(C7H13BF2N2)Cr(CO)3: a Vinamidine (1,5-Diazapenta-1,3-diene) Boron Difluoride as a Cyclohexadienide Type Ligand

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The vinamidine boron difluoride (difluorodiazaborinane) (1) acts as a 6-electron donor ligand in the tricarbonylchromium complex (3); the X-ray structure of (3) shows (1) to be a ligand analogous to cyclohexadienide.

Recently, the vinamidine boron difluoride (difluorodiazaborinane) (1)[1] has been demonstrated to be a stable heterocyclic analogue of the cyclohexadienide ion (2) whose stabilisation needs co-ordination at a metallic centre.[2,3] The synthesis and characterisation of the tricarbonylchromium complex (3)† enables us to investigate the influence of π-co-ordination in a comparison of (3) with the unco-ordinated ligand (1).

The X-ray structure of (3)‡ (Figure 1) shows [analogous to the structures of the isoelectronic complexes (4)[4] and (5)[5]] the
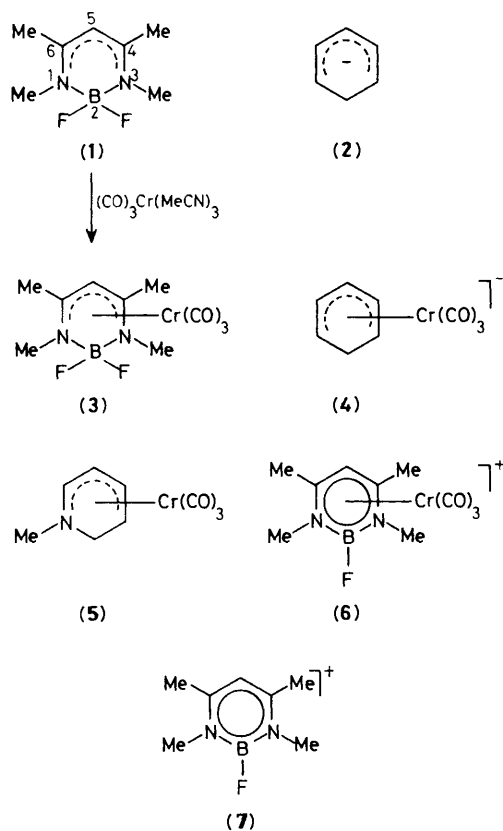
heterocyclic ligand to be folded about the N(1)–N(3) axis (angle of fold 41.6°). A minor deviation from planarity is also observed for C(5) [angle of fold about the C(4)–C(6) axis 6.0°], both B(2) and C(5) being oriented away from the co-ordination centre. The resulting boat structure is in contrast with the planar geometry of the unco-ordinated ligand (1).[1] In addition, co-ordination of (1) causes a remarkable lengthening of the ring bonds (Figure 2).[6]

Significant changes on co-ordination of (1) are also shown in n.m.r. spectra (see Table 1). [1]H N.m.r. shows an upfield shift of 5-H and a downfield shift of CCH3 on co-ordination. This is similar to the co-ordination shift of arenes. The upfield co-ordination shift of NCH3 may be influenced by a changed hybridisation of the nitrogen atoms in formation of the boat structure. As expected, in [13]C n.m.r. the ring carbon atoms are shifted upfield on co-ordination while deshielding is observed for the NCH3 groups. Surprisingly, no significant change is observed for the CCH3 groups here. The magnetic inequivalence of the fluorine atoms in (3) leads to a typical ABX pattern with marked differences both in chemical shift and in [19]F–[11]B coupling; in accordance with the assignment of the hydrogen shifts in the methylene group of cyclohexadienide complexes the downfield shifted signals may be assigned to F_{endo}. From the mean of F_{exo} and F_{endo} in (3), a downfield co-ordination shift of ca. 8 p.p.m. is observed in [19]F n.m.r. Only a minor influence of co-ordination is observed in the [11]B n.m.r. spectra of (1) and (3).
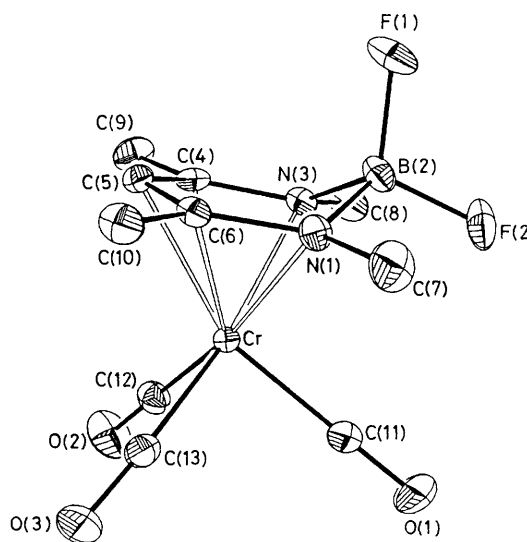

(1)   (2)

(3)   (4)

(5)   (6)

(7)

Figure 1. The structure of (C7H13BF2N2)Cr(CO)3 (3). Selected bond lengths (pm) and angles (°): Cr–C(4) 217.4(1), Cr–C(5) 219.8(1), Cr–C(6) 217.6(2), C(11)–O(1) 114.2(2), C(12)–O(2) 115.3(2), C(13)–O(3) 115.9(2), Cr ··· B(2) 268.2, Cr ··· F(2) 333.3, F(2) ··· C(11) 304.7, Cr–C(11)–O(1) 179.0(2), Cr–C(12)–O(2) 176.0(2), Cr–C(13)–O(3) 175.1(1), C(11)–Cr–C(12) 90.6(1), C(11)–Cr–C(13) 93.0(1), C(12)–Cr–C(13) 81.1(1).

Table 1. N.m.r. data of compounds (1) and (3) (δ in p.p.m., coupling constants in Hz).

Compound	^{1}H N.m.r.[a]	^{13}C N.m.r.[b]	^{19}F N.m.r.[a,f]	^{11}B N.m.r.[a,g]
(1)	1.37 (CCH_3), 2.87 (NCH_3) 4.37 (5-H)	20.49 (CCH_3), 31.87 (NCH_3), 94.40 (C-5), 163.76 (C-4)	-137.54 (q, ${}^{1}J$ 33.6)	1.74 (t)
(3)	1.70 (CCH_3), 2.37 (NCH_3), 4.13 (5-H)	19.89 (CCH_3), 35.28 (NCH_3),[c] 82.24 (C-5), 122.28 (C-4), 227.61, 233.38[d] (2 : 1, CO)[e]	-164.02 F_{exo} (dq, ${}^{1}J$ 17.0, ${}^{2}J$ 69.7); -127.44 F_{endo} (dq, ${}^{1}J$ 51.4)	-1.53 (dd)

[a] C_6D_6. [b] In CD_2Cl_2. [c] d, ${}^{3}J({}^{19}F-{}^{13}C)$ 1.63. [d] d, ${}^{4}J({}^{19}F-{}^{13}C)$ 4.29. [e] At $-30\,^{\circ}C$. [f] With respect to $CFCl_3$. [g] With respect to $BF_3\cdot Et_2O$.
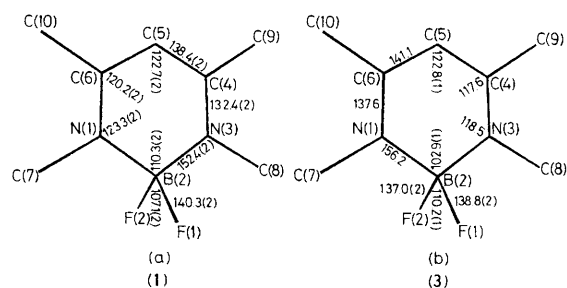
Figure 2. Schematic drawing of (a) (1) and (b) (3) (only the ring ligand is shown, mean values), distances and angles in pm and degrees.

The ligand to metal bond in (3) (Figure 1) is dominated by the short Cr–N bond length [mean Cr–N(1),N(3) 215.4 pm] which leads to an unexpectedly short distance for Cr to the centre of N(1),N(3),C(4),C(6) of 164.2(5) pm. The projection of the co-ordination centre on the plane N(1),N(3),C(4),C(6) is shifted towards the direction of the small nitrogen atoms. As a consequence, the Cr–F_{endo} distance (333.3 pm) is shortened to the range of the van der Waals radii, and the stability of (3) may be influenced by Cr–F_{endo} repulsion. For the vinamidine boron difluoride (1),[1] as well as for the cyclohexadienide ion (2),[7] the maximum of negative charge density has been calculated for the 1,3-position which causes a *trans*-orientation of the carbonyl ligands with respect to the N and C(5) atoms (Figure 1). The short distances Cr–C(12), C(13) [average 183.8 pm, *cf.* Cr–C(11) 187.5(2) pm] may be attributed to the donor properties of the nitrogen atoms in (1). However, the ^{13}C n.m.r. carbonyl shifts at 227.61 and 233.38 p.p.m. (relative intensities 2 : 1)[8] are in contrast with this interpretation. The asymmetric geometry of the $Cr(CO)_3$ fragment results in an angle between the planes C(11),C(12),C(13) and N(1),N(3),C(4),C(6) of 173.7°.

Use of spectroscopic and structural data of a series of $LCr(CO)_3$ complexes[4,5,9] implies the following order of donor–acceptor abilities: L = cyclohexadienide > cyclopentadienide > pyrrole ~ arene > (1) ~ dihydropyridine ~ pyridine > tropylium. This series does not represent the order of stability. In the case of (3), stability may be decreased by Cr–F_{endo} repulsion, which can also be seen by the relative shortening of the B–F_{endo} bond [F(1)–B 138.8(2), F(2)–B 137.0(2) pm].[10] Therefore fluoride abstraction from (3) should stabilise the ligand to chromium bond, forming the cationic complex (6). In fact, (3) reacts with $BF_3\cdot Et_2O$ but the only isolated product is the cationic heteroarene (7), which is also accessible by direct reaction of (1) with $BF_3\cdot Et_2O$.[11] Apparently, the donor properties of (7) are not sufficient to form a stable tricarbonylchromium complex.

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