Metal Complexes of 1,4-Difluoro-2,3,5,6-tetramethyl-2,5-diboracyclohexa-1,4-diene, an Analogue of Duroquinone. Crystal Structure of Bis(1,4-difluoro-2,3,5,6-tetramethyl-1,4-diboracyclohexa-2,5-diene)-nickel(0)

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1,4-Difluoro-2,3,5,6-tetramethyl-1,4-diboracyclohexa-2,5-diene, (I), displaces carbon monoxide from metal carbonyls directly or on photolysis to form complexes including $[(C_4Me_4B_2F_2)Ni(CO)_2]$ (II), $[(C_4Me_4B_2F_2)_2Ni]$ (III), $[(C_4Me_4B_2F_2)(C_5H_5)Co]$, and $[(C_4Me_4B_2F_2)Fe(CO)_3]$. A single-crystal *X*-ray study of (III) shows it to have a sandwich structure with idealised D_{2d} symmetry, the nearly planar rings being conversely orientated. All six atoms of each ring are bonded to the metal. Both the molecular structure and spectroscopic properties of the complexes are remarkably like those of the isoelectronic complexes of duroquinone. Crystals of (III) are monoclinic, space group $C2/c$, a = 17·569(3), b = 6·671(1), c = 17·270(3) Å, β = 116·06(1)°, Z = 4. The structure was solved by the heavy-atom method and refined by least-squares techniques R 0·057 for 2165 independent reflections measured by diffractometer.

THE reaction of boron monofluoride with but-2-yne at low temperatures yields 1,4-difluoro-2,3,5,6-tetramethyl-1,4-diboracyclohexa-2,5-diene, (I). This has been shown spectroscopically[1] to be isostructural with the isoelectronic compound duroquinone. Transition-metal complexes of duroquinone are well known[2,3] and we have therefore explored the possibility of using (I) similarly as a ligand.

EXPERIMENTAL

All the compounds made were air-sensitive and were handled by standard techniques on a vacuum line or under dry nitrogen.

Mass spectra were obtained by use of an A.E.I. MS30 or a VG MM12 spectrometer, with a glass vacuum-line inlet system. I.r. spectra were measured on Perkin-Elmer 225 or 457 instruments for mulls, solutions, or films condensed on a cooled silver-chloride window under vacuum; i.r. data listed give only the more intense bands, for complete data see ref. 4. Raman spectra were measured on a Coderg PHO spectrometer. Most n.m.r. measurements were made with a Varian HA 100, but some were obtained by use of a Jeol JNM PS 100 Fourier-transform instrument.

Photolysis was carried out in Pyrex tubes by use of a medium-pressure 250 W mercury arc lamp.

Preparations and Characterizations.—The ligand $C_4Me_4B_2F_2$, (I), was prepared from but-2-yne and BF as described previously.[1] It was initially contaminated with small amounts of $C_4Me_4B_3F_5$, but this decomposed slowly to (I) with liberation of BF_3.

$[(C_4Me_4B_2F_2)Ni(CO)_2]$ (II).—(I) (1 mmol) and $Ni(CO)_4$

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[1] P. L. Timms, *J. Amer. Chem. Soc.*, 1968, **90**, 4585.

[2] H. W. Sternberg, R. Markly, and I. Wender, *J. Amer. Chem. Soc.*, 1958, **80**, 1009.

[3] G. N. Schrauzer, *Adv. Organometallic Chem.*, 1964, **2**, 1.

[4] P. Maddren, Ph.D. Thesis, Bristol University, 1975.

(1 mmol) were condensed with dry degassed toluene (1 ml) into a tube on a vacuum line. The tube was sealed and allowed to warm to room temperature. The solution became yellow in a few minutes and bubbles of gas were seen. After 30 min the tube was re-opened to the vacuum line and it was found that CO (*ca.* 1·8 mmol) had been evolved. All volatiles were pumped out of the tube and *yellow crystals* of (II) (0·8 mmol) were collected in a trap at −30 °C; traces of oily materials were removed by repeated fractionation. It was found impossible to separate (I) from (II) on the vacuum line, hence the use of excess of $Ni(CO)_4$ to ensure complete reaction of (I) (Found: C, 42·8; H, 4·05; Ni, 20·6. $C_{10}H_{12}B_2F_2NiO_2$ requires C, 42·52; H, 4·25; Ni, 20·79%). I.r. spectrum (film on cold AgCl plate): 2079vs, 2035vs, 1512m, 1454m, 1444m, 1373m, 1331m, 1308s, 1287vs, 1275sh, 1262s, 1197vs, 1073s, 1020m, 616sh, 607m, 598vs, 491m, and 462m cm^{-1}; Raman spectrum (CCl_4 solution): 2079vs (pol), 2035vs, 1517m (pol), 1374m, 1267s (pol), 1003m (pol), 616sh, 608s (pol), and 395m cm^{-1}. Mass spectrum, relative ion intensities: $[C_4Me_4B_2F_2Ni(CO)_2]^+$ 3, $(P - CO)^+$ 8, $(P - 2CO)^+$ 100, $(C_4Me_4B_2F_2)^+$ 14, and Ni^+ 16.

$[(C_4Me_4B_2F_2)_2Ni]$ (III).—A solution of (I) (1 mmol) and (II) (1 mmol) in toluene (1 ml) was photolysed for 12 h in a sealed tube. The yellow solution darkened and orange crystals were deposited. On opening the tube it was found that CO (1·5 mmol) had been evolved. Solvent was drained off and the crystals washed with light petroleum (b.p. 40—60 °C) and dried under vacuum to give an *orange solid* (0·75 mmol, 75%) sparingly soluble in non-polar solvents. I.r. spectrum (Nujol and hexachlorobutadiene mulls): 1494m, 1459m, 1454m, 1379m, 1364m, 1359sh, 1310s, 1290vs, 1263sh, 1254s, 1202m 1196s, 1075m, 610m, 593vs, and 496m cm^{-1}; Raman spectrum (solid): 1487s, 1464m, 1441m, 1428m, 1381s, 1363m, 1279m, 1022s, 997s, 968s, 613m, 606s, 503m, 378m, and 330vs cm^{-1}. Mass spectrum, relative ion intensities: $[(C_4Me_4B_2F_2)_2Ni]^+$ 89, $(C_4Me_4B_2F_2Ni)^+$ 100, $(C_4Me_4B_2F_2)^+$ 9, and Ni^+ 9; mass matching on parent, molecular ion ^{58}Ni, ^{11}B peak; *m/e* found 394·155, calc. 394·155.

$[(C_4Me_4B_2F_2)$(cyclo-octa-1,5-diene)Ni] (IV).—A solution of redistilled cyclo-octa-1,5-diene (0·2 mmol) and (II) (0·1 mmol) in toluene (0·5 ml) was irradiated for 12 h. Liberated CO, solvent, and excess of reactants were then pumped off to leave an *orange-yellow solid* (0·08 mmol, 80%). Mass spectrum, relative ion intensities: $[(C_4Me_4B_2F_2)(C_8H_{12})Ni]^+$ 79, $(P - C_8H_{12})^+$ 5, $(C_4Me_4B_2F_2)^+$ 31, and $(P - C_4Me_4B_2F_2)^+$ 100.

$[(C_4Me_4B_2F_2)(C_5H_5)Co]$ (V).—$[(C_5H_5)Co(CO)_2]$ (1 mmol) and (I) (1 mmol) were dissolved in toluene (2 ml) and the solution irradiated for 36 h. *Ca.* 1·5 mmol of CO were evolved. Solvent and excess of reactants were evaporated from the filtrate to leave a red air-sensitive *solid* which was recrystallized from cold light petroleum (0·09 mmol, 90%) (Found: C, 52·9; H, 6·00; Co, 20·0. $C_{13}H_{17}B_2F_2Co$ requires C, 53·1; H, 5·87; Co, 20·2%). I.r. spectrum (CCl_4 solution): 1466m, 1442m, 1405m, 1372m, 1325s, 1309vs, 1277s, 1264s, 1194m, 1187s, 1069m, and 823m cm^{-1}. Mass spectrum, relative ion intensities: $[(C_4Me_4B_2F_2)(C_5H_5)Co]^+$ 100, $(P - CH_3)^+$ 42, $(P - 2CH_3)^+$ 38, $(P - 3CH_3)^+$ 24, $(P - C_5H_5)^+$ 3, $(C_4Me_3B_2F_2Co)^+$ 7, $(P - C_4Me_4B_2F_2)^+$ 43, and Co^+ 15.

$[(C_4Me_4B_2F_2)Fe(CO)_3]$ (VI).—A toluene solution (2 ml) containing $Fe(CO)_5$ (1 mmol) and (I) (1 mmol) was irradiated for 12 h; the solution darkened and small orange crystals appeared {$[Fe_2(CO)_9]$?}. The solution was then evaporated on a vacuum line and the volatile product collected in a trap at −20 °C as *orange crystals* which were purified by resublimation at room temperature (0·08 mmol, 80%) (Found: C, 42·9; H, 4·00. $C_{11}H_{12}B_2F_2FeO_3$ requires C, 42·9; H, 3·94%). I.r. spectrum (solutions in methyl bromide and cyclohexane): 2063vs, 2006vs, 1472m, 1460m, 1453m, 1441m, 1376m, 1329vs, 1312vs, 1286s, 1274s, 1072s, 1020m, 626s, 594m, and 559m cm^{-1}; Raman spectrum (toluene solution): 2060vs (pol) and 2001vs cm^{-1}. Mass spectrum: $[(C_4Me_4B_2F_2)Fe(CO)_3]^+$ 18, $(P - CO)^+$ 20, $(P - 2CO)^+$ 25, $(P - 3CO)^+$ 95, and $(C_4Me_4B_2F_2)^+$ 100.

Crystal Structure of (III)

Crystals were yellow prisms elongated along *b*. The crystal chosen, of dimensions 0·10 × 0·13 × 0·35 mm, was sealed in a Lindemann glass tube and mounted on a Syntex $P2_1$ four-circle diffractometer. By the procedure described in ref. 5, 3999 independent intensities (complete for $3·7° < 2\theta < 70·0°$) were collected with a 2θ—θ scan at speeds within the range 0·03255 to 0·977° s^{-1}. 2165 Reflections having $I \geqslant 2·5\sigma(I)$ were considered observed and were used in the refinement.

Standard reflection analysis indicated considerable *X*-ray damage to the crystal. During the 164 h of data collection, reflections 3,1,0, 0,0,12, and 12,0,0 decayed by 32—36%, but reflection 0,4,0 decayed by only 19%. A linear correction for 32% decay was made (an exponential correction fitted the data slightly worse), improving the standard deviation for the average intensity of each reflection by a factor of *ca.* 1·7. Out of 295 systematic absences also recorded, seven were significantly below zero $[I < -2·5\sigma(I)]$ and four would have been 'observed' under the 2·5σ criterion. The ratio $I:\sigma$ ranged from −5·0 to 3·0.

Crystal Data.—$C_{16}H_{24}B_4F_4Ni$, $M = 394·3$, Monoclinic, $a = 17·569(3)$, $b = 6·671(1)$, $c = 17·270(3)$ Å, $\beta = 116·06(1)°$, $Z = 4$, $D_c = 1·44$ g cm^{-3}, (D_m not measured), $F(000) = 816$. Space group $C2/c$. Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0·71069$ Å, μ(Mo-K_α) = 11·02 cm^{-1} (but see later). Space group $C2/c$.

Solution and Refinement of the Structure.—The Ni atom was found by Patterson methods to lie on the two-fold axis in space group $C2/c$. The possibility of space group *Cc* was ruled out by the subsequent structure solution, which used electron-density difference syntheses and least-squares refinement techniques. All non-hydrogen atoms were found on a difference synthesis phased on the metal atom. Two cycles of full-matrix isotropic refinement with unit weights led to *R* 0·139 (*R′* 0·150); inclusion of anisotropic thermal parameters for all non-hydrogen atoms and anomalous dispersion for the nickel atom caused the refinement to converge at *R* 0·098 (*R′* 0·121). Probable positions for all the hydrogen atoms were apparent from a further difference synthesis, and their refinement with isotropic temperature factors (giving a total of 162 variables) and a weighting scheme of the form: $1/w = a + b|F| + c|F|^2 + d|F|^{-1}$, where $a = -0·47$, $b = -0·05$, $c = 0·0116$, and $d = 179$, led to *R* 0·086 (*R′* 0·101). The largest peaks remaining on the difference map were located at (i) *ca.* *b*/2 from the Ni atom (2·1 e$Å^{-3}$) and (ii) around and in the plane of the ring atoms (0·4—0·9 e$Å^{-3}$). There were also a number of medium to strong intensities which showed large positive $(F_o - kF_c)$.

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[5] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

The inter- is almost identical to the intra-molecular ring–ring distance, a condition peculiarly favouring disorder in the nickel atom position. It is also known[6] that in crystals of [$(Me_4C_4B_2F_2)Ni(CO)_2$] extra molecules of ligand are incorporated to give an overall stoicheiometry [$(Me_4C_4B_2F_2)Ni(CO)_2$],$(Me_4C_4B_2F_2)$. The type (i) peak on the final electron-density difference synthesis, midway between rings of different molecules, prompted us to attempt a better refinement from disordered models, by introducing a second Ni atom into this vacant site. Three models were attempted: (1) refinement of the metal-population parameters with the constraint that their sum be unity (166 variables), (2) free refinement of the metal population parameters (167 variables), and (3) free refinement of the population parameter for the original Ni site only (163 variables). In each case the thermal parameters U_{11} and U_{33} were constrained to be the same for both Ni atoms. Electron-density difference syntheses after each refinement showed that the peak was still present after (3), disappeared after (2), and was replaced by a larger hole after (1). All three refinements reduced type (ii) peaks to at least half their original size. (2) also gave the best agreement indices at R 0·064 (R' 0·078), but the population parameter of the Ni atom fell to *ca.* 0·8 with a corresponding increase in the scale factor. Refinement was completed with a simpler (and better) weighting scheme of the type: $1/w = (A/F)^2$, $F < A$; $1/w = (F/A)^2$, $F > A$, with A = 17. Freeing the thermal parameters from their constraints (169 variables) caused this refinement to converge after two cycles at R 0·057 (R' 0·070). The mean shift-to-error ratio in the last cycle was 0·05, maximum 0·45. The population parameters for Ni(1) and Ni(2) were 0·772(4) and 0·026(2), and a final difference-Fourier synthesis showed residual densities of 0·6 eÅ^{-3} around Ni(1), no significant peak or hole around Ni(2), and a maximum of 0·3 eÅ^{-3} in the plane of the ligand. Refinement with scattering factors for

TABLE 1

Atomic positional and thermal parameters,* with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$U \times 10^2/Å^2$
Ni(1)	0·5000	0·5993(1)	0·2500	*
Ni(2) disorder	0·5000	0·0950(23)	0·2500	*
B(1)	0·5901(2)	0·8515(5)	0·2808(2)	*
F(1)	0·6757(1)	0·8562(4)	0·3109(2)	*
C(1)	0·5342(2)	0·8411(4)	0·1833(2)	*
C(10)	0·5745(3)	0·8353(8)	0·1218(3)	*
C(2)	0·5537(2)	0·8401(4)	0·3468(2)	*
C(20)	0·6121(3)	0·8327(7)	0·4426(2)	*
B(2)	0·5130(3)	0·3467(5)	0·3375(2)	*
F(2)	0·5257(2)	0·3428(4)	0·4210(1)	*
C(3)	0·5903(2)	0·3576(4)	0·3187(2)	*
C(30)	0·6792(3)	0·3656(8)	0·3921(4)	*
C(4)	0·5777(2)	0·3566(4)	0·2336(2)	*
C(40)	0·6519(3)	0·3635(7)	0·2114(4)	*
H(11)	0·545(3)	0·726(10)	0·067(4)	8·5(18) †
H(12)	0·634(4)	0·797(9)	0·153(3)	6·9(16)
H(13)	0·564(3)	0·949(9)	0·088(3)	7·4(18)
H(21)	0·674(4)	0·809(9)	0·454(3)	7·1(17)
H(22)	0·594(3)	0·724(9)	0·474(3)	6·3(14)
H(23)	0·609(3)	0·958(9)	0·470(3)	7·4(17)
H(31)	0·715(4)	0·480(11)	0·387(4)	8·7(19)
H(32)	0·681(4)	0·383(9)	0·445(4)	7·5(19)
H(33)	0·706(3)	0·230(9)	0·395(3)	5·6(13)
H(41)	0·683(3)	0·226(10)	0·235(4)	7·7(17)
H(42)	0·631(4)	0·398(10)	0·146(5)	9·9(23)
H(43)	0·698(3)	0·476(10)	0·252(3)	7·5(16)

* Anisotropic thermal parameters in the form: $\exp\{-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12} + hla^*c^*U_{13} + klb^*c^*U_{23})\}$, with parameters ($\times 10^3$) (for Ni $\times 10^4$). † $B = 8\pi^2U$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	306(3)	377(4)	291(3)	0	135(2)	0
Ni(2)	33(8)	22(7)	14(6)	0	10(5)	0
B(1)	39(2)	51(2)	48(2)	−04(1)	19(1)	−06(1)
F(1)	44(1)	92(2)	87(2)	−10(1)	26(1)	−12(1)
C(1)	55(2)	50(2)	43(1)	−04(1)	30(1)	01(1)
C(10)	90(3)	86(3)	69(2)	−10(3)	58(2)	00(2)
C(2)	53(2)	47(2)	34(1)	00(1)	16(1)	−05(1)
C(20)	81(3)	84(3)	35(1)	02(2)	11(2)	−10(2)
B(2)	62(2)	49(2)	44(2)	05(2)	24(2)	07(1)
F(2)	119(2)	94(2)	50(1)	10(2)	41(1)	17(1)
C(3)	40(1)	45(2)	52(2)	06(1)	08(1)	02(1)
C(30)	52(2)	87(3)	80(3)	12(2)	−07(2)	00(3)
C(4)	45(2)	45(2)	66(2)	01(1)	30(1)	−07(1)
C(40)	73(3)	73(3)	136(5)	00(2)	74(3)	−09(3)

TABLE 2

Interatomic distances (Å) and bond angles (°) *

(*a*) Distances

(i) Metal–ring

Ni(1)–B(1)	2·209(3)	Ni(1)–B(2)	2·207(4)
Mean Ni(1)–B 2·208			
Ni(1)–C(1)	2·213(3)	Ni(1)–C(3)	2·208(3)
Ni(1)–C(2)	2·208(3)	Ni(1)–C(4)	2·215(4)
		Mean Ni(1)–C	2·211

(ii) Ring

B(1)–F(1)	1·358(4)	C(1)–C(2$^{\mathrm{I}}$)	1·396(4)
B(2)–F(2)	1·395(5)	C(3)–C(4)	1·387(5)
Mean B–F	1·359	Mean C–C(ring)	1·392
B(1)–C(1)	1·532(4)	C(1)–C(10)	1·515(8)
B(1)–C(2)	1·534(6)	C(2)–C(20)	1·517(4)
B(2)–C(3)	1·531(6)	C(3)–C(30)	1·519(5)
B(2)–C(4$^{\mathrm{I}}$)	1·528(4)	C(4)–C(40)	1·512(8)
Mean B–C	1·531	Mean C–C(Me)	1·516
C(10)–H(11)	1·12(6)	C(30)–H(31)	1·02(7)
C(10)–H(12)	0·98(6)	C(30)–H(32)	0·91(8)
C(10)–H(13)	0·92(6)	C(30)–H(33)	1·02(6)
C(20)–H(21)	1·03(7)	C(40)–H(41)	1·06(6)
C(20)–H(22)	1·03(6)	C(40)–H(42)	1·05(8)
C(20)–H(23)	0·98(6)	C(40)–H(43)	1·10(6)
		Mean C–H	1·02

(*b*) Angles

C(1)–B(1)–C(2)	122·6(3)	B(2)–C(3)–C(30)	120·4(4)
B(1)–C(2)–C(1$^{\mathrm{I}}$)	118·5(2)	C(3)–C(4)–C(40)	120·9(3)
B(1)–C(1)–C(2$^{\mathrm{I}}$)	118·6(3)	B(2$^{\mathrm{I}}$)–C(4)–C(40)	120·6(4)
C(2$^{\mathrm{I}}$)–C(1)–C(10)	121·3(3)	C(3)–B(2)–F(2)	118·7(3)
B(1)–C(1)–C(10)	120·0(3)	C(4$^{\mathrm{I}}$)–B(2)–F(2)	118·6(4)
C(1$^{\mathrm{I}}$)–C(2)–C(20)	120·9(4)	B(1)–Ni(1)–B(1$^{\mathrm{I}}$)	80·8(1)
B(1)–C(2)–C(20)	120·6(3)	C(1)–Ni(1)–C(1$^{\mathrm{I}}$)	86·4(1)
C(1)–B(1)–F(1)	119·3(4)	C(2)–Ni(1)–C(2$^{\mathrm{I}}$)	86·7(1)
C(2)–B(1)–F(1)	118·0(3)	X–Ni(1)–X$^{\mathrm{I}}$	80·5(1)
C(3)–B(2)–C(4$^{\mathrm{I}}$)	122·5(3)	B(2)–Ni(1)–B(2$^{\mathrm{I}}$)	80·4(1)
B(2)–C(3)–C(4)	118·8(2)	C(3)–Ni(1)–C(3$^{\mathrm{I}}$)	86·1(1)
B(2$^{\mathrm{I}}$)–C(4)–C(3)	118·4(4)	C(4)–Ni(1)–C(4$^{\mathrm{I}}$)	86·1(1)
C(4)–C(3)–C(30)	120·8(4)	Y–Ni(1)–Y$^{\mathrm{I}}$	79·4(1)
Mean H–C–H	108	Mean C–C–H	111

(*c*) Non-bonded contacts

(i) Intramolecular

H(31) · · · H(43)	2·21(9)	F(1) · · · H(21)	2·50(7)
H(11) · · · H(22$^{\mathrm{I}}$)	2·22(8)	F(1) · · · H(12)	2·52(6)
F(2) · · · H(42$^{\mathrm{I}}$)	2·49(7)		

(ii) Intermolecular

B(1) · · · C(3$^{\mathrm{II}}$)	3·439(5)	C(2) · · · C(3$^{\mathrm{II}}$)	3·583(4)
B(1) · · · C(4$^{\mathrm{II}}$)	3·451(5)	B(2$^{\mathrm{II}}$) · · · C(2)	3·443(5)
C(1) · · · C(4$^{\mathrm{II}}$)	3·548(4)	H(11) · · · F(2$^{\mathrm{III}}$)	2·44(7)

X and Y are the midpoints of the C=C ring bonds. Superscripts refer to the following symmetry operations: I $1 - x, y, \frac{1}{2} - z$, II $x, y + 1, z$, III $x, 1 - y, z - \frac{1}{2}$.

* Estimated standard deviations include cell-parameter errors.

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[6] I. Kerr and P. Woodward, unpublished work.

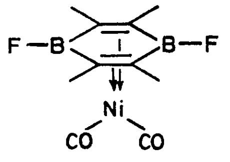
Ni^{2+} in place of Ni^0 showed no improvement in the agreement index.

Our interpretation of the results (see later) is that the crystal must contain, on average, about two extra ligand molecules for every four molecules of the sandwich compound (or, on average, one in five Ni atoms is missing). The Ni atoms which are present are only slightly disordered (*ca.* 3%). In the light of this probable conclusion, the crystal data should perhaps be: $C_{16}H_{24}B_4F_4Ni_{0.8}$, M = 382·4, D_c = 1·40 g cm^{-1}, $F(000)$ = 793·4, $\mu(\text{Mo-}K_\alpha)$ = 9·13 cm^{-1}.

Positional and thermal parameters are listed in Table 1 and interatomic distances in Table 2. No absorption correction was applied, and the scattering factors of ref. 7 were used for neutral nickel, fluorine, carbon, and boron, of ref. 8 for hydrogen, and of ref. 9 for Ni^{2+}. Calculations were made by use of the ' *X*-Ray ' system [10] on a CDC 7600 computer at the University of London. Observed and calculated structure factors and details of least-squares planes are listed in Supplementary Publication No. SUP 21263 (15 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Complexes with Nickel.—There is a rapid reaction between (I) and $[Ni(CO)_4]$ in toluene solution at room temperature. Carbon monoxide is liberated and the yellow solid formed is only slightly less volatile than is (I). The mass spectrum indicates a formula $[(C_4Me_4B_2F_2)Ni(CO)_2]$. Carbonyl stretching bands are found at 2037 and 2080 cm^{-1} in both the i.r. and Raman spectrum, and the ^{1}H, ^{19}F, and ^{11}B n.m.r. spectrum in each case shows a single resonance, although the ^{19}F and ^{11}B resonances are substantially shifted from the resonances in (I) (Table 4). This evidence suggests the structure (II), which is confirmed by a single-crystal *X*-ray study.[6] The compound is air sensitive, but stable in an inert atmosphere at room temperature. The corresponding duroquinone complex has not been reported, bis(duroquinone)nickel being the only isolable product of the duroquinone–$[Ni(CO)_4]$ reaction.



(II)

The two molecules of carbon monoxide in (II) are not displaced by treatment with excess of (I) in toluene at temperatures up to 100 °C, but u.v. irradiation causes a rapid reaction and precipitation of orange-brown needles. Mass spectrometry indicates the composition $[(C_4Me_4B_2F_2)_2Ni]$. The low solubility of the compound in most solvents makes n.m.r. measurements difficult but single ^{1}H, ^{19}F, and ^{11}B resonances have been observed with chemical shifts close to those for (II), suggesting a sandwich structure like that of bis(duroquinone)nickel. The structure (III) is confirmed by the single-crystal *X*-ray study (see Figures 1 and 2 and following discussion).

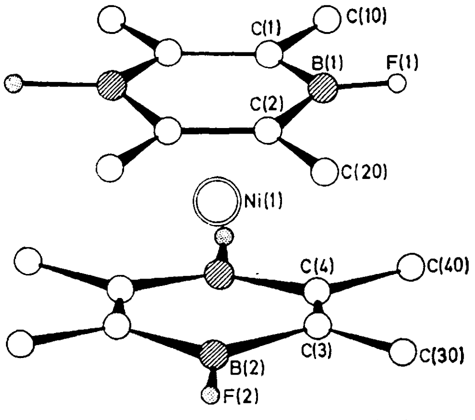


FIGURE 1 The molecule of (III) seen perpendicular to the B(1), B(2), B(1)′ plane, showing the atom numbering system

The compound (III), is thermally stable up to at least 150 °C. It is attacked by air, although large crystals are destroyed quite slowly.

Photolysis of a mixture of (II) and cyclo-octa-1,5-diene in toluene causes displacement of carbon monoxide and formation of a yellow solid which has been shown spectroscopically to be $[(C_4Me_4B_2F_2)(C_8H_{12})Ni]$, apparently an analogue of (cyclo-octa-1,5-diene)duroquinonenickel.[11] The compound is only slightly volatile under vacuum and decomposes with liberation of cyclooctadiene above 180°. There was no reaction between (III) and cyclo-octa-1,5-diene when the two compounds were heated together at 80—100 °C for 2 h. This is in contrast to the behaviour of bis(duroquinone)nickel which reacts with cyclo-octa-1,5-diene on heating to give (cyclo-octadiene)duroquinonenickel.

Complexes with Other Metals.—Photolysis of a toluene solution containing equimolar amounts of (I) and either dicarbonyl(cyclopentadienyl)cobalt or pentacarbonyliron, causes evolution of carbon monoxide and in each case a complex of (I) can be isolated in high yield. Spectroscopic evidence shows that the cobalt complex is $[(C_4Me_4B_2F_2)(C_5H_5)Co]$ and the iron complex is $[(C_4Me_4B_2F_2)Fe(CO)_3]$. Both compounds are apparently structural analogues of known duroquinone complexes.[2,12] The iron complex is stable at room temperature but loses carbon monoxide >50 °C *in vacuo*.

The iron complex is not formed when a mixture of pentacarbonyliron, diboron tetrafluoride, and but-2-yne react together. It was hoped that the diboron tetrafluoride would react with the iron carbonyl to form an unstable complex, which would then react with the alkyne to

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* For details see Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

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form the carborane complex. The preparation of tricarbonyl(duroquinone)iron by photolysis of a mixture of but-2-yne and $[Fe(CO)_5]$ is well known.[2]

Structures, Spectra, and Bonding.—The molecular configuration of (III) is shown, with the atom numbering system, in Figure 1. The nickel atom is sandwiched between two almost planar rings with converse orientation, in a distorted tetrahedral environment. The molecule has idealised symmetry D_{2d}. The mode of packing of the molecules in the monoclinic unit cell is shown in Figure 2. The perpendicular distance between the rings (*ca.* 3·3 Å) is of the same order as that found in BN or in a number of aromatic donor–acceptor complexes. The low volatility and sparing solubility of (III) may be dependent on these features. Each of the co-ordinated rings shows many of the structural features reported for duroquinone co-ordinated to nickel.[13,14]

The bond lengths of the free ligand (I) are known from a preliminary study of a crystal containing both (I) and (II).[6] The main changes in (I) after complex formation with nickel in (III) † are a lengthening of the C–C double bonds from 1·35 to 1·39 Å, lengthening of the B–F bonds from 1·30 to 1·36 Å, and shortening of the B–C ring bonds from 1·56 to 1·53 Å. The B–F groups are slightly bent out of the plane of the four carbon atoms in the ring, away from the nickel. Both the bond-length changes and the distortion from planarity in the ring mimic the changes which occur in duroquinone when it forms the complexes (cyclo-octa-1,5-diene)duroquinonenickel [13] and bis(duroquinone)nickel.[14] The mean nickel–ring-atom distance (2·21 Å) is the same as in the latter complex, which points to similar overall bonding properties for the two ligands. As the distances between the nickel atom and each of the ring atoms are almost equal, the rings must be bonded to the metal through all six atoms. In a qualitative view of the bonding, the carbon–carbon double bonds donate electrons to the nickel while vacant orbitals around the boron atoms accept electrons from the filled *d* orbitals on the nickel.

If the molecular-orbital scheme calculated by Schrauzer and Thyret for bis(duroquinone)nickel(0) can be taken as a guide,[15] back-donation of the *d* electrons from the nickel to the C_4B_2 rings will be mainly into a molecular orbital which is bonding with respect to the B–C and antibonding with respect to the B–F and olefinic C–C bonds. This would account for the observed differences in length of these bonds for the free and co-ordinated ligand. The more puckered ligand in bis(duroquinone)nickel suggests more involvement in back-bonding for the $>$B–F group than for the $>$C=O group, associated with a reduced olefin contribution to the antibonding orbitals of (I). As a result, the Ni–C(olefin) distance in the bisduroquinone complex [14] is 0·04 Å shorter, and the Ni–C(O) distance 0·10 Å longer, than the corresponding bonds in (III), notwithstanding the larger radius expected for boron (which may be reduced by the inductive effect of the attached fluorine atom).

Table 3 shows the frequencies of the bands tentatively assigned to the asymmetric C=C and ^{11}B–F stretching frequencies for the free and co-ordinated ligand. The shift to lower frequency on co-ordination corresponds to the lengthening of these bonds from (I) to (III). The marked upfield shifts in the ^{19}F and ^{11}B n.m.r. resonances (Table 4) which occur when (I) forms a metal complex point to an increase in the electron density on the boron and fluorine atoms. This is consistent with

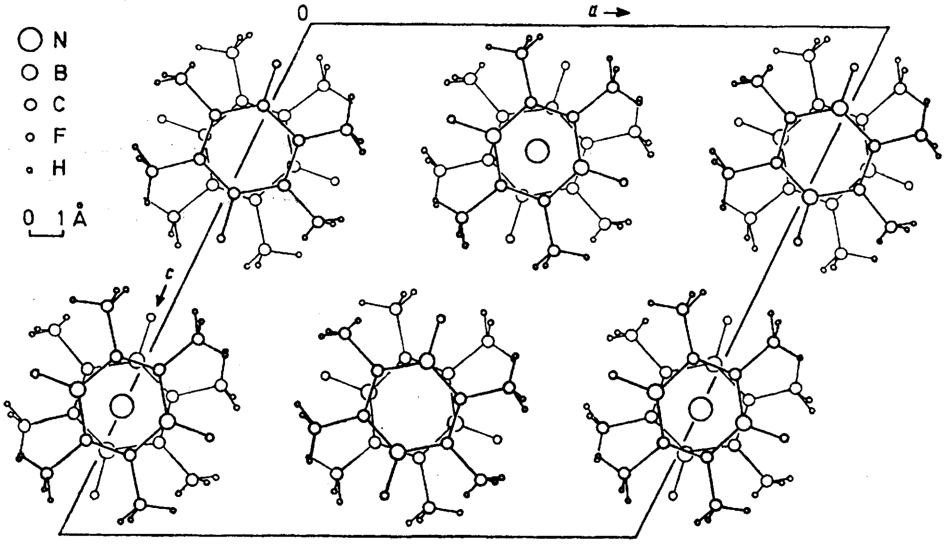

FIGURE 2 The contents of the unit cell of (III) seen in projection down *b* looking towards the origin

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† For a full discussion of the possible effects of molecular disorder on the bond lengths in (III) see A. Modinos, Ph.D. Thesis, University of Bristol, 1974.

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the observation from the *X*-ray structure of (III) that the boron atoms of the ligand are bonded to the metal. The positions of the ^{19}F resonances correspond better to fluorine atoms joined to four- rather than to three-co-ordinate boron. The upfield shift of the ^{19}F resonance for the nickel complexes is less than for the iron and cobalt complexes. It is known [16,17] that in cobalt and rhodium complexes, the duroquinone rings are markedly less planar than in duroquinone–nickel complexes,[13,14] reflecting the reduced contribution of $\rangle$C=O orbitals to the ligand antibonding MO's. The extra distortion may also occur in the iron and cobalt complexes of (I), for which the i.r. spectra indicate stronger B–F but weaker C–C bonds compared with (III), and the underlying electronic changes could cause the ^{19}F chemical shifts. The nickel–ring-atom bonds for complexes of duroquinone are known to be longer than comparison with Co and Rh complexes would suggest. Schrauzer and Thyret [12] have discussed the reason for this difference in MO terms and they argue that the duroquinone–cobalt bonding is stronger than the duroquinone–nickel bonding. The mass spectrum of [($C_4Me_4B_2F_2$)(C_5H_5)Co] shows loss of successive methyl groups from the co-ordinated ring, an ionization process not found in the nickel complexes; the observation could indicate stronger ring–cobalt than –nickel bonding.

TABLE 3

Asymmetric C=C and ^{11}B–F stretching frequencies (cm^{-1})

	ν(C=C)	ν(^{11}B–F)
(I)	1576	1362
(II)	1511	1287
(III)	1497	1294
(V)	1465	1307
(VI)	1474	1312

TABLE 4

N.m.r. data for $C_4Me_4B_2F_2$ and complexes (in benzene soln)

Compound	^{1}H/p.p.m.[a]	^{19}F/p.p.m.[b]	^{11}B/p.p.m.[c]
(I)	−1·67	67·8	−40·2
(III)	−1·66	142·7	−21·7
(II)	−1·74	144·8	−24·9
(VI)	−1·52	161·0	−22·7
(V)	−1·69 −3·92 [d]	161·2	−23·1
(IV)	−1·70 −2·31 −3·98 [e]		−22·0

[a] From tetramethylsilane. [b] From trichlorofluoromethane. [c] From trifluoroboron etherate. [d] Ratio 12 : 5. [e] Ratio 3 : 2 : 1.

The strong band at 2080 cm^{-1} in the i.r. spectrum of (II) is assigned to the symmetric A_1 CO-stretching mode. This is at slightly higher frequency than the corresponding A_1 mode of [Ni(CO)$_4$] but slightly lower than the frequency for [(PF_3)$_2$Ni(CO)$_2$]. Force constants calculated by use of the Cotton–Kraihanzel approximations follow the same sequence, with the value for (II) falling between those of [Ni(CO)$_4$] and [(PF_3)$_2$Ni(CO)$_2$]. These results imply that (I) is a rather stronger π acceptor than CO but less strong than PF_3. The CO-stretching bands in [($C_4Me_4B_2F_2$)Fe(CO)$_3$] (2061 and 2003 cm^{-1}) are close to those in tricarbonyl(duroquinone)iron (2066 and 2012 cm^{-1}).

The behaviour of (I) and duroquinone as ligands are more closely comparable than we had expected from the relative electronegativities of the atoms in the isoelectronic groups $\rangle$C=O and $\rangle$B–F. The electron-density changes which occur in duroquinone and (I) on complex formation must compensate for the initial differences between the two ring systems. It should be possible to form complexes of (I) with the more electropositive transition metals which are oxidised by duroquinone.

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