounds stable on storage under ordinary conditions and on heating in benzene, toluene, and acetic acid. They react with *N*-phenylazodicarboximide and *N*-phenylmaleimide to form the adducts **5** and **6**, respectively. Compound **6** was formed stereospecifically as a single, presumably *endo*, diastereoisomer. This assignment is based on previously established criteria.[8,18,19] Thus, the signal of one of the protons of the C_5H_4 group of the ferrocene unit in the ^{1}H NMR spectrum of compound **6** is present at higher field relative to the singlet of the C_5H_5 protons, which is typical of *endo* isomers.

The action of tetrafluoroboric acid−diethyl ether on the dienes **4a** and **4b** afforded crystalline 2-acetyl-1-ferrocenyl-3,3-dimethylallylium tetrafluoroborates (**7a** and **7b**; Scheme 4), which are sufficiently stable (up to 24 h) when



Scheme 3

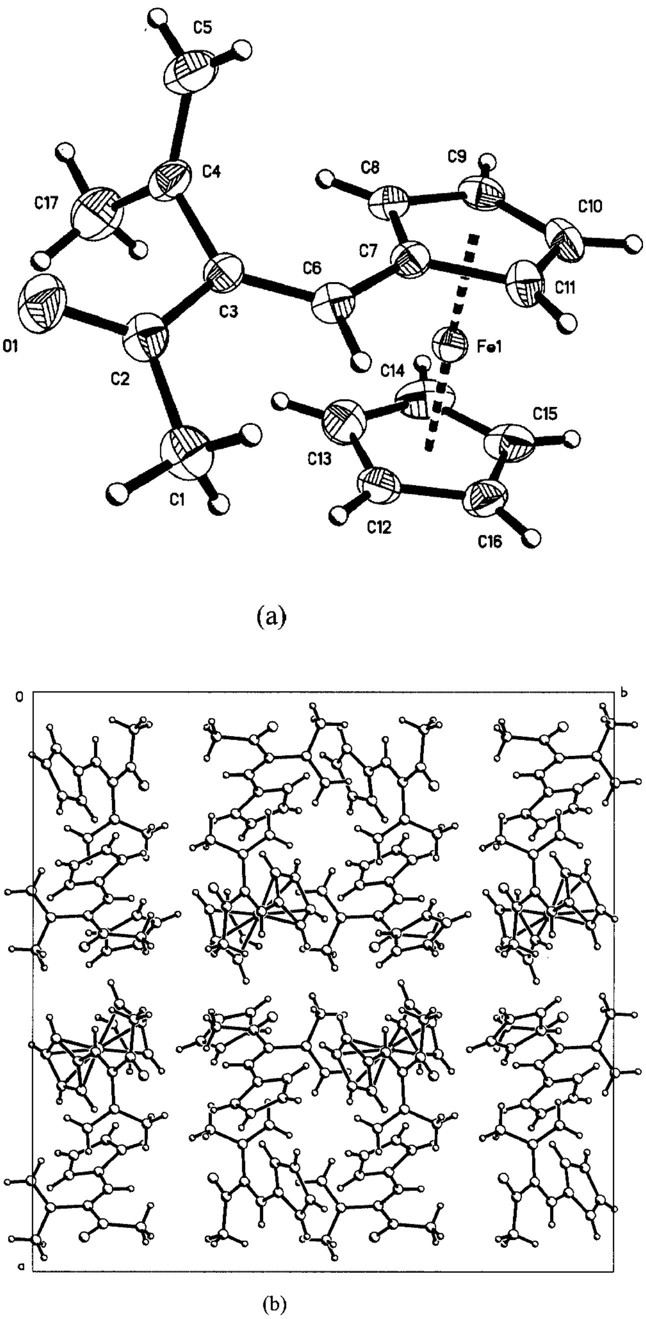
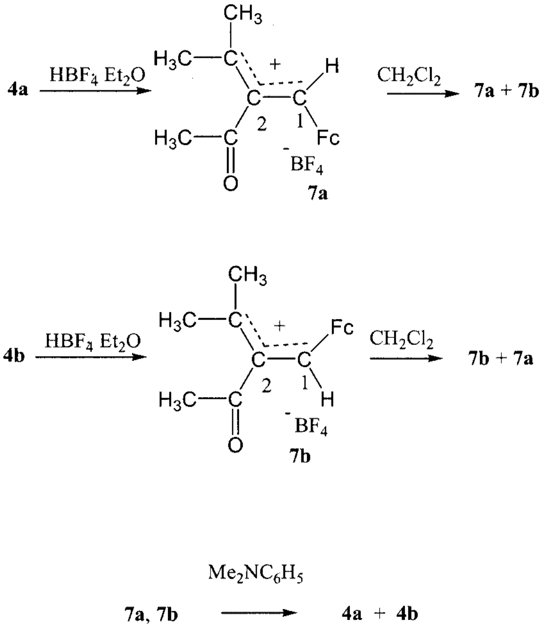


Figure 1. (a) Crystal structure and (b) crystal packing of **4b**



Scheme 4

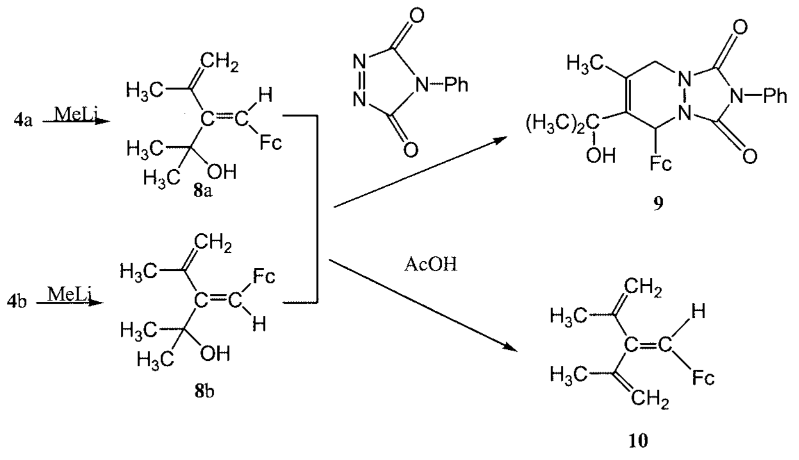
stored in their crystalline forms under ordinary conditions. These salts underwent isomerization in solution in CH_2Cl_2, as determined from their ^1H NMR spectroscopic data, to give an equilibrium mixture of the two isomers (**7a** ⇄ **7b**) in a ca. 1:2 ratio (**7a/7b**; Scheme 4). Treatment of the solutions of the tetrafluoroborates **7a** and **7b** in CH_2Cl_2 with *N*,*N*-dimethylaniline resulted in their deprotonation and formation of mixtures of the dienes **4a** and **4b** in a ca. 1:2 ratio (Scheme 4).

We believe that the transition of the initial (*Z*) or (*E*) configuration of the ferrocenylallylium cations into the (*E*) and (*Z*) isomers, respectively, occurs because of rotation around the sesquilateral C(1)−C(2) bond despite the rather high energy barrier.[20−23] Similar isomerizations have been observed earlier for ferrocenylmethylidene-substituted camphor, quinuclidinone, and menthone in acidic media.[24]

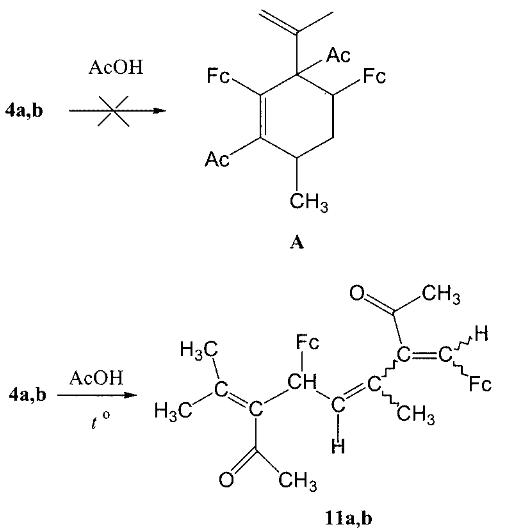
Addition of methyllithium to 2-acetyl-1-ferrocenylbutadienes **4a** and **4b** afforded the corresponding (*Z*)- and (*E*)-(1-hydroxy-1-methyl)ethylbutadienes **8a** and **8b**, which were characterized from a Diels−Alder adduct (**9**). Their dehydration under the action of acetic acid resulted in a cross-conjugated ferrocenyltriene **10** (Scheme 5). The triene **10** is an crystalline, orange compound that is storage-stable in air.

Our studies on the chemical behavior of the (acetyl)ferrocenylbutadienes **4a** and **4b** demonstrate that, unlike the *s-trans-/s-cis*-1,3-diferrocenyl- and *s-trans-/s-cis*-1,3-(aryl)ferrocenylbuta-1,3-dienes, which undergo cyclodimerization in acidic media to give 1,3,4,5-tetrasubstituted cyclohexenes,[9,10] compounds **4a** and **4b** do not form cyclodimers of type A even after heating under reflux in acetic acid — conditions that would be expected to induce acid-induced cyclodimerization (Scheme 6). The only reaction product was a mixture of two isomers of the linear dimer **11** (**11a/11b**, ca. 3:1, as deduced from ^1H NMR spectroscopic data).

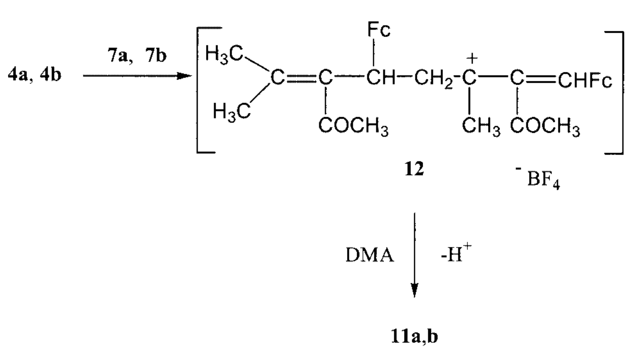
The isomers **11a** and **11b** were separated by chromatography and their structures, except for the stereochemistry [(*Z*) or (*E*)], was established from their ^1H and ^{13}C NMR spectra. Thus, the ^1H NMR spectra of compounds **11a** and **11b** display five singlets for the five methyl groups, one singlet and one doublet for the olefinic protons, one doublet for the proton of the −CH− fragment, and signals for protons of the two ferrocenyl substituents. The ^{13}C NMR spectra of compounds **11a** and **11b**, which also corroborate their structures, each display four signals for carbon atoms bearing no hydrogen atoms, two signals for carbonyl carbon



Scheme 5

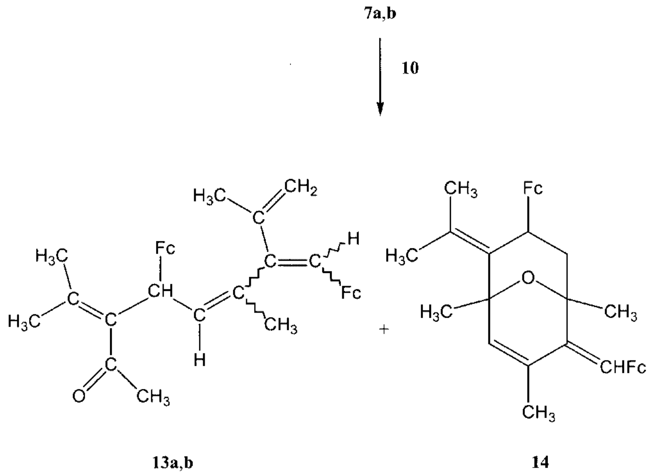


Scheme 6



Scheme 7

atoms, two signals for $-CH=$ groups, and two signals for the C_{ipso}Fc carbon atoms of the ferrocene units. The number of signals for the $-CH=$, C_5H_5, C_5H_4-, and Me groups and their chemical shifts correspond completely to structure **11**.



Scheme 8

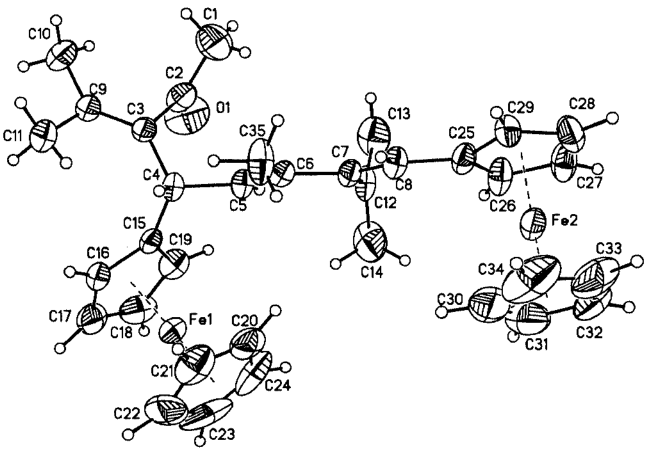


Figure 2. Crystal structure of **13a**

We also obtained the linear dimer **11** by coupling the dienes **4a** and **4b** with the tetrafluoroborates **7a** and **7b**. The product obtained (Scheme 7) represents a mixture of the two isomers **11a** and **11b** in nearly the same ratio (ca. 3:1, ^1H NMR spectroscopic data).

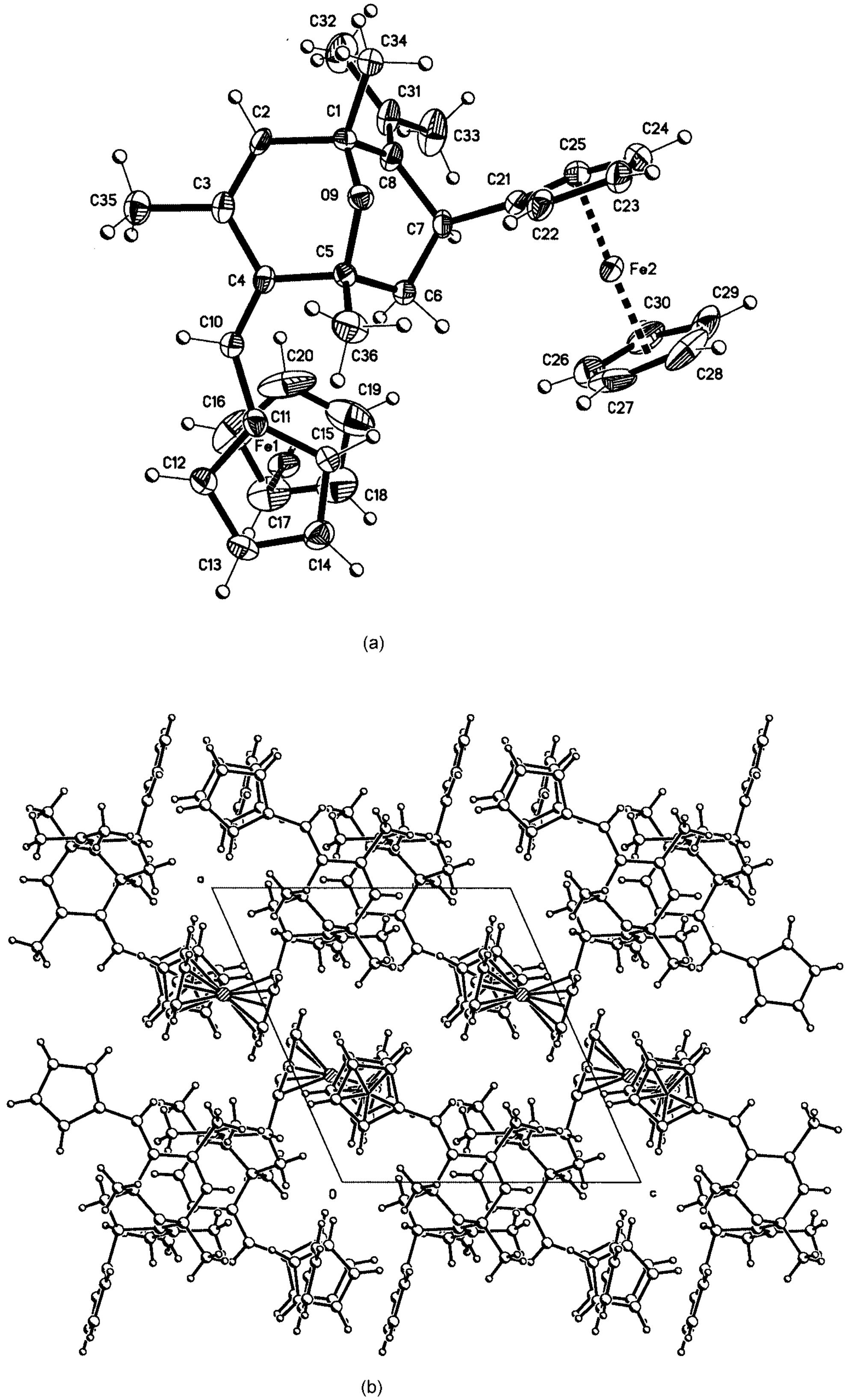


Figure 3. (a) Crystal structure and (b) crystal packing of **14**

The linear dimer **11** forms, apparently, from deprotonation of the intermediate dimeric allylic cations **12**, which are formed upon addition of the cation **7**, through its secondary carbocationic center, to the methylidene group of the diene **4**. This type of deprotonation of dimeric allylic carbocations has been observed earlier in the cationic dimerizations of *s-cis*-ferrocenylbutadienes, viz., 2-(ferrocenylmethylidene)-3-methylidenequinuclidine and 3-(ferrocenylmethylidene)-2-methylidenecamphane.[25,26]

Under similar conditions, the tetrafluoroborates **7a** and **7b** react with the triene **10** to give two products, viz., the linear dimer **13** (as a ca. 2:1 mixture of two isomers, **13a** and **13b**) and the cyclodimer **14** (Scheme 8).

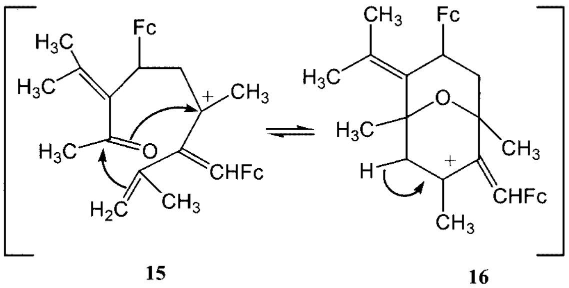
The isomers **13a** and **13b** were separated by chromatography. X-ray crystallographic analysis of a single crystal of **13a**, prepared from $CHCl_3$, indicates its (*E*,*E*) configuration (Figure 2). The linear dimer **11a** seems to have an analogous spatial structure.

Compound **14** was isolated in one stereoisomeric form in ca. 20% yield. Its ^1H NMR spectrum contains five singlets for the five methyl groups, an ABX system for the protons of the $CH-CH_2$ fragment, two singlets for the olefinic protons, and signals for the protons of the two ferrocenyl substituents. Signals for carbon atoms of the two ferrocene units, five methyl substituents, six carbon atoms bearing no hydrogen atoms, two olefinic carbon atoms, one methylene unit, and one methine group are all present in the ^{13}C NMR spectrum.

We obtained final proof that the structure of the cyclodimer **14** is that of 7-ferrocenyl-4-(ferrocenylmethylidene)-8-[isopropylidene-1,3,5-trimethyl-9-oxabicyclo[3.3.1]non-2-ene, having two fused six-membered heterocycles, by X-ray crystallographic analysis (Figure 3, a and b) of a single crystal obtained from a chloroform solution. The lengths of the C−C, C=C, and C−O bonds in the heterocyclic fragments and of the C−Fe and C−C bonds in the ferrocenyl substituents, as well as the geometric parameters of the ferrocene sandwiches, are all close to standard values.[27]

Compound **14** is formed, presumably, by intramolecular transformation of a transient dimeric linear allylic cation **15** according to the tentative mechanism depicted in Scheme 9.

The deprotonation of the linear carbocation **15** by *N*,*N*-dimethylaniline results in the linear dimers **13a**,**b**, whereas the deprotonation of a bicyclic carbocation **16**, which is in equilibrium with the linear cation **15**, affords the product **14**.



15 **16**

$$\mathbf{13a,b} \xleftarrow[-H^+]{DMA} \mathbf{15} \rightleftharpoons \mathbf{16} \xrightarrow[-H^+]{DMA} \mathbf{14}$$

Scheme 9

In the cycloaddition reaction studied, the high diastereoselectivity observed in the formation of compound **14** is worth special mention. The molecule of **14** contains several chiral centers, yet this compound was isolated as a single diastereoisomer. The high diastereoselectivity of this cycloaddition probably can be attributed to the configurational features of the dimeric linear allylic cation **15**, in which the carbocationic center and the oxygen atom of the carbonyl group, positioned on one side, and the terminal methylidene fragment and the carbon atom of the carbonyl group, on the other, become close enough spatially to enable intramolecular double alkylation.

This kind of processes in unprecedented in the literature. Elucidation of the roles of the various factors that characterize the stepwise cationic dimerization/cyclodimerization involving cross-conjugated trienes, and isolation of the reaction products at each step, deserves, in our opinion, further studies.

Experimental Section

The ^1H and ^{13}C NMR spectra were recorded with a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$ using Me_4Si as the internal standard. The ^1H NMR spectra of the tetrafluoroborates **7a** and **7b** were recorded from their solutions in CD_2Cl_2. The IR spectra were measured with a Specord IR-75 instrument using KBr pellets. The mass spectra were obtained with a Varian MAT CH-6 instrument (EI MS, 70 eV). Column chromatography was carried out on Al_2O_3 (Brockmann activity III). The following reagents were purchased from Aldrich: Ferrocenecarbaldehyde, 99%; pentane-2,4-dione, 99%; 1.6 M methyllithium in diethyl ether; glacial acetic acid, 99.99%, *N*,*N*-dimethylaniline, 99%; piperidine, 99%; and pyridine, 99%. Tetrafluoroboric acid−diethyl ether (50−52%) was purchased from Alfa AESAR.

Condensation of Ferrocenecarbaldehyde with Pentane-2,4-dione: A mixture of FcCHO (4.3 g, 0.02 mol), acetylacetone (3 mL), piperidine (1 mL), and pyridine (1 mL) in dry benzene (100 mL) was heated under reflux for 10 h. The reaction mixture was washed with 5% HCl to remove the amines and then the organic layer was concentrated to dryness. Diethyl ether (100 mL) was added to the residue and the precipitate was filtered off and dried on a filter to give 3-(ferrocenylmethylidene)pentane-2,4-dione (**1**) (4.21 g, 71%) as violet crystals. M.p. 142 °C (ref.[28] m.p. 142 °C). IR (KBr): $\tilde{\nu}$ = 821, 850, 1100, 1480, 1662, 1690, 1850, 1720, 3030 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 4.21 (s, 5 H, C_5H_5), 4.42 (m, 2 H, C_5H_4), 4.51 (m, 2 H, C_5H_4), 7.30 (s, 1 H, CH=) ppm. $C_{16}H_{16}FeO_2$ (296): calcd. C 64.89, H 5.45, Fe 18.86; found C 64.71, H 5.69, Fe 18.74.

The ethereal filtrate was concentrated to dryness and the residue was chromatographed (Al_2O_3; hexane/diethyl ether, 1:1) to give 6-ferrocenyl-3-(ferrocenylmethylidene)hex-5-ene-2,4-dione (**2**, 0.3 g, 12%) as a violet powder. M.p. 234−235 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 3 H, CH_3), 4.02 (s, 5 H, C_5H_5), 4.21 (s, 5 H, C_5H_5), 4.45 (m, 4 H, C_5H_4), 4.47 (m, 4 H, C_5H_4), 6.47 (d, *J* = 15.9 Hz, 1 H, CH=), 7.34 (d, *J* = 15.9 Hz, 1 H, CH=), 7.61 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.2 (CH_3), 69.1, 71.2, 71.8, 72.1 (2 × C_5H_4), 69.7, 69.9 (2 × C_5H_5), 76.1, 78.0 (2 × C_{ipso}Fc), 124.9, 141.8, 149.2 (3 × CH=), 135.0 (C), 194.8, 198.1 (2 × C=O) ppm. $C_{27}H_{24}Fe_2O_2$ (492): calcd. C 65.88, H 4.92, Fe 22.70; found C 65.64, H 4.71, Fe 22.97.

(*Z*)- and (*E*)-2-Acetyl-1-ferrocenyl-3-methylbut-1-en-3-ols (3a and 3b): A solution of MeLi (1.6 M in diethyl ether, 25 mL) was added dropwise over 30 min under an inert atmosphere to a stirred solution of compound **1** (2.86 g, 0.01 mol) in dry THF (100 mL) at 20 °C. The mixture was stirred for an additional 2 h before the excess MeLi was quenched by addition of water (50 mL) and then the organic layer was separated, dried with Na_2SO_4, and concentrated. The residue was chromatographed (Al_2O_3; hexane/diethyl ether, 2:1) to give the hydroxy ketone **3a** [0.94 g, 30%; (*Z*) isomer] and the hydroxy ketone **3b** [1.96 g, 63%; (*E*)].

Compound 3a: Yellow powder, m.p. 78−79 °C. IR (KBr): ṽ = 816, 1101, 1155, 1259, 1445, 1528, 1645, 1719, 2931, 3090, 3340−3450 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (s, 6 H, 2 CH_3), 2.21 (s, 3 H, CH_3), 2.89 (br. s, 1 H, OH), 4.14 (s, 5 H, C_5H_5), 4.25 (m, 2 H, C_5H_4), 4.28 (m, 2 H, C_5H_4), 6.56 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.5 (2 × CH_3), 32.6 (CH_3), 69.0, 69.8 (C_5H_4), 69.3 (C_5H_5), 72.5 (C−OH), 80.3 ($C_{ipso}Fc$), 125.4 (CH=), 145.5 (C), 210.2 (C=O) ppm. $C_{17}H_{20}FeO_2$ (312): calcd. C 65.40, H 6.46, Fe 17.89; found C 65.61, H 6.29, Fe 17.73.

Compound 3b: Orange crystals, 1.96 g (63%), m.p. 97−99 °C. IR (KBr): ṽ = 825, 1115, 1148, 1245, 1451, 1518, 1640, 1711, 2919, 3089, 3345−3430 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 6 H, 2 CH_3), 2.19 (s, 3 H, CH_3), 2.96 (br. s, 1 H, OH), 4.11 (s, 5 H, C_5H_5), 4.15 (m, 2 H, C_5H_4), 4.18 (m, 2 H, C_5H_4), 6.33 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.7 (2 × CH_3), 32.2 (CH_3), 67.9, 70.3 (C_5H_4), 69.1 (C_5H_5), 75.8 (C-OH), 83.8 ($C_{ipso}Fc$), 120.2 (CH=), 151.8 (C), 210.1 (C=O) ppm. $C_{17}H_{20}FeO_2$ (312): calcd. C 65.40, H 6.46, Fe 17.89; found C 65.26, H 6.70, Fe 18.03.

(*Z*)-2-Acetyl-1-ferrocenyl-3-methylbuta-1,3-diene (4a): A solution of the hydroxy ketone **3a** (1.56 g, 5 mmol) in benzene (50 mL) and AcOH (20 mL) was stirred at 20 °C for 5 h. Water (50 mL) was then added and the organic layer was separated, washed with 5% $NaHCO_3$, and concentrated. The residue was chromatographed (Al_2O_3; hexane) to give the diene **4a** (1.03 g, 70%) as orange crystals. M.p. 58−60 °C. IR (KBr): ṽ = 816, 883, 1002, 1030, 1053, 1105, 1178, 1201, 1349, 1382, 1415, 1606, 1660, 1703, 2923, 2963, 3091 cm^{-1}. UV ($CHCl_3$, 20 °C): $\lambda_{max.}$ = 211, 248, 293, 458 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (dd, *J* = 0.6, 1.2 Hz, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 4.14 (s, 5 H, C_5H_5), 4.29 (m, 4 H, C_5H_4), 4.80 (dd, *J* = 0.6, 1.2 Hz, 1 H, CH_2=), 5.09 (m, 1 H, CH_2=), 6.27 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.4, 31.5 (2 CH_3), 68.9, 69.9 (C_5H_4), 69.3 (C_5H_5), 79.8 ($C_{ipso}Fc$), 114.0 (CH_2=), 124.4 (CH=), 139.4, 141.2 (2 C), 208.9 (C=O) ppm. $C_{17}H_{18}FeO$ (294): calcd. C 69.40, H 6.16, Fe 19.00; found C 69.19, H 6.28, Fe 18.73. MS: *m*/*z* = 294 [M]$^{+}$.

(*E*)-2-Acetyl-1-ferrocenyl-3-methylbuta-1,3-diene (4b): 4b was obtained from the hydroxy ketone **3b** (1.56 g, 5 mmol) in an analogous manner as red crystals (1.12 g, 76%). M.p. 84−85 °C. IR (KBr): ṽ = 824, 895, 1002, 1026, 1049, 1103, 1184, 1254, 1331, 1355, 1429, 1604, 1649, 1698, 2910, 2970, 3085 cm^{-1}. UV ($CHCl_3$, 20 °C): $\lambda_{max.}$ = 221, 245, 283, 451 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98 (q, *J* = 1.2 Hz, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 4.14 (s, 5 H, C_5H_5), 4.41 (m, 2 H, C_5H_4), 4.62 (m, 2 H, C_5H_4), 4.90 (m, 1 H, CH_2=), 5.27 (m, 1 H, CH_2=), 7.25 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.8, 26.6 (2 × CH_3), 70.9, 71.1 (C_5H_4), 69.6 (C_5H_5), 77.6 ($C_{ipso}Fc$), 116.5 (CH_2=), 138.8 (CH=), 139.0, 142.5 (2 × C), 197.7 (C=O) ppm. $C_{17}H_{18}FeO$ (294): calcd. C 69.40, H 6.16, Fe 19.00; found C 69.19, H 6.28, Fe 18.73. MS: *m*/*z* = 294 [M]$^{+}$.

Condensation of the Dienes 4a and 4b with *N*-Phenylazodicarboximide: *N*-Phenylazodicarboximide (0.2 g, 1.22 mmol) was added portionwise to a stirred solution of the diene **4a** or **4b** (0.3 g, 1 mmol) in benzene (30 mL) at 0−5 °C as the solution discolored. Stirring was continued for an additional 1 h and the solvent was then evaporated. Column chromatography of the residue (Al_2O_3; hexane/dichloromethane, 2:1) gave adduct **5**. From **4a**: 0.32 g (70%), yellow crystals, m.p. 123−125 °C. From **4b**: 0.35 g (74%), m.p. 123−124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 (br. s, 3 H, CH_3), 2.59 (s, 3 H, CH_3), 3.96 (d, *J* = 18.0 Hz, 1 H, CH_2), 4.35 (d, *J* = 18.0 Hz, 1 H, CH_2), 4.10 (s, 5 H, C_5H_5), 3.94 (m, 1 H, C_5H_4), 4.15 (m, 1 H, C_5H_4), 4.19 (m, 1 H, C_5H_4), 4.36 (m, 1 H, C_5H_4), 5.99 (s, 1 H, CH), 7.32−7.48 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.2, 31.0 (2 × CH_3), 48.1 (CH_2), 53.5 (CH), 66.9, 67.6, 67.9, 69.1 (C_5H_4), 69.3 (C_5H_5), 85.2 ($C_{ipso}Fc$), 125.5 (2 × C), 128.2, 129.1 (2 × C) (C_6H_5), 131.0, 133.3, 133.8 (3 × C), 151.3, 152.5, 199.2 (3 × C=O) ppm. $C_{25}H_{23}FeN_3O_3$ (469): calcd. C 63.98, H 4.94, Fe 11.90, N 8.95; found C 64.09, H 5.12, Fe 11.73, N 8.75. MS: *m*/*z* = 469 [M]$^{+}$.

Condensation of the Dienes 4a and 4b with *N*-Phenylmaleimide: A solution of the diene **4a** or **4b** (0.3 g, 1 mmol) and *N*-phenylmaleimide (0.2 g, 1.24 mmol) in toluene (50 mL) was heated under reflux for 3 h and then concentrated. The residue was chromatographed (Al_2O_3; hexane/dichloromethane, 3:1) to give the adduct **6** as yellow crystals. From **4a**: 0.34 g (72%); from **4b**: 0.32 g (68%). M.p. 167−168 °C. IR (KBr): ṽ = 770, 826, 1001, 1035, 1103, 1158, 1186, 1383, 1436, 1496, 1625, 1685, 1711, 1776, 2852, 2937, 3081 cm^{-1}. UV ($CHCl_3$, 20 °C): λ_{max} = 214, 378, 507 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.18 (d, *J* = 1.0 Hz, 3 H, CH_3), 2.54 (s, 3 H, CH_3), 2.55 (dd, *J* = 10.1, 17.4 Hz, 1 H, CH_2), 2.94 (ddd, *J* = 1.0, 6.9, 17.4 Hz, 1 H, CH_2), 3.18 (m, 1 H, CH), 3.27 (dd, *J* = 5.8, 9.6 Hz, 1 H, CH), 4.02 (s, 5 H, C_5H_5), 3.81 (m, 1 H, C_5H_4), 4.10 (m, 2 H, C_5H_4), 4.14 (m, 1 H, C_5H_4), 4.63 (d, *J* = 5.8 Hz, 1 H, CH), 6.99 (dm, 2 H, C_6H_5), 7.30−7.41 (m, 3 H, C_6H_5) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2, 30.6 (2 × CH_3), 29.8 (CH_2), 38.0, 38.3, 47.3 (3 × CH), 67.8, 68.2, 68.5, 68.9 (C_5H_4), 68.9 (C_5H_5), 84.0 ($C_{ipso}Fc$), 126.6 (2 × C), 128.5, 128.8 (2 × C, C_6H_5), 131.5, 137.2, 142.0 (3 × C), 176.6, 178.1, 200.2 (3 × C=O) ppm. $C_{27}H_{25}FeNO_3$ (467): calcd. C 69.39, H 5.39, Fe 11.95, N, 3.00; found C 69.53, H 5.21, Fe 12.13, N 2.75. MS: *m*/*z* = 467 [M]$^{+}$.

(*Z*)- and (*E*)-2-Acetyl-1-ferrocenyl-3,3-dimethylallylium Tetrafluoroborates (7a and 7b): These compounds were prepared by addition of tetrafluoroboric acid−diethyl ether to a solution of either diene **4a** or **4b** in dry diethyl ether. The crystalline residues that precipitated were filtered off, washed with dry diethyl ether, and dried in vacuo. The yields of the salts were quantitative. All operations with solid salts were carried out in an atmosphere of dry nitrogen.

Compound 7a: Black crystals, m.p. 186−188 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.87 (s, 3 H, CH_3), 1.96 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 4.76 (s, 5 H, C_5H_5), 4.67 (m, 1 H, C_5H_4), 5.00 (m, 1 H, C_5H_4), 5.93 (m, 1 H, C_5H_4), 6.00 (m, 1 H, C_5H_4), 8.13 (s, 1 H, CH) ppm. $C_{17}H_{19}BF_4FeO$ (382): calcd. C 53.45, H 5.01, F 19.90, Fe 14.62; found C 53.73, H 4.83, F 20.07, Fe 14.38.

Compound 7b: Black crystals, m.p. 197−198 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.82 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 4.90 (s, 5 H, C_5H_5), 4.72 (m, 1 H, C_5H_4), 4.81 (m, 1 H, C_5H_4), 6.09 (m, 1 H, C_5H_4), 6.19 (m, 1 H, C_5H_4), 8.00 (s, 1 H, CH) ppm. $C_{17}H_{19}BF_4FeO$ (382): calcd. C 53.45, H 5.01, F 19.90, Fe 14.62; found C 53.19, H, 5.23, F 19.69, Fe 14.79.

Isomerization of (*Z*)-Tetrafluoroborate 7a into 7b: A solution of the salt **7a** (0.38 g, 1 mmol) in dry dichloromethane (30 mL) was kept at room temperature for 4 h and then *N*,*N*-dimethylaniline (0.2 mL) was added. The mixture was stirred for 30 min at 20 °C, washed with 5% HCl (2 × 10 mL) and water (2 × 10 mL), and dried with Na_2SO_4. The solvent was removed and the residue was chromatographed on Al_2O_3 (hexane) to give 0.08 g (27%) of the diene **4a**, m.p. 58−59 °C, and 0.16 g (54%) of the diene **4b**, m.p. 84−85 °C.

Isomerization of (*E*)-7b Tetrafluoroborate 7b into 7a: This reaction was carried out analogously to give, following deprotonation and chromatography, diene **4a** (30%; m.p. 59−60 °C) and the diene **4b** (61%; m.p. 84−86 °C).

Reactions of Dienes 4a and 4b with Methyllithium: A solution of MeLi (1.6 M in diethyl ether, 20 mL) was added to a stirred solution of compound **4a** (1.47 g, 5 mmol) in dry diethyl ether (100 mL). The mixture was stirred for an additional 30 min at 20 °C and then the excess MeLi was quenched by the addition of water (50 mL). The organic layer was separated, washed with water (2 × 20 mL), and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was purified by crystallization from hexane to give the alcohol **8a** (1.25 g, 80%) as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.45$ (s, 6 H, 2 CH_3), 1.95 (dd, $J = 0.9$, 1.5 Hz, 3 H, CH_3), 2.22 (br. s, 1 H, OH), 4.12 (s, 5 H, C_5H_5), 4.21 (m, 2 H, C_5H_4), 4.41 (m, 2 H, C_5H_4), 4.76 (dd, $J = 0.9$, 2.4 Hz, 1 H, $CH_2=$), 4.88 (dd, $J = 1.5$, 2.4 Hz, 1 H, $CH_2=$), 6.07 (s, 1 H, CH=) ppm. $C_{18}H_{22}FeO$ (310): calcd. C 69.69, H 7.15, Fe 18.00; found C 69.47, H 7.28, Fe 17.83. MS: $m/z = 310$ $[M]^+$.

Analogously, the reaction of the diene **4b** (1.47 g, 5 mmol) with MeLi gave the alcohol **8b** (1.17 g, 75%) as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.42$ (s, 6 H, 2 CH_3), 1.75 (br. s, 1 H, OH), 1.98 (dd, $J = 0.9$, 1.5 Hz, 3 H, CH_3), 4.07 (s, 5 H, C_5H_5), 4.17 (m, 2 H, C_5H_4), 4.44 (m, 2 H, C_5H_4), 4.86 (dd, $J = 0.9$, 2.4 Hz, 1 H, $CH_2=$), 5.18 (dd, $J = 1.5$, 2.4 Hz, 1 H, $CH_2=$), 6.20 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 24.4$ (CH_3), 30.0 (2 × CH_3), 68.5, 68.6, 68.9, 73.3 (C_5H_4), 69.0 (C_5H_5), 69.1 (C-OH); 81.4 (C_{ipso}Fc), 115.4 ($CH_2=$), 119.7 (CH=), 144.7, 146.8 (2 C) ppm. $C_{18}H_{22}FeO$ (310): calcd. C 69.69, H 7.15, Fe 18.00; found C 69.78, H 6.88, Fe 18.13. MS: $m/z = 310$ $[M]^+$.

Condensation of the hydroxyalkyldienes **8a** and **8b** with *N*-phenylazodicarboximide was carried out as described for the preparation of **5** to give the adduct **9** in 71 and 69% yields, respectively, as yellow crystals. M.p. 171−173 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.42$ (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3), 1.91 (s, 3 H, CH_3), 2.18 (br. s, 1 H, OH), 4.05 (d, $J = 16.2$ Hz, 1 H, CH_2), 4.18 (d, $J = 16.2$ Hz, 1 H, CH_2), 4.21 (s, 5 H, C_5H_5), 4.07 (m, 1 H, C_5H_4), 4.15 (m, 1 H, C_5H_4), 4.19 (m, 2 H, C_5H_4), 5.89 (s, 1 H, CH), 7.34−7.58 (m, 5 H, C_6H_5) ppm. $C_{26}H_{27}FeN_3O_3$ (485): calcd. C 64.34, H 5.61, Fe 11.51, N 8.66; found C 64.57, H 5.48, Fe 11.36, N 8.95. MS: $m/z = 485$ $[M]^+$.

Dehydration of alcohols **8a** and **8b** was performed under the conditions described above for the dehydration of the hydroxy ketones **3a** and **3b**. The yields of the triene **10**, following chromatography (Al_2O_3; hexane) were 72 and 71%, respectively. Orange crystals, m.p. 78−79 °C. IR (KBr): $\tilde{\nu} = 506$, 817, 887, 1001, 1029, 1053, 1103, 1229, 1281, 1369, 1447, 1601, 1640, 1772, 2916, 2944, 2967, 3089 cm^{-1}. UV ($CHCl_3$, 20 °C): $\lambda_{max.} = 207$, 251, 298, 449, 455 nm. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.93$ (dd, $J = 0.9$, 1.5 Hz, 3 H, CH_3), 2.00 (dd, $J = 0.6$, 1.5 Hz, 3 H, CH_3), 4.08 (s, 5 H, C_5H_5), 4.21 (m, 2 H, C_5H_4), 4.50 (m, 2 H, C_5H_4), 4.84 (m, $J = 0.6$ Hz, 1 H, 0.9, 2.4 Hz, $CH_2=$), 4.98 (m, $J = 0.6$ Hz, 1 H, 2.4 Hz, $CH_2=$), 5.07 (m, $J = 0.6$ Hz, 1 H, 1.5 Hz, $CH_2=$), 5.21 (m, $J = 1.5$ Hz, 1 H, 2.4 Hz, $CH_2=$), 6.13 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.8$, 23.0 (2 × CH_3), 68.9, 69.4 (C_5H_4), 69.1 (C_5H_5), 81.5 (C_{ipso}Fc), 113.5, 115.5 (2 × $CH_2=$), 122.7 (CH=), 141.5, 142.5, 144.2 (3 × C) ppm. $C_{18}H_{20}Fe$ (292): calcd. C 73.99, H 6.90, Fe 19.11; found C 74.18, H 6.78, Fe 19.33. MS: $m/z =$ 292 $[M]^+$.

Dimerization of 2-Acetyl-1-ferrocenyl-3-methylbuta-1,3-dienes. A: A solution of the diene **4a** or **4b** (0.3 g) in glacial acetic acid was heated under reflux for 4 h and then cooled to room temperature and diluted with water (100 mL). The reaction products were extracted with ethyl acetate (3 × 50 mL) and then the extracts were washed with water (2 × 50 mL), 5% $NaHCO_3$, and water, and dried (Na_2SO_4). The solvent was distilled off and the residue was chromatographed (Al_2O_3; hexane/dichloromethane, 2:1) to give dimer **11** [from **4a**: 0.25 g (80%); from **4b**: 0.23 g, 77%] as a mixture of two isomers, **11a** and **11b** (ca. 3:1) as violet crystals (m.p. 186−187 °C).

The isomers were separated by preparative TLC (Al_2O_3; hexane/benzene, 1:1) to give **11a** (0.15 g, 50%) and **11b** (0.07 g, 24%).

Compound 11a: Violet powder, m.p. 218−219 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.74$ (s, 3 H, CH_3), 1.89 (s, 3 H, CH_3), 1.97 (s, 3 H, CH_3), 1.99 (d, $J = 1.5$ Hz, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 4.17 (s, 5 H, C_5H_5), 4.18 (s, 5 H, C_5H_5), 4.07 (m, 1 H, C_5H_4), 4.11 (m, 2 H, C_5H_4), 4.15 (m, 1 H, C_5H_4), 4.39 (m, 2 H, C_5H_4), 4.54 (m, 1 H, C_5H_4), 4.62 (m, 1 H, C_5H_4), 4.85 (d, $J = 9.9$ Hz, 1 H, CH), 5.58 (dd, $J = 1.5$, 9.9 Hz, 1 H, CH=), 7.30 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 17.4$, 21.1, 22.4, 26.9, 32.6 (5 × CH_3), 39.3 (CH), 66.9, 67.5, 67.6, 67.7, 70.4, 70.7, 71.0, 71.6 (2 × C_5H_4), 68.8, 69.6 (2 × C_5H_5), 78.1, 91.1 (2 × C_{ipso}Fc), 129.5, 138.9 (2 × CH=), 130.8, 132.0, 140.3, 140.6 (4 × C), 198.0, 207.2 (2 × C=O) ppm. $C_{34}H_{36}Fe_2O_2$ (588): calcd. C 69.40, H 6.16, Fe 19.00; found C 69.61, H 6.02, Fe 18.83. MS: $m/z = 588$ $[M]^+$.

Compound 11b: Violet needles, m.p. 207−208 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.68$ (s, 3 H, CH_3), 1.89 (s, 3 H, CH_3), 1.95 (s, 3 H, CH_3), 1.99 (d, $J = 1.5$ Hz, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 4.16 (s, 5 H, C_5H_5), 4.19 (s, 5 H, C_5H_5), 4.05 (m, 1 H, C_5H_4), 4.10 (m, 2 H, C_5H_4), 4.16 (m, 1 H, C_5H_4), 4.39 (m, 2 H, C_5H_4), 4.51 (m, 1 H, C_5H_4), 4.57 (m, 1 H, C_5H_4), 4.82 (d, $J = 9.9$ Hz, 1 H, CH), 5.65 (dd, $J = 1.5$, 9.3 Hz, 1 H, CH=), 7.28 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.8$, 20.5, 22.6, 29.0, 31.6 (5 × CH_3), 36.1 (CH), 68.6, 68.7, 69.0, 69.1, 69.2, 69.3, 70.1, 71.5 (2 × C_5H_4), 69.0, 69.8 (2 × C_5H_5), 87.1, 92.0 (2 × C_{ipso}Fc), 122.4, 130.0 (2 × CH=), 126.4, 130.8, 132.0, 140.6 (4 × C), 198.0, 207.1 (2 × C=O) ppm. $C_{34}H_{36}Fe_2O_2$ (588): calcd. C 69.40, H 6.16, Fe 19.00; found C 69.47, H 6. 26, Fe 18.87. MS: $m/z = 588$ $[M]^+$.

B: The diene **4a** or **4b** (0.15 g, 5 mmol) was added to a solution of the tetrafluoroborate **7a** or **7b** (0.19 g, 0.5 mmol) in dry dichloromethane (50 mL) under an inert atmosphere. The mixture was stirred for 2 h at 20 °C and then *N*,*N*-dimethylaniline (0.3 mL) was added; stirring was continued for 1 h. The reaction mixture was washed with water, 5% HCl, and water and then dried (Na_2SO_4). The solvent was evaporated in vacuo and the residue was chromatographed Al_2O_3; hexane/dichloromethane, 2:1) to give the dimer **11** (0.22−0.27 g) as a mixture of two isomers, **11a** and **11b**, in nearly the same ratio in both cases (ca. 3:1) as a violet powder (m.p. 186−188 °C).

Condensation of the Tetrafluoroborates 7a and 7b with the Triene 10: This reaction was carried under analogous conditions. The reaction of the salt **7a** with the triene **10** (0.30 g) afforded, following chromatography Al_2O_3; hexane/dichloromethane, 3:1), the cyclodimer **14** (0.13 g, 21%) and the linear dimer **13** (0.37 g, 61%) as a mixture of two isomers **13a** and **13b** in a ca. 2:1 ratio (^1H NMR spectroscopic data). The isomers were separated upon rechromatography, Al_2O_3; hexane/benzene, 1:1) to yield isomer **13a** (0.2 g) isomer **13b** (0.1 g).

Compound 13a: Violet crystals, m.p. 246−247 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.66 (s, 3 H, CH_3), 1.88 (s, 3 H, CH_3), 1.97 (s, 3 H, CH_3), 1.99 (s, 3 H, CH_3), 2.01 (s, 3 H, CH_3), 4.10 (s, 5 H, C_5H_5), 4.11 (s, 5 H, C_5H_5), 4.12 (m, 2 H, C_5H_4), 4.15 (m, 1 H, C_5H_4), 4.16 (m, 1 H, C_5H_4), 4.24 (m, 2 H, C_5H_4), 4.53 (m, 1 H, C_5H_4), 4.55 (m, 1 H, C_5H_4), 4.65 (d, J = 9.9 Hz, 1 H, CH), 4.89 (br. s, 1 H, CH_2=), 5.29 (br. s, 1 H, CH_2=), 5.87 (d, J = 9.9 Hz, 1 H, CH=), 6.34 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.4, 22.4, 23.2, 32.7 (5 × CH_3), 39.2 (CH), 67.3, 67.4, 67.6, 67.9, 68.9, 69.0, 69.2, 69.5 (2 × C_5H_4), 68.9, 69.4 (2 × C_5H_5), 82.6, 92.1 (2 × C_{ipso}Fc), 116.0 (CH_2=), 121.5, 128.5 (2 × CH=), 128.9, 133.5, 141.1, 143.0, 144.4 (5 × C), 207.7 (C=O) ppm. $C_{35}H_{38}Fe_2O$ (586): calcd. C 71.69, H 6.53, Fe 19.05; found C 71.45, H 6.32, Fe 18.81. MS: m/z = 586 $[M]^+$.

Compound 13b: Violet powder, crystals, m.p. 227−229 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3), 1.95 (s, 3 H, CH_3), 1.97 (s, 3 H, CH_3), 4.08 (s, 5 H, C_5H_5), 4.09 (s, 5 H, C_5H_5), 4.06 (m, 2 H, C_5H_4), 4.13 (m, 1 H, C_5H_4), 4.23 (m, 2 H, C_5H_4), 4.48 (m, 1 H, C_5H_4), 4.52 (m, 2 H, C_5H_4), 4.66 (d, J = 9.6 Hz, 1 H, CH), 4.91 (br. s, 1 H, CH_2=), 5.21 (br. s, 1 H, CH_2=), 5.93 (d, J = 9.6 Hz, 1 H, CH=), 6.15 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3, 20.6, 22.2, 23.0, 33.4 (5 × CH_3), 39.3 (CH), 66.6, 67.1, 67.2, 67.6, 68.2, 68.8, 68.9, 69.6 (2 × C_5H_4), 68.6, 69.1 (2 × C_5H_5), 81.8, 92.3 (2 × C_{ipso}Fc), 115.8 (CH_2=), 121.9, 128.9 (2 × CH=), 129.1, 140.5, 144.0, 144.2, 144.5 (5 × C), 209.0 (C=O) ppm. $C_{35}H_{38}Fe_2O$ (586): calcd. C 71.69, H 6.53, Fe 19.05; found C 71.87, H 6.37, Fe 19.21. MS: m/z = 586 $[M]^+$.

Compound 14: Brown crystals, m.p. 228−249 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.76 (s, 3 H, CH_3), 1.89 (s, 3 H, CH_3), 1.90 (d, J = 1.2 Hz, 3 H, CH_3), 2.40 (dd, J = 7.2, 13.2 Hz, 1 H, CH_2), 2.63 (dd, J = 1.2, 13.2 Hz, 1 H, CH_2), 4.00 (dd, J = 1.2, 7.2 Hz, 1 H, CH), 4.12 (s, 5 H, C_5H_5), 4.13 (s, 5 H, C_5H_5), 4.03 (m, 2 H, C_5H_4), 4.18 (m, 1 H, C_5H_4), 4.27 (m, 2 H, C_5H_4), 4.32 (m, 1 H, C_5H_4), 4.36 (m, 1 H, C_5H_4), 4.41 (m, 1 H, C_5H_4), 6.10 (q, J = 1.2 Hz, 1 H, CH), 6.14 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 22.2, 22.9, 27.3, 29.1 (5 × CH_3), 35.9 (CH_2), 42.3 (CH), 66.4, 66.8 (2 × C), 68.5, 69.0, 69.5 (2 × C_5H_4), 68.6, 69.2 (2 × C_5H_5), 73.4, 83.3 (2 × C_{ipso}Fc), 119.6, 133.7 (2 × CH=), 123.5, 128.1, 138.7, 142.7 (4 × C) ppm. $C_{35}H_{38}Fe_2O$ (586): calcd. C 71.69, H 6.53, Fe 19.05; found C 71.44, H 6.27, Fe 19.15. MS: m/z = 586 $[M]^+$.

Crystal Structure: The unit cell parameters and the X-ray diffraction intensities were recorded with a Siemens P4/PC/ω diffractometer (compounds **4b** and **14**) and a Bruker Smart Apex AXS CCD area detector/ω diffractometer (compound **13a**). The structures of compounds **4b**, **13a**, and **14** were solved by the direct methods (SHELXS) and refined using a full-matrix least-squares method on F^2.

Crystal Data for $C_{17}H_{18}FeO$ (4b): M_r = 294.16 g·mol^{-1}, tetragonal $I4_1/a$, a = 22.992(1), b = 22.992(1), c = 10.696(1) Å, α = 90, β = 90, γ = 90°, V = 5654.2(6) Å^3, T = 293(2) K, Z = 16, ρ = 1.382 Mg·m^{-3}, λ (Mo-K_α) = 0.71073 Å, F(000) = 2464, absorption coefficient 1.055 mm^{-1}, index ranges $0 \leq h \leq 27$, $0 \leq k \leq 27$, $0 \leq l \leq 12$, scan range $2.10 \leq \theta \leq 25.00°$, 2483 independent reflections, R_{int} = 0.0385, 2621 total reflections, 174 refinable parameters, final R indices [$I > 2\sigma(I)$] R_1 = 0.0429, wR_2 = 0.0877, R indices (all data) R_1 = 0.0722, wR_2 = 0.1005, largest difference peak and hole 0.239/−0.212 e·Å^{-3}.

Crystal Data for $C_{35}H_{38}Fe_2O$ (13a): M_r = 586.35 g·mol^{-1}, monoclinic Cc, a = 26.814(2), b = 7.4570(5), c = 18.8642(12) Å, α = 90, β = 129.225(1), γ = 90°, V = 2922.0(3) Å^3, T = 291(2) K, Z = 4, ρ = 1.333 Mg·m^{-3}, λ (Mo-K_α) = 0.71073 Å, F(000) = 1232, absorption coefficient 1.018 mm^{-1}, index ranges $-31 \leq h \leq 31$, $-8 \leq k \leq 8$, $-22 \leq l \leq 22$, scan range $2.17 \leq \theta \leq 25.00°$, 5117 independent reflections, R_{int} = 0.0287, 11514 total reflections, 349 refinable parameters, final R indices [$I > 2\sigma(I)$] R_1 = 0.0303, wR_2 = 0.0633, R indices (all data) R_1 = 0.0339, wR_2= 0.0643, largest difference peak and hole 0.267/−0.185 e·Å^{-3}.

Crystal Data for $C_{35}H_{38}Fe_2O$ (14): M_r = 586.35 g·mol^{-1}, monoclinic $P2_1/c$, a = 11.737(1), b = 24.740(3), c = 10.853(1) Å, α = 90, β = 113.90(1), γ = 90°, V = 2881.2(5) Å^3, T = 293(2) K, Z = 4, ρ = 1.352 Mg·m^{-3}, λ (Mo-K_α) = 0.71073 Å, F(000) = 1232, absorption coefficient 1.033 mm^{-1}, index ranges $-13 \leq h \leq 12$, $-29 \leq k \leq 0$, $0 \leq l \leq 12$, scan range $1.90 \leq \theta \leq 25.00°$, 5053 independent reflections, R_{int} = 0.1031, 5338 total reflections, 348 refinable parameters, final R indices [$I > 2\sigma(I)$] R_1 = 0.0739, wR_2 = 0.1429, R indices (all data) R_1 = 0.1536, wR_2 = 0.1835, largest difference peak and hole 0.375/−0.363 e·Å^{-3}.

CCDC-223084 (for **4b**), -228066 (for **13a**), and -223085 (for **14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/const/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] A. Togni, R. L. Halterman, *Metallocenes*, Wiley-VCH, Weinheim, **1998**, Vol. 2.

[2] *Ferrocenes* (Eds: A. Togni, T. Hayashi), Wiley-VCH, Weinheim, **1995**, 497−530.

[3] R. W. Heo, F. B. Somoza, T. R. Lee, *J. Am. Chem. Soc.* **1998**, *120*, 1621−1622.

[4] E. Stankovic, S. Toma, R. V. Boxel, I. Asselberghs, A. Persoons, *J. Organomet. Chem.* **2001**, *637*−*639*, 426−434.

[5] L. M. Tolbert, X. Zhao, Y. Ding, L. A. Bottomley, *J. Am. Chem. Soc.* **1995**, *117*, 12891−12892.

[6] B. Bildstein, W. Skibar, M. Schweiger, H. Kopacka, K. Wurst, *J. Organomet. Chem.* **2001**, *622*, 135−142.

[7] A. E. Kaifer, S. Mendoza, *Comprehensive Supramolecular Chemistry I* (Ed.: G. W. Gokel), Pergamon, Oxford, **1996**, *701*, 138−157.

[8] A. N. Pushin, E. I. Klimova, V. A. Sazonova, *Zh. Obshch. Khim.* **1987**, *57*, 1102−1109.

[9] E. G. Prevalova, E. I. Klimova, V. V. Kryuchkova, *Zh. Obshch. Khim.* **1989**, *59*, 873−881.

[10] V. N. Postnov, E. I. Klimova, A. N. Pushin, N. N. Meleshonkova, *Metalloorg. Khim.* **1991**, *4*, 116−122.

[11] E. I. Klimova, A. N. Pushin, V. A. Sazonova, *J. Organomet. Chem.* **1984**, *270*, 319−325.

[12] E. I. Klimova, L. Ruíz Ramírez, M. Martínez García, P. G. Espinosa, N. N. Meleshonkova, *Izv. Akad. Nauk. Ser Khim.* **1996**, 2743−2750 [*Russ. Chem. Bull.* **1996**, *45*, 2602−2609].

[13] E. I. Klimova, M. Martínez García, C. Alvarez Toledano, R. Alfredo Toscano, L. Ruíz Ramírez, *J. Organomet. Chem.* **2000**, *598*, 254−261.

[14] G. Wittig, U. Schöllkopf, *Org. Syn.* **1960**, *40*, 66−68.

[15] E. I. Klimova, V. N. Postnov, N. N. Meleshonkova, A. S. Zaks, E. M. Chukichev, *Khim.-Farm. Zh.* **1992**, *26*, 34−35.

[16] E. I. Klimova, M. Martínez García, L. Ruíz Ramírez, N. N. Meleshonkova, *Dokl. Akad. Nauk* **1999**, *365*, 630−635.
[17] E. I. Klimova, M. Martínez García, T. Klimova, J. M. Méndez Stivalet, *J. Organomet. Chem.* **2000**, *602*, 105−114.
[18] B. N. Postnov, E. I. Klimova, N. N. Meleshonkova, M. Martínez García, *Dokl. Akad. Nauk* **1992**, *326*, 113−116.
[19] A. N. Chekhlov, V. N. Solov'ev, A. N. Pushin, V. A. Sazonova, E. I. Klimova, I. V. Martynov, *Izv. Akad. Nauk. Ser Khim.* **1986**, 701−703.
[20] G. A. Olah, R. J. Spear, *J. Am. Chem. Soc.* **1975**, *97*, 1539−1546.
[21] W. G. Young, S. U. Sharman, S. Winstein, *J. Am. Chem. Soc.* **1960**, *82*, 1376−1382.
[22] M. J. A. Habib, J. Park, W. E. Watts, *J. Chem. Soc., C* **1970**, 2556−2563.
[23] G. A. Olah, M. Mayer, *J. Am. Chem. Soc.* **1976**, *98*, 7333−7340.
[24] E. I. Klimova, L. Ruíz Ramírez, T. Klimova, M. Martínez García, *J. Organomet. Chem.* **1998**, *559*, 43−53.
[25] V. N. Postnov, E. I. Klimova, M. Martínez García, N. N. Meleshonkova, V. V. Rybakov, L. A. Aslanov, *J. Organomet. Chem.* **1994**, *476*, 189−195.
[26] E. I. Klimova, L. Ruíz Ramírez, M. Martínez García, N. N. Meleshonkova, A. Marín Becerra, *Dokl. Akad. Nauk* **1996**, *351*, 776−779.
[27] V. N. Postnov, E. I. Klimova, A. N. Pushin, N. N. Meleshonkova, *Metalloorg. Khim.* **1992**, *5*, 564−569.
[28] V. N. Postnov, Yu. N. Polivin, D. V. Baschenov, V. A. Sazonova, *Dokl. Akad. Nauk SSSR* **1984**, *276*, 373−376.

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