Crystal Structure of Dicarbonyl(1,4-difluoro-2,3,5,6-tetramethyl-1,4-diboracyclohexa-1,5-dienyl)nickel(0): A Complex with a Ligand analogous to Duroquinone

By **Judith A. K. Howard, Ian W. Kerr,** and **Peter Woodward,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Crystals of the title compound were found to contain two crystallographically distinct molecules of free ligand for every two molecules of the nickel dicarbonyl complex. These crystals were monoclinic, space group *A*2/*m*, with $Z = 4$, in a unit cell of dimensions $a = 11.904(7)$, $b = 15.505(8)$, $c = 12.584(4)$ Å, $\beta = 110.07(4)°$. The structure has been elucidated by conventional heavy-atom methods from 950 independent diffracted intensities measured on a diffractometer and refined to *R* 0.069 (*R'* 0.067). The nickel atom is in a tetrahedral environment if the main bonding directions are considered to be to the two carbonyl groups and to the ethylenic bonds of the diborahexadiene ring, although all six atoms of the ring are within bonding distance of the metal atom. As in the sandwich analogue, $[Ni(C_4Me_4B_2F_2)_2]$, the ligand ring is significantly non-planar, the B atoms bending away from the metal. Differences in bond lengths between the free ligand, the carbonyl complex, and the sandwich compound are discussed.

We have already reported the *X*-ray structure of the sandwich compound $[Ni(C_4Me_4B_2F_2)_2]$ and compared this with the formally analogous complexes of duroquinone ($C_6Me_4O_2$).[1] Here we describe a further structural investigation of a carbonyl complex of the same ligand. It transpired that the crystals investigated contained not only $[Ni(C_4Me_4B_2F_2)(CO)_2]$ but also molecules of the free ligand. We are able, therefore, to compare the geometry of the ligand in the uncomplexed, singly bound, and doubly bound states.

EXPERIMENTAL

Crystals of $[Ni(C_4Me_4B_2F_2)(CO)_2]$ were prepared as described earlier;[1] they are air-sensitive. Several were mounted individually in sealed tubes on a vacuum line. A suitable single crystal was found by *X*-ray examination and mounted on a Syntex $P2_1$ four-circle diffractometer, according to methods already described.[2] No attempt was made to measure the crystal dimensions accurately, and as μ(Mo-K_α) was 9.4 cm^{-1} an absorption correction was considered unnecessary. The density of the crystal was estimated by analogy with $[Ni(C_4Me_4B_2F_2)_2]$.[1] The number of reflections for which $I > 2.5\sigma(I)$ in the range $3.7° < 2\theta < 50°$ was 950, and only these were used in the structure solution and refinement. Three check reflections were remeasured after every 30 intensity measurements.

Crystal Data.—$C_{18}H_{24}B_4F_4NiO_2$, $M = 450.1$, Monoclinic, $a = 11.904(7)$, $b = 15.505(8)$, $c = 12.584(4)$ Å, $\beta = 110.07(4)°$, $Z = 4$, $D_c = 1.37$ g cm^{-3}, D_m not measured, $F(000) = 928$. Space group *A*2/*m* (C^3_{2h}, No. 12). Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å; μ(Mo-K_α) = 9.4 cm^{-1}.

Structure Solution.—The structure was solved by conventional heavy-atom methods, and in the final refinement (by full-matrix least squares) anisotropic thermal parameters were used for the nickel and fluorine atoms, and for the carbon and oxygen atoms of the carbonyl groups. Hydrogen atoms were incorporated at positions estimated from the electron-density maps, but neither their positional nor thermal parameters were refined. Weights were applied according to the scheme $1/w = \sigma(F)^2$. Refinement converged at *R* 0.069 (*R'* 0.067) and a final electron-density difference synthesis showed no peaks > 0.7 or < -1.4 eÅ^{-3}, with an average density very much less than this. Positional and thermal parameters are in Table 1, interatomic

TABLE 1

Atomic positional (fractional co-ordinates) and thermal parameters, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	$10^2U/Å^2$ *
Co-ordination complex				
Ni	0.22597(14)	0.0	0.42323(11)	†
C(1)	0.2794(7)	0.0933(5)	0.5119(6)	†
O(1)	0.3161(6)	0.1495(4)	0.5690(4)	†
B(1)	0.1469(8)	0.0899(5)	0.2749(6)	4.6(2)
F(1)	0.1448(4)	0.1801(2)	0.2716(3)	†
C(2)	0.0472(6)	0.0446(4)	0.3038(4)	4.2(2)
C(3)	−0.0494(7)	0.0942(5)	0.3298(6)	7.0(2)
H(31)	−0.0349	0.1384	0.3229	6.3
H(32)	−0.0906	0.0566	0.3848	6.3
H(33)	−0.1132	0.0883	0.2697	6.3
C(4)	0.2558(6)	0.0451(4)	0.2635(5)	6.3
C(5)	0.3614(7)	0.0957(6)	0.2528(6)	6.3
H(51)	0.3367	0.1000	0.1982	6.3
H(52)	0.4215	0.0779	0.3079	6.3
H(53)	0.3766	0.1401	0.3046	6.3
Free ligand (A)				
B(2)	0.4200(12)	0.0	0.8858(10)	5.6(4)
F(2)	0.3536(6)	0.0	0.7789(4)	†
C(6)	0.4629(6)	0.0893(4)	0.9474(5)	4.7(2)
C(7)	0.4119(8)	0.1725(6)	0.8773(7)	8.4(3)
H(71)	0.4017	0.2000	0.9253	6.3
H(72)	0.3980	0.1400	0.8600	6.3
H(73)	0.4891	0.1800	0.9625	6.3
Free ligand (B)				
B(3)	0.1110(13)	0.0	−0.0190(10)	5.2(3)
F(3)	0.2108(6)	0.0	−0.0391(6)	†
C(8)	0.0530(5)	0.0883(4)	−0.0081(5)	3.9(2)
C(9)	0.1188(7)	0.1720(5)	−0.0145(6)	7.1(2)
H(91)	0.1782	0.1506	0.0000	6.3
H(92)	0.1179	0.1800	−0.0847	6.3
H(93)	0.0679	0.2400	−0.0271	6.3

* $B = 8\pi^2U$. † Anisotropic thermal parameters in the form: $\exp\{-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]\}$, with parameters ($\times 10^2$):

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	5.20(11)	4.86(8)	3.81(7)	0.0	1.12(6)	0.0
C(1)	7.0(7)	8.3(7)	4.6(5)	−0.8(6)	0.3(4)	0.9(5)
O(1)	12.2(6)	7.6(4)	6.9(4)	−0.8(4)	0.6(5)	−2.4(3)
F(1)	9.8(4)	3.7(2)	7.7(3)	−0.3(2)	3.2(3)	−0.3(2)
F(2)	9.3(5)	6.9(4)	4.8(3)	0.0	0.2(3)	0.0
F(3)	6.3(6)	8.6(5)	11.5(6)	0.0	5.6(4)	0.0

Values for which no standard deviation is given have been treated as invariant in the least-squares cycles.

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[1] P. S. Maddren, A. Modinos, P. L. Timms, and P. Woodward, *J.C.S. Dalton*, 1975, 1272.

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

distances and bond angles in Table 2. The atomic scattering factors used were those of ref. 3 for nickel (corrected for anomalous dispersion),[4] boron, carbon, fluorine, and oxygen, and those of ref. 5 for hydrogen. All computational work was carried out at the University of London Computing Centre with the '*X*-Ray' System of programmes.[6] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21504 (10 pp., 1 microfiche).*

TABLE 2

Bond lengths (Å) and angles (°)

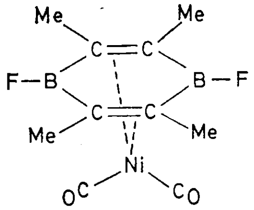
(*a*) Distances			
(i) Co-ordination complex			
Ni–C(1)	1.804(7)	B(1)–C(2)	1.531(10)
C(1)–O(1)	1.117(8)	B(1)–C(4)	1.524(10)
Ni–B(1)	2.268(6)	C(2)–C(2′)	1.388(7)
Ni–C(2)	2.253(5)	C(4)–C(4′)	1.402(7)
Ni–C(4)	2.268(6)	C(2)–C(3)	1.511(13)
B(1)–F(1)	1.385(8)	C(4)–C(5)	1.520(13)
[Mean C=C 1.39_5; C–B 1.52_7; B–F 1.38_6]			
(ii) Free ligand (A)			
B(2)–F(2)	1.306(10)	C(6)–C(6′)	1.329(7)
B(2)–C(6)	1.577(7)	C(6)–C(7)	1.524(14)
(iii) Free ligand (B)			
B(3)–F(3)	1.303(15)	C(8)–C(8′)	1.350(8)
B(3)–C(8)	1.558(8)	C(8)–C(9)	1.523(11)
[Mean C=C 1.33_9; C–B 1.56_7; B–F 1.30_5]			
(*b*) Angles			
(i) Co-ordination complex			
Ni–C(1)–O(1)	117.5(6)	C(1)–Ni–C(1′)	106.6(3)
F(1)–B(1)–C(2)	117.6(6)	F(1)–B(1)–C(4)	117.9(6)
B(1)–C(2)–C(3)	122.0(6)	B(1)–C(4)–C(5)	121.4(6)
C(3)–C(2)–C(2′)	120.3(6)	C(5)–C(4)–C(4′)	121.1(6)
C(2′)–C(2)–B(1)	117.7(6)	C(4′)–C(4)–B(1)	117.5(6)
C(2)–B(1)–C(4)	117.9(6)		
(ii) Free ligand (A)			
F(2)–B(2)–C(6)	118.6(3)	C(7)–C(6)–C(6′)	122.8(7)
C(6)–B(2)–C(6′)	122.7(6)	C(6′)–C(6)–B(2)	118.6(5)
B(2)–C(6)–C(7)	118.5(6)		
(iii) Free ligand (B)			
F(3)–B(3)–C(8)	118.2(5)	C(9)–C(8)–C(8′)	122.7(6)
C(8)–B(3)–C(8′)	123.6(9)	C(8′)–C(8)–B(3)	118.2(6)
B(3)–C(8)–C(9)	119.1(7)		

The co-ordination complex has crystallographic *m* symmetry, and the free ligands 2/*m* symmetry. A prime has been used, as the context is simplistically clear, to mean either 2 or *m*.

RESULTS AND DISCUSSION

Condensation of the ligand $C_4Me_4B_2F_2$ with excess of $Ni(CO)_4$ and dry degassed toluene into a tube on a vacuum line gives a reaction product which analyses as $[Ni(C_4Me_4B_2F_2)(CO)_2]$.[1] It was not appreciated at first that separation of the complex from the free ligand by distillation is exceedingly difficult, so that unwittingly the single crystals used for the *X*-ray investigation contained extra ligand incorporated into the structure. This fortuitous circumstance, however, enables us to to give an analysis of the geometry of the ligand as well as of the co-ordination complex. It is not known whether the material which gave a good chemical analysis for $[Ni(C_4Me_4B_2F_2)(CO)_2]$ is in fact a different structural type, but several crystals were *X*-rayed and all were identical with the one reported here. The chemical analysis, however, was performed on microcrystalline material. If at any stage we are able to prepare crystals of reasonable dimensions which give accurate chemical analysis for $[Ni(C_4Me_4B_2F_2)(CO)_2]$, further *X*-ray investigations will be carried out.

With space group symmetry *A*2/*m*, and $Z = 4$, molecular symmetry 2 or *m* is required. [Although symmetry $\bar{1}$ is also possible in principle, it can be ruled out in this instance on chemical grounds: see (I).]



(I)

The structure determination shows (Figure 1) that the crystallographic asymmetric unit comprises half a molecule of $[Ni(C_4Me_4B_2F_2)(CO)_2]$ with the Ni atom in the mirror plane, and two crystallographically distinct quarter-molecules of $(C_4Me_4B_2F_2)$. These free-ligand molecules, (A) and (B), lie astride sites of 2/*m* symmetry. The relationships between these units are best seen looking down the *b* axis of the monoclinic cell (Figure 2).

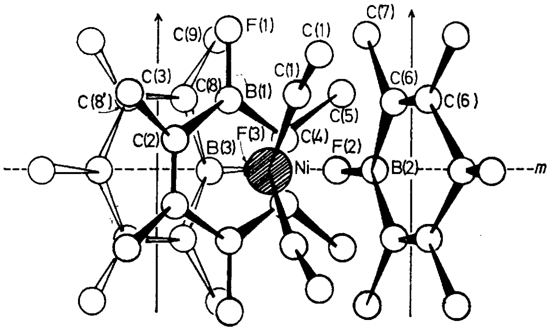


FIGURE 1 A view of the complex and of the free ligand molecules as seen along the crystallographic *c* direction; the atom numbering sequence is also shown, but hydrogen atoms are omitted for clarity

The $[Ni(C_4Me_4B_2F_2)(CO)_2]$ molecule contains an Ni atom in tetrahedral co-ordination. Two of the bonds, to the carbonyl groups, are at an angle of 107° (with Ni–C 1.805(8) and C–O 1.117(10) Å), while the other two bonds can be envisaged as donor bonds from the –C=C– links in the ligand ring. This determines the orientation of the ring relative to the carbonyl groups. It is clear from the interatomic distances, however (Table 2), that

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

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[4] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[5] R. F. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[6] Technical Report TR 192, Computer Science Center, University of Maryland, June 1972.

all six atoms of the ligand ring are within bonding distance of the Ni atom. Presumably vacant orbitals on the boron atoms accept electrons from filled orbitals on the nickel, making the boron atoms effectively four-co-ordinate. This view accords well with the observed changes in bond length of the co-ordinated ligand as compared with the free molecule: the –C=C– bonds lengthen from 1.34 to 1.39 Å, B–F from 1.30 to 1.39, while the B–C ring bonds shorten from 1.57 to 1.53 Å. This pattern exactly parallels that observed for [Ni-($C_4Me_4B_2F_2)_2$],[1] and is also closely similar to the changes observed in duroquinone when it forms complexes such as bis(duroquinone)nickel[7] and cyclo-octa-1,5-diene-(duroquinone)nickel.[8] A molecular orbital scheme for bis(duroquinone)nickel has been presented.[9]

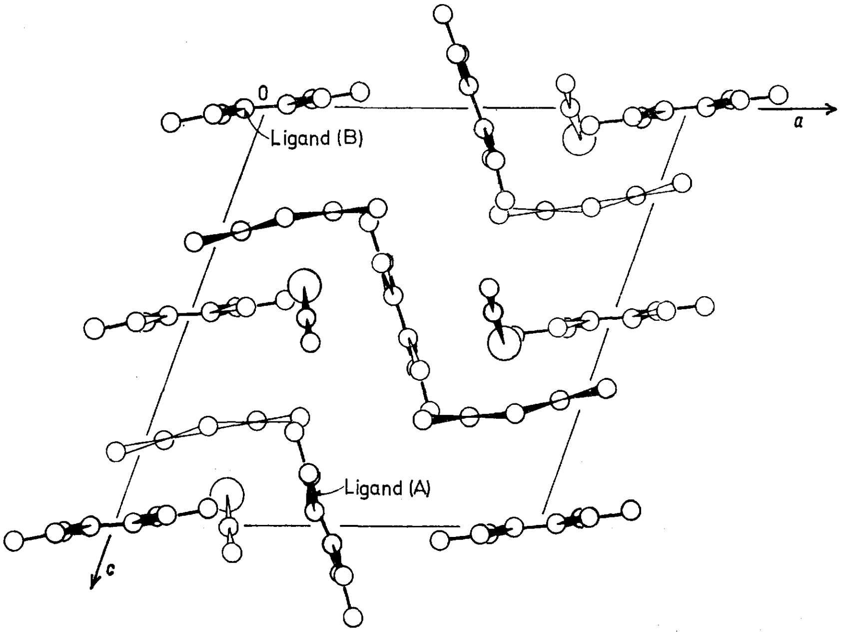

FIGURE 2 One unit cell seen in projection down *b* looking towards the origin

The ligand in the co-ordinated state is non-planar: the C–B–C portion of the ring bends along the C · · · C ' hinge ' away from the nickel atom by some 8.5°, and a further bend occurs between the B–F bond and the C–B–C plane to bring the B · · · F vector back towards the plane of the carbon atoms, making an angle of 7° with the C–B–C plane. In the crystal the whole [Ni-($C_4Me_4B_2F_2$)(CO)$_2$] molecule lies astride a mirror plane which passes through the Ni atom and the mid-points of the C=C bonds: the plane defined by the Ni(CO)$_2$ unit is at an angle of 86.6° to the central C_4 plane of the [$C_4Me_4B_2F_2$] ligand. Steric considerations in this tightly packed crystal may explain the deviation from 90°. The overall symmetry of the molecule is ideally C_{2v} (*mm*).

The two molecules of free ligand which are also incorporated into the crystal structure lie on sites of 2/*m* symmetry, the two-fold axis running (in both cases) from centre to centre of the C=C bonds (so that the mirror plane passes through the B–F bonds). Any deviation from planarity results, of necessity, in a *trans*-configuration for the ligand, and will only arise as a result of intermolecular forces. Ligand (B) lies parallel to, and at a distance of only 3.2 Å from, the co-ordinated ligand of the [Ni($C_4Me_4B_2F_2$)(CO)$_2$] molecule. Indeed, the relationship between ligand (B) and the ligand of the complex is closely similar to that found between the two ligand molecules in [Ni($C_4Me_4B_2F_2)_2$]:[1] a converse orientation and a distance apart of only 3.2 Å, comparable with (*e.g.*) the interplanar spacing of graphite. The angle between the plane of the C–B–C portion of the ring and the central (planar) C_4 moiety of the ligand is only 1.7°, and the B–F bond again bends back towards the C_4 plane to make an angle of 0.7° with the C–B–C section. Ligand (A), on the other hand, lies in a position approximately perpendicular to the plane of ligand (B) and of the co-ordinated ligand. The six-membered ring and the four attached methyl carbon atoms are effectively planar (deviation *ca.* 0.5°) but the B–F bond is bent out of this plane by some 4.5°. This bending is almost certainly a packing phenomenon, as the distance of closest approach between ligands (A) and (B), namely B(2) · · · F(3) 2.97 Å, is one of the few intermolecular contacts in the crystal <3 Å. For ligand (B) and for the co-ordinated ligand the methyl groups bend in the opposite direction to the C–B–C fold, and to about the same extent relative to the central C_4 plane.

The degree of bending in the ligand ring gives some indication of its ability to function as a π-acceptor, and

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[7] G. G. Aleksandrov and Yu. T. Struchkov, *J. Struct. Chem.*, 1974, 1001.

[8] M. D. Glick and L. F. Dahl, *J. Organometallic Chem.*, 1965, **3**, 200.

[9] G. N. Schrauzer and H. Thyret, *Z. Naturforsch.*, 1961, **16b**, 353; *Theor. Chim. Acta*, 1963, **1**, 172.

the fact that the bending in $[Ni(C_4Me_4B_2F_2)(CO)_2]$ (8.5°) is greater than in $[Ni(C_4Me_4B_2F_2)_2]$ (5.5°) suggests that the diboracyclohexadiene ligand is a better π-acceptor than are two carbonyl groups. This is borne out by the increase in stretching frequency of the CO ligand in $[Ni(C_4Me_4B_2F_2)(CO)_2]$: ν 2 080, 2 037, *vs.* 2 050, 2 043 cm^{-1} in $Ni(CO)_4$.[10]

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[10] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378.