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Synthesis and properties of novel substituted 4,5,6,7-tetrahydroindenes and selected metal complexes ☆

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Abstract

The synthesis of a complete series of substituted 4,5,6,7-tetrahydroindenes (4,5,6,7-tetrahydroindene, **1**; 1-methyl-, 1,3-dimethyl- and 1,2,3-trimethyl-4,5,6,7-tetrahydroindene, **2–4**) is reported. The synthesis of ferrocenes (**8–11**) from these substituted cyclopentadienes is described. The electrochemistry of these ferrocenes indicates that these complexes are more readily oxidized than ferrocene and that the effect of methyl or alkyl substituents on the ease of oxidation is additive. A single crystal X-ray structure of two of the ferrocenes, bis(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)iron(II), **10**, and bis(1,2,3-trimethyl-4,5,6,7-tetrahydroindenyl)iron(II), **11**, indicates that steric hindrance causes the alkyl substituents to be bent away from the plane of the cyclopentadienyl ring. However, the structures differ in that the cyclopentadienyl rings in **10** are staggered wheras those in **11** are eclipsed. The synthesis of the cyclopentadienyltricarbonylmethyl compounds of molybdenum and tungsten from **3** and **4** is also described.

Keywords: Iron; Molybdenum; Tungsten; Indenes; Metallocenes; Electrochemistry

1. Introduction

Complexes of 4,5,6,7-tetrahydroindene have been the focus of great interest recently owing to the catalytic activity of their zirconium compounds [1]. These complexes have been synthesized by the hydrogenation of the six-membered aromatic ring of the corresponding complexed indenyl ligands [2]. This route limits the synthesis of an extensive range of such complexes, especially those which contain other moieties that are sensitive to hydrogenation. We report here on the synthesis of 4,5,6,7-tetrahydroindene and its 1-methyl-, 1,3-dimethyl-, and 1,2,3-trimethyl-cogeners via the methylation of the corresponding cyclopentenones. Metal complexes of these ligands are also described.

2. Results and discussion

2.1. Synthesis of 4,5,6,7-tetrahydroindenes

We have devised a straightforward, two-step synthesis of 4,5,6,7-tetrahydroindene, Cp^0H, **1**, and its methylated cogeners 1-methyl-, 1,3-dimethyl- and 1,2,3-trimethyl-4,5,6,7-tetrahydroindene, **2–4**, Cp^1H, Cp^2H and Cp^3H, respectively. These are synthesized via the intermediate bicyclic cyclopentenones, **5–7**, [3], which can be easily isolated in 20–40% yield using the method reported by Dev for **5** and **6** [4], Scheme 1, which is a modification of the Nazarov cyclization reaction. Nucleophilic addition of hydride (from $LiAlH_4$) or methyl (from methyllithium) anions give allylic alcohols, that are dehydrated in situ, using acid catalysis. This addition–dehydration process yields the 4,5,6,7-tetrahydroindenes, **1–4**, in 30–60%, Scheme 1. These 4,5,6,7-tetrahydroindenes are formed as mixtures of isomer as indicated by GC analysis. The possibility exists that

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☆ Dedicated to the memory of Professor Jeffery M. Chance.
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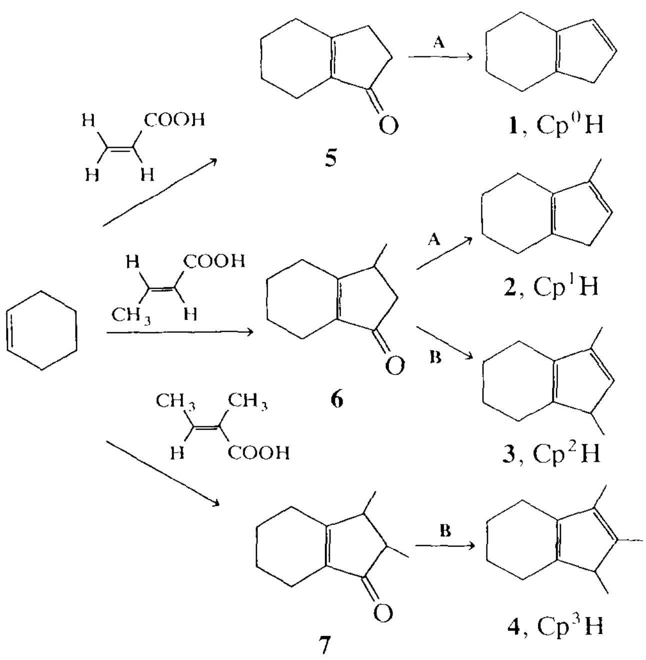

Scheme 1. Synthesis of 4,5,6,7-Tetrahydroindenes. **5**–**7** synthesized by reaction in polyphosphoric acid at 60° for 2 h [3]. A = $LiAlH_4$ in diethyl ether followed by hydrolysis and acid catalyzed dehydration. B = MeLi in diethyl ether followed by hydrolysis and acid catalyzed dehydration.

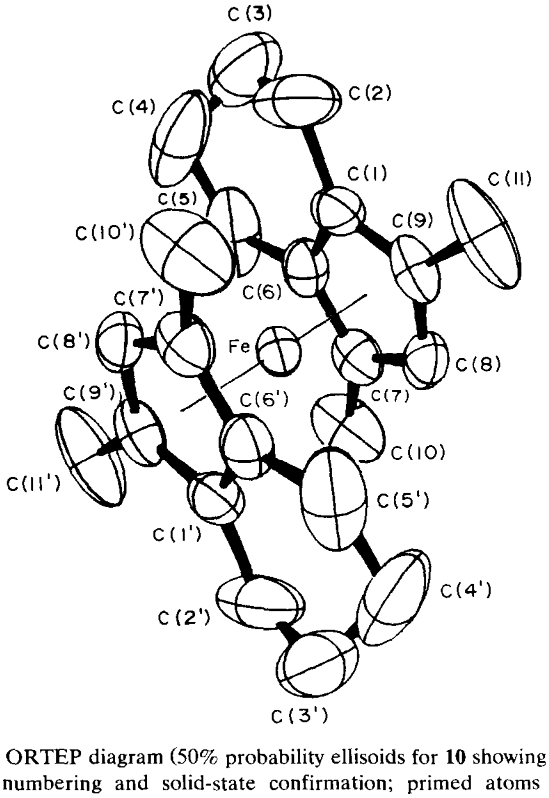

Fig. 1. ORTEP diagram (50% probability ellisoids for **10** showing the atom numbering and solid-state confirmation; primed atoms are related to the unprimed atoms by a crystallographic center of symmetry. Hydrogen atoms have been omitted for clarity.

some of these isomers will not have acidic hydrogens, which may explain the low yields of transition metal complexes derived from their reaction with *n*-butyllithium or dibutylmagnesium

$$\mathbf{1\text{–}4} \xrightarrow[(ii)\ \mathrm{FeCl_2\ or\ Fe(acac)_2py_2}]{(i)\ \mathrm{BuLi\ or\ Bu_2Mg}} \mathrm{Cp}^x_2\mathrm{Fe} \qquad (1)$$

8	$x = 0$	37% yield
9	$x = 1$	35% yield
10	$x = 2$	60% yield
11	$x = 3$	25% yield

2.2. Synthesis of 4,5,6,7-tetrahydroindenyliron(II) and its methylated cogeners

To demonstrate the synthetic utility of these novel ligands, we have synthesized the complete series of ferrocenes, **8**–**11**, in the usual fashion using Cp^xLi or Cp^x_2Mg, Eq. (1). The ferrocene **8** has been previously synthesized by hydrogenation of the corresponding bis(indenyl)iron(II) compound or from the reaction of iron atoms with spiro[4,4]nona-1,3-diene [5].

2.3. Single crystal X-ray structural determination of 10 and 11

The structures of **10** and **11** were determined by single crystal X-ray diffraction studies and details are included in the experimental section.

The structure of **10**, Fig. 1, indicates that the cyclopentadienyl rings are staggered, as are those in $(C_5Me_5)_2Fe$, **12** [6], and $(C_5Me_4H)_2Fe$, **13** [7]. The cyclohexyl rings, as expected, are *trans* to one another. The average Fe–C(ring) distances are 2.050 (4) Å compared with values of 2.064 (3) Å and 2.054 (3) Å for **12** and **13**, respectively. The average C(ring)–C(ring) bond lengths are similar in **10**, **12** and **13** being 1.411 (6) Å, 1.419 (2) Å, and 1.428 (4) Å respectively, as are the C(ring)–C(methyl) bond lengths (1.504 (8) Å, 1.502 (3) Å and 1.496 (6) Å, respectively). The steric bulk of the substituents causes the carbons of the two methyl groups and the two carbons of the cyclohexyl ring adjacent to the five-membered ring to deviate from the plane of the cyclopentadienyl ring away from the iron atom by an average of 0.057 Å (range: 0.050–0.076 Å). The stuctures of **12** and **13** show similar distortions of the carbon atoms of the methyl groups with average deviations of 0.064 Å (range: 0.036–0.077 Å), and 0.060 Å (range: 0.043–0.090 Å), respectively. The iron atom–cyclopentadienyl centroid distance is 1.662 Å in **10**, compared with 1.657 Å in both **12** and **13**. The cyclohexyl hexyl ring is puckered with average C–C bond distances of 1.504 (8) Å with the following deviations from the cyclopentadienyl plane (Å):C(2) −0.076; C(3) −0.503; C(4) 0.223; C(5) −0.057.

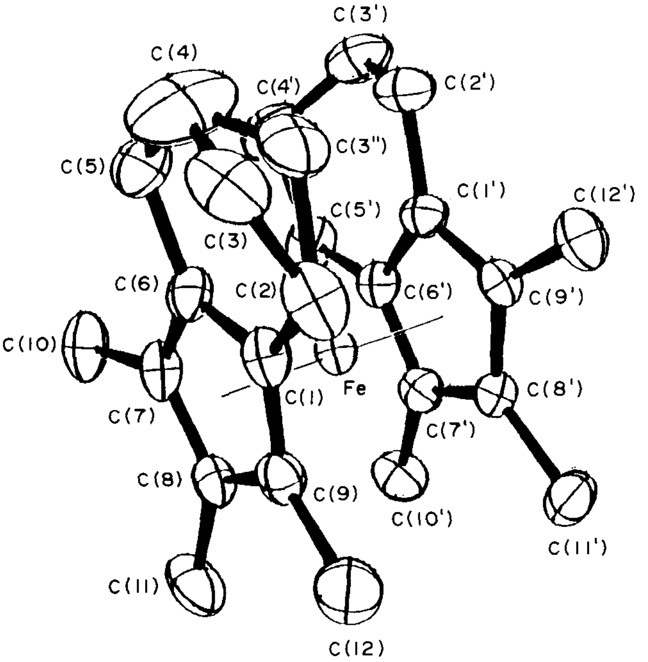

Fig. 2. ORTEP diagram (40% probability ellipsoids) for 11 showing the atom numbering scheme and solid state conformation; one of the carbon atoms is disordered over two positions, C(3) and C(3"). Hydrogen atoms have been omitted for clarity.

In contrast, in the structure of **11**, Fig. 2, the cyclopentadienyl and cyclohexyl rings are eclipsed. The average Fe–C(ring), C(ring)–C(ring) and C(ring)–C(methyl) distances are similiar to those in **10** being 2.062 (4), 1.424 (5) and 1.495 (6) Å respectively. However, the carbons of the three methyl substituents and the two carbons of the cyclohexyl ring adjacent to the cyclopentadienyl ring are deviated even farther away from the cyclopentadienyl plane, with average deviations of 0.118 Å (range 0.088–0.157 Å) away from the iron atom. Presumably, this greater deviation is caused by the more severe steric interactions in **11** due to the eclipsed conformation. The iron atom–cyclopentadienyl centroid distance is 1.669 Å in **11** which is similiar to that in **10**. The cyclohexyl ring in **11** is puckered and the torsion angles are similiar in size and sign to those for **10**.

The fact that the conformations of **10** and **11** are different is at first surprising, but the stability of the favored staggered conformation for **12** is estimated to be only 4.2 kJ mol^{-1} relative to the eclipsed form [8]. Therefore it seems that the difference in conformation can be rationalized by small differences in forces such as crystal packing forces perhaps caused by interlocking of the puckered cyclohexyl rings in **11**.

2.4. *Electrochemical investigations of substituted ferrocenes*

In order to investigate the electronic properties of these 4,5,6,7-tetrahydroindenyl ligands, the electrochemistry of **8–10** was investigated by cyclic voltammetry in acetonitrile using the standard calomel electrode, SCE, as a reference and tetraethylammonium perchlorate, TEAP, as the supporting electrolyte. The ease of oxidation of substituted ferrocenes relative to ferrocene can be expressed in terms of $\Delta E^0_{1/2}$, which is the difference between $E^0_{1/2}$ for the substituted ferrocene and ferrocene itself [9]. The values of $\Delta E^0_{1/2}$ for **8**, **9** and **10** are −249, −340 and −430 mV, respectively. As expected, the electron donating alkyl substituents make **8**, **9** and **10** easier to oxidize compared with ferrocene. The values are in accord with those reported for ferrocenes with equivalent numbers of alkyl groups, for example, the value of $\Delta E^0_{1/2}$ for 1,1',3,3'-tetrakis(*tert*-butyl)ferrocene is −239 mV [10] compared with a value of −249 mV for **8**. The value of $\Delta E^0_{1/2}$ for 1,1',2,2',3,3'4,4'-octaethylferrocene is −440 mV [11], close to that obtained for **10**. The addition of each methyl group to the cyclopentadienyl ring of **8–10** decreases $\Delta E^0_{1/2}$ by approximately 45 mV, which is comparable with the value of 47 mV per alkyl substituent found for other substituted ferrocenes [12].

2.5. *Synthesis of 1,3-dimethyl-4,5,6,7-tetrahydroindenyltungsten and 1,2,3-trimethyl-4,5,6,7-tetrahydroindenyltricarbonylmethylmolybdenum(II) and tungsten(II)* ***14–16***

The synthesis of these complexes was acheived using the reaction of the cyclopentadienyl anions derived

Table 1
Crystallographic Data for **10**

Molecular formula	$C_{24}H_{34}Fe$
Formula weight	378.39
Crystal system	Orthorhombic
Space group	$Pbca(D^{15}_{2h})$-No. 61
a (Å)	18.051(2)
b (Å)	19.408(2)
c (Å)	11.408(2)
No. of orientation refls.; θ(°) range	25; 35–40
V (Å^3)	3997(2)
Z	8
$D_{calcd.}$ (g cm^{-3})	1.258
μ (Cu-Kα radiation, $\lambda = 1.5418$ Å)	60.6
Temp. (°C)	25
Crystal dimensions (mm^3)	$0.21 \times 0.25 \times 0.50$
$T_{max} : T_{min}$	1.00 : 0.75
Scan type	ω-2θ
Scanwidth (°)	$1.00 + 0.14 \tan \theta$
θ_{max}. (°)	75
Intensity control refls.;	131, 241, 321, 411;
Variation; repeat time (hr)	< 1%; 2
Total no. of refls. ($+h$, $+k$, $+l$) recorded	4119
No. of refls. retained [$I > 3.0\ \sigma(I)$]	2215
No. of parameters refined	356
Extinction correction	$1.1(4) \times 10^{-7}$
$R(R_w)$	0.041 (0.055)
Goodness-of-fit	1.20
Max. shift : esd in final least-squares cycle	0.02
Final $\Delta\rho$ (e Å^{-3}) max.; min.	0.40; −0.54

from **3** or **4** with tris(propionitrile)tricarbonylmolybdenum(0) or tungsten(0) in refluxing tetrahydrofuran (THF) for 3 h followed by addition of iodomethane, Eqs. (2) and (3).

$$Cp^{x}Li + M(EtCN)_3(CO)_3 \longrightarrow Cp^{x}M(CO)_3Li + 3EtCN \qquad (2)$$

$$Cp^{x}M(CO)_3Li + MeI \longrightarrow Cp^{x}M(CO)_3Me + LiI \qquad (3)$$

14 $x = 3$, M = Mo; 48% yield
15 $x = 2$, M = W; 70% yield
16 $x = 3$, M = W; 22% yield

We are currently investigating other ligands containing these tetrahydroindene groups, other transition metal complexes, and the catalytic activity of these complexes.

3. Experimental

3.1. General

All manipulations of moisture and air sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk and vacuum techniques.

Table 2
Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for **10** with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq} (Å^2)
Fe	0.0000(–) [a]	0.0000(–) [a]	0.0000(–) [a]	3.62(1)
C(1)	0.1457(4)	0.1328(4)	0.1331(3)	5.4(1)
C(2)	0.3387(6)	0.1662(6)	0.1763(5)	10.5(2)
C(3)	0.4437(7)	0.1051(8)	0.3074(7)	14.1(2)
C(4)	0.4010(8)	–0.0251(7)	0.3134(7)	13.7(2)
C(5)	0.2108(9)	–0.0439(6)	0.2998(5)	9.8(2)
C(6)	0.0880(5)	0.0351(4)	0.1915(3)	5.2(1)
C(7)	–0.0971(5)	0.0325(4)	0.1339(3)	5.3(1)
C(8)	–0.1515(4)	0.1293(4)	0.0415(3)	5.3(1)
C(9)	–0.0038(5)	0.1910(4)	0.0377(4)	5.6(1)
C(10)	–0.2125(7)	–0.0528(6)	0.1711(4)	9.2(1)
C(11)	–0.0046(9)	0.3027(5)	–0.0441(5)	10.7(2)

[a] Fixed by symmetry.

THF, hexane and diethyl ether were pre-dried over powdered potassium hydroxide and freshly distilled from sodium benzophenone ketyl. Dibutylmagnesium (1M in heptane) was a gift from FMC Corporation, Lithium Division, Gastonia, NC, and was used as received. ^{1}H NMR spectra were recorded on Varian 60MHz EM-360 and JOEL FX-90 MHz spectrometers. IR spectra were recorded on a Perkin Elmer 1320

Table 3
Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses for **10**

Fe–C(1)	2.054(3)	C(3)–C(4)	1.411(11)
Fe–C(6)	2.061(3)	C(4)–C(5)	1.548(11)
Fe–C(7)	2.057(4)	C(5)–C(6)	1.497(6)
Fe–C(8)	2.040(4)	C(6)–C(7)	1.412(5)
Fe–C(9)	2.038(4)	C(7)–C(8)	1.402(5)
C(1)–C(2)	1.522(6)	C(7)–C(10)	1.502(8)
C(1)–C(6)	1.413(6)	C(8)–C(9)	1.411(6)
C(1)–C(9)	1.418(5)	C(9)–C(11)	1.498(7)
C(2)–C(3)	1.543(9)		
(b) Bond angles			
C(2)–C(1)–C(6)	122.3(3)	C(5)–C(6)–C(7)	128.7(5)
C(2)–C(1)–C(9)	129.4(4)	C(6)–C(7)–C(8)	107.1(4)
C(6)–C(1)–C(9)	108.3(3)	C(6)–C(7)–C(10)	120.0(3)
C(1)–C(2)–C(3)	108.9(5)	C(8)–C(7)–C(10)	126.9(3)
C(2)–C(3)–C(4)	113.1(5)	C(7)–C(8)–C(9)	109.8(3)
C(3)–C(4)–C(5)	112.8(6)	C(1)–C(9)–C(8)	106.5(4)
C(4)–C(5)–C(6)	109.7(5)	C(1)–C(9)–C(11)	126.6(4)
C(1)–C(6)–C(5)	123.0(4)	C(8)–C(9)–C(11)	126.8(4)
C(1)–C(6)–C(7)	108.3(3)		
(c) Torsion angles [a]			
C(6)–C(1)–C(2)–C(3)	–14.7(7)	C(3)–C(4)–C(5)–C(6)	46.3(7)
C(9)–C(1)–C(2)–C(3)	162.5(5)	C(4)–C(5)–C(6)–C(1)	–13.5(7)
C(2)–C(1)–C(6)–C(5)	–0.3(6)	C(4)–C(5)–C(6)–C(7)	169.6(5)
C(2)–C(1)–C(6)–C(7)	177.2(4)	C(1)–C(6)–C(7)–C(8)	–0.5(4)
C(9)–C(1)–C(6)–C(5)	–177.9(4)	C(1)–C(6)–C(7)–C(10)	–177.1(4)
C(9)–C(1)–C(6)–C(7)	–0.5(4)	C(5)–C(6)–C(7)–C(8)	176.7(4)
C(2)–C(1)–C(9)–C(8)	–176.1(4)	C(5)–C(6)–C(7)–C(10)	0.2(7)
C(2)–C(1)–C(9)–C(11)	–0.3(7)	C(6)–C(7)–C(8)–C(9)	1.4(4)
C(6)–C(1)–C(9)–C(8)	1.3(4)	C(10)–C(7)–C(8)–C(9)	177.9(4)
C(6)–C(1)–C(9)–C(11)	177.1(4)	C(7)–C(8)–C(9)–C(1)	–1.7(5)
C(1)–C(2)–C(3)–C(4)	47.6(7)	C(7)–C(8)–C(9)–C(11)	–177.5(4)
C(2)–C(3)–C(4)–C(5)	–66.1(7)		

[a] The torsion angle A–B–C–D is defined as positive if, when viewed along the B–C bond, atom A must be rotated clockwise to eclipse atom D.

spectrometer. The purity of all volatile materials was confirmed using a Varian 3300 GC with a thermal conductivity detector using a 6ft. 5% OV 101 Chromasorb column. Cyclic voltammetry was carried with a Cypress Systems CS 1087 electrochemical analyzer using a platinum bead electrode, TEAP as the supporting electrolyte, and acetonitrile as the solvent. Microanalyses were carried out by Desert Analytics, Tucson, AZ.

3.2. Syntheses

3-Methyl-2,3,4,5,6,7-hexahydroind-8(9)-en-1-one, **6.** This compound was prepared as described by Dev [4]: crotonic acid (28.7 g, 0.333 mol), cyclohexene (27.3 g, 0.332 mol) and polyphosphoric acid (500 g) were mechanically stirred at 60°C for 30 min. The slurry was poured onto solid ammonium sulfate (250 g, 1.89 mol) and allowed to stand until the polyphosphoric acid decomposed. The mixture was extracted three times with 30–60° petroleum ether (100 ml), and the combined organic extracts were washed with 5% ammonium hydroxide, then twice with saturated sodium chloride. The solution was dried over magnesium sulfate and concentrated. Distillation at reduced pressure afforded **6** as a colorless oil: 17.7 g (36%); b.p. 80–85°/15 mm. ^{1}H NMR ($CDCl_3$) δ 0.7–3.0 (14H). (Ref. [3] 2.13(d, $J = 7$ Hz, 3H); 1.6–2.8(M, 11H).

Table 4
Crystallographic data for **11**

Molecular formula	$C_{22}H_{30}Fe$
Formula weight	350.33
Crystat system	monoclinic
Space group	$P2_1/c(C^5_{2h})$-No. 14
a (Å)	8.380(1)
b (Å)	10.407(1)
c (Å)	11.590(1)
β (°)	114.47(1)
No. of orientation refls.; θ(°) range	25; 36–40
V (Å^3)	920.0(4)
Z	2
$D_{calcd.}$ (g cm^{-3})	1.265
μ (Cu-Kα radiation, $\lambda = 1.5418$ Å)	65.4
Temp. (°C)	25
Crystal dimensions (mm^3)	$0.18 \times 0.20 \times 0.50$
$T_{max} : T_{min}$	1.00 : 0.67
Scan type	ω-2θ
Scanwidth (°)	$0.60 + 0.14 \tan \theta$
$\theta_{max.}$(°)	75
Intensity control refls.;	213, 231, $14\bar{4}$, $32\bar{2}$;
variation; repeat time (hr)	< 1%; 2
Total no. of refls. ($+h$, $+k$, $+l$) recorded	1983
No. of non-equiv. refls. recorded	1887
R_{merge} (on I)	0.026
No. of refls. retained [$I > 3.0\ \sigma(I)$]	1286
No. of parameters refined	107
Extinction correction	$8.5(5) \times 10^{-6}$
R (R_w)	0.048 (0.066)
Goodness-of-fit	1.67
Max. shift:esd in final least-squares cycle	0.02
Final $\Delta\rho$(e Å^3) max.; min.	0.35; −0.59

Table 5
Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for **11** with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq} (Å^2)
Fe	0.41440(3)	0.11827(3)	0.23472(4)	2.41(1)
C(1)	0.4158(2)	0.0131(2)	0.2043(3)	3.2(1)
C(2)	0.4036(3)	−0.0460(2)	0.2865(4)	4.6(1)
C(3)	0.3325(6)	−0.0812(4)	0.2580(9)	5.4(2)
C(3″)	0.3184(6)	−0.0518(5)	0.3154(9)	5.2(2)
C(4)	0.2701(3)	−0.0395(3)	0.2264(6)	9.2(2)
C(5)	0.2786(2)	0.0198(2)	0.1461(4)	4.7(1)
C(6)	0.3577(2)	0.0447(2)	0.1395(3)	3.2(1)
C(7)	0.3884(2)	0.0944(2)	0.0634(3)	3.3(1)
C(8)	0.4670(2)	0.0939(2)	0.0805(3)	3.2(1)
C(9)	0.4835(2)	0.0438(2)	0.1680(3)	3.2(1)
C(10)	0.3489(3)	0.1360(2)	−0.0264(4)	4.8(1)
C(11)	0.5223(3)	0.1325(2)	0.0089(4)	5.3(1)
C(12)	0.5604(3)	0.0218(3)	0.2042(5)	5.2(1)
C(1′)	0.3449(2)	0.1644(2)	0.3561(3)	2.9(1)
C(2′)	0.2640(2)	0.1528(2)	0.3849(4)	4.2(1)
C(3′)	0.2173(2)	0.2129(3)	0.3364(5)	5.4(1)
C(4′)	0.2381(3)	0.2304(3)	0.2113(5)	5.6(1)
C(5′)	0.3174(2)	0.2576(2)	0.2025(4)	3.9(1)
C(6′)	0.3690(2)	0.2136(2)	0.2725(3)	2.8(1)
C(7′)	0.4479(2)	0.2166(2)	0.2778(3)	2.9(1)
C(8′)	0.4719(2)	0.1685(2)	0.3640(3)	2.9(1)
C(9′)	0.4082(2)	0.1356(2)	0.4131(3)	2.8(1)
C(10′)	0.4947(3)	0.2655(2)	0.2103(4)	4.3(1)
C(11′)	0.5507(2)	0.1580(2)	0.4040(4)	4.1(1)
C(12′)	0.4073(3)	0.0854(2)	0.5116(4)	4.0(1)

1,3-Dimethyl-2,3,4,5,6,7-hexahydroind-8(9)-en-1-one **7**. This compound was prepared in a similar manner to **6**, using tiglic acid, cyclohexene, and polyphosphoric acid. After hydrolysis, washing and drying, vacuum distillation give **7** as a colorless oil (24%); b.p. 96–99°/12 mmHg. ^{1}H NMR ($CDCl_3$) δ 1.0–2.5 (broad multiplets).

2,3,4,5,6,7-Hexahydroind-8(9)-en-1-one, **5** [3]. This compound was prepared in a similar manner to **6**, using acrylic acid, cyclohexene and polyphosphoric acid. The usual purification procedures yielded **5** as a colorless oil (20%); b.p. 78–80°C/10 mmHg. ^{1}H NMR ($CDCl_3$) δ 2.5–1.3 (broad multiplets).

1,3-Dimethyl-4,5,6,7-tetrahydroindene, **3**. A solution of methyllithium (1.5 M, 96 ml, 0.14 mol) was added dropwise to a solution of **6**, (17.7 g, 0.120 mol) in diethyl ether (50 ml) and the mixture was refluxed for 18 h. The mixture was hydrolyzed, and extracted twice with diethyl ether (50 ml). The combined ether extracts were dried ($MgSO_4$) and filtered. Hydrochloric acid (6 M, 0.5 ml) was added and the mixture was stirred for 2 h. The ether solution was washed with water, dried

($MgSO_4$) and concentrated. Distillation at reduced pressure afforded **3** as a mixture of double bond isomers, 8.0 g, (45%); b.p. 57–59°/15 mmHg. ^1H NMR ($CDCl_3$) δ 5.2 (m, 1H), 0.8–2.7 (m, 15H).

1,2,3-Trimethyl-4,5,6,7-tetrahydroindene, **4**. This compound was prepared from **7** and methyllithium in a manner analogous to **3**. Vacuum distillation of the oil remaining after purification yielded **4** as a colorless oil (45%); b.p. 62–66°/12 mmHg. ^1H NMR ($CDCl_3$) δ 1.0–2.7 (broad series of multiplets).

4,5,6,7-Tetrahydroindene, **1**. Lithium aluminum hydride (4.04 g, 0.106 mol) was suspended in diethyl ether (200 ml) and cooled in ice. A solution of **5** (14.5 g, 0.106 mol) in diethyl ether (100 ml) was added dropwise over 1 h. The resulting slurry was refluxed for 2 h, cooled in ice and hydrolyzed cautiously with water (250 ml) and subsequently enough 6 M hydrochloric acid to dissolve all precipitates. After refluxing the two layers for 4 h, the organic layer was separated, washed with water and saturated sodium bicarbonate solution, dried over $MgSO_4$, concentrated to give **1**, 3.81 g (30%) as a mixture of isomers in reasonable purity. This crude mixture of isomers was used for synthetic work because of the rapid polymerization of **1**. A more pure sample could be isolated by chromatography on alumina yielding a colorless oil. The ^1H NMR spectrum of this oil was in agreement with that previously reported [12].

1-Methyl-4,5,6,7-tetrahydroindene, **2**. This compound was prepared from **6** in a manner analogous to **1**. Vacuum distillation of the oil remaining after purification yielded **2** as a colorless oil (58%), b.p. 47°/20 mmHg. Analysis by GC indicates the presence of isomers. ^1H NMR ($CDCl_3$) δ 5.1–5.3 (m, 2H), 0.6–2.8 (m, 12H).

Bis(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)iron(II), **10**. 1,3-Dimethyl-4,5,6,7-tetrahydroindene, **3**, (2.0 g, 14 mmol.) and di-*n*-butylmagnesium (7.0 mmol.) were refluxed in THF (20 ml) for 1 h. Iron(II) chloride (0.86 g, 7.0 mmol.) was added at 0° and the mixture was stirred for 6 h at 25°C followed by 1 h reflux. The reaction mixture was hydrolyzed, extracted with diethyl ether, and the ether layer was dried ($MgSO_4$) and concentrated. The resulting oil was chromatographed on alumina using hexane as the eluent. Recrystallization from low boiling petroleum ether gave **10** as orange crystals, 1.43 g, 60%, m.p. 114–116°. ^1H NMR ($CDCl_3$) δ(ppm) 3.1 (s, 1H), 1.6 (s, 6H), 1.3–2.4 (m, 8H). Anal. found: C 75.64; H 8.79. $C_{22}H_{30}Fe$ calcd.: C 75.43; H 8.63.

Bis(1-methyl-4,5,6,7-tetrahydroindenyl)iron(II), **9**. This preparation was carried out as for **10**, using **2**, yielding **9** as an orange solid (35%); m.p. 100–103°C. ^1H NMR ($CDCl_3$) δ 3.6(br.m, 2H), 2.28(br, m, 4 H), 1.71(br.s, 7H). Anal. found: C, 74.59; H, 8.30. $C_{20}H_{26}Fe$ calcd.: C, 74.52; H, 8.15%.

Bis(1,2,3-trimethyl-4,5,6,7-tetrahydroindenyl)iron(II), **11**. This preparation was carried out as for **10**, using **4**, yielding **11** as an orange solid (25%); m.p. 180–183°C. ^1H NMR ($CDCl_3$) δ 2.10(br.s, 4H); 1.75(s, 3H); 1.45(br.m, 10H). Anal. found: C, 75.96; H, 8.91. $C_{24}H_{34}Fe$ calcd.: C, 76.18; H, 9.06%.

Bis(4,5,6,7-tetrahydroindenyl)iron(II), **8**. This preparation was carried out as for **10** using **1**, yielding **8** as an orange oil (37%). ^1H NMR ($CDCl_3$ δ3.6(br.s, 3H); 2.3–1.6(br.m, 8H). (Ref. [5]: 3.80(d, 2H); 3.70(t, 2H); 2.42(br.s, 4H); 1.75(br.s, 4H)).

(1,2,3-Trimethyl-4,5,6,7-tetrahydroindenyl)tricarbonylmethylmolybdenum(II), **14**. A solution of 2.5 M butyllithium (3.7 ml, 9.3 mmol) in hexane was added to

Table 6
Interatomic distances (Å) and angles (°), with estimated standard deviations in parenthesis for **11**

(a) Bond lengths			
Fe–C(1)	2.071(4)	Fe–C(1′)	2.072(4)
Fe–C(6)	2.065(4)	Fe–C(6′)	2.069(4)
Fe–C(7)	2.063(3)	Fe–C(7′)	2.061(4)
Fe–C(8)	2.054(4)	Fe–C(8′)	2.050(4)
Fe–C(9)	2.055(4)	Fe–C(9′)	2.066(3)
C(1)–C(2)	1.498(6)	C(1′)–C(2′)	1.514(5)
C(1)–C(6)	1.422(5)	C(1′)–C(6′)	1.418(5)
C(1)–C(9)	1.421(5)	C(1′)–C(9′)	1.429(5)
C(2)–C(3)	1.49(1)	C(2′)–C(3′)	1.542(7)
C(2)–C(3″)	1.58(1)		
C(3)–C(4)	1.43(1)	C(3′)–C(4′)	1.514(8)
C(3″)–C(4)	1.36(1)		
C(4)–C(5)	1.479(7)	C(4′)–C(5′)	1.529(7)
C(5)–C(6)	1.509(5)	C(5′)–C(6′)	1.495(5)
C(6)–C(7)	1.411(5)	C(6′)–C(7′)	1.427(5)
C(7)–C(8)	1.432(5)	C(7′)–C(8′)	1.423(5)
C(7)–C(10)	1.487(6)	C(7′)–C(10′)	1.486(6)
C(8)–C(9)	1.425(5)	C(8′)–C(9′)	1.430(5)
C(8)–C(11)	1.492(5)	C(8′)–C(11′)	1.508(5)
C(9)–C(12)	1.510(7)	C(9′)–C(12′)	1.487(6)
(b) Bond angles			
C(2)–C(1)–C(6)	123.2(4)	C(2′)–C(1′)–C(6′)	122.8(3)
C(2)–C(1)–C(9)	129.0(4)	C(2′)–C(1′)–C(9′)	127.9(3)
C(6)–C(1)–C(9)	107.6(3)	C(6′)–C(1′)–C(9′)	108.9(3)
C(1)–C(2)–C(3)	109.9(5)	C(1′)–C(2′)–C(3′)	109.7(3)
C(1)–C(2)–C(3″)	109.2(5)		
C(2)–C(3)–C(4)	118.2(6)	C(2′)–C(3′)–C(4′)	111.9(4)
C(2)–C(3″)–C(4)	117.2(8)		
C(3)–C(4)–C(5)	120.9(6)	C(3′)–C(4′)–C(5′)	111.8(4)
C(3″)–C(4)–C(5)	122.2(6)		
C(4)–C(5)–C(6)	112.2(4)	C(4′)–C(5′)–C(6′)	110.6(4)
C(1)–C(6)–C(5)	122.3(3)	C(1′)–C(6′)–C(5′)	123.6(3)
C(1)–C(6)–C(7)	109.0(3)	C(1′)–C(6′)–C(7′)	107.8(3)
C(5)–C(6)–C(7)	128.4(3)	C(5′)–C(6′)–C(7′)	128.4(3)
C(6)–C(7)–C(8)	107.5(3)	C(6′)–C(7′)–C(8′)	107.8(3)
C(6)–C(7)–C(10)	127.4(4)	C(6′)–C(7′)–C(10′)	124.9(4)
C(8)–C(7)–C(10)	124.9(4)	C(8′)–C(7′)–C(10′)	127.2(4)
C(7)–C(8)–C(9)	107.9(3)	C(7′)–C(8′)–C(9′)	108.6(3)
C(7)–C(8)–C(11)	125.8(3)	C(7′)–C(8′)–C(11′)	125.8(3)
C(9)–C(8)–C(11)	125.9(3)	C(9′)–C(8′)–C(11)	125.4(3)
C(1)–C(9)–C(8)	108.1(3)	C(1′)–C(9′)–C(8′)	106.9(3)
C(1)–C(9)–C(12)	126.3(4)	C(1′)–C(9′)–C(12′)	126.3(4)
C(8)–C(9)–C(12)	125.2(4)	C(8′)–C(9′)–C(12′)	126.7(4)

Table 6 (continued)

(c) Torsion angles [a]

C(6)-C91)-C(2)-C(3)	20.3(6)	C(6')-C(1')-C(2')-C(3')	-14.5(5)
C(6)-C(1)-C(2)-C(3'')	-16.0(6)		
C(9)-C(1)-C(2)-C(3)	-153.7(5)	C(9')-C(1')-C(2')-C(3')	158.2(4)
C(9)-C(1)-C(2)-C(3'')	170.0(5)		
C(2)-C(1)-C(6)-C(5)	-1.6(6)	C(2')-C(1')-C(6')-C(5')	-1.5(6)
C(2)-C(1)-C(6)-C(7)	-175.0(4)	C(2')-C(1')-C(6')-C(7')	173.2(3)
C(9)-C(1)-C(6)-C(5)	173.5(3)	C(9')-C(1')-C(6')-C(5')	-175.5(4)
C(9)-C(1)-C(6)-C(7)	0.1(4)	C(9')-C(1')-C(6')-C(7')	-0.8(4)
C(2)-C(1)-C(9)-C(8)	174.4(4)	C(2')-C(1')-C(9')-C(8')	-172.9(4)
C(2)-C(1)-C(9)-C(12)	1.2(7)	C(2')-C(1')-C(9')-C(12')	2.4(6)
C(6)-C(1)-C(9)-C(8)	-0.3(4)	C(6')-C(1')-C(9')-C(8')	0.6(4)
C(6)-C(1)-C(9)-C(12)	-173.6(4)	C(6')-C(1')-C(9')-C(12')	175.9(4)
C(1)-C(2)-C(3)-C(4)	-39.9(9)	C(1')-C(2')-C(3')-C(4')	46.4(5)
C(1)-C(2)-C(3'')-C(4)	38.4(9)		
C(2)-C(3)-C(4)-C(5)	42.9(11)	C(2')-C(3')-C(4')-C(5')	-64.9(5)
C(2)-C(3'')-C(4)-C(5)	-45.3(10)		
C(3)-C(4)-C(5)-C(6)	-20.4(8)	C(3')-C(4')-C(5')-C(6')	45.7(6)
C(3'')-C(4)-C(5)-C(6)	24.2(8)		
C(4)-C(5)-C(6)-C(1)	0.2(6)	C(4')-C(5')-C(6')-C(1')	-13.7(6)
C(4)-C(5)-C(6)-C(7)	172.2(4)	C(4')-C(5')-C(6')-C(7')	172.7(4)
C(1)-C(6)-C(7)-C(8)	0.1(4)	C(1')-C(6')-C(7')-C(8')	0.6(4)
C(1)-C(6)-C(7)-C(10)	175.1(4)	C(1')-C(6')-C(7')-C(10')	-175.3(4)
C(5)-C(6)-C(7)-C(8)	-172.8(4)	C(5')-C(6')-C(7')-C(8')	175.0(4)
C(5)-C(6)-C(7)-C(10)	2.3(7)	C(5')-C(6')-C(7')-C(10')	-1.0(6)
C(6)-C(7)-C(8)-C(9)	-0.3(4)	C(6')-C(7')-C(8')-C(9')	-0.3(4)
C(6)-C(7)-C(8)-C(11)	172.7(4)	C(6')-C(7')-C(8')-C(11')	-175.7(4)
C(10)-C(7)-C(8)-C(9)	-175.5(4)	C(10')-C(7')-C(8')-C(9')	175.6(4)
C(10)-C(7)-C(8)-C(11)	-2.5(6)	C(10')-C(7')-C(8')-C(11')	0.2(6)
C(7)-C(8)-C(9)-C(1)	0.4(4)	C(7')-C(8')-C(9')-C(1')	-0.2(4)
C(7)-C(8)-C(9)-C(12)	173.7(4)	C(7')-C(8')-C(9')-C(12')	-175.5(4)
C(11)-C(8)-C(9)-C(1)	-172.6(4)	C(11')-C(8')-C(9')-C(1')	175.3(4)
C(11)-C(8)-C(9)-C(12)	0.8(6)	C(11')-C(8')-C(9')-C(12')	0.0(8)

a solution of **4** (1.48 g, 9.1 mmol) in THF (20 ml) at 0°C. After 1 h, a solution of tris(propionitrile)tricarbonylmolybdenum [13] (3.14 g, 9.1 mmol) in THF (50 ml) was added via canula and the resulting mixture refluxed for 4 h. A solution of iodomethane (1.24 g, 9.1 mmol) in THF (10 ml) was added and the mixture stirred for 24 h. The resulting mixture was concentrated in vacuo and purified by chromatography under nitrogen on silica using petroleum ether as eluent to provide pure product as a yellow solid: 1.56 g (48%); m.p. 80–83°C. ^{1}H NMR (CDCl$_3$) δ 2.35(br.m, 4 H), 1.41(s, 3H), 1.85(s, 6H), 1.69(br.m, 4H), 0.08(s, 3H). Anal. found: C, 53.87; H, 5.67. $C_{16}H_{20}O_3Mo$ calcd.: C, 53.93; H, 5.67%.

(1,3-Dimethyl-4,5,6,7-tetrahydroindenyl)tricarbonylmethyltungsten(II), **15**. This synthesis was carried out as for **14**, using **3** and tris(propionitrile)tricarbonyltungsten [14] yielding **15** as a pale lemon solid (20%); m.p. 94–96°C. ^{1}H NMR (CDCl$_3$) δ 5.14(s, 1H) 2.50(br.m, 4H), 2.00(s, 6H), 1.74(br.m, 4H), 0.07(s, 3H). Anal. found: C, 42.17; H, 4.23. $C_{15}H_{18}O_3W$ calcd.: C, 41.88; H, 4.23%.

(1,2,3-Trimethyl-4,5,6,7-tetrahydroindenyl)tricarbonylmethyltungsten(II), **16**. This synthesis was carried out as for **14**, using **4** and tris(propionitrile)tricarbonyltungsten [14] yielding **16** as a pale lemon solid (22%); m.p. 102–104°C. ^{1}H NMR (CDCl$_3$) δ 2.46(br.m, 4H), 2.01(s, 3H), 1.94(s, 6H), 1.68(br.m, 4H), 0.15(s, 3H). Anal. found: C, 43.33; H, 4.55. $C_{16}H_{20}O_3W$ calcd.: C 43.27; H 4.54%.

3.3. X-ray structure determination of 10 and 11

These structures were determined by single crystal X-ray diffraction studies and were carried out on an Enraf-Nonius CAD-4 diffractometer (Cu-Kα radiation, graphite monochromator, $\lambda = 1.5418$ Å) at 298 K. Intensity data were corected for the usual Lorentz and polarization effects; an empirical absorption correction was also applied. Crystallographic calculations were performed on PDP11/44 and MicroVax computers by use of the Enraf-Norris structure determination package (SDP). For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from *International Tables for X-Ray Crystallography* [15].

X-ray structures, **10**. The space group was established uniquely from the Laue symmetry and systematic absences: $0kl$ when $k = 2n$, $h0l$ when $l = 2n$. The crystal structure was solved by the heavy-atom approach. With $Z = 2$, the asymmetric crystal unit is half of the complex molecule with the iron atom lying on a crystallographic center of symmetry. The iron atom was placed at the origin of the cell and positions for the other non-hydrogen atoms were obtained from a weighted F_0 Fourier synthesis phased by the iron atom. Several rounds of full-matrix least-squares refinement of positional and thermal parametersof the non-hydrogen atoms (at first isotropic, then anisotropic) followed. A difference Fourier synthesis indicated that the methyl group hydrogen atoms were disordered over two orientations. All hydrogen atoms were incorporated at their calculated positions and an extinction correction was included as a variable in the subsequent least-squares iterations which converged at $R = 0.048$ ($R_w = 0.066$). A final difference Fourier synthesis contained no unusual features.

Further details are given in Table 1. Atom positions are listed in Table 2, and bond lengths are given in Table 3. Tables of complete bonds and angles, H atom positions, thermal parameters are available from the Cambridge Crystallographic Data Centre.

X-ray structure of **11**. The space group was determined unambiguously from Laue symmetry and systematic absences: $0kl$ when $k = 2n$, $h0l$ when $l = 2n$, $hk0$ when $h = 2n$. The crystal structure was solved by the heavy-atom approach. Initial coordinates for the iron atom were derived from a Patterson map. Approximate positions for the carbon atoms were obtained from a weighted F_0 Fourier synthesis phased by the iron atom. Several rounds of full-matrix least-squares adjustment of positional and thermal parameters of all non-hydrogen atoms (at first isotropic and anisotropic) indicated that C(3) was disordered as possibly also was C(4). When both of these atoms were omitted from the structure–factor calculations, a difference Fourier synthesis contained two approximately equal maxima corresponding to C(3) whereas only one broad peak was present for C(4), and thus the former was included at two positions with 50% occupancy in all further calculations. Following several more least-squares iterations, hydrogen atoms, other than those associated with C(3) and C(4), were located in a difference Fourier synthesis. Subsequent least-squares cycles involved refinement of non-hydrogen atom positional and anisotropic temperature factor parameters and positional and isotropic thermal parameters for the hydrogne atoms, except those bonded to C(3) and C(4) where they were incorporated at their calculated positions. In addition, an extinction correction was included in later iterations which converged at $R = 0.041$ ($R_w = 0.055$). A final difference Fourier synthesis contained no unusual features.

Further details are given in Table 4. Atom positions are listed in Table 5, and bond lengths are given in Table 6. Tables of complete bonds and angles, H atom parameters, thermal parameters are available from the Cambridge Crystallographic Data Centre.

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