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Journal of Organometallic Chemistry 509 (1996) 189–196

Journal of Organometallic Chemistry

Synthesis and transformation of iron and tungsten complexes with tetrahydropentalenyl ligands

Wolfgang Malisch [a,*], Norbert Gunzelmann [a], Michael Neumayer [a], Axel G. Griesbeck [b,*,1], Thomas Deufel [b]

[a] *Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany*
[b] *Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany*

Received 28 April 1995

Abstract

New half-sandwich complexes of iron and tungsten carbonyl fragments with tetrahydropentalenyl ligands were synthesized, their stereochemistry determined and several ligand transformations performed in order to demonstrate the ability of these groups to control the relative stereochemistry of complex formation. The ligands L^1 and L^2 are derived from the diastereomerically pure (*rac*)-*cis*-1-methyl-3-phenyl-tetrahydropentalene (**1**) and (*rac*)-1,1-dimethyl-3-(2-methoxyphenyl)tetrahydropentalene (**2**). The following iron complexes were synthesized: $[(L^1)(CO)_2Fe]_2$ (**3**), $[(L^2)(CO)_2Fe]_2$ (**4**), $Na[Fe(CO)_2(L^1)]$ (**5**), $Na[Fe(CO)_2(L^2)]$ (**6**), $(L^1)(CO)_2FeC(O)CH_3$ (**7**) and $(L^2)(CO)_2FeC(O)CH_3$ (**8**). The following were obtained as tungsten complexes: $(L^1)(CO)_3WX$ [X = H (**9**), Cl (**10**)], $(L^2)(CO)_3WH$ (**11**) and $Li[W(CO)_3(L^1)]$ (**12**). In the case of **10**, one diastereoisomer could be separated; in the case of the acetyl complexes **7** and **8**, both diastereoisomers have been isolated in the pure state.

Keywords: Iron; Tungsten; Tetrahydropentalenyl; Transition metal anions; Diastereoselectivity

1. Introduction

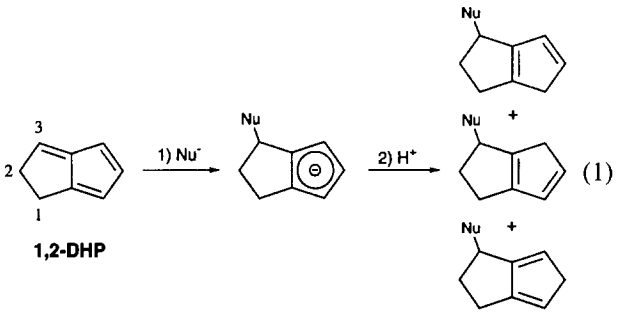
The design of new and effective ligands for organometallic complexes is still a worthwhile activity due to the impressive amount of new applications for these compounds in stoichiometric and catalytic asymmetric organic synthesis [1]. The term 'effective' can be understood in several ways: (a) the flexible and efficient synthesis of the ligand systems, (b) a diastereo- and enantio-selective approach to different derivatives from a standard ligand system, (c) highly regio- and stereoselective addition of metal fragments to neutral and/or anionic ligands and (d) selective transformations of metal complexes and subsequent decomplexation in order to generate useful products for organic syntheses.

A promising approach to chiral 1,2-disubstituted cyclopentadienyl ligands is the use of 1,2-dihydropentalenes (DHPs) as substrates. These compounds are versatile building blocks in organic synthesis as well as suitable precursors for diastereomerically pure ligands for metal complexes. A variety of syntheses are known which lead to 1,2-dihydropentalene systems, the most flexible of which is the addition/condensation sequence of α,β-unsaturated carbonyl compounds with cyclopentadiene in the presence of stoichiometric or catalytic amounts of pyrrolidine [2], similar to the pentafulvene synthesis developed by Stone and Little [3]. Donor- as well as acceptor-substituted aryl groups may be introduced at the stereogenic carbon atom C-1 whereas position C-3 can be functionalized with a multitude of organic substituents. The 1,2-dihydro isomers can be transformed into the corresponding 1,5-isomers via acid catalysis or thermolysis. Both types of compound are excellent substrates for Diels-Alder reactions [4] and versatile for the synthesis of isodicyclopentadiene derivatives and their addition products [5]. Due to their electrophilic nature, 1,2-DHP substrates easily react with different nucleophiles by addition towards C-3. These additions proceed in most cases highly diastereoselec-

* Corresponding authors.
[1] Present address: Institut für Organische Chemie der Universität zu Köln, Greinstr. 4, D-50939 Köln, Germany.

SSDI 0022-328X(95)05807-9

tively *anti* with respect to the phenyl substituent at position C-1 [see Eq. (1)]:

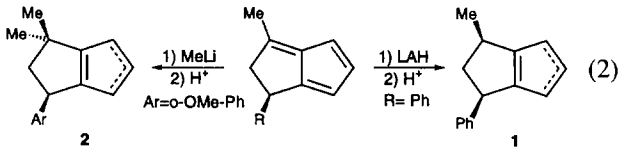


(1)

To date, pentalenes have been used only seldomly as ligands in organometallic chemistry. C_2-chiral ansa-ferrocene and several binuclear iron complexes, where pentalenes act as η^8- and σ,η^6-ligands have been characterized [6]. A homologous binuclear iron complex with η^6-bicyclo[4.3.0]nonadiene ligands is available from spiro[4.4]octadiene [7]. Half-sandwich complexes containing η^5-coordinated pentalenes have not as yet been described in the literature, and for this reason we decided to examine the synthesis of iron and tungsten compounds. We focused our interest primarily on metal species of the anionic type which should offer broad access to complexes with ligated main group element units [8]. The transformation of these complexes under stereocontrol of the tetrahydropentalenyl metal fragment is the subject of current investigations which contribute to stereocontrolled metal-mediated organic chemistry, an area of growing interest [9,10].

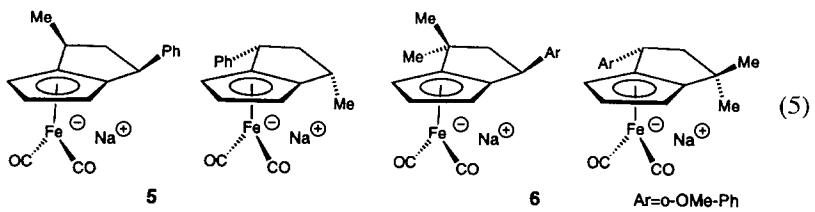
2. Results and discussion

To investigate diastereofacial selectivity in organometallic transformations, we decided to use two tetrahydropentalenyl ligands with a different number of stereogenic centres. The precursor to the first ligand (L^1) was synthesized from 1-phenyl-3-methyl-1,2-dihydropentalene via reduction with lithium aluminium hydride and subsequent protonation. The tetrahydropentalene **1** produced consists of a mixture of three constitutional isomers, all in diastereomerically pure (*cis*) form [2a]. It was known from a multitude of experiments that diastereofacial selectivity is remarkably high for cycloaddition reactions with this bicyclic diene [2b]. This could be due to the predominant steric effects of the phenyl group, the methyl group, or of both. To clarify this question we have investigated another model ligand L^2. Addition of methyl lithium to 1-(2-methoxyphenyl)-3-methyl-1,2-dihydropentalene and subsequent protonation led to **2** which has only one stereogenic benzylic centre [11]. Thus, any additional diastereofacial control which derives from the methylated stereogenic centre in L^1 should vanish in substrates with L^2 as a ligand [see Eq. (2)].



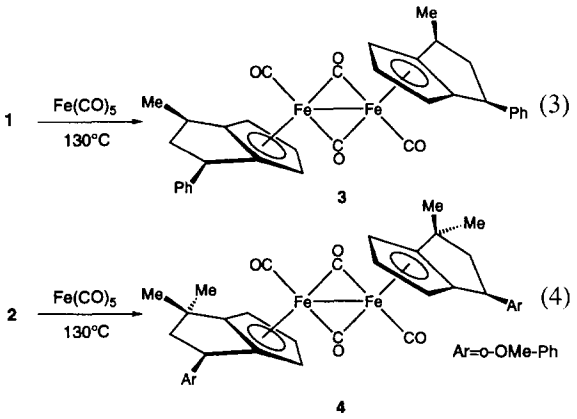
(2)

By analogy to the extensively investigated chemistry of $Cp(CO)_2Fe$ [8], deriving from the well-known dinuclear complex $[Cp(OC)_2Fe]_2$ [12], dienes **1** and **2** were used to generate the analogous species **3** and **4** as basic starting materials [Eqs. (3) and (4)]. On refluxing **1** in methylcyclohexane in the presence of iron pentacarbonyl, only poor yields (9%) were obtained under such drastic conditions, but these were increased in the case of **2** through the use of toluene as a solvent (29%). Purification of the crude material by column chromatography on alumina gave deep red crystals of **3** and **4** which are air-stable. In comparison to $[Cp(CO)_2Fe]_2$ [12], the solubility of **3** and **4**, which show significantly lower melting points, is improved in non-polar solvents. Although CO scrambling [13] leads to fast interconversion of isomers with the *cis*- and *trans*-coordinated tetrahydropentalenyl ligand, the ^1H and ^{13}C NMR spectra of **3** and **4** still exhibit a high complexity [14]. Hence, estimation of the diastereofacial selectivity and



(5)

relative configuration seemed not to be reasonable at this stage.



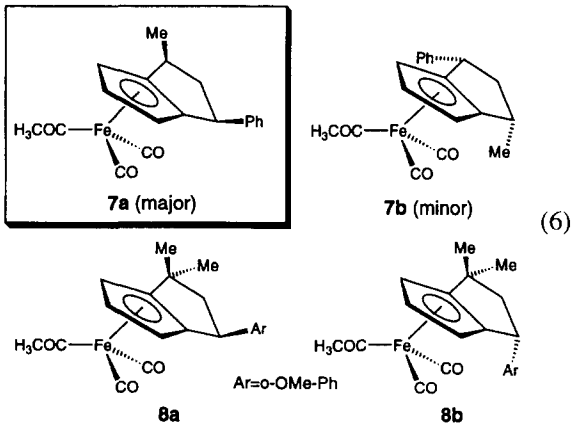
(3)

(4)

Reductive cleavage of **3** and **4** with sodium amalgam in THF gave the sodium salts of the iron complexes **5** and **6** in nearly quantitative yield after a reaction time of 2 d [Eq. (5)].

The less complicated stereochemical situation for the anionic iron complexes — two diastereomerically pairs of enantiomers are possible — could not be established due to the high lability of **5** and **6** even in THF solution, allowing characterization only by means of IR spectroscopy. Because of the four $\tilde{\nu}$(CO) bands found [$\tilde{\nu}$(CO): 1876 (s), 1855 (sh), 1803 (s), 1768 (m) (**5**); 1876 (s), 1855 (sh), 1803 (s), 1765 (m) (**6**)], **5** and **6** exist as a mixture of the two expected contact ion pairs described in the literature for Na[Fe(CO)$_2$Cp] [15]; a solvent-separated ion pair was not detected. In order to perform heterogenous metallation reactions in nonpolar solvents, **5** and **6** were isolated as ochre-coloured pyrophoric powders after removing the solvent in vacuo.

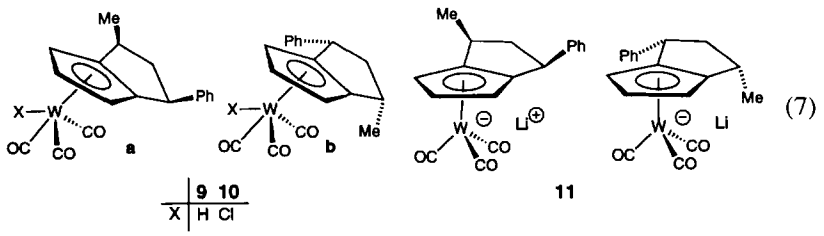
Treatment of a suspension of **5** and **6** in petroleum ether with excess acetyl chloride leads to the neutral acetyl complexes **7** and **8** which were isolated in 52% and 60% yield, respectively, as yellowish oils [Eq. (6)].



(6)

The diastereomeric ratio of **7**/**8**, as determined from the ^{1}H NMR spectra using the C(O)CH$_3$-signals, amounts to 3.85 : 1 (**7**) or 1.66 : 1 (**8**). A third diastereoisomer (epimerization-sensitive stereogenic centre C-3 [2e]) was not detected, thus demonstrating that no epimerization at the benzylic stereogenic centre occurred during reductive cleavage and nucleophilic substitution. Purification of the acetyl complexes was performed by chromatography on alumina, which in addition guaranteed separation of the diastereoisomers using a petroleum ether/toluene (1 : 1) mixture as eluant. In both cases, the predominant pair of enantiomers was isolated from the first fraction. The next phase contained a mixture of both diastereoisomers and the third the other pair of enantiomers also obtained diastereomerically pure. The stereochemistry is assumed to be the same as established for the tungsten derivatives **9a,b** (see discussion below). This means that in **7a** (major diastereoisomer) both the methyl and the aryl group are situated at sites opposite to the metal–carbonyl moiety, while in **7b** (minor diastereoisomer) they are associated with the metal centre site. An analogous situation is obtained for **8a,b** and all the following complexes.

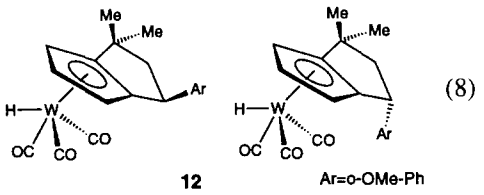
By expanding the investigations from iron to tungsten, a practicable route to the metal anion was realized



(7)

via lithiation of hydrido tungsten complexes [16]. The hydrido complex **9** was synthesized from $(EtCN)_3W(CO)_3$ and **1** in methanol at room temperature with a yield of 53% [17]. The diastereomeric ratio as determined from the ^1H NMR spectrum (W–H signals) was 3:1. Separation of the respective diastereoisomers, however, could not be performed due to the pronounced lability of the tungsten–hydrogen bond under chromatographic conditions. For this reason, the chloro complex **10** was prepared from **9** by treatment with tetrachloromethane [Eq. (7)]. After separation of impurities by passing through a column of alumina with toluene as eluant, a 4:1 ratio of diastereoisomers was determined by comparing the intensities of the benzylic signals (^1H NMR spectroscopy). Changing to petroleum ether/toluene (1:3) as an eluant led to pure **10a** being obtained as the first fraction. The second and third phase contained mixtures of **10a** and **10b**.

The relative configuration of the hydrido complexes **9a,b** could be determined by means of NOE spectroscopy. The pronounced enhancement (8%) of the W–H signal on saturation of the benzylic hydrogen signal (and vice versa) in **9a** and the lack of such effects in **9b** provides stringent proof for the above-mentioned stereochemistry. Complex **9** was converted into the lithium salt **11** by deprotonation with n-butyl-lithium in pentane. As for the iron complexes $(L^2)(CO)_2FeC(O)CH_3$ (**8a,b**), the hydrido tungsten complexes **12** (41% yield), derived from the pentalene **2**, were formed but with a lower degree diastereoisomeric ratio (3:2) relative to **7** and **9**, respectively, [Eq. (8)].



(8)

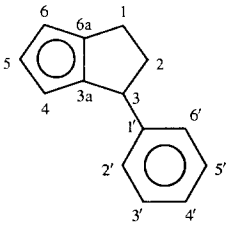
12 Ar=o-OMe-Ph

These findings provide evidence that the additional stereogenic centre in **1** leads to a pronounced higher degree of diastereofacial control and makes this tetrahydropentalene a useful ligand for organometallic chemistry. In particular, the access to the metallating reagents **5**, **6** and **11**, as described in this paper, offers the opportunity to generate a vast number of compounds bearing, for example, a σ-bonded carbon [8], silicon [18] or phosphorus [19] moiety under stereo-controlled conditions, and thereby attractive for further transformations.

3. Experimental details

All experiments were carried out under dinitrogen gas using solvents purified by standard procedures. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX-400 instrument and IR spectra on a Perkin-Elmer (model 283) instrument. Melting points (DTA: DuPont Thermal Analyzer 9000) and microanalysis were carried out by the Analytical Department of the Inorganic Laboratory at the University of Würzburg. $(EtCN)_3W(CO)_3$ [17], (*rac*)-*cis*-1-methyl-3-phenyltetrahydropentalene, $C_{15}H_{16}$ (**1**) [2a], and (*rac*)-1,1-dimethyl-3-(2-methoxyphenyl)tetrahydropentalene, $C_{17}H_{20}O$ (**2**) [2d], were prepared by published methods.

The following numbering scheme is used for assignment of the NMR data:



The diastereotopic hydrogen atoms at C-2 are numbered 2-H and 2*-H, respectively.

3.1. Preparation of bis{dicarbonyl[η^5-(cis-1-methyl-3-phenyl)bicyclo[3.3.0]octadienyl]}iron (3)

A solution consisting of 3.71 g (18.98 mmol) of $C_{15}H_{16}$ (**1**) and 5.58 g (28.47 mmol) of $Fe(CO)_5$ in 12 cm^3 of methylcyclohexane was refluxed for 12 h at 125°C. After evaporation to dryness, the residue was worked-up by column chromatography (column 20 × 1.5 cm, Al_2O_3, grade II, toluene/diethyl ether = 1:1). Elution with petroleum ether separated unreacted **1** first followed by **3**, which was obtained as red powder after evaporation of solvent and washing with pentane (2 × 5 cm^3). Yield, 1.03 g (9%), m.p. 76°C. Anal. Found: C, 66.37; H, 5.01%. $C_{34}H_{30}Fe_2O_4$ (614.30) calc.: C, 66.48; H, 4.92%. ^1H NMR (400.1 MHz, C_6D_6) δ: 7.65–6.95 (m, 5H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H); 4.56–0.85 (m, 10H, 1-H, 2-H, 2*-H, 3-H, 3a-H, 4-H, 5-H, 6-H, 6a-H) ppm. ^{13}C NMR (100.6 MHz, C_6D_6) δ: 145.93, 145.91, 145.88, 145.83, 140.69, 140.65 (s, C-1'); 129.26, 128.79, 128.71, 128.67, 128.51, 128.12, 127.88, 127.39, 127.28, 127.01, 126.97, 126.91, 126.56, 126.50, 125.64 (s, C-2', C-3', C-4', C-5', C-6'); 119.68, 119.63, 119.58, 118.56, 119.51, 119.45, 119.39, 116.67, 116.44, 115.80, 115.69, 114.39, 114.35, 143.31, 114.27, 114.14, 114.10 (s, C-3a, C-6a); 93.94, 93.75, 93.54, 88.64, 88.26, 86.93, 86.90, 81.32, 81.04, 80.59, 78.80, 78.46 (s, C-4, C-5, C-6); 48.64, 48.49, 48.46, 48.43, 44.94 (s, C-2); 43.02, 42.96, 42.83, 42.77, 42.75 (s, C-1); 32.80, 32.72, 32.63 (s, C-3); 22.32, 22.26, 19.03, 18.97, 18.87, 18.80 (s, CH_3C-1) ppm. IR (Et_2O) (cm^{-1}): $\tilde{\nu}$(CO) = 1988 (vs), 1947 (s), 1775 (vs).

3.2. Preparation of bis{dicarbonyl[η^5-1,1-dimethyl-3-anisylbicyclo[3.3.0]octadienyl]}iron (4)

This was obtained as for **3** from 1.27 g (5.26 mmol) of $C_{17}H_{20}O$ (**2**) and 894 mg (4.56 mmol) of $Fe(CO)_5$ in 10 cm^3 of methylcyclohexane (8 h, 128°C). Yield, 916 mg (29%). Red powder, M.p. 104°C. Anal. Found: C, 65.29; H, 5.53%. $C_{38}H_{38}Fe_2O_6$ (702.41) calc. C, 64.98; H, 5.45%. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 7.90–7.81, 7.20–6.68 (m, 4H, 3'-H, 4'-H, 5'-H, 6'-H); 4.81–2.07 (m, 3H, 4'-H, 5'-H, 6'-H); 3.79, 3.79, 3.78, 3.77, 3.74, 3.71 (s, 3H, H_3CO); 1.55, 1.55, 1.52, 1.52, 1.46, 1.45, 1.43, 1.25, 1.22, 1.10, 1.09, 1.07 [s, 6H, $(CH_3)_2CH$] ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 157.49, 156.93, 156.90, 156.87, 137.83, 133.42, 133.34, 133.31 (s, C-1', C-2'); 129.01, 128.36, 128.20, 127.99, 127.84, 127.63, 127.61, 127.35, 127.14, 127.10, 125.28, 122.74, 122.41, 122.28, 122.20, 120.65, 119.95, 119.93, 119.87, 119.59, 119.20, 119.08, 115.53, 115.40, 115.34, 115.25, 115.14, 110.14, 109.76, 109.73 (s, C-3', C-4', C-5', C-6'); 92.81, 92.72, 92.53, 88.51, 87.86, 87.74, 86.84, 82.08, 78.01, 77.76, 77.21 (s, C-3a, C-4, C-5, C-6, C-6a); 55.28, 55.23, 55.16, 55.12, 54.99 (s, H_3CO); 52.57, 52.50, 52.35, 49.65, 49.32, 49.16, 49.05 (s, C-2). 39.20, 39.14, 37.70, 37.65 (s, C-1); 36.81, 36.70, 36.61, 36.51, 36.47 (s, C-3); 32.12, 32.00, 31.97, 30.15, 30.01, 29.85, 28.77, 28.70, 28.65, 28.53, 28.50, 28.44 [s, $CH_3)_2C$] ppm. IR (cyclohexane) (cm^{-1}): $\tilde{\nu}$(CO) = 1995 (vs), 1947 (s), 1782 (vs).

3.3. Preparation of sodium {dicarbonyl[η^5-(cis-methyl-3-phenyl)bicyclo[3.3.0]octadienyl]iron(0)} (5)

To a solution of 928 mg (1.51 mmol) of $[C_{15}H_{15}(OC)_2Fe]_2$ (**3**) in 20 cm^3 of THF was added 44.32 g of sodium amalgam (sodium content, 1.02 g). The mixture was stirred for 5 d while being protected from light. After filtration and removal of the solvent, **5** was suspended in 20 cm^3 pentane and stirred for 2 d, separated and dried in vacuo. Yield, 989 mg (99%). Brown, pyrophoric powder. IR (THF) (cm^{-1}): $\tilde{\nu}$(CO) = 1876 (s), 1855 (sh), 1803 (s), 1768 (m).

3.4. Preparation of sodium {dicarbonyl[η^5-1,1-dimethyl-3-anisylbicyclo[3.3.0]octadienyl]iron(0)} (6)

This was obtained as for **5** from 760 mg (1.08 mmol) of $[C_{17}H_{19}(OC)_2Fe]_2$ (**4**) and 25.19 g of sodium amalgam (sodium content: 567 mg) in 20 cm^3 of THF (60 h). Yield, 798 mg (98%). Brown, pyrophoric powder. IR (THF) (cm^{-1}): $\tilde{\nu}$(CO) = 1876 (s), 1855 (sh), 1803 (s), 1765 (m).

3.5. Preparation of anti-acetyl{dicarbonyl[η^5-(cis-1-methyl-3-phenyl)bicyclo[3.3.0]octadienyl]}iron(II) (7a) and syn-acetyl{dicarbonyl[η^5-(cis-1-methyl-3-phenyl)-bicyclo[3.3.0]octadienyl]}iron(II) (7b)

A suspension of 989 mg (3.00 mmol) of Na $[Fe(CO)_2C_{15}H_{15}]$ (**5**) in 25 cm^3 of petroleum ether was added to 500 mg (6.37 mmol) of acetyl chloride and the reaction mixture stirred at room temperature for 12 h. Filtration and removal of the solvent in vacuo yielded **7a** and **7b** in a ratio of 3.85 : 1 [as determined from the $CH_3C(O)$ signal in the ^{1}H NMR spectra]. Purification by column chromatography (column 15 × 1 cm, Al_2O_3, grade III, petroleum ether/toluene = 1 : 1, ca. 1.5 dm^3) led to a long, third fraction containing pure **7a**, which could be isolated after removal of the solvent and drying in vacuo. Yield, 409 mg (39%) (**7a**). Anal. Found: C, 64.92; H, 5.53%. $C_{19}H_{18}FeO_3$ (350.20) calc.: C, 65.17; H, 5.18%. Further eluation of the column led to two additional fractions being isolated, one containing a mixture of **7a** and **7b** in the ratio of 2 : 3 and the other containing pure **7b**. Yield, 51 mg (5%) (**7a/7b**); 81 mg (8%) (**7b**). Anal. Found: C, 65.23, H, 5.11%. $C_{19}H_{18}FeO_3$ (350.20) calc.: 65.17; H, 5.18%. Yellow oils.

Complex **7a**: ^{1}H NMR (400.1 MHz, C_6D_6) δ: 7.08–6.91 (m, 5H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H); 4.27 (dd, $^3J_{H^5CCH^6}$ = 2.6 Hz, $^3J_{H^5CCH^4}$ = 2.6 Hz, 1H, 5-H); 3.97 (dd, $^3J_{H^3CCH^{2\cdot}}$ = 2.7 Hz, $^3J_{H^3CCH^2}$ = 9.0 Hz, 1H, 3-H); 3.93 (d, $^3J_{H^4CCH^5}$ = 2.6 Hz, 1H, 4-H); 3.92 (d, $^3J_{H^6CCH^5}$ = 2.6 Hz, 1H, 6-H); 2.92 (ddd, $^2J_{H^2CH^2}$ = 13.4 Hz, $^3J_{H^2CCH^3}$ = 8.6 Hz, $^3J_{H^2CCH^1}$ = 8.6 Hz, 1H, 2-H); 2.60 (ddq, $^3J_{H^1CCH^{2\cdot}}$ = 2.5 Hz, $^3J_{H^1CCH}$ = 7.7 Hz, $^3J_{H^1CCH^2}$ = 7.7 Hz, 1H, 1-H); 2.50 [s, 3H, $H_3CC(O)$]; 1.69 (ddd, $^3J_{H^{2\cdot}CCH^3}$ = 2.7 Hz, $^3J_{H^{2\cdot}CCH^1}$ = 2.7 Hz, $^2J_{H^{2\cdot}CH^2}$ = 13.4 Hz, 1H, 2*-H); 0.77 (d, $^2J_{HCCH^1}$ = 7.2 Hz, 3H, H_3CCH^1) ppm. ^{13}C NMR (100.6 MHz, C_6D_6) δ: 250.84 [s, $C(O)CH_3$]; 215.84, 215.74 (s, CO); 145.53 (s, C-1', C_6H_5); 128.69 (s, C-2', C-6', C_6H_5); 127.42 (s, C-3', C-5', C_6H_5); 126.58 (s, C-4', C_6H_5); 120.57 (s, C-3a); 114.66 (s, C-6a); 89.72, 79.07, 75.81 (s, C-4, C-5, C-6); 51.56 [s, $CH_3C(O)$]; 47.95 (s, C-2); 43.22 (s, C-3); 32.80 (s, C-1); 22.38 (s, CH_3C-1) ppm. IR (cyclohexane) (cm^{-1}): $\tilde{\nu}$(CO) = 2006 (s), 1956 (s); $\tilde{\nu}$[C(O)] = 1664 (br).

Complex **7b**: ^{1}H NMR (400.1 MHz, C_6D_6) δ: 7.19–7.12 (m, 5H, 1'-H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H); 4.17 (dd, $^3J_{H^5CCH^6}$ = 2.4 Hz, $^3J_{H^5CCH^4}$ = 2.4 Hz, 1H, 5-H); 4.08 (d, $^3J_{H^4CCH^5}$ = 2.2 Hz, 1H, 4-H); 4.07 (d, $^3J_{H^6CCH^5}$ = 2.2 Hz, 1H, 6-H); 3.40 (dd, $^3J_{H^3CCH^2}$ = 6.6 Hz, $^3J_{H^3CCH^{2\cdot}}$ = 11.0 Hz, 1H, 3-H); 2.29 [s, 3H, $H_3CC(O)$]; 2.23 (ddq, $^3J_{H^1CCH}$ = 6.5 Hz, $^3J_{H^1CCH^2}$ = 6.5 Hz, $^3J_{H^1CCH^{2\cdot}}$ = 10.3 Hz, 1H, 1-H); 2.06 (ddd, $^3J_{H^2CCH^1}$ = 6.5 Hz, $^3J_{H^2CCH^3}$ = 6.5 Hz, $^2J_{H^2CH^{2\cdot}}$ = 12.4 Hz, 1H, 2-H); 1.78 (ddd, $^3J_{H^{2\cdot}CCH^3}$ = 10.7 Hz, $^3J_{H^{2\cdot}CCH^1}$ = 10.7 Hz, $^2J_{H^{2\cdot}CH^2}$ = 12.0 Hz, 1H, 2*-H); 1.05 (d, $^3J_{HCCH^1}$ =

6.6 Hz, 3H, H_3CCH^1) ppm. ^{13}C NMR (100.6 MHz, C_6D_6) δ: 249.18 [s, $C(O)CH_3$]; 216.07, 215.59 (s, CO); 140.26 (s, C-1'); 128.71 (s, C-2', C-6'); 127.29 (s, C-3', C-5'); 127.14 (s, C-4'); 118.06 (s, C-3); 115.82 (s, C-1); 86.75, 80.81, 80.43 (s, C-4, C-5, C-6); 51.21 [s, $CH_3C(O)$]; 43.89 (s, C-2); 42.45 (s, C-3); 32.14 (s, C-1); 18.69 (s, CH_3C-1) ppm. IR (cyclohexane) (cm^{-1}): $\tilde{\nu}$(CO) = 2006 (s), 1956 (s); $\tilde{\nu}$[C(O)] = 1664 (br).

3.6. Preparation of anti-acetyl{dicarbonyl[η^5-1,1-dimethyl-3-anisylbicyclo[3.3.0]octadienyl]}iron(II) (8a) and syn-acetyl{dicarbonyl[η^5-1,1-dimethyl-3-anisylbicyclo[3.3.0]octadienyl]}iron(II) (8b)

A suspension of 798 mg (2.13 mmol) of $Na[Fe(CO)_2C_{17}H_{19}]$ (**6**) in 25 cm^3 of petroleum ether was added to 500 mg (6.37 mmol) of acetyl chloride at −78°C. The reaction mixture was warmed up to room temperature over a period of 2 h and stirred for 12 h while being protected from light. Work-up and separation was followed by column chromatography (column 15 × 1.5 cm, Al_2O_3, grade III, petroleum ether/toluene = 1:1 ca. 1.5 dm^3) analogously to **7**. Yield 279 mg (33%) (**8a**); 112 mg (13%) (**8a**/**8b**, ratio 1:2.29); 110 mg (13%) (**8b**). Anal. Found: C, 63.18; H, 5.98%. $C_{21}H_{22}FeO_4$ (394.25) calc.: C, 63.98; H, 5.62%.

Complex **8a**: ^1H NMR (400.1 MHz, C_6D_6) δ: 7.04 (dt, $^3J_{HCCH}$ = 7.7 Hz, $^4J_{HCCCH}$ = 1.5 Hz, 1H, $H_4C_6OCH_3$); 6.92 (dd, $^3J_{HCCH}$ = 7.6 Hz, $^4J_{HCCCH}$ = 1.3 Hz, 1H, $H_4C_6OCH_3$); 6.74 (dt, $^3J_{HCCH}$ = 7.5 Hz, $^4J_{HCCCH}$ = 0.9 Hz, 1H, $H_4C_6OCH_3$); 6.51 (dd, $^3J_{HCCH}$ = 8.1 Hz, $^4J_{HCCCH}$ = 0.5 Hz, 1H, $H_4C_6OCH_3$); 4.37 (d, $^3J_{H^3CCH^2}$ = 8.6 Hz, 1H, 3-H); 4.28 (dd, $^3J_{H^5CCH^6}$ = 2.6 Hz, $^3J_{H^5CCH^4}$ = 2.6 Hz, 1H, 5-H); 4.06 (dd, $^3J_{H^4CCH^5}$ = 2.6 Hz, $^4J_{H^4CCCH^6}$ = 1.0 Hz, 1H, 4-H); 4.05 (dd, $^3J_{H^6CCH^5}$ = 2.6 Hz, $^4J_{H^6CCCH^4}$ = 1.0 Hz, 1H, 6-H); 3.29 (s, H_3CO); 2.79 (dd, $^2J_{H^2CH^{2\cdot}}$ = 13.4 Hz, $^3J_{H^2CCH^3}$ = 9.3 Hz, 1H, 2-H); 2.50 [s, 3H, $H_3CC(O)$]; 2.06 (dd, $^2J_{H^{2\cdot}CH^2}$ = 13.4 Hz, $^3J_{H^{2\cdot}CCH^3}$ = 1.4 Hz, 1H, 2*-H); 1.23 (s, 3H, H_3^1C); 0.88 (s, 3H, $H_3^{1*}C$) ppm. ^{13}C NMR (100.6 MHz, C_6D_6) δ: 250.14 [s, $C(O)CH_3$]; 216.18, 215.99 (s, CO); 157.16 (s, C-1'); 133.22 (s, C-6'); 123.47 (s, C-3a); 115.87 (s, C-6a); 127.84, 127.21, 120.20, 110.43 (s, C-2', C-3', C-4', C-5'); 88.87, 79.17, 77.03 (s, C-4, C-5, C-6); 54.78 (s, $CH_3OC_6H_4$); 52.93 (s, C-2); 51.41 [s, $CH_3C(O)$]; 38.53 (s, C-1); 37.65 (s, C-3); 30.94, 30.72 (s, CH_3^1, CH_3^{1*}) ppm. IR (cyclohexane) (cm^{-1}): $\tilde{\nu}$(CO) = 2005 (s), 1954(s); $\tilde{\nu}$[C(O)] = 1662.

Complex **8b**: ^1H NMR (400.1 MHz, C_6D_6) δ: 7.49 (dd, $^3J_{HCCH}$ = 7.7 Hz, $^4J_{HCCCH}$ = 0.9 Hz, 1H, $H_4C_6OCH_3$); 7.08 (dt, $^3J_{HCCH}$ = 7.8 Hz, $^4J_{HCCCH}$ = 1.6 Hz, 1H, $H_4C_6OCH_3$); 6.96 (dt, $^3J_{HCCH}$ = 7.5 Hz, $^4J_{HCCCH}$ = 1.1 Hz, 1H, $H_4C_6OCH_3$); 6.51 (dd, $^3J_{HCCH}$ = 8.1 Hz, $^4J_{HCCCH}$ = 0.9 Hz, 1H, $H_4C_6OCH_3$); 4.30 (d, $^3J_{H^4CCH^5}$ = 2.5 Hz, 1H, 4-H); 4.29 (dd, $^3J_{H^3CCH^2}$ = 11.1 Hz, $^3J_{H^3CCH^{2\cdot}}$ = 6.4 Hz, 1H, 3-H); 4.21 (dd, $^3J_{H^5CCH^6}$ = 2.5 Hz, $^3J_{H^5CCH^4}$ = 2.5 Hz, 1H, 5-H); 4.05 (dd, $^3J_{H^6CCH^5}$ = 2.5 Hz, $^4J_{H^6CCCH^4}$ = 1.0 Hz, 1H, 6-H); 3.26 (s, H_3CO); 2.35 (dd, $^2J_{H^2CH^{2\cdot}}$ = 11.7 Hz, $^3J_{H^2CCH^3}$ = 11.7 Hz, 1H, 2-H); 2.30 [s, 3H, $H_3CC(O)$]; 1.95 (dd, $^2J_{H^{2\cdot}CH^2}$ = 12.2 Hz, $^3J_{H^{2\cdot}CCH^3}$ = 5.8 Hz, 1H, 2*-H); 1.25 (s, 3H, H_3^1C); 0.92 (s, 3H, $H_3^{1*}C$) ppm. ^{13}C NMR (100.6 MHz, C_6D_6) δ: 249.58 [s, $C(O)CH_3$]; 216.28, 215.81 (s, CO); 157.77 (s, C-1'); 128.61 (s, C-6'); 121.75 (s, C-3a); 115.10 (s, C-6a); 128.15, 127.02, 120.95, 110.15 (s, C-2', C-3', C-4', C-5'); 85.77, 81.96, 79.43 (s, C-4, C-5, C-6); 54.59 (s, $CH_3OC_6H_4$); 51.08 [s, $CH_3C(O)$]; 48.91 (s, C-2); 37.14 (s, C-1); 35.95 (s, C-3); 28.51, 27.62 (s, CH_3^1, CH_3^{1*}) ppm. IR (cyclohexane) (cm^{-1}): $\tilde{\nu}$(CO) = 2005 (s), 1954(s); $\tilde{\nu}$[C(O)] = 1662.

3.7. Preparation of anti-tricarbonyl(hydrido)[η^5-(cis-1-methyl-3-phenyl)bicyclo[3.3.0]octadienyl]tungsten(II) (9a) and syn-tricarbonyl(hydrido)[η^5-(cis-1-methyl-3-phenyl)bicyclo[3.3.0]octadienyl]tungsten(II) (9b)

A suspension of 4.25 g (9.81 mmol) of $(EtCN)_3W(CO)_3$ in 50 cm^3 of methanol was combined with 963 mg (4.91 mmol) of $C_{15}H_{16}$ (**1**) in 5 cm^3 of diethyl ether and stirred for 24 h with protection against light. After evaporating to dryness in vacuo, **9** remained (diastereomeric ratio = 3:1 from the W–H signals in the ^1H NMR spectrum). Work-up by column chromatography for purification and separation of the diastereoisomers was unsuccessful because of the lability of the tungsten–hydrogen bond. Yield, 1.20 g (53%). Orange oil. Anal. Found: C, 45.36; H, 4.43%. $C_{18}H_{16}O_3W$ (464.17) calc. C, 46.58; H, 3.47%.

Complex **9a**: ^1H NMR (400.1 MHz, C_6D_6) δ: 7.14–6.79 (m, 5H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H); 4.60–4.52 (m, 3H, 4-H, 5-H, 6-H); 3.91 (bd, 1H, 3-H); 3.18–2.81 (m, 2H, 1-H, 2-H); 1.81–1.61 (m, 1H, 2*-H); 0.67 [d, $^3J_{HCCH}$ = 7.2 Hz, 3H, H_3C]; −6.78 [s, $^1J_{HW}$ = 38.0 Hz, 1H, HW] ppm. IR (pentane) (cm^{-1}): $\tilde{\nu}$(CO) = 2016 (s), 1946 (vs).

Complex **9b**: ^1H NMR (400.1 MHz, C_6D_6) δ: 7.14–6.79 (m, 5H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H); 4.60–4.52 (m, 3H, 4-H, 5-H, 6-H); 3.94 (bd, 1H, 3-H); 3.18–2.81 (m, 2H, 1-H, 2-H); 1.81–1.61 (m, 1H, 2*-H); 0.96 [d, $^3J_{HCCH}$ = 7.2 Hz, 3H, H_3C]; −7.00 [s, ^1J(HW) = 38.0 Hz, 1H, HW] ppm. IR (pentane) (cm^{-1}): $\tilde{\nu}$(CO) = 2016 (s), 1946 (vs).

3.8. Preparation of anti-tricarbonyl(chloro)[η^5-(cis-1-methyl-3-phenyl)bicyclo[3.3.0]octadienyl]tungsten(II) (10a) and syn-tricarbonyl(chloro)[η^5-(cis-1-methyl-3-phenyl)bicyclo[3.3.0]octadienyl]tungsten(II) (10b)

To a solution of 490 mg (1.06 mmol) of $(C_{15}H_{15})(CO)_3WH$ (**10**) in 20 cm^3 of toluene, 10 cm^3 of

CCl_4 was added at 0°C and the reaction mixture warmed up to room temperature over a period of 2 h. The solvent and excess CCl_4 were removed in vacuo, the residue eluted in toluene and passed through a column of alumina (grade III). The two expected diastereoisomers were detected in a ratio of 4:1. Subsequent column chromatography (column 15 × 1 cm, Al_2O_3, grade III, petroleum ether/toluene = 1:3) gave pure **10a** as the first zone. The second and third zones contained mixtures of **10a** and **10b**. Yield, 433 mg (82%). Red oil. Anal. Found: C, 42.67; H, 3.98%. $C_{18}H_{15}ClO_3W$ (498.62) calc. C, 43.36; H, 3.03%.

Complex **10a**: ^{1}H NMR (400.1 MHz, C_6D_6) δ: 7.51–7.28 (m, 5H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H); 5.55–5.54, 5.44–5.42, 5.42–5.41 (m, 3H, 4-H, 5-H, 6-H); 4.27 (dd, 1H, 3-H); 3.20–3.11 (m, 2H, 1-H, 2-H); 2.05–1.92 (m, 1H, 2*-H); 1.43 [d, $^2J_{HCCH}$ = 7.0 Hz, 3H, H_3C] ppm. ^{13}C NMR (100.6 MHz, C_6D_6) δ: 230.75, 216.42, 216.33 (s, CO); 143.95 (s, C-1′); 128.76 (s, C-2′, C-6′); 127.34 (s, C-3′, C-5′); 126.84 (s, C-4′); 86.28, 81.47, 80.48 (s, C-4, C-5, C-6); 48.16 (s, C-2); 44.50 (s, C-3); 33.78 (s, C-1); 21.91 (s, CH_3) ppm. IR (pentane) (cm^{-1}): $\tilde{\nu}$(CO) = 2040 (s), 1964 (vs), 1943 (vs).

Complex **10b**: ^{1}H NMR (400.1 MHz, C_6D_6) δ: 7.51–7.28 (m, 5H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H); 6.09–6.07, 5.64–5.63, 5.23–5.22 (m, 3H, 4-H, 5-H, 6-H); 4.54 (dd, 1H, 3-H); 3.39–3.37 (m, 2H, 1-H, 2-H); 2.24–2.20 (m, 1H, 2*-H); 1.49 [d, $^2J_{HCCH}$ = 6.6 Hz, 3H, H_3C] ppm. ^{13}C NMR (100.6 MHz, C_6D_6) δ: 230.66, 216.53, 216.41 (s, CO); 139.45 (s, C-1′); 128.26 (s, C-2′, C-6′); 127.27 (s, C-3′, C-5′); 126.78 (s, C-4′); 97.58, 94.43, 84.23 (s, C-4, C-5, C-6); 42.09 (s, C-2); 43.40 (s, C-3); 34.61 (s, C-1); 19.85 (s, CH_3) ppm. IR (pentane) (cm^{-1}): $\tilde{\nu}$(CO) = 2040 (s), 1964 (vs), 1943 (vs).

3.9. Preparation of tricarbonyl(hydrido)[η^5-1,1-dimethyl-3-anisylbicyclo[3.3.0]octadienyl]tungsten(II) (11)

Using the procedure described for **9**, complex **11** was prepared from 4.08 g (9.42 mmol) of $(Et_3CN)W(CO)_3$ and 1.32 g (4.71 mmol) of $C_{17}H_{19}O$ (**2**). The resulting two diastereoisomers were obtained in a ratio of 1.5:1. Yield, 980 mg (41%). Yellow oil. Anal. Found: C, 46.88; H, 3.67%. $C_{20}H_{20}O_4W$ (508.23) calc. C, 47.27; H, 3.97%. ^{1}H NMR (400.1 MHz, C_6D_6) δ: 7.56–6.38 (m, 4H, 3′-H, 4′-H, 5′-H, 6′-H); 4.95–4.58 (m, 3H, 4-H, 5-H, 6-H); 4.55–4.46 (m, 1H, 3-H); 3.51, 3.45 (s, 3H, OCH_3); 2.86–2.59 (m, 2H, 1-H, 2-H); 2.22–2.15 (m, 1H, 2*-H); 1.45–0.27 [m, 6H, $C(CH_3)_2$]; −6.59 [s, $^1J_{HW}$ = 38.4 Hz, 1H, HW]; −6.81 [s, $^1J_{HW}$ = 38.0 Hz, 1H, HW] ppm. IR (pentane) (cm^{-1}): $\tilde{\nu}$(CO) = 2017 (s), 1945 (vs).

3.10. Preparation of lithium {tricarbonyl[η^5-(cis-1-methyl-3-phenyl)bicyclo[3.3.0]octadienyl]tungsten} (12)

A solution of 105 mg (0.23 mmol) of **9** in 20 cm^3 of pentane was carefully treated with 0.1 cm^3 of a 2.5 M solution of ^{n}BuLi in hexane. After 30 min, the precipitated **12** was separated, washed three times with 10 cm^3 portions of pentane and dried in vacuo. Yield, 83 mg (77%). Beige powder. IR (THF) (cm^{-1}): $\tilde{\nu}$(CO) = 1898 (s), 1798 (s), 1712 (m).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (SFB 347 'Selektive Reaktionen Metall-aktivierter Moleküle'), the Fonds der Chemischen Industrie and the Universitätsbund Würzburg for generous financial support.

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[14] In the NMR spectra of **3** and **4**, the averaged signals between the *cis* and *trans* forms are observed. It is therefore possible to find two forms with the methyl and phenyl (**3**) or aryl (**4**) ligands being on the opposite side to the metal–carbonyl moiety and two in which they are adjacent to the metal centre, resulting in four sets of signals. If the substituents at the chiral centres of the two tetrahydropentalenyl ligands in **3** or **4** lie in different directions, two forms again result, each giving rise to two sets of signals. The resulting eight sets of signals lead to the complexity of the NMR spectra.

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