35. Stereoselective Double *Friedel-Crafts* Acylation of *trans*-μ-(2,3,6,7-Tetramethylidenebicyclo[3.2.1]octane)bis(tricarbonyliron). Crystal Structure of *trans*-μ-{(1*RS*,2*RS*,3*SR*,5*RS*,6*SR*,7*SR*)-*C*,2,3,*C*-η:*C*,6,7,*C*-η-[(*Z*,*Z*)-1,1′-(3,7-Dimethylidenebicyclo[3.2.1]octane-2,6-diylidene)di(2-propanone)]}bis(tricarbonyliron)

by **A. Alan Pinkerton**[1]) and **Dieter Schwarzenbach**

Institut de cristallographie de l'Université de Lausanne, Bâtiment des Sciences Physiques, CH-1015 Lausanne

and **Raphy Gabioud**[2]) and **Pierre Vogel***

Institut de chimie organique de l'Université de Lausanne, 2, rue de la Barre, CH-1005 Lausanne

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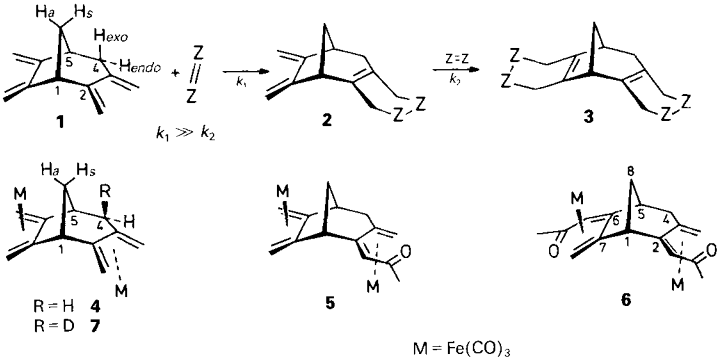
The *Friedel-Crafts* mono and double acylations of *trans*-μ-[(1*RS*,2*RS*,3*SR*,5*RS*,6*SR*,7*SR*)-*C*,2,3,*C*-η:*C*,6,7,*C*-η-(2,3,6,7-tetramethylidenebicyclo[3.2.1]octane)]bis(tricarbonyliron) (**4**) are highly stereoselective and yield *trans*-μ-{(1*RS*,2*RS*,3*SR*,5*RS*,6*SR*,7*RS*)-*C*,2,3,*C*-η:*C*,6,7,*C*-η-[(*Z*)-1-(3,6,7-trimethylidenebicyclo[3.2.1]oct-2-ylidene)-2-propanone]}bis(tricarbonyliron) (**5**) and *trans*-μ-{(1*RS*,2*RS*,3*SR*,5*RS*,6*SR*,7*SR*)-*C*,2,3,*C*-η:*C*,6,7,*C*-η-[(*Z*,*Z*)-1,1′-(3,7-dimethylidenebicyclo[3.2.1]octane-2,6-diylidene)di(2-propanone)]}bis(tricarbonyliron) (**6**) whose structure has been established by single-crystal X-ray diffraction.

Introduction. – The 2,3,6,7-tetramethylidenebicyclo[3.2.1]octane (**1**) is a new type of exocyclic double diene. It adds to strong dienophiles Z=Z to give selectively the monoadducts **2** resulting from the reaction of the s-*cis*-butadiene group at C(2),C(3). The addition of a second equivalent of dienophile to the diene moiety at C(6),C(7) leading to the bis-adducts **3** is significantly less rapid than reaction **1** + Z=Z→**2** [1]. Tetraene **1** would be a useful synthetic intermediate in tandem *Diels-Alder* additions if its two diene moieties could be substituted in a stereoselective fashion. We report here our first results toward this objective. We shall show that under *Friedel-Crafts* conditions, the dimetallic complex



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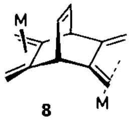
[1]) Present address: Department of Chemistry, The University of Toledo, Toledo, Ohio 43606, USA.

[2]) Present address: *Orgamol SA*, CH-1902 Evionnaz.

4, a direct synthetic precursor of **1** [1], can be acylated stereoselectively to give **5**. The double acylation of **4** is also highly stereoselective and yields the diketone **6** whose structure was determined by single-crystal X-ray diffraction.

Results and Discussion. – Oxidative hydroboration of the readily available diiron complex **8** [2] gave **9** whose mesylate **10**, obtained on treating **9** with MsCl and pyridin (20°, 20 min), was reduced and rearranged into **4** (73 %) with $NaBH_4$ in hexafluoroisopropyl alcohol ($(CF_3)_2CHOH$; 20°, 8 min) [1]. When $NaBD_4$ and $(CF_3)_2CHOD$ were used, the deuterated complex **7** was obtained. In $(CF_3)_2CHOH$, the $NaBD_4$ reduction of **10** led to a 2:1 mixture of **7** and **4**. In tetrahydrofuran (THF), the $NaBH_4$ reduction of **10** yielded the unrearranged derivative **11**. When using $NaBD_4$ in THF, the deuterated compound **12** was isolated. The rate of the latter reactions was dependent on the concentration of $NaBH_4$ (and $NaBD_4$), in agreement with an S_N2 type of mechanism for the displacement reactions **10**→**11** and **10**→**12**. The relative configuration of the D-atom in **12** was given by the comparison of its 360-MHz-^{1}H-NMR spectrum with that recorded for the deuterated isomer **15** (see *Fig. 1*) prepared from **8** by oxidative deuteroboration (giving alcohol **13**), followed by $NaBH_4$ reduction in THF of the corresponding mesylate **14**. The direct S_N2 displacement reaction **10** + $NaBD_4$→**12** is expected to be sterically hindered because of the '*exo*'-$Fe(CO)_3$ moiety which flanks the ethano C(2),C(3) bridge in **10** with two CO groups. One can however imagine the borohydride anion adding first to one of the



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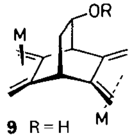
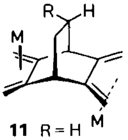
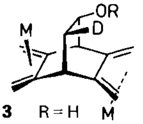


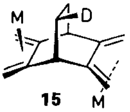
9 R=H
10 R=Ms



11 R=H
12 R=D



13 R=H
14 R=Ms



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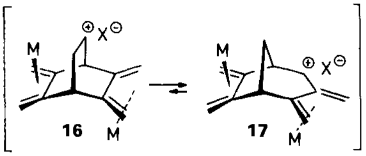


M = $Fe(CO)_3$

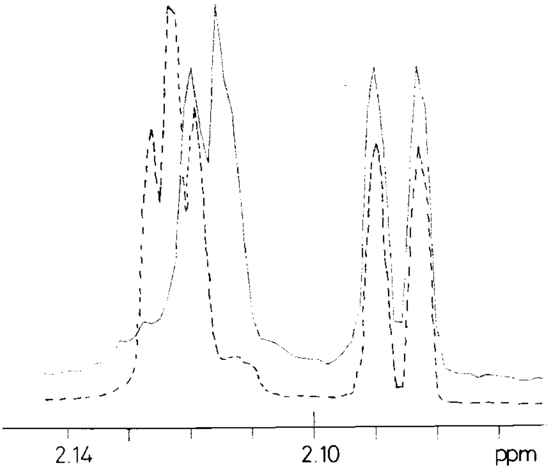


Fig. 1. *Portion of the 360-MHz-^{1}H-NMR spectra ($CDCl_3$) or deuterated bicyclo[2.2.2]octane derivatives* **12** (– – – –) *and* **15** (———)

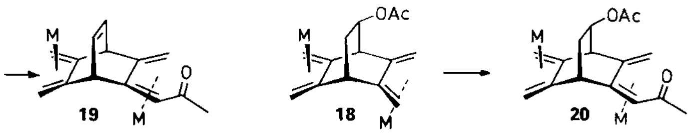
carbonyl group of the *'exo'*-Fe(CO)$_3$ moiety and then being transferred to C(2) in an S_Ni type of mechanism. Our data is consistent with either mechanism.

Our results in the more ionizing solvent (CF$_3$)$_2$CHOH can be interpreted in terms of an S_N1 mechanism. This implies formation of the relatively stable, delocalized [(butadien-2-yl)carbinyl]tricarbonyliron cation **17** [3] which arises from the less stable intermediate **16** *via* a *Wagner-Meerwein* rearrangement [4]. Because of the participation of the *endo*-Fe(CO)$_3$ group in the charge delocalization, only the face *anti* to the metal centre is accessible to the nucleophile, thus leading to the stereoselective deuteration **10**→**7**. The *exo*-position of the D-atom in **7** was given by the 360-MHz-^{1}H-NMR spectrum. The H,H-coupling constants measured for **4** suggested an envelope or half-chair conformation for the six-membered ring C(1),C(2),C(3),C(4),C(5),C(8) (see also the X-ray structure of **6**). The proton H_{exo}–C(4) couples with H–C(5) (^3J(H,H) = 4.5 Hz), whereas H_{endo}–C(4) does not couple with H–C(5). The distinction between the signals attributed to the bridgehead protons H–C(1) and H–C(5) was based on their multiplicity and NOE measurements.

When **4** was treated with 1 equiv. of AlCl$_3$ in pure CH$_3$COCl, the monoacylated compound **5** was isolated in moderate yield (40–60%) after quenching with aqueous NaHCO$_3$. In the presence of 2 equiv. of AlCl$_3$ in CH$_3$COCl, **4** gave a 1:3 mixture of **4** and **5** after 2 min at 20°. A 1:2:2 mixture of **4**, **5**, and **6** was obtained after 5 min at 20°. If the reaction was allowed to go for 10 min before quenching with aqueous NaHCO$_3$, only the doubly acylated compound **6** was isolated in 40–55% yield. We found also that pure **5** treated under the above *Friedel-Crafts* conditions gave **6** as the unique product isolated in 45–55% yield. No trace of other isomeric acetylated products could be detected by 360-MHz ^{1}H-NMR spectroscopy and/or chromatography of the crude reaction mixtures, thus confirming the high stereoselectivity of the acylations **4**→**5** and **5**→**6**. The moderate yields of these reactions must be attributed to the instability of **5** and **6** and their tendency to give products of aldol condensation under our workup conditions.

The structure of **6** was established by single-crystal X-ray crystallography (see below). That of **5** was deduced from that of **6** and confirmed by ^{1}H-NMR spectroscopy. The (*Z*)-configuration of the exocyclic double bond substituted by the acyl group in **5** was given by the NOE's measured between the signals at 2.95 ppm (*d*, *J* = 4.5 Hz) of H–C(1) and 3.39 ppm (*s*) of H–C=C(2). Similarly, NOE's were measured for the proximal proton pairs H–C(1)/H–C=C(2) (2.87 (*d*, *J* = 5 Hz) and 3.48 ppm (*s*)) and H–C(5)/H–C=C(6) (2.8 (*t*, *J* = 5 Hz) and 3.30 ppm (*s*) in **6**. The relative configuration of the Fe(CO)$_3$ moieties in **4** and **5** was also deduced from that in **6**.

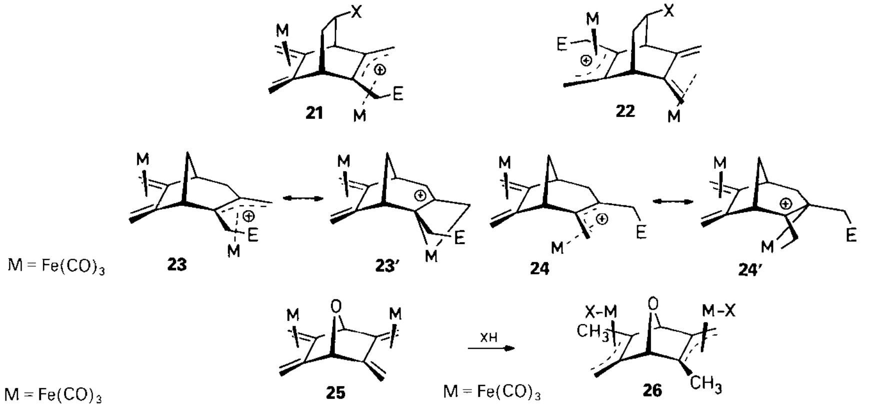
The stereoselectivities of the acylations **4**→**5** and **5**→**6** are remarkable. Out of 4 possible modes of attacks by the acylating agent, only one leads to a substitution product for the monoacylation **4**→**5**. The preference for the diene moiety coordinated to the *endo*-Fe(CO)$_3$ group was expected by analogy with the monoacylations of **8** and **18** that we had also found to be stereoselective and to give the monoacylated products **19** [5] and **20**, respectively [6]. The preference for the *'endo'*-Fe(CO)$_3$ coordinated diene was attributed to an electronic factor [7]: the hypothetical intermediate **21** of the *Friedel-Crafts*



19 **18** **20**

acylation is expected to be more stable then the isomeric species **22** because of the destabilizing effect of the $Fe(CO)_3$ dipole on remote allylic cations. This effect was proposed to be stronger in **22** than in **21**.

The preference for acylation of the $CH_2{=}C(2)$ rather than the $CH_2{=}C(3)$ moiety in **4** is difficult to interprete. If one assumes that most of the positive charge in the $Fe(CO)_3$-coordinated allyl cation resides on the central C-atom rather than on the terminal allylic centres, as suggested by ^{13}C-NMR spectroscopy of $Fe(CO)_4$-coordinated allyl cations [8], one can forsee that in **24**↔**24'**, the positive charge will be closer to the destabilizing homoconjugated diene $Fe(CO)_3$ moiety than in the regioisomeric intermediate **23**↔**23'**.



The stereoselectivity of the double acylation **4**→**6** is more difficult to explain. It can be compared with that observed for the acid additions **25**→**26** [9]. The regioselectivity of reaction **5**→**6** is not obvious. Further experimental results are required to approach an interpretation.

Determination of the Crystal Structure $Fe_2C_{22}H_{18}O_8$ (6). – Compound **6** crystallizes as orange plates from AcOEt/hexane solution. The crystal used for structure determination was cleaved from a larger plate in order to

Table 1. *Crystal Data of* **6**, *Intensity Measurements, Structure Solution and Refinement*

Formula	$Fe_2C_{22}H_{18}O_8$	λ [Å]	0.71069
Molecular weight	522.07	μ [cm^{-1}]	13.5
Crystal dimensions [mm]	0.32 × 0.21 × 0.09	Scan method	*2θ–θ*
Crystal system	Monoclinic	$(\sin\theta/\lambda)_{max}$	0.55
a [Å]	11.911(2)	No. of unique reflections	6135
b [Å]	26.580(5)	No. of reflections < 3σ	3022
c [Å]	13.976(2)	No. of observations/No. of variables	8.9(7.0)[a]
β [°]	90.05(1)	Structure solution	*Patterson* and *Fourier*
U [$Å^3$]	4424.6	Refinement method	Blocked matrix least squares
Z	8		
$d_{obs.}$ [$g\cdot cm^{-3}$]	1.56	Function minimized	$\Sigma w(\lvert Fo\rvert - \lvert Fc\rvert)^2$
$d_{calc.}$ [$g\cdot cm^{-3}$]	1.57	w	$1/\sigma^2$
F_{000}	2128	R	0.045
Space group	$P2_1/n$	R_w	0.031
Radiation	Mo-$K\alpha$	Goodness of fit	1.27

[a]) Only those reflections with $I < 3\sigma$ with $\lvert Fc\rvert > \lvert Fo\rvert$ were included in the refinement.

Table 2. *Final Atomic Coordinates for* $Fe_2C_{22}H_{18}O_8$ (**6**)

Molecule A				Molecule B			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1A)	0.46358(7)	0.37121(3)	0.87299(6)	Fe(1B)	0.71557(8)	0.15051(4)	0.81408(6)
Fe(2A)	0.01651(7)	0.38799(3)	0.81497(6)	Fe(2B)	0.26837(7)	0.10916(3)	0.85388(6)
C(1A)	0.2545(5)	0.4438(2)	0.7980(4)	C(1B)	0.5112(5)	0.1043(2)	0.9475(4)
C(2A)	0.3770(5)	0.4365(2)	0.8329(4)	C(2B)	0.6290(4)	0.1259(2)	0.9358(3)
C(3A)	0.3956(5)	0.4367(2)	0.9334(4)	C(3B)	0.6422(5)	0.1786(2)	0.9393(4)
C(4A)	0.2985(6)	0.4405(3)	1.0044(4)	C(4B)	0.5411(6)	0.2123(3)	0.9503(5)
C(5A)	0.1844(5)	0.4442(2)	0.9553(4)	C(5B)	0.4303(5)	0.1850(2)	0.9613(4)
C(6A)	0.1511(5)	0.3950(2)	0.9077(4)	C(6B)	0.3921(5)	0.1623(2)	0.8661(4)
C(7A)	0.1913(4)	0.3949(2)	0.8136(4)	C(7B)	0.4415(4)	0.1149(2)	0.8574(3)
C(8A)	0.1971(5)	0.4789(2)	0.8690(5)	C(8B)	0.4517(5)	0.1378(3)	1.0220(4)
C(9A)	0.4675(5)	0.4274(2)	0.7692(4)	C(9B)	0.7253(5)	0.0955(2)	0.9194(4)
C(10A)	0.5741(6)	0.4556(3)	0.7626(5)	C(10B)	0.8292(5)	0.0940(2)	0.9781(5)
C(11A)	0.6585(8)	0.4334(5)	0.6926(7)	C(11B)	0.9206(7)	0.0605(4)	0.9397(7)
C(12A)	0.5068(5)	0.4298(3)	0.9677(4)	C(12B)	0.7513(6)	0.1987(2)	0.9278(5)
C(13A)	0.0814(5)	0.3566(2)	0.9439(4)	C(13B)	0.3131(5)	0.1811(2)	0.7997(4)
C(14A)	0.1000(6)	0.3017(3)	0.9333(4)	C(14B)	0.3248(6)	0.1819(3)	0.6941(5)
C(15A)	0.0045(7)	0.2673(3)	0.9636(7)	C(15B)	0.221(1)	0.2025(4)	0.6421(8)
C(16A)	0.1609(5)	0.3582(2)	0.7456(4)	C(16B)	0.4113(6)	0.0807(2)	0.7828(5)
C(17A)	0.4110(6)	0.3336(2)	0.9692(5)	C(17B)	0.6624(6)	0.1997(3)	0.7414(5)
C(18A)	0.4146(5)	0.3268(2)	0.7844(4)	C(18B)	0.6669(6)	0.1032(3)	0.7327(5)
C(19A)	0.6051(6)	0.3523(3)	0.8767(5)	C(19B)	0.8592(6)	0.1553(3)	0.7792(5)
C(20A)	−0.0040(5)	0.4323(2)	0.7210(4)	C(20B)	0.2657(6)	0.0523(3)	0.9200(5)
C(21A)	0.0658(6)	0.3364(3)	0.7707(4)	C(21B)	0.1770(5)	0.1387(2)	0.9378(4)
C(22A)	−0.0826(6)	0.4209(3)	0.8886(5)	C(22B)	0.1749(5)	0.0911(3)	0.7583(5)
O(1A)	0.5957(4)	0.4937(2)	0.8065(3)	O(1B)	0.8389(4)	0.1157(2)	1.0536(3)
O(2A)	0.1859(4)	0.2830(2)	0.9009(3)	O(2B)	0.4079(4)	0.1673(2)	0.6530(3)
O(3A)	0.3807(4)	0.3114(2)	1.0339(3)	O(3B)	0.6327(5)	0.2335(2)	0.6961(4)
O(4A)	0.3923(4)	0.2982(2)	0.7271(3)	O(4B)	0.6386(5)	0.0722(2)	0.6819(3)
O(5A)	0.6978(4)	0.3405(2)	0.8834(4)	O(5B)	0.9512(4)	0.1600(2)	0.7610(4)
O(6A)	−0.0192(4)	0.4602(2)	0.6606(3)	O(6B)	0.2688(5)	0.0157(2)	0.9624(4)
O(7A)	−0.1134(4)	0.3022(2)	0.7415(3)	O(7B)	0.1218(4)	0.1568(2)	0.9946(3)
O(8A)	0.1454(4)	0.4415(2)	0.9357(4)	O(8B)	0.1196(4)	0.0790(2)	0.6968(4)
H(1A)	0.692(7)	0.450(3)	0.656(5)	H(1B)	0.957(6)	0.074(3)	0.889(5)
H(2A)	0.637(7)	0.408(3)	0.663(6)	H(2B)	0.899(6)	0.027(3)	0.959(5)
H(3A)	0.707(7)	0.436(4)	0.727(6)	H(3B)	0.969(6)	0.055(3)	0.977(6)
H(4A)	0.448(4)	0.412(2)	0.711(3)	H(4B)	0.711(4)	0.063(2)	0.895(3)
H(5A)	0.563(4)	0.448(2)	0.939(3)	H(5B)	0.814(4)	0.185(2)	0.972(3)
H(6A)	0.513(4)	0.414(2)	1.038(3)	H(6B)	0.752(4)	0.233(2)	0.907(3)
H(7A)	0.307(4)	0.412(2)	1.057(3)	H(7B)	0.550(4)	0.234(2)	1.001(3)
H(8A)	0.312(4)	0.474(2)	1.042(3)	H(8B)	0.545(4)	0.239(2)	0.898(3)
H(9A)	0.258(3)	0.455(2)	0.730(3)	H(9B)	0.503(4)	0.067(1)	0.965(3)
H(10A)	0.134(4)	0.456(2)	0.998(3)	H(10B)	0.374(4)	0.208(2)	0.990(3)
H(11A)	0.124(3)	0.491(2)	0.846(3)	H(11B)	0.368(3)	0.124(2)	1.046(3)
H(12A)	0.240(4)	0.509(2)	0.882(3)	H(12B)	0.496(4)	0.141(2)	1.070(3)
H(13A)	0.168(4)	0.323(2)	0.766(3)	H(13B)	0.417(4)	0.093(2)	0.718(3)
H(14A)	0.178(4)	0.372(2)	0.676(3)	H(14B)	0.430(4)	0.047(2)	0.794(3)
H(15A)	0.029(3)	0.364(1)	1.011(3)	H(15B)	0.266(4)	0.213(2)	0.821(3)
H(16A)	−0.064(6)	0.280(3)	0.956(6)	H(16B)	0.233(9)	0.222(4)	0.613(6)
H(17A)	−0.025(7)	0.279(3)	1.024(4)	H(17B)	0.216(6)	0.173(2)	0.594(5)
H(18A)	0.041(6)	0.240(3)	0.985(5)	H(18B)	0.191(7)	0.231(3)	0.674(5)

Table 3. *Bond Lengths* (Å) *and Angles* (°) *for* $Fe_2C_{22}H_{18}O_8$ (**6**) *with Estimated Standard Deviations in Parentheses*

Distances			
Fe(1A)–C(17A)	1.789(7)	Fe(1B)–C(17B)	1.771(8)
Fe(1A)–C(18A)	1.807(6)	Fe(1B)–C(18B)	1.792(7)
Fe(1A)–C(19A)	1.759(7)	Fe(1B)–C(19B)	1.784(7)
Fe(1A)–C(2A)	2.094(5)	Fe(1B)–C(2B)	2.095(5)
Fe(1A)–C(3A)	2.098(6)	Fe(1B)–C(3B)	2.095(6)
Fe(1A)–C(9A)	2.083(6)	Fe(1B)–C(9B)	2.078(6)
Fe(1A)–C(12A)	2.108(6)	Fe(1B)–C(12B)	2.085(7)
Fe(2A)–C(20A)	1.780(6)	Fe(2B)–C(20B)	1.771(7)
Fe(2A)–C(21A)	1.796(7)	Fe(2B)–C(21B)	1.782(6)
Fe(2A)–C(22A)	1.795(7)	Fe(2B)–C(22B)	1.803(7)
C(17A)–O(3A)	1.139(8)	C(17B)–O(3B)	1.16(1)
C(18A)–O(4A)	1.136(8)	C(18B)–O(4B)	1.138(9)
C(19A)–O(5A)	1.152(8)	C(19B)–O(5B)	1.132(8)
C(20A)–O(6A)	1.138(8)	C(20B)–O(6B)	1.142(8)
C(21A)–O(7A)	1.145(8)	C(21B)–O(7B)	1.139(8)
C(22A)–O(8A)	1.137(8)	C(22B)–O(8B)	1.129(8)
C(1A)–C(2A)	1.550(8)	C(1B)–C(2B)	1.525(8)
C(1A)–C(7A)	1.517(8)	C(1B)–C(7B)	1.534(7)
C(1A)–C(8A)	1.525(8)	C(1B)–C(8B)	1.543(8)
C(2A)–C(3A)	1.421(8)	C(2B)–C(3B)	1.410(8)
C(2A)–C(9A)	1.420(8)	C(2B)–C(9B)	1.422(8)
C(3A)–C(4A)	1.527(8)	C(3B)–C(4B)	1.509(9)
C(3A)–C(12A)	1.420(9)	C(3B)–C(12B)	1.415(9)
C(4A)–C(5A)	1.526(9)	C(4B)–C(5B)	1.515(9)
C(5A)–C(6A)	1.519(8)	C(5B)–C(6B)	1.530(8)
C(5A)–C(8A)	1.527(8)	C(5B)–C(8B)	1.536(9)
C(6A)–C(7A)	1.400(7)	C(6B)–C(7B)	1.395(8)
C(6A)–C(13A)	1.411(8)	C(6B)–C(13B)	1.413(8)
C(7A)–C(16A)	1.409(8)	C(7B)–C(16B)	1.429(8)
C(9A)–C(10A)	1.477(9)	C(9B)–C(10B)	1.485(9)
C(10A)–C(11A)	1.52(1)	C(10B)–C(11B)	1.51(1)
C(10A)–O(1A)	1.212(9)	C(10B)–O(1B)	1.207(8)
C(13A)–C(14A)	1.483(9)	C(13B)–C(14B)	1.483(9)
C(14A)–C(15A)	1.52(1)	C(14B)–C(15B)	1.53(1)
C(14A)–O(2A)	1.225(8)	C(14B)–O(2B)	1.209(8)
Bond angles			
C(17A)–Fe(1A)–C(18A)	92.1(3)	C(17B)–Fe(1B)–C(18B)	92.2(3)
C(17A)–Fe(1A)–C(19A)	98.9(3)	C(17B)–Fe(1B)–C(19B)	97.6(3)
C(17A)–Fe(1A)–C(9A)	158.8(3)	C(17B)–Fe(1B)–C(9B)	160.9(3)
C(17A)–Fe(1A)–C(2A)	119.4(3)	C(17B)–Fe(1B)–C(2B)	121.3(3)
C(17A)–Fe(1A)–C(3A)	91.5(3)	C(17B)–Fe(1B)–C(3B)	93.8(3)
C(17A)–Fe(1A)–C(12A)	91.5(3)	C(17B)–Fe(1B)–C(12B)	93.2(3)
C(18A)–Fe(1A)–C(19A)	98.2(3)	C(18B)–Fe(1B)–C(19B)	100.8(3)
C(18A)–Fe(1A)–C(9A)	89.9(3)	C(18B)–Fe(1B)–C(9B)	88.5(3)
C(18A)–Fe(1A)–C(2A)	101.4(3)	C(18B)–Fe(1B)–C(2B)	97.9(3)
C(18A)–Fe(1A)–C(3A)	133.9(3)	C(18B)–Fe(1B)–C(3B)	130.2(3)
C(18A)–Fe(1A)–C(12A)	172.5(3)	C(18B)–Fe(1B)–C(12B)	168.8(3)
C(19A)–Fe(1A)–C(9A)	101.7(3)	C(19B)–Fe(1B)–C(9B)	101.0(3)
C(19A)–Fe(1A)–C(2A)	135.7(3)	C(19B)–Fe(1B)–C(2B)	135.8(3)
C(19A)–Fe(1A)–C(3A)	126.5(3)	C(19B)–Fe(1B)–C(3B)	127.1(3)
C(19A)–Fe(1A)–C(12A)	87.7(3)	C(19B)–Fe(1B)–C(12B)	88.2(3)
C(9A)–Fe(1A)–C(2A)	39.7(2)	C(9B)–Fe(1B)–C(2B)	39.8(2)
C(9A)–Fe(1A)–C(3A)	72.2(2)	C(9B)–Fe(1B)–C(3B)	71.4(2)
C(9A)–Fe(1A)–C(12A)	84.4(2)	C(9B)–Fe(1B)–C(12B)	83.2(2)
C(2A)–Fe(1A)–C(3A)	39.6(2)	C(2B)–Fe(1B)–C(3B)	39.3(2)
C(2A)–Fe(1A)–C(12A)	71.1(2)	C(2B)–Fe(1B)–C(12B)	70.9(2)
C(3A)–Fe(1A)–C(12A)	39.5(2)	C(3B)–Fe(1B)–C(12B)	39.6(2)

Table 3 (continued)

C(20A)–Fe(2A)–C(21A)	100.2(3)	C(20B)–Fe(2B)–C(21B)	91.2(3)
C(20A)–Fe(2A)–C(22A)	90.6(3)	C(20B)–Fe(2B)–C(22B)	98.5(3)
C(20A)–Fe(2A)–C(13A)	158.8(3)	C(20B)–Fe(2B)–C(13B)	163.4(3)
C(20A)–Fe(2A)–C(6A)	120.5(3)	C(20B)–Fe(2B)–C(6B)	123.9(3)
C(20A)–Fe(2A)–C(7A)	94.1(2)	C(20B)–Fe(2B)–C(7B)	93.9(3)
C(20A)–Fe(2A)–C(16A)	91.2(3)	C(20B)–Fe(2B)–C(16B)	87.4(3)
C(21A)–Fe(2A)–C(22A)	102.2(3)	C(21B)–Fe(2B)–C(22B)	103.2(3)
C(21A)–Fe(2A)–C(13A)	100.9(3)	C(21B)–Fe(2B)–C(13B)	89.5(3)
C(21A)–Fe(2A)–C(6A)	135.0(3)	C(21B)–Fe(2B)–C(6B)	94.7(3)
C(21A)–Fe(2A)–C(7A)	127.4(3)	C(21B)–Fe(2B)–C(7B)	124.1(3)
C(21A)–Fe(2A)–C(16A)	90.0(3)	C(21B)–Fe(2B)–C(16B)	163.7(3)
C(22A)–Fe(2A)–C(13A)	86.8(3)	C(22B)–Fe(2B)–C(13B)	97.5(3)
C(22A)–Fe(2A)–C(6A)	96.1(3)	C(22B)–Fe(2B)–C(6B)	133.6(3)
C(22A)–Fe(2A)–C(7A)	128.2(3)	C(22B)–Fe(2B)–C(7B)	130.7(3)
C(22A)–Fe(2A)–C(16A)	167.2(3)	C(22B)–Fe(2B)–C(16B)	93.1(3)
C(13A)–Fe(2A)–C(6A)	39.2(2)	C(13B)–Fe(2B)–C(6B)	39.5(2)
C(13A)–Fe(2A)–C(7A)	71.4(2)	C(13B)–Fe(2B)–C(7B)	72.1(2)
C(13A)–Fe(2A)–C(16A)	87.0(2)	C(13B)–Fe(2B)–C(16B)	87.3(2)
C(6A)–Fe(2A)–C(7A)	39.3(2)	C(6B)–Fe(2B)–C(7B)	39.6(2)
C(6A)–Fe(2A)–C(16A)	72.1(2)	C(6B)–Fe(2B)–C(16B)	72.9(2)
C(7A)–Fe(2A)–C(16A)	39.0(2)	C(7B)–Fe(2B)–C(16B)	40.0(2)
C(2A)–C(1A)–C(7A)	108.3(4)	C(2B)–C(1B)–C(7B)	109.9(4)
C(2A)–C(1A)–C(8A)	107.1(5)	C(2B)–C(1B)–C(8B)	106.2(5)
C(7A)–C(1A)–C(8A)	102.0(4)	C(7B)–C(1B)–C(8B)	101.5(4)
C(1A)–C(2A)–C(3A)	117.2(5)	C(1B)–C(2B)–C(3B)	118.2(5)
C(1A)–C(2A)–C(9A)	122.6(5)	C(1B)–C(2B)–C(9B)	123.0(5)
C(3A)–C(2A)–C(9A)	120.2(5)	C(3B)–C(2B)–C(9B)	118.7(5)
C(2A)–C(3A)–C(4A)	121.7(5)	C(2B)–C(3B)–C(4B)	120.3(5)
C(2A)–C(3A)–C(12A)	118.5(5)	C(2B)–C(3B)–C(12B)	118.3(5)
C(4A)–C(3A)–C(12A)	119.7(5)	C(4B)–C(3B)–C(12B)	121.3(6)
C(3A)–C(4A)–C(5A)	112.7(5)	C(3B)–C(4B)–C(5B)	114.9(5)
C(4A)–C(5A)–C(6A)	111.9(5)	C(4B)–C(5B)–C(6B)	111.1(5)
C(4A)–C(5A)–C(8A)	107.8(5)	C(4B)–C(5B)–C(8B)	107.7(5)
C(6A)–C(5A)–C(8A)	101.6(4)	C(6B)–C(5B)–C(8B)	101.9(5)
C(5A)–C(6A)–C(7A)	108.9(5)	C(5B)–C(6B)–C(7B)	107.9(4)
C(5A)–C(6A)–C(13A)	128.3(5)	C(5B)–C(6B)–C(13B)	128.9(5)
C(7A)–C(6A)–C(13A)	122.5(5)	C(7B)–C(6B)–C(13B)	122.9(5)
C(1A)–C(7A)–C(6A)	107.7(5)	C(1B)–C(7B)–C(6B)	108.8(4)
C(1A)–C(7A)–C(16A)	128.5(5)	C(1B)–C(7B)–C(16B)	128.2(5)
C(6A)–C(7A)–C(16A)	123.2(5)	C(6B)–C(7B)–C(16B)	122.1(5)
C(1A)–C(8A)–C(5A)	100.9(5)	C(1B)–C(8B)–C(5B)	100.1(4)
C(2A)–C(9A)–C(10A)	127.3(5)	C(2B)–C(9B)–C(10B)	126.7(5)
C(9A)–C(10A)–C(11A)	114.2(7)	C(9B)–C(10B)–C(11B)	114.9(6)
C(9A)–C(10A)–O(1A)	125.1(6)	C(9B)–C(10B)–O(1B)	123.3(6)
C(11A)–C(10A)–O(1A)	120.7(7)	C(11B)–C(10B)–O(1B)	121.7(6)
C(6A)–C(13A)–C(14A)	126.0(5)	C(6B)–C(13B)–C(14B)	126.5(5)
C(13A)–C(14A)–C(15A)	116.9(6)	C(13B)–C(14B)–C(15B)	113.6(7)
C(13A)–C(14A)–O(2A)	124.1(6)	C(13B)–C(14B)–O(2B)	123.1(6)
C(15A)–C(14A)–O(2A)	119.0(6)	C(15B)–C(14B)–O(2B)	123.3(7)
Torsion angles			
H(9A)–C(1A)–C(8A)–H(11A)	47.4(7)	H(9B)–C(1B)–C(8B)–H(11B)	–42.7(7)
H(9A)–C(1A)–C(8A)–H(12A)	–71.1(7)	H(9B)–C(1B)–C(8B)–H(12B)	81.8(7)
H(10A)–C(1A)–C(8A)–H(11A)	–111.2(7)	H(10B)–C(1B)–C(8B)–H(11B)	105.2(7)
H(10A)–C(1A)–C(8A)–H(12A)	130.3(7)	H(10B)–C(1B)–C(8B)–H(12B)	–130.3(7)
H(10A)–C(1A)–C(8A)–H(7A)	34.7(7)	H(10B)–C(1B)–C(8B)–H(7B)	–52.3(7)
H(10A)–C(1A)–C(8A)–H(8A)	57.5(7)	H(10B)–C(1B)–C(8B)–H(8B)	–34.4(7)

have sufficient thickness. X-Ray intensity data collection was carried out at room temperature with an *Enraf-Nonius CAD-4* automatic diffractometer. The crystal data, intensity collection, structure solution and refinement methods are summarized in *Table 1*. The measured intensities were corrected for absorption as before [10], and the variances of the intensities were derived from counting statistics and the fluctuations of three periodically measured check reflections.

The computer programs used for data reduction and structure solution were taken from the 'XRAY-72' program system [11]. The scattering factors for the neutral non-H-atoms were taken from *Cromer* and *Mann* [12], and for the H-atoms from *Stewart et al.* [13]. Anomalous scattering coefficients were taken from *Cromer* and *Liberman* [14]. The structure was solved by *Patterson* and *Fourier* methods and refined by blocked matrix least squares to $R = 0.045$. In the last cycles all non-H-atoms were refined anisotropically, and like H-atoms were constrained to have the same isotropic temperature factor. The final atomic coordinates for the two independent molecules are reported in *Table 2*. Calculated bond lengths, bond angles, and torsion angles are reported in *Table 3* with equivalent values for molecules A and B on the same line.

A perspective drawing of one of the two independent molecules in the asymmetric unit prepared by the program ORTEP [15] is shown in *Fig. 2*. Angles between least-squares planes in **6** are shown in *Fig. 3*. A list of the observed and calculated structure factors as well as tables of temperature factors are available as supplementary material.

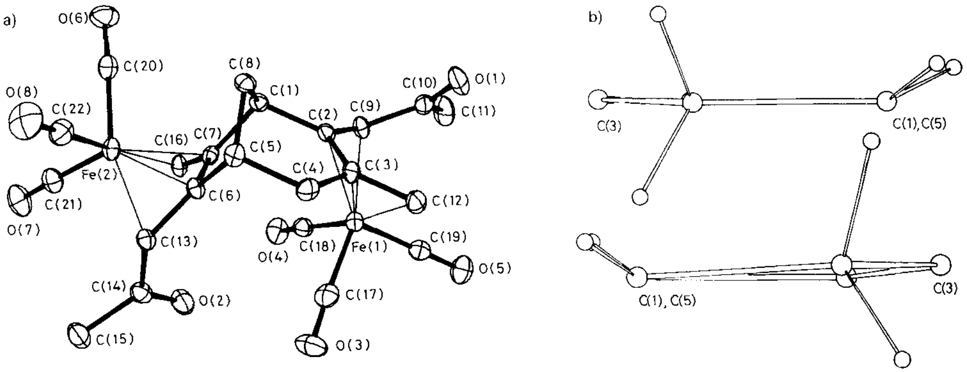


Fig. 2. a) *ORTEP representation of diketone* **6**. b) *Projections of the portion C(1) to C(5) of molecules A and B in a plane perpendicular to the axis C(1)–C(5)* (envelope conformation of the six-membered ring)

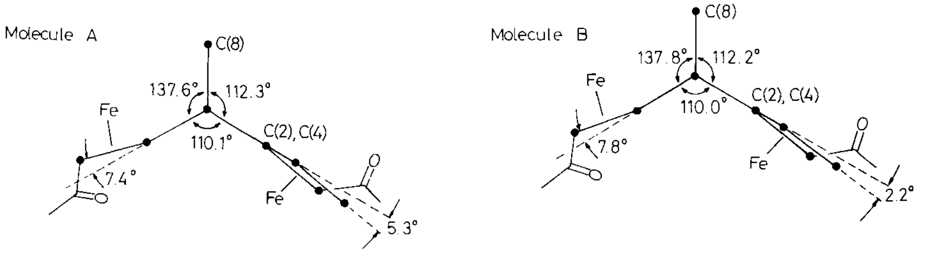


Fig. 3. *Angles between least-squares planes in* **6**. Two independent molecules A and B in the asymmetric unit.

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Experimental Part

General. See [16].

Preparation of **4**. See [1].

trans-μ-{*(1*RS,*2*RS,*3*SR,*5*RS,*6*SR,*7*RS*)*-C,*2,3*,C-η:C,*6,7*,C-η-*[(*Z*)-1-(3,6,7-trimethylidenebicyclo[3.2.1]oct-2-ylidene)-2-propanone]*}*bis(tricarbonyliron)* (**5**). The dimetallic complex **4** (100 mg, 0.23 mmol) was dissolved in freshly distilled CH_3COCl (0.33 ml) under N_2. $AlCl_3$ (33 mg, 0.25 mmol) was added and the mixture stirred at 20° for 10 min. The mixture was then poured to a vigorously stirred ice-cold sat. aq. $NaHCO_3$ soln. (10 ml) and extracted with CH_2Cl_2 (10 ml, 3 times). After drying ($MgSO_4$), the solvent was evaporated and the residue taken in anh. CH_2Cl_2 (5 ml) and stirred at 20° until obtention of a yellow soln. After solvent evaporation, the crude **5** was purified by flash chromatography on silica gel (1 g, CH_2Cl_2) yielding 45 mg (41%) of yellow crystals, m.p. 116.5–177°. UV (95% EtOH): 261 (sh, 10600), 231 (sh, 25500), IR (KBr): 2940, 2060, 2000, 1970, 1960, 1950, 1660, 1415, 1195, 1170. ^1H-NMR (360 MHz, $CDCl_3$): 3.39 (*s*, CH=C(2)); 3.35 (*dd*, *J* = 17, 4.5, H_{exo}–C(4)); 2.95 (*d*, *J* = 4.5, H–C(1)); 2.91 (*t*, *J* = 4.5, H–C(5)); 2,60 (*dtd*, *J* = 11, 4.5, 1 H_{anti}–C(8)); 2.53 (*dd*, *J* = 17, 1, H_{endo}–C(4)); 2.42 (*d*, *J* = 11, H_{syn}–C(8)); 2.12 (*s*, CH_3CO); 2.06, 1.92, 1.90, 1.05, 0.57, 0.33 (6*d*, *J* = 3). MS (70 eV): 480 (1), 452 (5), 396 (16), 368 (11), 341 (11), 340 (48), 313 (20), 312 (100), 310 (19), 284 (8), 270 (9), 259 (9), 258 (54), 257 (13), 256 (29), 240 (14), 238 (26), 228 (12), 226 (14), 200 (8), 198 (8), 186 (15), 185 (9), 184 (24), 171 (9), 170 (14), 159 (8), 156 (17), 155 (11), 149 (16), 148 (14), 141 (8), 134 (9), 129 (19), 128 (26), 115 (15), 112 (14), 105 (10), 95 (10), 91 (23). Anal. calc. for $C_{20}H_{16}Fe_2O_7$ (480.04): C 50.04, H 3.35; found: C 50.13, H 3.45.

trans-μ-{*(1*RS,*2*RS,*3*SR,*5*RS,*6*SR,*7*RS*)*-C,*2,3*,C-η:C,*6,7*,C-η-*[(*Z,Z*)-1,1'-(3,7-dimethylidenebicyclo[3.2.1]octane-2,6-diyliden)di(2-propanone)]*}*bis(tricarbonyliron)* (**6**). Same procedure as for the preparation of **5**, but using 67 mg (0.5 mmol) of $AlCl_3$. Yield: 60 mg (50%), yellow crystals, m.p. 169–170°. UV (95% EtOH): 332 (sh, 2450), 245 (sh, 18800). IR (KBr): 2980, 2060, 1990, 1970, 1960, 1660, 1450, 1410, 1340, 1200, 1170. ^1H-NMR (360 MHz, $CDCl_3$): 3.48 (*s*, CH=C(2)); 3.30 (*s*, CH=C(6)); 3.28 (*dd*, *J* = 17.5, 5, H_{exo}–C(4)); 2.87 (*d*, *J* = 5, H–C(1)); 2.80 (*t*, *J* = 5, H–C(5)); 2.62 (*dt*, *J* = 11, 5, H_{anti}–C(8)); 2.49 (*d*, *J* = 17, H_{endo}–C(4)); 2.43 (*d*, *J* = 11, H_{syn}–C(8)); 2.30 (*d*, *J* = 3); 2.12, 2.11 (2*s*, 2 CH_3CO); 1.78, 1.67, 1.06 (3*d*, *J* = 3). MS (70 eV): 494 (2), 466 (3), 438 (2), 411 (3), 410 (16), 382 (6), 355 (22), 354 (100), 352 (13), 334 (4), 326 (4), 300 (17), 298 (31), 276 (19), 258 (15), 257 (10), 256 (12), 244 (12), 243 (12), 242 (12), 226 (11), 204 (14). Anal. calc. for $C_{22}H_{18}Fe_2O_8$ (522.08): C 50.61, H 3.47; found: C 50.75, H 3.53.

trans-μ-*[(1*RS,*2*SR,*3*RS,*4*RS,*5*SR,*6*RS,*7*SR*)*-C,*2,3*,C-η:C,*6,7*,C-η-*(2,3,6,7-tetramethylidene(4-*exo-*D*)-bicyclo[3.2.1]octane)]bis(tricarbonyliron)* (**7**). Mesylate **10** [1] (20 mg, 0.04 mmol) was added to a stirred soln. of $NaBD_4$ (61 mg, 1.4 mmol) in $(CF_3)_2CHOD$ (2 ml). After stirring at 20° for 8 min, the mixture was filtered through silica gel (1 g). The solvent was evaporated and the residue purified by column chromatography on silica gel (1 g, hexane). The crude **7** was recrystallized from hexane yielding 12 mg (73%) of yellow crystals, m.p. 98–99°. IR (KBr): 2990, 2950, 2920, 2030, 1990, 1970, 1950, 1480, 1470, 1450, 1440, 1280, 1215, 1120, 1015. ^1H-NMR (360 MHz, $CDCl_3$): 3.05 (*d*, *J* = 4.5, H–C(1)); 2.90 (*d*, *J* = 4.5, H–C(5)); 2.75 (*dt*, *J* = 11, 4.5, H_{anti}–C(8)); 2.70 (br. *s*, $^4J(H_{anti}$–C(8), H_{endo}–C(4)) < 1, H_{endo}–C(4)); 2.36 (*d*, *J* = 11, H_{syn}–C(8)); 2.07, 1.90, 1.89, 1.57, 0.58, 0.56, 0.54, 0.07 (8*d*, *J* = 3). MS (70 eV): 439 (2), 411 (33), 409 (8), 383 (81), 381 (12), 355 (38), 353 (11), 327 (10), 299 (63), 297 (12), 271 (100), 269 (23), 243 (19), 215 (54), 213 (21), 164 (40), 149 (31), 91 (67). Anal. calc. for $C_{18}H_{13}DFe_2O_6$ (439.01): C 49.25, H 3.44; found: C 49.80, H 3.48.

trans-μ-*[(1*RS,*2*RS,*3*SR,*4*SR,*5*SR,*6*RS,*7*SR*)*-C,*2,3*,C-η:C,*5,6*,C-η-*(2,3,5,6-tetramethylidene(7-*D*)bicyclo[2.2.2]octane)]bis(tricarbonyliron)* (**12**). The mesylate **10** [1] derived from the alcohol **9** [17] (20 mg, 0.04 mmol) was added to a stirred soln. of $NaBD_4$ (58 mg, 1.4 mmol) in anh. THF (2 ml). The mixture was stirred at 60° for 1 h and then filtered through silica gel (1 g). The solvent was evaporated and the residue purified by flash chromatography on silica gel (1 g, CH_2Cl_2). The crude **12** was recrystallized from hexane yielding 6 mg (36%) of yellow crystals. Same properties as those reported for **11** [18], except for its 360-MHz-^1H-NMR, see *Fig. 1*.

trans-μ-*[(1*RS,*2*RS,*3*RS,*4*SR,*5*SR,*6*RS,*7*RS,*8*SR*)*-C,*5,6*,C-η:C,*7,8*,C-η-*(5,6,7,8-tetramethylidene(3-*D*)-bicyclo[2.2.2]oct-2-yl methanesulfonate)]bis(tricarbonyliron)* (**14**). The alcohol **13** [19] (228 mg, 0.5 mmol) was dissolved at 20° in anh. pyridin (1 ml). After cooling to 0°, methanesulfonyl chloride (74 mg, 0.6 mmol) was added under stirring. After stirring at 20° for 30 min under N_2, CH_2Cl_2 (15 ml) was added. The soln. was washed with 1N HCl (10 ml, 4 times) and H_2O (10 ml, 3 times) and dried ($MgSO_4$). The solvent was evaporated and the residue recrystallized from CH_2Cl_2/hexane yielding 210 mg (79%) of yellow crystals, m.p. 152–153°. IR (KBr): 3030, 3000, 2940, 2040, 1990, 1970, 1470, 1450, 1360, 1340, 1300, 1250, 1225, 1180, 1140, 1010, 970, 935, 890, 850, 830, 790, 750. ^1H-NMR (360 MHz, $CDCl_3$): 5.41 (*m*, H–C(2)); 3.90 (*d*, *J* = 3, H–C(1)); 3.51 (*d*, *J* = 3, H–C(4)); 3.07 (*s*, CH_3); 2.74 (*m*, H–C(3)); 2.18, 2.10, 1.94, 1.88 (4*d*, *J* = 3); 0.67, 0.63, 0.41, 0.33 (4*d*, *J* = 3). MS (70 eV): 533 (9), 505 (15), 477 (407), 499 (11), 439 (41), 421 (12), 409 (20), 397 (7), 381 (100), 365 (17). Anal. calc. for $C_{19}H_{15}DFe_2O_9S$ (533.10): C 42.80, H 3.21; found: C 42.95, H 3.08.

trans-μ-*[(1*RS,*2*RS,*3*SR,*4*SR,*5*SR,*6*RS,*7*RS*)*-C,*2,3,*C-η:C,*5,6,*C-η-*(2,3,5,6-tetramethylidene(7-D)bicyclo[2.2.2]octane)]bis(tricarbonyliron)* (**15**). Mesylate **14** (20 mg, 0.04 mmol) was added to a soln. of $NaBH_4$ (55 mg, 1.4 mmol) in anh. THF (2 ml). After stirring at 20° for 20 min, the mixture was filtered through silica gel (1 g). The solvent was evaporated and the residue purified by column chromatography on silica gel (1 g, CH_2Cl_2) yielding 6 mg (36%) of yellow crystals, m.p. 92–94°. IR (KBr): 3000, 2975, 2960, 2890, 2040, 1985, 1975, 1465, 1450, 1420, 1300, 1220, 1140, 950. ^1H-NMR ($CDCl_3$): 3.43 (*s*, H–C(1), H–C(4)); 2.13 (*m*, H–C(2), CH_2(3)); 2.09, 1.89, 0.50, 0.29 (4*d*, $J = 3$). MS (70 eV): 439 (5), 411 (38), 383 (78), 381 (11), 355 (36), 327 (12), 299 (100), 297 (13), 271 (90), 269 (19), 243 (15), 215 (44), 213 (11), 164 (24), 163 (16), 112 (14). Anal. calc. for $C_{18}H_{13}DFe_2O_6$ (439.01): C 49.25, H 3.44; found: C 49.38, H 3.56.

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