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Iron complexes of dioxoborolanylbutadienes

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Abstract

The first [2,3-dialkyl-1,4-bis(1,3-dioxo-4,4,5,5-tetramethyl-2-borolanyl]-1,3-butadiene]Fe(CO)₃ complexes (2, alkyl = n-butyl; 3, alkyl = cyclopentyl; 4, 'alkyl' = phenyl; 5, alkyl = 3-chloropropyl) have been prepared from the reaction of bis(*cis*-cyclooctadiene)Fe(CO)₃ (1) with the borolanylbutadienes. The X-ray crystal structures of 2 and 3 are reported. The geometries of the coordinated ligands are compared with those of the free ligands. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Borolanylbutadiene complexes; Butadiene complexes; Iron complexes

1. Introduction

Reihlen et al. prepared the first metal complexes of butadienes in 1930 [1]. Many examples of metal-butadiene complexes are now known [2]. In 1996, Srebnik et al. [3] prepared and characterized a series of [2,3-dialkyl-1,4-bis(1,3-dioxo-4,4,5,5-tetramethyl-2-borolanyl]-1,3butadiene]Fe(CO)₃ complexes (2, alkyl = n-butyl; 3,alkyl = cyclopentyl; 4, 'alkyl' = phenyl; 5, alkyl = 3chloropropyl). Zirconocene-induced coupling on a series of 1-alkenyl pinacolboronates resulted in a mixture of two regioisomers: 1,3-(1,3-dioxo-2-borolanyl)butadienes and 1,4-(1,3-dioxo-2-borolanyl)-butadienes both as S-trans isomers. No S-cis isomers were obtained. The S-trans-1,4-(1,3-dioxo-2-borolanyl)butadienes could be separated from the crude reaction mixture by crystallization at -20° C. These highly crystalline borolanylbutadienes are very stable to air, water and heat. Prolonged heating at 150°C or more under an inert atmosphere did not cause any noticeable decomposition or isomerization.

The X-ray crystal structure of 2,3-di-n-butyl-1,4bis(1,3 - dioxo - 4,4,5,5 - tetramethyl - 2 - borolanyl] - 1,3butadiene]Fe(CO)₃ [3a] showed that the molecule has high planarity and linearity. These structural features make it a good candidate for evaluation as a liquid crystal [4]. Moreover, metal complexes of S-*trans* borolanylbutadienes might also make good liquid crystals. Since no metal complexes of borolanylbutadienes had been previously reported, we explored reactions of these species to Fe(CO)₃ groups to show that complexation could occur. These complexes would be expected to have (and did indeed show) an S-*cis* geometry for the coordinated butadienes. The results of these investigations are reported here.

2. Experimental

All reactions were carried out under an Ar atmosphere using Schlenk techniques. Solvents were obtained from ACROS or Fischer Scientific (ACS reagent grade) and were dried before use. Benzene and methylene chloride were refluxed over phosphorus pentoxide and distilled. Tetrahydrofuran (THF), pentane, hexane and toluene were dried over potassium benzophenone ketyl and distilled. Anhydrous diethyl ether was used as received.

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Low temperature photolysis was carried out in a custom-made immersion well using a large Dewar as a low-temperature bath. Acetonitrile/dry ice (about -42° C) and n-decane/dry ice(about -30° C) were used as cooling baths. Storage tubes made of Pyrex glass were used as reaction vessels.

Chromatography was accomplished on alumina (basic, grade I) or on silica gel.

The borolanylbutadienes were prepared by literature methods [3].

NMR Solvents were purchased from ACROS (C_6D_6 , 99.5% D, without internal standard) Cambridge Isotope Laboratories (C₂D₆CO, 99.9%, without internal standard) and Aldrich (CDCl₃, 99.8%D, with TMS as internal standard). The following abbreviations are used: singlet (s), doublet (d), triplet (t), multiplet (m), coupling constant (J). Chemical shifts for H and C are reported in parts per million downfield from TMS. For NMR spectra in C₆D₆ the solvent signal was used as the standard ($\delta = 7.15$ ppm). ¹¹B chemical shifts are reported in parts per million downfield relative to BF₃OEt₂ as an external standard. NMR spectra were recorded on a Bruker AC 250 MHZ instrument and the IR spectra on a Perkin-Elmer FT-IR 1600. X-ray data were collected on a Siemens P3/PC diffractometer. Mass spectra were obtained on a VG-30-250 quadrupole mass spectrometer. Elemental analysis was performed by M-H-W Laboratories, Phoenix, AZ.

2.1. Preparation of $Fe(CO)_3(cis-cyclo-C_8H_{14})_2$ (1)

This compound was prepared by a literature procedure [5]; however, we were unable to dry the crystals in vacuo below 0°C without their decomposing. Hence, the workup was modified as follows: the reaction solution was cooled to -78° C, let settle for a day and the solvent removed via syringe. Pre-cooled hexane was added; the solution allowed to warm to -45° C, stirred and cooled again. By repeating this procedure twice, *cis*-cyclooctene (CCO) was removed almost completely. The crystals could be stored covered by hexane over dry ice under argon for months. The product was used as a suspension in hexane.

2.2. Preparation of [2,3-dialkyl-1,4-bis(1,3-dioxo-4,4,5,5-tetramethyl-2-borolanyl]-1,3-butadiene]Fe(CO)₃ complexes (2, alkyl = n-butyl; 3, alkyl = cyclopentyl; 4, 'alkyl' = phenyl; 5, alkyl = 3-chloropropyl)

A typical reaction for the synthesis is given followed by more detail for each individual compound. A solution containing a weighed amount of diborolanylbutadiene in hexane was cooled below -60° C under an Ar atmosphere. The scale on which reactions were run was dictated by the quantities of borolanylbutadienes available. 1 was added and the resulting yellow solution stirred and allowed to warm to 0°C over a period of 1-2 h. An IR spectrum was then taken; if no bands due to 1 were present, the solution was re-cooled and a second portion of 1 added in order to consume the borolanylbutadiene completely. When the IR spectrum showed bands attributable to the desired product. 1 and $Fe(CO)_4(CCO)$, the reaction was stopped. The solution was concentrated and filtered through a fine glass frit to yield a dark green solution; by cooling to -10° C it was possible to crystallize $Fe_3(CO)_{12}$ which could then be filtered off. The pale green solution was chromatographed. Two bands were eluted with hexane: the first yellow band contained Fe(CO)₄(CCO) and the second green band contained more $Fe_3(CO)_{12}$. The third yellow band contained the desired product and was eluted with hexane/THF. Solvent was removed from this fraction in a stream of Ar. The resulting yellow oil was dissolved in pentane and the solvent again removed with Ar. This procedure was repeated twice to yield yellow crystals which were recrystallized from pentane at -5° C and dried in vacuo at room temperature. Solvent evaporation in vacuo results in decomposition; only crystals pre-dried in a stream of Ar could be dried further in vacuo without complications. The products are stable in solution at room temperature for periods up to 4 days.

2: Scale 1.00 mmol; total reaction time 1.5 h; chromatography on Grade I basic alumina; product eluted with 5% THF in hexane; yield 30%; *Anal.* Calc. For $C_{27}H_{44}B_2FeO_7$: C, 58.11; H, 7.95. Found: C, 58.00; H, 7.80%. M.p. 68–72°C; IR (n-pentane): v(CO) 2052 (s), 1991 (s), 1977 (s) cm⁻¹. δ (¹H, in C₆D₆) = 3.02 [m, 2H, CHH), 2.75 (m, 2H, CHH), 1.64 (m, 4H, CH₂), 1.47 (m, 4H, CH₂), 1.08 (s, 24H, CH₃), 0.96 (t, 6H, *J* = 7 Hz, CH₂CH₃), -0.12 (s, 2H, C=CH-B); δ (¹³C{¹H}, in C₆D₆) = 111.1, 82.8, 36.5, 31.5, 24.9, 24.3, 23.5, 14.3); δ (¹³CO{¹H}, in C₃D₆O, 211.4 at 25°C; 207.5, 213.8 at -65°C; δ (¹¹B) = 30.4. Mass spectrum: *m/e* 559 (*M*H⁺), 558 (*M*⁺), 531, 503, 475, 460, 416.

3: Scale 0.005 mmol; total reaction time 1.5 h; chromatography on silica gel; product eluted with 1:1 THF/ hexane; yield 95%; M.p. 65–66°C; IR (n-pentane): ν (CO) 2050 (s), 1989 (s), 1976 (s) cm⁻¹. δ (¹H) = 3.51 [m, 2H, J = 9.1 Hz, =C–CH), 2.33–1.99 and 1.92–1.75 (m, 12H), 1.71–1.60 (m, 4H), CH(CH₂)₄, 1.09 (s, 24H, CH₃), -0.09 (s, 2H, C =CH–B); δ (¹³C{¹H}) = 114.8, 83.0, 42.6, 36.0, 34.8, 27.8, 26.8, 24.8, 24.4). Mass spectrum: m/e 583.3 (MH⁺), 582 (M⁺), 567, 554, 526, 498, 483, 370.

4: Scale 0.0065 mmol; total reaction time 3 h; chromatography on silica gel; product eluted with THF; yield 30%. *Anal.* Calc. For $C_{31}H_{38}B_2FeO_7$: C, 62.29; H, 6.07. Found: C, 62.86; H, 6.22%. M.p. 91–93°C; IR (n-pentane): v(CO) 2056 (s), 1996 (s), 1985 (s) cm⁻¹. $\delta({}^{1}\text{H}) = 7.40/7.37$ (d, 5H, phenyl), 6.93/6.90 (d, 5H, phenyl), 0.94 (s, 12H, CH₃), 0.87 (s, 12H, CH₃), 0.36 (s, 2H, C=CH-B); $\delta({}^{13}\text{C}\{{}^{1}\text{H}\}) = 213.8, 207.5, 138.2, 132.7, 128.5, 127.1, 127.0, 114.6, 82.9, 30.4, 24.8, 24.0.$ Mass spectrum: m/e 599 (MH⁺), 571, 543, 515, 416.

5: Scale 0.0065 mmol; total reaction time 2 h; chromatography on silica gel; product eluted with hexane; yield 30%; *Anal.* Calc. For C₂₅H₃₈B₂Cl₂FeO₇: C, 50.16; H, 6.40. Found: C, 50.46; H, 6.12%. M.p. 101–104°C; IR (n-pentane): ν (CO) 2055 (s), 1996 (s), 1980 (s) cm⁻¹. δ (¹H) = 3.33 [t, 4H, *J* = 6.6 Hz, CH₂Cl), 2.96 (m, 2H, =C-CH₂-CH₂), 2.72 (m, 2H, =C-CH₂-CH₂), 1.86 (m, 4H, -CH₂-CH₂-CH₂Cl), 1.06 (s, 24H, CH₃), -0.03 (s, 2H, C=CH-B); δ (¹³C{¹H}) = 109.7, 83.0, 44.7, 36.8, 29.2, 24.9, 24.3). Mass spectrum: *m/e* 599 (*M*H⁺), 514.

2.3. Crystal structure analysis

Crystal data and numerical details of the structure determinations of **2** and **3** are given in Table 1. Suitable crystals of **2** $(0.30 \times 0.30 \times 0.10 \text{ mm})$ and **3** $(0.85 \times 0.60 \times 0.60 \text{ mm})$ were grown from pentane, coated with a light film of epoxy resin and mounted on a glass fiber. Intensity data were collected at 24°C on a Siemens P3/PC diffractometer with graphite- monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Lattice parameters were obtained by least squares refinement of the angular settings from 25 to 30 reflections lying in a 2 θ range

Table 1	
Crystallographic da	ata for 2 and 3

Compound	2	3
Empirical formula	C ₂₇ H ₄₄ B ₂ FeO ₇	C ₂₉ H ₄₄ B ₂ FeO ₇
Formula weight	558.09	582.11
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_{1}/c$
a (Å)	13.187(6)	9.887(7)
b (Å)	17.071(7)	17.527(13)
<i>c</i> (Å)	14.122(4)	17.471(7)
β (°)	96.81(3)	94.91(5)
$V(Å^3)$	3157(2)	3016(3)
Ζ	4	4
F(000)	1192	1240
Density (calc.) (Mg m^{-3})	1.174	1.282
Absorption coeff. (mm^{-1})	0.516	0.543
Decay correction (min./max.)	0.9410/1.0089	0.9657/1.0064
Transmission factors (min./max.)		0.2117/0.2555
Independent reflections	6274	6954
	$(R_{\rm int} = 0.1124)$	$(R_{\rm int} = 0.0529)$
Data/parameters	6274/334	6942/352
Goodness-of-fit on F^2	0.998	1.043
Final R indices $[I > 2\sigma(I)]$ (%)	$R_1 = 6.75,$	$R_1 = 4.79,$
	$wR_2 = 11.26$	$wR_2 = 10.61$
R indices (all data) (%)	$R_1 = 20.25,$	$R_1 = 8.80,$
	$wR_2 = 15.90$	$wR_2 = 17.22$

of $10-30^{\circ}$. Intensity data in the 2θ range of $3.5-55^{\circ}$ (2: $0 \le h \le 12$, $-22 \le k \le 22$, $-18 \le l \le 18$; **3**: $0 \le h \le 12$, $0 \le k \le 22$, $-22 \le l \le 22$) were collected using variable speeds (3.0-29.0° min⁻¹ with respect to ω). The data for **2** and **3** were corrected for decay, Lorentz and polarization effects. An empirical absorption correction was applied to the data based on measured ψ -scans for **3**; no correction was applied to the data for **2**.

The structures were solved by a combination of direct methods for 2 and Patterson methods for 3 using SHELXTL 5.03 and the difference Fourier technique and refined by full-matrix least squares on F^2 . All unique reflections were used in the refinement of 2. In the case or 3, 12 reflections were omitted from the refinement due to very negative F^2 values or because they suffered from systematic errors. All non-hydrogen atoms were refined with anisotropic displacement parameters. Weights were assigned as $\omega^{-1} = \sigma^2(F_{\alpha}^2) +$ $(aP)^2 + bP$, where $P = 0.33333F_0^2 + 0.66667F_c^2$ and a = 0.0494, b = 0.0114 for **2** and a = 0.0476, b = 1.7539for 3. Hydrogen atom positions were either located directly from the electron density map or calculated based on a geometric criterion and all were allowed to ride on their respective atoms. Hydrogen atom isotropic temperature factors were defined as $U(C)^*a = U(H)$, where a = 1.5 for methyl hydrogens and a = 1.2 for the remaining hydrogens. Large thermal motion indicative of disorder is associated with a number of the methyl groups and with O2 and O3 for 2; however a reasonable disorder model could not be sorted out. The final difference Fourier maps for both structures appeared featureless with the largest residual electron density of 0.216 and 0.358 eD⁻³ for **2** and **3**, respectively. The refinements for 2 and 3 converged with crystallographic agreement factors indicated in Table 1.

3. Results and discussion

We tried several methods which had been successful with other butadienes for preparing diborolanylbutadiene iron tricarbonyl complexes. In particular, irradiation of Fe(CO)₅ and a diborolanylbutadiene in benzene at 50°C for 2.5 days gave no product. Treatment of $Fe(CO)_5$ with trimethylamine N-oxide in the presence of borolanylbutadienes in hexane, benzene, THF and diethyl ether at temperatures from 0 to 65°C gave either no product or only traces of product detectable by IR. Only displacement of cis-cyclooctene (CCO) from previously prepared $Fe(CO)_3(CCO)_2$ at low temperatures resulted in isolation of the desired complexes. As shown in Eq. (1), byproducts of the synthesis are $Fe_3(CO)_{12}$ and Fe(CO)₄(CCO), both of which presumably result from decomposition of (excess) Fe(CO)₃(CCO)₂. Evidently, the diborolanylbutadienes can displace only

Table 2

Selected $^1\mathrm{H}$ NMR data for 2,3-dialkyl-1,4-bis(1,3-dioxo-4,4,5,5-te-tramethyl-2-borolanyl)-1,3-butadiene]Fe(CO)_3 complexes

(ppm)	(ppm)
-0.12 -0.09 +0.36	1.08 singlet 1.09 singlet 0.94/0.87 2 singlets
1	(ppm) 1 - 0.12 entyl - 0.09 + 0.36 ropropyl - 0.03

very weakly coordinating ligands such as CCO from $Fe(CO)_3$, perhaps for steric reasons. Because we were unable to dry 1 without decomposition, the reactions were conducted using weighed amounts of the dioxaborolanylbutadienes to which portions of 1 were added until the dioxaborolanylbutadiene was consumed as indicated by the presence of unreacted 1 detected in the IR spectrum of the reaction mixture. Thus, the yields are based on the masses of diborolanylbutadienes employed in the reactions.





(1)

Complexes 2–5 display IR spectra consisting of three carbonyl stretching bands consistent with the overall C_s symmetry of the complexes. NMR spectra were recorded in C₆D₆ or C₂D₆O since much better resolution was obtained in these solvents than in CDCl₃ where decomposition was apparent after 1–2 h. Table 2 reports selected ¹H NMR data for 2–5.

As expected, 2, 3 and 5 show a singlet for the methyl groups of the dioxaborolanyl rings indicating that some dynamic process renders the two sets of methyl protons equivalent. Presumably free rotation about the C–B bond is possible. Unexpectedly, the methyl signal of 4

consists of two singlets, indicating that the energy barrier for rotation of the dioxaborolanyl ring around the bond must be higher than that in the other derivatives due to interactions of the five-membered ring with the phenyl rings which are in close proximity. This also very likely explains the appearance of one more aromatic peak than expected in the ¹³C NMR. A variable temperature NMR study of 4 between -10 and +45°C showed no change in the NMR spectrum. Similarly, no changes were detected in the spectrum of 3 over this temperature range. Lowering the temperature of a solution of 3 in CDCl₃ to -58° C resulted in broadening, but no splitting of the methyl signal. Cyclopentyl groups are apparently less effective at slowing the dioxaborolanyl ring rotation. This may be due to possibilities for ring folding which are not present for phenyl rings (vide infra).

Also interesting is the chemical shift for the H attached to the butadiene double bond. The chemical shifts of these protons occur at about 6 ppm in the free ligands and are seen at slightly negative values in complexes 2, 3 and 5. Again, 4 shows a major deviation with $\delta = +0.36$ ppm. Possibly responsible for this observation are the two phenyl rings which could delocalize a significant amount of electron density from the butadiene system, making the ligand a less effective donor and the iron less negative; consequently, the signal would be shifted less far upfield than in cases where R is saturated. In the literature, chemical shifts for hydrogens attached to the terminal carbons of butadiene complexes have been reported to range from $\delta = +0.3$ to -0.3 ppm [6].

Table 3 shows selected ¹³C NMR data. The only values of some surprise are the ones for the C's substituted with two methyl groups in the dioxaborolanyl ring; one would expect the chemical shift to be in the range of 60–85 ppm. In the free ligands, the shifts are at 82 ± 1 ppm. The upfield shifts seen here may indicate that electron delocalization in the π -system extends to the O atoms in the dioxaborolanyl rings.

Chemical shifts for the double bond carbons in the free ligands are in the range of 115-125 ppm for C4 and 160-172 ppm for C5 (labels from Figs. 2 and 3). The upfield shift observed in our complexes can be explained by the redistribution of electron density toward the iron center on coordination of the ligands. In

Table 3

Selected ¹³C{¹H} NMR data for 2,3-dialkyl-1,4-bis(1,3-dioxo-4,4,5,5-tetramethyl-2-borolanyl)-1,3-butadiene]Fe(CO)₃ complexes

Complex	R	$\delta(C-CH_3)$	δ (C–CH ₃)	δ(C= C -B)	δ (C=C-B)
2	n-butyl	24.3	31.5	82.8	111.1
3	cyclopentyl	24.4	34.8	83.0	114.8
4	phenyl	24.0/24.8	30.4	82.9	114.6
5	3-chloropropyl	24.3	29.2	83.0	109.7

Table 4 Mass spectrometry data for parent peak of 5

Peak mass (Da)	Calculated abundance	Measured abundance
594	0.29	0.32
595	2.52	2.6
596	10.54	11.0
597	42.51	44.7
598	100.00	100.0
599	54.75	55.0
600	67.54	65.8
601	23.31	22.3
602	13.67	12.8
603	3.49	3.0
604	0.65	0.42
605	0.08	

(butadiene)Fe(CO)₃ the chemical shifts for C4 and C5 are seen at 40.53 and 85.49 ppm, respectively. In none of the ¹³C{H} NMR spectra at room temperature in C₆D₆ could peaks corresponding to CO groups be observed, although the pulse width of the spectrometer was increased to 7 μ s and the relaxation time to 25 s. However, the spectrum of **2** in C₃D₆O showed a very weak signal at 210.8. On cooling to -65° C, two signals were visible at 207.5 and 213.8 ppm in a 2:1 ratio. Similar behavior has been observed for other butadiene complexes containing the Fe(CO)₃ group [7].

In all FAB⁺ MS, peaks corresponding to the molecular ion M^+ (for 2 and 3) or MH^+ for (4 and 5) could be observed. Peaks corresponding to the loss of three CO groups were also present in all spectra.

The general fragmentation pattern is successive loss of CO groups, sometimes with loss of a methyl group before the loss of the next CO. Loss of the $Fe(CO)_3$ groups and the dioxaborolane rings also occurred.

As a check on the composition of the complexes, the isotope pattern in the molecular ion peak of **5** was investigated. The isotopic pattern arises from the relative abundances of the isotopes of chlorine [35 Cl (75.5%) and 37 Cl (24.5%)], boron [10 B (19.8%) and 11 B (80.2%)],

iron [⁵⁴Fe (5.8%), ⁵⁶Fe (91.7%) and ⁵⁷Fe (2.2%)] and C [¹²C (98.9%) and ¹³C (1.1%)]. Table 4 presents a comparison of the calculated and measured data for this peak. Only ¹⁶O (99.763% abundance) was assumed to be present in the calculations. For example, the relative abundance of a peak containing ¹⁶O₇ and one containing ¹⁶O₆¹⁸O is 1: 2×10^{-3} . Likewise, the natural abundance of deuterium has been ignored since the relative abundance of a peak containing ¹H₄₄ and one containing ¹H₄₃H₁ is 1: 1.6×10^{-4} . The 12 calculated peaks of highest abundance. The measured and observed parent isotopic peaks are presented in Table 4 and displayed in Fig. 1.

3.1. X-ray crystal structures of 2 and 3

The single crystal X-ray structures of **2** and **3** both reveal η^4 -bonded diborolylbutadienes in the S-*cis* geometry on Fe(CO)₃ units. Figs. 2 and 3 show ORTEP drawings of **2** and **3**, respectively. Selected bond distances are given in Table 5 and bond angles in Table 6.

The structure of $(\eta^4$ -butadiene)Fe(CO)₃ has been determined both by X-ray diffraction [8] and by gas-phase electron diffraction [9]. The overall features of this compound are very similar to those found for all $(\eta^4$ -butadiene)Fe(CO)₃ complexes [10–12] including those prepared by us. The geometry for $(\eta^4$ -butadiene)Fe(CO)₃ complexes is derived from a square pyramid with axial CO. This CO is parallel to the butadiene plane and directed to the open side of the butadiene. The four butadiene carbon atoms are coplanar with a distance of about 161 pm from the Fe to the plane. The double bonds of the organic ligand occupy two basal positions with the other two occupied by CO's.

In 2 the four butadiene carbons are planar within 0.62 pm and in 3 within 0.13 pm. Fe lies about 161 pm above the center of the planes with nearly equal distances from Fe to C4 and C7 and to C5 and C6. In 2 the



Fig. 1. Calculated and observed abundances for the parent peak of 5.



Fig. 2. ORTEP view of (2,3-di-n-butyl-1,4-bis(1,3-dioxo-4,4,5,5-tetramethyl-2-borolanyl)-1,3-butadiene)Fe(CO)₃ (2).



Fig. 3. ORTEP view of (2,3-dicyclopentyl-1,4-bis(1,3-dioxo-4,4,5,5-tetramethyl-2-borolanyl)-1,3-butadiene)Fe(CO)₃ (3).

Fe- C_{outer} bonds are nearly equal and at the average of the range observed for symmetrically substituted (butadiene)Fe(CO)₃ complexes (Table 7). The Fe- C_{inner} bonds differ by 2.4 pm and both are shorter by 4.55 pm than the Fe- C_{outer} bonds. In contrast the Fe- C_{outer} bonds in 3 differ by 1.1 pm and the Fe- C_{inner} bonds by about half that (0.5 pm).

The angle C_{basal} -Fe- C_{basal} for 2 and 3 is smaller than the usual range seen in (diene)Fe(CO)₃ complexes (Table 7). In 2 the Fe(CO)₃ unit is almost symmetric and close to the average structure. 3 exhibits a fairly distorted Fe(CO)₃ unit with one axialbasal angle close to the average, one at the lower limit and the basal-basal angle below the lower limit. In 2,3-di-n-butyl-1,4-bis(1,3-dioxo-4,5,5-tetramethyl-2-borolanyl)buta-1,3-diene [3a] the heterocycle exhibits a slight envelope conformation with one carbon 36 pm out of the plane defined by the remaining four atoms. The dioxaboloranyl rings in **2** have geometries similar to those in the free ligand, however the complexes do tend to be less planar. C9 lies 38.5 pm below the plane defined by the other four atoms while C23 lies 47.0 pm below the corresponding plane in the second ring. The dihedral angles between the butadiene and the nearest dioxaborolanyl rings are 20.0 and 18.1° in contrast to the 4.48° observed for the free ligand. All the non-H substituents on the butadiene are displaced toward the Fe atom (20 pm for B1, 31 pm for B2, 8 pm for C14 and 4 pm for C18).

The crystal structure of 2,3-dicyclopentyl-bis-1,4-(1,3dioxo-4,5,5-tetramethyl-2-borolanyl)-1,3-butadiene [3b] shows a twisted conformation for the pinacol borate ring. The cyclopentyl rings adopt a slight envelope conformation with C1 deviating by 53.7 pm. In contrast, the coordinated 2,3-dicyclopentyl-1,4-bis(2,3dioxo-4,4,5,5-tetramethyl-2-borolanyl)-1,3-butadiene in **3** exhibits different conformations for the cyclopentyl groups. One cyclopentyl group adopts an envelope

Table 5 Selected bond distances for **2** and **3** (Å)

2 (R = n-but	tyl)	3 ($R = cyclop$	bentyl)
Fe-C1	1.787(7)	Fe–C1	1.790(3)
Fe–C2	1.779(7)	Fe–C2	1.783(3)
Fe–C3	1.785(6)	Fe–C3	1.800(3)
C1O1	1.144(6)	C1O1	1.147(3)
C2–O2	1.143(6)	C2–O2	1.138(3)
C3–O3	1.138(5)	C3–O3	1.141(3)
Fe–C4	2.123(5)	Fe–C4	2.115(3)
Fe–C5	2.067(5)	Fe–C5	2.086(3)
Fe–C6	2.091(5)	Fe–C6	2.091(3)
Fe–C7	2.126(5)	Fe–C7	2.104(3)
C4-C5	1.440(6)	C4–C5	1.447(3)
C5–C6	1.421(6)	C5–C6	1.438(3)
C6–C7	1.442(6)	C6–C7	1.449(3)

Table 6

Selected bond angles for 2 and 3 (°)

2 (R = n-buty)	1)	3 ($R = cyclope$	entyl)
C1–Fe–C2	100.9(3)	C1–Fe–C2	102.86(13)
C1-Fe-C3	101.2(3)	C1-Fe-C3	86.94(13)
C2–Fe–C3	88.4(3)	C2–Fe–C3	99.85(13)

Table 7

Selected structural parameters for symmetrically substituted (butadiene)Fe(CO)₃ complexes

Bond lengths	Range (pm)	Mean (pm)
Fe-C(inner)	203–208	205
Fe-C(outer)	210-216	213
C-C(inner)	138.6-142.6	140.9
C–C (outer)	139.4–143.4	141.9
Bond angles	Range (°)	Mean (°)
C _{basal} -Fe-C _{basal}	89–94	92
C _{basal} -Fe-C _{axial}	95–103	100

Displacements of substituents out of the butadiene plane (pm) (+ = away from Fe) (

C-1, C-4 syn	-15 to $+20$
C-1, C-4 anti	+50 to $+65$
C-2, C-3	-5 to -15

configuration with C19 twisted out of the plane defined by C20-C21-C22-C23; the other is twisted with C17 and C18 above and below the plane defined by C14-C15-C16. The dioxaboloranyl rings in 3 have geometries similar to those found in 2, C9 extends out of the plane by 40.2 while C25 lies 40.8 pm out of the corresponding plane. The dihedral angles between the butadiene and the nearest dioxaborolanyl rings are 22.2 and 48.7°, the larger angle corresponding to the ring nearer the twisted cyclopentyl group. Note that in the free ligand the corresponding angle is 94.4°, a configuration which is almost orthogonal but more transoid than *cisoid*. Three of the butadiene substituents in 3 are displaced toward Fe: B1 by 45.7 pm, C14 by 4.5 pm and B2 by 34.3 pm. C19 is displaced 14.0 pm away from Fe.

4. Supplementary material

Crystallographic data (excluding structure factors) for structures **2** and **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103316 and CCDC-103317, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + 44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk). Structure factors are available upon request from author J. K-B.

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References

- H. Reihlen, A. Gruhl, G. von Hessling, O. Pfrengle, Liebigs Ann. 482 (1930) 161.
- [2] (a) R.B. King, in: F.W. Grevels, I. Fischer (Eds.), The Organic Chemistry of Iron, Academic Press, NY, 1978. (b) A.J. Deeming, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 4, Chapter 31.3, Pergamon Press, NY, 1982. (c) R.C. Kerber, in: G. Wilkinson, F.G.A. Stone, E.W. Abel, (Eds.), Comprehensive Organometallic Chemistry, Vol. 7, Chapter 2, Pergamon, New York, 1995. D.F. Shriver and M.L. Bruce, Volume Eds.
- [3] (a) G. Desurmont, R. Klein, S. Uhlenbrock, E. Laloe, L. Deloux, D.M. Giolando, Y.W. Kim, S. Pereira, M. Srebnik, Organometallics 15 (1996) 3323. (b) R. Klein, S. Uhlenbrock, E. Gifford, G. Desurmont, D.M. Giolando, M. Srebnik, J. Organomet. Chem., submitted for publication.

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- [4] A.-M. Giroud-Godquin, P.M. Maitlis, Angew. Chem., Int. Ed. Engl. 30 (1991) 375.
- [5] H. Fleckner, F.-W. Grevels, D. Hess, J. Am. Chem. Soc. 106 (1984) 2027.
- [6] Gmelin's, Handbuch der anorganischen Chemie, Vol. B6, Springer, NY, 1981, p. 138.
- [7] L. Kruczynski, J. Takats, Inorg. Chem. 20 (1976) 299.
- [8] O.S. Mills, G. Robinson, Acta Crystallogr. 16 (1963) 758.
- [9] M.I. Davis, C.S. Speed, J. Organomet. Chem. 21 (1970) 401.
- [10] F.A. Cotton, V.W. Day, B.A. Frenz, K.I. Hardcastle, J.M. Troup, J. Am. Chem. Soc. 95 (1973) 4522.
- [11] F.H. Herbstein, M.G. Reiser, Acta Crystallogr., Sect. B 33 (1977) 3304.
- [12] G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemisty, Vol. 13, Pergamon, New York, 1995. M.L. Bruce, Volume Ed.