Structural Characterization of Charge Transfer Complexes of the Nickel(IV) Bis-(3,1,2-dicarbollyl) Sandwich Compound

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Dedicated to Professor Göran Bergson on the occasion of his 65th birthday

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The charge transfer complexes of $commo$-Ni$(3,1,2,$-C$_2$B$_9$H$_{11}$)$_2$ (1) with naphthalene (1 · C$_{10}$H$_8$), pyrene (1 · C$_{16}$H$_{10}$) and N,N-dimethylaniline (1 · C$_6$H$_5$NMe$_2$) were structurally characterized by X-ray diffraction studies. 1 · C$_{10}$H$_8$ crystallized in the orthorhombic space group $Pnma$ with $a = 9.825(7)$, $b = 13.257(10)$ and $c = 18.114(14)$ Å, $V = 2359$ Å^3, and $Z = 4$. Data were collected to a maximum $2\theta = 115°$, giving 1426 unique reflections. The final discrepancy index was $R = 0.077$, $R_w = 0.090$ for 919 independent reflections with $I > 2\sigma(I)$. 1 · C$_{16}$H$_{10}$ was crystallized in the orthorhombic space group $P2_12_12_1$ with $a = 6.967(1)$, $b = 14.804(2)$ and $c = 26.200(4)$ Å, $V = 2702$ Å^3, and $Z = 4$. Data were collected to a maximum of $2\theta = 50°$, giving 2751 unique refections. The final discrepancy index was $R = 0.075$, $R_w = 0.094$ for 1812 independent refections with $I > 3\sigma(I)$. 1 · C$_6$H$_5$NMe$_2$ crystallized in the orthorhombic space group $Pn2_1a$ (standard setting $Pna2_1$) with $a = 9.476(2)$, $b = 13.160(2)$ and $c = 18.389(4)$ Å, $V = 2304$ Å^3, and $Z = 4$. Data were collected to a maximum of $2\theta = 45°$, giving 1581 unique reflections. The final discrepancy index was $R = 0.055$, $R_w = 0.070$ for 1152 independent reflections with $I = 3\sigma(I)$. Crystallographic data, in combination with molecular orbital calculations, demonstrate that in each case the nickelacarborane acceptor orients itself with respect to the donor molecule to maximize orbital overlap, thereby facilitating charge transfer.

In contrast to cyclopentadiene-derived metallocene compounds, the corresponding metallacarborane sandwich compounds derived from dicarbollide, [$nido$-C$_2$B$_9$H$_{11}$]$^{2-}$, cages generally exhibit greater thermal, chemical and redox stability.[1] Notably, dicarbollide cages and their C-substituted derivatives often serve to stabilize unusual oxidation states and coordination geometries of the central atoms in sandwich molecules.[1,2] An excellent example is found in the highly robust nickel bis(3,1,2-dicarbollyl) sandwich compounds of the type [Ni(C$_2$B$_9$H$_{11}$)$_2$]$^{n-}$, for which room temperature stable species can be isolated containing formal Ni^{4+}, Ni^{3+} and Ni^{2+} centers ($n = 0$–2).[3] The facile electrochemical interconversion of these species by reversible one-electron transfer reactions has been described previously.[3a]

Although nickelocene, Ni(η-C$_5$H$_5$)$_2$, can be observed via cyclic voltammetry to exhibit similar redox behavior, the formal Ni^{4+} species, [Ni(C$_5$H$_5$)$_2$]$^{2+}$, is stable in electrolyte solutions only at temperatures below 0 °C.[4]

The electron transfer reactions of [Ni(3,1,2-C$_2$B$_9$H$_{11}$)$_2$]$^{n-}$ ($n = 0$–2) involve intriguing structural changes which appear to be general for most transition and post-transition metal bis-dicarbollide sandwich compounds. The formal d^8 nickel (2+) and d^7 nickel (3+) complexes have been shown to have 'slipped' (C_{2h} symmetry) and nonslipped 'transoid' sandwich structures, respectively, as shown schematically in Fig. 1a and 1b.[3b] The bright orange, diamagnetic, formal d^6 Ni^{4+} species [Ni(3,1,2-C$_2$B$_9$H$_{11}$)$_2$] (1) is formed by the air oxidation of the Ni^{3+} analogue in solution.

This air-stable compound possesses an unusual 'cisoid' (C_2 symmetry) sandwich structure in which both pairs of
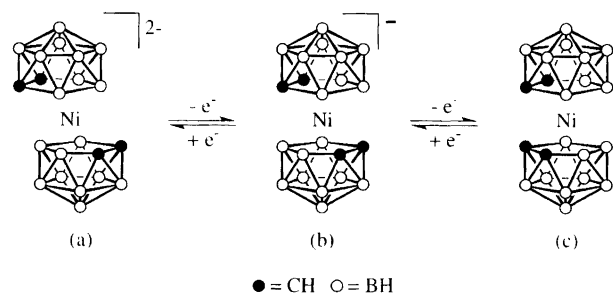
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● = CH ○ = BH

Fig. 1. The bis(dicarbollide) formal nickel d^8, d^7 and d^6 sandwich compound series: (a) [*commo*-3,3'-Ni(3,1,2-NiC$_2$B$_9$H$_{11}$)$_2$]$^{2-}$, (b) *commo*-3,3'-Ni(3,1,2-NiC$_2$B$_9$H$_{11}$)$_2$]$^-$, and (c) [*commo*-3,3'-Ni(3,1,2-NiC$_2$B$_9$H$_{11}$)$_2$ (1), and their electrochemical interconversion.

cage carbon atoms reside on the same side of the molecule in a staggered arrangement as shown schematically in Fig. 1c.[5] It has been shown previously that 1 may serve as a catalyst for the air-oxidation of ethanol to acetaldehyde in a catalytic cycle presumably involving the reversible Ni^{3+}–Ni^{4+} couple.[3a]

The unusual cisoid structure of 1 leads to a significant dipole moment which has been measured at 6.16 ± 0.05 D.[3c] As a result, 1 forms highly colored 1 : 1 charge transfer adducts with soft Lewis bases. Adduct formation has been observed for a variety of neutral donors including aromatic hydrocarbons, such as naphthalene, phenanthrene, 1,3,5-trimethoxybenzene, pyrene, and *N,N*-dimethylaniline, as well as anionic donors such as the chloride, bromide, and thiocyanate ions. Diethyl sulfide, tetrathiafulvene and dicyclohexylthiourea also form adducts with 1.[3d,6] It is notable that, as a rule, organometallic and coordination compounds act as donors in charge transfer complexes;[7] however, the adducts of 1 represent unique examples of charge transfer complexes in which the metal centered species acts as an acceptor.

The electronic spectra of these adducts have been discussed previously.[3a] In particular, the pyrene and *N,N*-dimethylaniline adducts of 1 exhibit broad absorptions in the 650–900 nm region, which is lower in energy than the absorption maximum of uncomplexed 1 at 425 nm. A preliminary X-ray structure determination for the pyrene adduct of 1 was carried out by Wing more than 25 years ago, the details of which were never published.[3a]

Results and discussion

The addition of excess naphthalene to a yellow solution of 1 in benzene affords a red–orange solution from which a 1 : 1 red adduct was crystallized. Similarly, addition of excess pyrene or *N,N*-dimethylaniline to a yellow solution of 1 in dichloromethane results in the immediate formation of dark green solutions from which greenish black and dark green 1 : 1 crystalline adducts, respectively, can be isolated. When dissolved in dichloromethane in the absence of excess Lewis base the intense color of these

compounds is lost, giving yellow solutions indicative of a high degree of adduct dissociation. The structures of the naphthalene, pyrene and *N,N*-dimethylaniline adducts of 1 have now been determined by single crystal X-ray diffraction studies, the details of which are reported herein.

Crystallographic analysis

The metallacarborane in the naphthalene, pyrene, and *N,N*-dimethylaniline complexes of 1 was not found to be significantly distorted when compared to the uncomplexed nickelacarborane. In each case, the long axis of the metallocarborane molecule lies nearly parallel to the plane of the aromatic molecule, and the two dicarbollide cages are oriented such that the cage carbon atoms lie in a staggered cisoid relationship, as found in the free sandwich molecule. The carbon atoms of the nickelacarborane acceptor were found to be on the same side of the molecule as the aromatic donor species.

1 · $(C_{10}H_8)$. The structure of the naphthalene adduct of 1 is shown in Fig. 2. Selected interatomic distances and angles are listed in Table 1. Position and displacement parameters for 1 · $(C_{10}H_8)$ are given in Table 2. A mirror
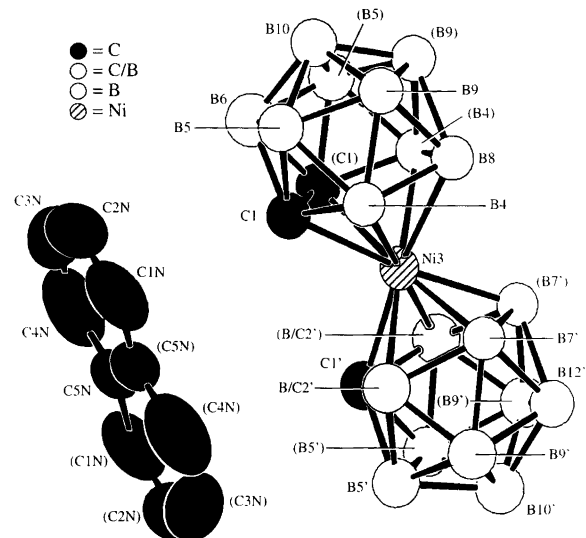

● = C
○ = C/B
○ = B
⊘ = Ni

Fig. 2. The structure of 1 · (C$_{10}$H$_8$), with hydrogen atoms omitted for clarity. Symmetrically equivalent positions are indicated by parentheses.

Table 1. Selected interatomic distances (in Å) and angles (in °) for 1 · C$_{10}$H$_8$.

Ni3–C1	2.074(8)	Ni3–B8	2.102(14)
Ni3–Cl'	2.090(12)	C1–C1	1.631(11)
Ni3–B/C2'	2.085(10)	C1–B4	1.724(13)
Ni3–B4	2.085(11)	B4–B8	1.864(13)
Ni3–B7'	2.102(14)	B5–C2N	3.82(2)
C1–C4N	3.80(2)	B6–C3N	3.88(3)
C1–C5N	3.81(2)	B/C2'–C3N	3.88(2)
C1–C3N	3.88(2)	B5'–C2N	3.81(2)
C1–Ni3–C2	46.3(3)	B10–Ni3–B10'	176.2(2)

Table 2. Position and displacement parameters for $1 \cdot (C_{10}H_8)$.[a-c]

Atom	x	y	z	U_{11} or $\langle u^2 \rangle$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U(eq)
C1N	0.4408(13)	0.5735(11)	0.0795(8)	0.109(11)	0.138(14)	0.105(10)	−0.046(10)	0.064(10)	−0.066(12)	0.117(5)
C2N	0.5063(20)	0.5258(18)	0.1339(10)	0.185(23)	0.298(38)	0.052(7)	−0.154(23)	0.007(14)	−0.019(17)	0.178(12)
C3N	0.5870(20)	0.4449(19)	0.1188(13)	0.133(22)	0.219(30)	0.151(20)	−0.075(17)	−0.068(18)	0.131(24)	0.168(10)
C4N	0.6055(16)	0.4110(14)	0.0493(12)	0.086(11)	0.114(12)	0.201(17)	−0.011(9)	0.018(14)	0.043(15)	0.134(6)
C5N	0.5402(9)	0.4594(6)	−0.0085(7)	0.061(6)	0.058(6)	0.069(7)	−0.005(5)	0.009(7)	0.006(7)	0.063(3)
Ni3	0.10957(17)	0.25000	−0.00019(11)	0.0525(13)	0.0546(15)	0.0342(12)	0	0.0058(12)	0	0.0471(6)
C1*	0.2455(8)	0.1885(6)	0.0750(4)	0.052(2)						
B4*	0.0834(10)	0.1391(8)	0.0802(5)	0.050(3)						
B5*	0.1952(10)	0.1432(8)	0.1604(6)	0.059(3)						
B6*	0.2993(16)	0.2500	0.1544(9)	0.073(5)						
B8*	−0.0326(13)	0.2500	0.0865(8)	0.050(4)						
B9*	0.0243(10)	0.1820(8)	0.1691(5)	0.056(3)						
B10*	0.1543(15)	0.2500	0.2115(8)	0.060(4)						
C1'*	0.2265(12)	0.2500	−0.0966(6)	0.058(4)						
C2'*	0.1330(10)	0.1465(8)	−0.0859(5)	0.063(3)						
B2'*	0.1330(10)	0.1465(8)	−0.0859(5)	0.063(3)						
B5'*	0.1807(11)	0.3155(8)	−0.1767(5)	0.063(3)						
B7'*	−0.0403(9)	0.1793(7)	−0.0648(5)	0.049(3)						
B9'*	0.0134(11)	0.3587(9)	−0.1576(6)	0.064(3)						
B10'*	0.0386(16)	0.2500	−0.2108(9)	0.066(5)						
B12'*	−0.0917(14)	0.2500	−0.1458(8)	0.056(4)						

[a] Units of U_{ij}, U(eq) and isotropic $\langle u^2 \rangle$ are Å². Units of each e.s.d., in parentheses, are those of the least significant digit of the corresponding parameter. U(eq) is defined as: $(1/3)[U_{11}(aaa^*a^*) + U_{22}(bbb^*b^*) + U_{33}(ccc^*c^*) + 2U_{12}(aba^*b^* \cos \gamma) + 2U_{13}(aca^*c^* \cos \beta) + 2U_{23}(bcb^*c^* \cos \alpha)]$. [b] The anisotropic temperature factor is defined as: $\exp\{-2\pi^2[U_{11}(a^*a^*hh) + U_{22}(b^*b^*kk) + U_{33}(c^*c^*ll) + 2U_{12}(a^*b^*hk) + 2U_{13}(a^*c^*hl) + 2U_{23}(b^*c^*kl)]\}$. [c] The carborane has mirror symmetry relating C2, B7, B11 and B12 to atoms C1, B4, B5 and B9, respectively, and B4', B8', B6', B9' to atoms C2', B7', B5' and B9', respectively. Atoms refined isotropically are denoted by*.

plane passes through B10, B6, B8, Ni3, C1', B12' and B10'. As a result of this crystallographic symmetry, the mirror-related positions B/C2' and (B/C2') have half boron, half carbon occupancy. A redundant numbering scheme has been used to label the figure with parentheses to indicate symmetry equivalent positions. The bonding C_2B_3 faces of the two carborane cages are planar to within 0.02 Å and the normals to these faces form an angle of 8°. The nickel atom is located 1.46 Å from each face. The angle B10–Ni3–B10' is 176.2°. The nickelacarborane molecule is oriented such that the C1, B4, B5 face and the atoms B/C2' and B5' are closest to the naphthalene molecule.

The naphthalene molecule is centrosymmetric and is planar to within 0.01 Å. The angle formed by the normal to this plane and the vector B10–B10' is 89°. The closest carborane approaches to the plane are C1 (3.63 Å°), B5 (3.81 Å), B6 (3.86 Å), B/C2' (3.85 Å) and B5' (3.62 Å). The shortest intermolecular distances, not involving hydrogen, are C1–C4N, C1–C5N, and B5'–C2N (Table 1). The shortest hydrogen atom–naphthalene plane distance is 3.1 Å, for both H6 and H1'.

Figure 3a shows the orientation of the long axis of 1 (B10 Ni3–B10') with respect to naphthalene. The view is along an axis normal to the plane of the naphthalene. As can be seen, the nickelacarborane is not centered over the top of the donor as might be expected, but is instead shifted down. Additionally, the long axis of the nickelacarborane is tilted away from the long axis of the donor. A view down the B10–Ni3–B10' axis of the nickelacarborane (Fig. 4a) reveals that the carbon atoms of the acceptor are rotated away from the face of the naphthalene donor.

1 · $(C_{16}H_{10})$. The structure of the pyrene adduct of 1 is shown in Fig. 5. Selected interatomic distances and angles are given in Table 3. Position and displacement parameters for 1 · $(C_{16}H_{10})$ are given in Table 4. The bonding C_2B_3 faces of the carborane cages are planar to within 0.02 Å and the normals of the planes form an angle of 7°. The nickel atom is located 1.47 Å from each face. The angle B10–Ni3–B10' is 178.8°. The nickelacarborane molecule is oriented such that the C1', C2', B6' face and the C1 atom are closest to the pyrene molecule.
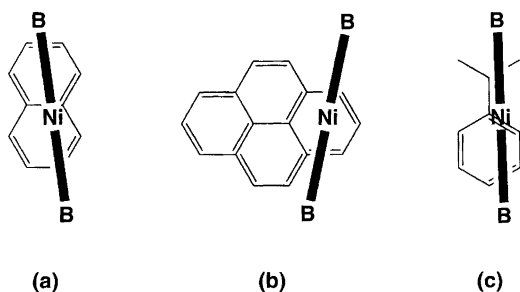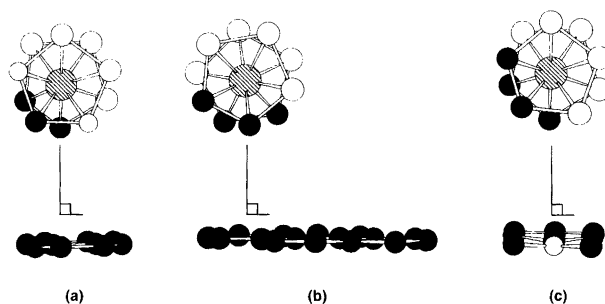

Fig. 4. Orientation of 1 with respect to the donor molecules (a) $C_{10}H_8$, (b) $C_{16}H_{10}$, and (c) $C_6H_5NMe_2$ as viewed down the long axis (B10–Ni3–B10') of 1. For clarity, only Ni and the two C_2B_3 rings of the nickelacarborane in each complex have been shown.
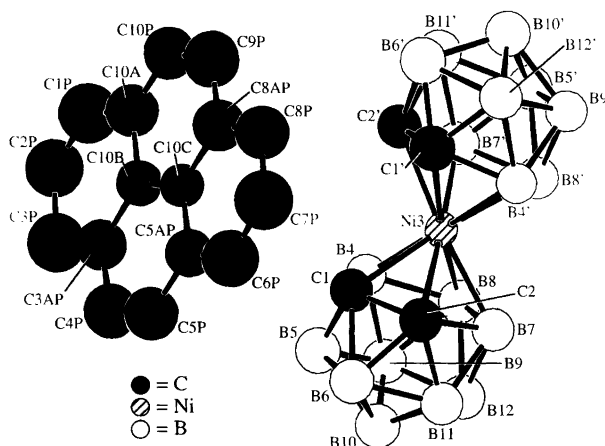

● = C
⊘ = Ni
○ = B

Fig. 5. The structure of 1 · $(C_{16}H_{10})$, with hydrogen atoms omitted for clarity.

Table 3. Selected interatomic distances (in Å) and angles (in °) for 1 · $C_{16}H_{10}$.

Ni3–C1	2.077(12)	C1–C2	1.590(16)
Ni3–C2	2.061(11)	C1'–C2'	1.64(2)
Ni3–C01'	2.114(12)	C1–B4	1.71(2)
Ni3–C2'	2.070(12)	C1'–B4'	1.71(2)
Ni3–B4	2.094(14)	C2–B7	1.73(2)
Ni3–B4'	2.108(13)	C2'–B7'	1.73(2)
Ni3–B7	2.092(14)	B7–B8	1.86(2)
Ni3–B7'	2.077(15)	B7'–B8'	1.83(2)
Ni3–B8	2.131(14)	B4–B8	1.85(2)
Ni3–B8'	2.094(14)	B4'–B8'	1.80(2)
C1–Ni3–C2	45.2(5)	B10–Ni3–B10'	178.8(3)
C1'–Ni3–C2'	46.1(5)		

The pyrene molecule is planar to within 0.02 Å. The angle formed by the normal to this plane and the vector B10–B10' is 87°. The distance between the nickel center and the mean plane of the pyrene molecule is 4.74 Å. The C1', C2', B6', and C1 atoms lie 3.43, 3.67, 3.08, and 3.46 Å, respectively, from the mean plane of the aromatic molecule. The shortest hydrogen atom–pyrene plane distance is 2.04 Å, involving H6'.

Figure 3b shows the orientation of the long axis of 1 (B10–Ni3–B10') with respect to pyrene. As was observed

Fig. 3. Views normal to the hydrocarbon mean plane depicting the orientation of 1 with respect to (a) $C_{10}H_8$, (b) $C_{16}H_{10}$, and (c) $C_6H_5NMe_2$. For the purposes of clarity, 1 has been depicted by the vectors Ni3–B10 and Ni3–B10'.

in the case of the naphthalene complex above, the nickelacarborane is tilted with respect to the donor molecule. In addition, **1** is translated away from the center of the molecule. In a view down the long axis of **1** (Fig. 3b), the carbon atoms of the carborane are again found to be rotated away from the face of the poly-aromatic donor molecule. However, the rotation observed in **1**·($C_{16}H_{10}$) is not as pronounced as that observed in **1**·($C_{10}H_8$).

1·*($C_6H_5NMe_2$)*. The structure of the *N,N*-dimethyl-aniline adduct of **1** is shown in Fig. 6. Selected interatomic distances and angles are listed in Table 5. Position and displacement parameters for **1**·($C_6H_5NMe_2$) are given in Table 6. Each of the C_2B_3 bonding faces of the carborane cages is planar to within 0.02 Å. The angle between normals to these faces is 8° and the nickel atom is 1.46 Å from each. The angle B10–Ni3–B10' is 177.1°. The nickelacarborane molecule is oriented with the C1, B5, B6 face and the B11' atom closest to the aniline molecule.

The nonhydrogen atoms of *N,N*-dimethylaniline are all coplanar to within 0.08 Å, and the angle formed by the normal to this plane and the vector B10–B10' is 86.9°. The distance between the nickel center and the mean plane of the aniline molecule is 5.02 Å. The C1, B5, B6, and B11' atoms lie 3.54, 3.67, 3.59 and 3.71 Å, respectively, from the mean plane of the aromatic molecule. The shortest hydrogen atom–aromatic plane distance is 2.58 Å, involving H5.

The orientation of the long axis of **1** (B10–Ni3–B10') with respect to the long axis of *N,N*-dimethylaniline is shown in Fig. 3c. The axes of both molecules in the complex are nearly parallel. However, the carbon atoms of the two dicarbollide cages are rotated from the plane of the donor as seen in Fig. 4c.
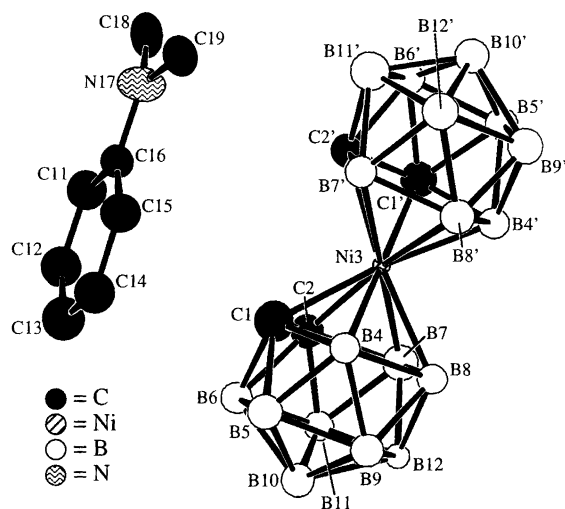

● = C
⊘ = Ni
○ = B
⊗ = N

Fig. 6. The structure of **1**·(C₆H₅NMe₂), with hydrogen atoms omitted for clarity.

Molecular orbital calculations. Molecular orbital calculations for all molecules were obtained from 6-31G* Hartree–Fock calculations using the GAUSSIAN 94 program.[8] A geometry of C2 was imposed on **1** in order to simplify the calculation. The lowest unoccupied molecular orbital (LUMO) for **1** and the highest occupied molecular orbital (HOMO) for each of the donor molecules (napthalene, pyrene, and *N,N'*-dimethylaniline) are shown in Fig. 7. A more detailed view depicting the three-dimensional nature of the LUMO of **1** is shown in Fig. 8. Based on frontier orbital type arguments, the orientation of **1** with respect to the donor molecules shows a strong correlation. Comparisons of the orientation of **1** with respect to each of the donor molecules (Figs. 3 and 4) with the calculated molecular orbitals (LUMO and HOMO, Figs. 7 and 8) reveals that the nickelacarborane is oriented in such a way as to maximize orbital overlap between the donor and acceptor. While crystal packing forces may also apply to the translational and rotational anomalies observed in these complexes, molecular orbital calculations present a compelling argument for configurations based on electronic interactions.

Geometric distortion of **1**. The two dicarbollide cages of **1** show a distortion in which the carbon atoms are displaced slightly toward the geometric centers of their respective icosahedra. This distortion results in a tilt of the C_2B_3 planes of the two dicarbollide cages by 6° with respect to one another without producing a bending of the overall complex along the axis passing through the nickel center and the two dicarbollide cage apical B10 and B10' atoms. Unlike most dicarbollide sandwich compounds, the nickel atom is not significantly slipped away from the cage face carbon atoms in the direction of the unique boron atom, B8. The Ni–C and Ni–B interatomic distances in **1** average 2.07 and 2.10 Å, respectively. Distortions from idealized geometry in *commo*-metallacarboranes are often described in terms of the 'slipping' parameter Δ,[9] and the 'folding' parameters θ and φ.[10] The slip parameter, Δ, is defined as the displacement of the metal atom from the normal through the centroid of the least-squares plane of the lower B_5 ring of the dicarbollide cage. The folding parameters, θ and φ, which measure the lack of coplanarity of the C_2B_3 bonding face of the dicarbollide cage with respect to the lower B_5 plane, are defined as the dihedral angles between the normals to the least-squares plane of the lower B_5 ring and the B(4)–C(1)–C(2)–B(7) and B(4)–B(8)–B(7) planes, respectively, for 3,1,2-MC_2B_9-type complexes. However, the mode of dicarbollide cage distortion in compound **1** is different from that found in most metallacarborane complexes. In general *commo*-metallacarborane complexes exhibit varying degrees of slip along an axis which passes between the two carboranyl carbon atoms and through the B8 atom, and folding along a line that passes through the B4 and B7 atoms. The free nickelacarborane **1** is essentially unslipped (Δ = 0.10 Å) and does not fold in a regular

Table 4. Position and displacement parameters for $1 \cdot (C_{16}H_{10})$.[a,b]

Atom	x	y	z	U_{11} or $\langle U^2 \rangle$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$U(\text{eq})$
Ni3	−0.2461(2)	−0.16603(8)	−0.18471(5)	0.0336(7)	0.0360(7)	0.0418(7)	−0.0041(10)	0.0038(10)	−0.0017(7)	0.0371(3)
C1*	−0.1410(17)	−0.1476(8)	−0.1112(5)	0.064(3)						
C2*	−0.0139(17)	−0.2147(7)	−0.1445(4)	0.063(3)						
B4*	−0.3806(20)	−0.1734(9)	−0.1134(5)	0.060(4)						
B5*	−0.2337(26)	−0.1968(8)	−0.0593(5)	0.073(4)						
B6*	0.0123(23)	−0.2221(10)	−0.0786(5)	0.072(4)						
B7*	−0.1493(21)	−0.2983(9)	−0.1735(5)	0.064(4)						
B8*	−0.4012(21)	−0.2767(9)	−0.1530(5)	0.066(4)						
B9*	−0.3909(22)	−0.2801(9)	−0.0834(6)	0.070(4)						
B10*	−0.1549(22)	−0.3118(9)	−0.0630(6)	0.073(4)						
B11*	−0.0051(21)	−0.3176(9)	−0.1184(5)	0.066(4)						
B12*	−0.2458(26)	−0.3589(8)	−0.1199(5)	0.072(3)						
C1*	−0.1190(18)	−0.0571(8)	−0.2244(4)	0.073(4)						
C2*	−0.3363(17)	−0.0370(8)	−0.2035(4)	0.068(3)						
B4*	−0.1096(19)	−0.1575(9)	−0.2564(5)	0.058(3)						
B5*	−0.1047(21)	−0.0530(9)	−0.2881(5)	0.067(4)						
B6*	−0.2380(26)	0.0276(9)	−0.2530(5)	0.076(4)						
B7*	−0.4964(22)	−0.1214(9)	−0.2196(5)	0.069(4)						
B8*	−0.3511(20)	−0.2003(9)	−0.2570(5)	0.063(4)						
B9*	−0.2511(25)	−0.1375(8)	−0.3105(4)	0.064(3)						
B10*	−0.3442(21)	−0.0241(9)	−0.3067(5)	0.071(4)						
B11*	−0.4843(23)	−0.0095(10)	−0.2521(6)	0.071(4)						
B12*	−0.4937(22)	−0.1162(9)	−0.2869(5)	0.070(4)						
C1P*	−0.5745(27)	0.1819(11)	−0.0195(6)	0.128(6)						
C2P*	−0.5889(26)	0.1470(10)	0.0262(6)	0.117(5)						
C3P*	−0.4396(24)	0.0878(10)	0.0505(6)	0.119(5)						
C3AP*	−0.2762(23)	0.0725(8)	0.0169(5)	0.087(4)						
C4P*	−0.1225(23)	0.0165(9)	0.0326(6)	0.101(5)						
C5P*	0.0266(23)	0.0032(9)	0.0027(5)	0.096(4)						
C5AP*	0.0433(19)	0.0403(10)	−0.0474(5)	0.078(4)						
C6P*	0.1959(25)	0.0237(10)	−0.0766(5)	0.111(5)						
C7P*	0.2098(26)	0.0616(10)	−0.1229(6)	0.120(5)						
C8P*	0.0664(22)	0.1155(10)	−0.1449(6)	0.101(5)						
C8AP*	−0.0985(23)	0.1335(10)	−0.1145(6)	0.095(4)						
C9P*	−0.2519(26)	0.1881(9)	−0.1315(5)	0.104(4)						
C10P*	−0.4039(22)	0.2060(9)	−0.1022(5)	0.089(4)						
C10A*	−0.4245(22)	0.1717(10)	−0.0537(6)	0.097(4)						
C10B*	−0.2720(21)	0.1091(7)	−0.0330(4)	0.071(3)						
C10C*	−0.1087(17)	0.0961(7)	−0.0650(4)	0.063(3)						

[a] Units of U_{ij}, $U(\text{eq})$ and isotropic $\langle U^2 \rangle$ are Å^2. Units of each e.s.d., in parentheses, are those of the least significant digit of the corresponding parameter. $U(\text{eq})$ is defined as: $(1/3)|U_{11}(aaa^*a^*) + U_{22}(bbb^*b^*) + U_{33}(ccc^*c^*) + 2U_{12}(aba^*b^* \cos \gamma) + 2U_{13}(aca^*c^* \cos \beta) + 2U_{23}(bcb^*c^* \cos \alpha)|$. [b] The anisotropic temperature factor is defined as: $\exp\{-2\pi^2[U_{11}(a^{*2}h^2) + U_{22}(b^{*2}k^2) + U_{33}(c^{*2}l^2) + 2U_{12}(a^*b^*hk) + 2U_{13}(a^*c^*hl) + 2U_{23}(b^*c^*kl)]\}$. Atoms refined isotropically are denoted by*.

Table 5. Selected interatomic distances (in Å) and angles (in °) for $1 \cdot C_6H_5NMe_2$.

Ni3–C1	2.051(16)	C1–C2	1.60(2)
Ni3–C2	2.060(14)	C1'–C2'	1.54(2)
Ni3–C1'	2.057(15)	C1–B4	1.71(2)
Ni3–C2'	2.073(9)	C1'–B4'	1.74(2)
Ni3–B4	2.063(15)	C2–B7	1.66(2)
Ni3–B4'	2.070(15)	C2'–B7'	1.78(3)
Ni3–B7	2.10(2)	B7–B8	1.78(3)
Ni3–B7'	2.10(2)	B7'–B8'	1.80(2)
Ni3–B8	2.101(11)	B4–B8	1.88(2)
Ni3–B8'	2.066(16)	B4'–B8'	1.82(3)
C1–Ni3–C2	45.9(6)	B10–Ni3–B10'	177.1(3)
C1'–Ni3–C2'	43.9(6)		

fashion. Nevertheless, the folding parameters do give some measurement of the extent of the distortions in the two C_2B_3 dicarbollide cage bonding faces in 1. In the case of free 1, the two cages show dissimilar θ folding parameters of 5 and 2.2°. The φ parameters for free 1 are 0.4 and 0.9°.

The distortion parameters for the $1 \cdot$ naphthalene, $1 \cdot$ pyrene and $1 \cdot N,N$-dimethylaniline complexes are given in Table 7. A lessening of the distortions of 1 in these complexes could be taken as evidence of partial reduction by electron transfer from the aromatic component. However, only very slight structural changes are found. The complexes contain nickel centers which are essentially unslipped (average $\Delta = 0.09$ Å). No regular pattern seems to emerge for the folding parameters. For the $1 \cdot$ naphthalene complex, only values for the 'unprimed' $C_2B_9H_{11}$ cage are given, because of disorder in the 'primed' cage (Fig. 2). In comparison with uncomplexed 1, the value of θ is identical and the value for φ is reduced to 0.2°. For the $1 \cdot$ pyrene complex the average θ value is reduced from 3.6 to 2.9° and the average φ value remains unchanged at 0.65°. In the case of the $1 \cdot N,N$-dimethylaniline complex the average θ value is reduced to 2.6°, and the average φ value is increased from 0.65 to 1.05°. These relatively minor changes in distortion parameters between the complexed and uncomplexed forms of 1 do not indicate an overall trend and can be explained by crystallographic packing forces.

Table 6. Position and displacement parameters for $1 \cdot (C_6H_5NMe_2).$[a,b]

Atom	x	y	z	U_{11} or $\langle u^2 \rangle$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U(eq)
Ni3	0.60641(10)	0.25206	0.49952(9)	0.0072(6)	0.0085(6)	0.0075(6)	0.0009(17)	0.0000(6)	−0.0001(6)	0.0077(2)
N17	1.0056(14)	0.5062(13)	0.5929(4)	0.054(6)	0.059(7)	0.035(5)	0.014(6)	−0.008(8)	0.003(10)	0.049(3)
C18	1.0741(16)	0.4258(15)	0.6340(10)	0.045(10)	0.076(14)	0.056(12)	−0.025(10)	0.003(8)	0.019(11)	0.059(5)
C19	0.9126(14)	0.5724(12)	0.6319(9)	0.045(9)	0.027(8)	0.041(10)	−0.007(7)	0.007(7)	−0.001(8)	0.038(4)
C1*	0.7306(18)	0.3189(15)	0.4217(7)	0.044(5)						
C2*	0.7364(16)	0.1973(12)	0.4187(7)	0.030(4)						
B4*	0.5595(19)	0.3613(12)	0.4227(7)	0.027(4)						
B5*	0.6616(18)	0.3714(14)	0.3422(8)	0.037(4)						
B6*	0.7841(11)	0.2682(11)	0.3415(6)	0.030(3)						
B7*	0.5792(20)	0.1422(15)	0.4180(9)	0.038(5)						
B8*	0.4520(12)	0.2414(14)	0.4178(6)	0.027(3)						
B9*	0.4828(17)	0.3172(15)	0.3378(8)	0.032(5)						
B10*	0.6264(12)	0.2604(19)	0.2886(6)	0.032(3)						
B11*	0.6840(17)	0.1535(12)	0.3374(8)	0.027(4)						
B12*	0.5059(16)	0.1794(12)	0.3365(7)	0.018(4)						
C1'*	0.6490(18)	0.1530(12)	0.5832(7)	0.035(4)						
C2'*	0.7377(9)	0.2510(17)	0.5897(5)	0.030(2)						
B4'*	0.4706(15)	0.1758(13)	0.5688(8)	0.029(4)						
B5'*	0.5361(18)	0.1408(14)	0.6558(8)	0.030(4)						
B6'*	0.7071(20)	0.1847(15)	0.6678(8)	0.029(5)						
B7'*	0.6343(19)	0.3628(15)	0.5805(8)	0.029(4)						
B8'*	0.4583(17)	0.3139(15)	0.5691(8)	0.036(5)						
B9'*	0.4175(11)	0.2453(16)	0.6485(7)	0.036(3)						
B10*	0.5665(12)	0.2476(20)	0.7099(6)	0.035(3)						
B11'*	0.7024(24)	0.3200(19)	0.6676(9)	0.045(6)						
B12'*	0.5241(19)	0.3616(16)	0.6565(9)	0.039(5)						
C11*	1.0889(14)	0.4300(13)	0.4815(9)	0.044(4)						
C12*	1.0911(16)	0.4266(14)	0.4064(9)	0.044(5)						
C13*	1.0126(18)	0.4988(16)	0.3661(6)	0.049(3)						
C14*	0.9300(17)	0.5678(14)	0.4007(9)	0.046(5)						
C15*	0.9295(15)	0.5708(13)	0.4778(10)	0.044(4)						
C16*	1.0049(16)	0.5070(14)	0.5192(4)	0.029(3)						

[a] Units of U_{ij}, U(eq) and isotropic $\langle u^2 \rangle$ are Å². Units of each e.s.d., in parentheses, are those of the least significant digit of the corresponding parameter. U(eq) is defined as: $(1/3)[U_{11}(aaa^*a^*) + U_{22}(bbb^*b^*) + U_{33}(ccc^*c^*) + 2U_{12}(aba^*b^* \cos \gamma) + 2U_{13}(aca^*c^* \cos \beta) + 2U_{23}(bcb^*c^* \cos \alpha)]$. [b] The anisotropic temperature factor is defined as: $\exp\{-2\pi^2[U_{11}(a^*a^*hh) + U_{22}(b^*b^*kk) + U_{33}(c^*c^*ll) + 2U_{12}(a^*b^*hk) + 2U_{13}(a^*c^*hl) + 2U_{23}(b^*c^*kl)]\}$. Atoms refined isotropically are denoted by*.
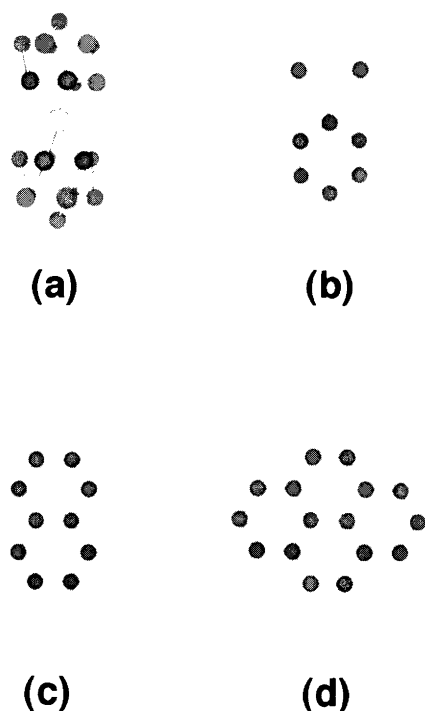
(a)   **(b)**

(c)   **(d)**

Fig. 7. The (a) LUMO of 1 and the HOMO's of (b) $C_6H_5NMe_2$, (c) $C_{10}H_8$, and (d) $C_{16}H_{10}$ were obtained from 6-31G* Hartree–Fock calculations using the GAUSSIAN 94 program.[8] Nodal surfaces are depicted of each.

Fig. 8. Detailed view of the nodal surface of the LUMO of 1 obtained from a 6-31G* Hartree–Fock calculation using the GAUSSIAN 94 program.[8]

Experimental

Materials and general methods. Naphthalene, pyrene and N,N-dimethylaniline were commercial reagents that were used without further purification. Dichloromethane was distilled from phosphorus pentoxide. Benzene and n-

hexane were distilled from sodium. The naphthalene adduct of 1 was prepared by adding a tenfold excess of naphthalene to a solution of 1 in benzene. The color of the solution immediately changed from yellow to red orange. The solution was concentrated by slow evaporation at room temperature to yield deep red crystals of $1 \cdot C_{10}H_8$. The pyrene $(1 \cdot C_{16}H_{10})$ and N,N-dimethylaniline $(1 \cdot C_6H_5NMe_2)$ adducts of 1 were prepared by a modification of the method described in Ref. 4a. The addition of a ten-fold molar excess of pyrene or N,N-dimethylaniline to a yellow dichloromethane solution of 1 resulted in the immediate formation of a dark green solution. Layering of these solutions with n-hexane and cooling these solutions to 20 °C resulted in greenish black and dark green crystals, respectively. $1 \cdot C_{10}H_8$ and $1 \cdot C_{16}H_{10}$ were stable indefinitely in air. However, upon standing in air, $1 \cdot C_6H_5NMe_2$ slowly decomposed via loss of dimethylaniline.

General methods of crystallographic analyses. Data for $1 \cdot C_{10}H_8$, $1 \cdot C_{16}H_{10}$ and $1 \cdot C_6H_5NMe_2$ were collected on modified Syntex $P\bar{1}$, Huber and Picker FACS-1 diffractometers, respectively. Calculations were performed in the J. D. McCullough X-ray Crystallographic Laboratory using the UCLA crystallographic programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; ABSCOR, locally written absorption correction program based on psi-scans; SHELX76 (Sheldrick), crystal structure package; MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declerq, and Woolfson), direct methods; and ORTEP (Johnson), figure plotting. Data were corrected for Lorentz and polarization effects. Additionally, $1 \cdot C_{10}H_8$ and $1 \cdot C_6H_5NMe_2$ were corrected for absorption and $1 \cdot C_{10}H_8$ was corrected for secondary extinction. The structures of $1 \cdot C_{10}H_8$, and $1 \cdot C_{16}H_{10}$ were solved using heavy-atom methods, and the structure of $1 \cdot C_6H_5NMe_2$ by direct methods (MULTAN80). Remaining atoms were located by use of difference electron density maps. In the course of refinement all cage C and B atoms were initially assigned scattering factors for boron. After refinement, carboranyl carbon atom positions could be distinguished by their anomalously low temperature factors and by shorter interatomic distances. Scattering factors for hydrogen were obtained from Stewart *et al.*,[10] and those for other atoms were taken from Ref. 11. Details of the individual data collections are given in Table 8.

X-Ray analysis of $1 \cdot C_{10}H_8$. A red crystal of 1 · naphthalene was affixed to a fiber using epoxy cement. Systematic absences were found for $hk0$ reflections for which $h = 2n + 1$, and for $0k1$ reflections for which $k + 1 = 2n + 1$. Unit-cell parameters were determined from a least-squares fit of 27 accurately centered reflections $(18.8 < 2\theta < 40.0°)$. These dimensions and other

Table 7. Distortion parameters for the metallacarborane moiety, **1** · (donor).[a]

Compound	$\Delta/\text{Å}$ [b]	$\theta/^\circ$ [c]	$\phi/^\circ$ [d]
[(C$_2$B$_9$H$_{11}$)$_2$Ni]	0.10, 0.09	5, 2.2	0.9, 0.4
[(C$_2$B$_9$H$_{11}$)$_2$Ni] · naphthalene	0.10(1)[e]	2.2(3)[e]	0.2(3)[e]
[(C$_2$B$_9$H$_{11}$)$_2$Ni] · pyrene	0.09, 0.07(2)	3.2, 2.6(3)	1.3, 0.0(3)
[(C$_2$B$_9$H$_{11}$)$_2$Ni] · *N,N*-dimethylaniline	0.11, 0.08(2)	3.0, 2.2(4)	1.4, 0.7(4)

[a] Units of e.s.d., in parentheses, are those of the least significant digit of the corresponding parameter. [b] Δ is the displacement of the metal from the normal through the centroid to the least-squares plane of the lower B$_5$ belt of the dicarbollide cage. [c] θ is the angle between the normals to the least-squares planes of the C(01), C(02), B(04), B(07) set and the lower B$_5$ belt. [d] ϕ is the angle between the normal to the plane of the B(04), B(07), B(08) set and the least-squares plane of the lower B$_5$ ring. [e] The value reported is for the unprimed cage only (Fig. 2). Calculated values of Δ, θ and ϕ derived from the primed cage are not valid because of disorder due to symmetry.

Table 8. Details of crystallographic collections.

	1 · (C$_{10}$H$_8$)	**1** · (C$_{16}$H$_{10}$)	**1** · (C$_6$H$_5$NMe$_2$)
Chemical formula	C$_{14}$B$_{18}$H$_{30}$Ni	C$_{20}$B$_{18}$H$_{32}$Ni	C$_{12}$B$_{18}$H$_{33}$NNi
Formula weight	451.7	525.8	444.7
Space group	*Pnma*	*P2$_1$2$_1$2$_1$*	*Pn2$_1$a*
T/K	297	298	128
a/Å	9.825(7)	6.967(1)	9.476(2)
b/Å	13.257(10)	14.804(2)	13.160(2)
c/Å	18.114(14)	26.200(4)	18.389(4)
V/Å^3	2359	2702	2304
Z	4	4	4
ρ(calcd)/g cm^{-3}	1.27	1.29	1.29
μ/cm^{-1}	11.3	7.3	8.52
λ/Å	1.5418	0.7107	0.7107
R [a]	0.077	0.075	0.055
R_w [b]	0.090	0.094	0.070
GOF [c]	2.51	2.45	2.12

[a] $R = \Sigma \| F_o | - | F_c \| / | F_o |$. [b] $R_w = [\Sigma w (| F_o | - | F_c |)^2 / \Sigma w (| F_o |)^2]^{1/2}$. [c] GOF $= [\Sigma w (| F_o | - | F_c |)^2 / (N_o - N_v)]^{1/2}$, where $w = 1/(\sigma^2 | F_o |)$.

parameters, including conditions of data collection, are summarized in Table 8. Data were collected at 25 °C in the θ–2θ scan mode using Cu K$_\alpha$ radiation. Three intense reflections (1 3 1, 0 0 4, 4 0 –2) were monitored every 97 reflections to check stability. Intensities of these reflections decayed 23% during the course of the experiment (21.9 h). Of the 1426 unique reflections measured, 919 were considered observed [$I > 2\sigma(I)$] and were used in the subsequent structure analysis.

Atoms were located by use of heavy atom methods. Nickel and cation non-hydrogen atoms were refined with anisotropic parameters. All other non-hydrogen atoms were refined isotropically. Carboranyl H were located and were included in structure factor calculations but parameters were not refined. Cation H were placed in calculated positions (C–H = 1.0 Å). Hydrogen atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Anomalous dispersion terms were included for nickel. The largest peak on a final difference electron density map was 0.26 e Å^{-3}. Final position and thermal

parameters for nonhydrogen atoms are provided in the supporting information.

X-Ray analysis of **1** · *C$_{16}$H$_{10}$*. A deep green crystal of **1** · pyrene was affixed to a fiber using epoxy cement. Systematic absences were found for reflections h00, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and for $00l$, $l = 2n + 1$. Unit-cell parameters were determined from a least-squares fit of 21 accurately centered reflections ($10.1 < 2\theta < 20°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table 8. Data were collected at 25 °C in the θ–2θ scan mode using Mo K$_\alpha$ radiation. Three intense reflections (1 6 –2, 1 1 8, –2 1 5) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated only slightly, ca. ± 5%, with less than 2% decay during the course of the experiment (50.0 h). Of the 2751 unique reflections measured, 1812 were considered observed [$I > 3\sigma(I)$], and were used in the subsequent structure analysis.

Atoms were located by use of heavy atom methods, and calculations were performed on a VAX 11/750 computer. Only Ni atoms were included with anisotropic thermal parameters. All pyrene hydrogens were included in calculated positions with an assigned B dependent on the value of the attached atom. All carboranyl hydrogens were included in located positions in structure factor calculations with an assigned B dependent on the value of the attached atom. Parameters for hydrogen atoms were not refined. Anomalous dispersion terms were applied to the scattering of Ni. The maximum on a final difference electron density map was 0.2 e Å^{-3}. Final position and thermal parameters for nonhydrogen atoms are provided in the supporting information.

X-Ray analysis of **1** · *C$_6$H$_5$NMe$_2$*. A deep green needle of **1** · *N,N*-dimethylaniline was affixed to a fiber. Systematic absences were found for reflections $0kl$, $k + l = 2n + 1$, and for $hk0$, $h = 2n + 1$. Unit cell parameters were determined from a least-squares fit of 21 accurately centered reflections ($9.6 < 2\theta < 20.4°$). These dimensions

and other parameters, including conditions of data collection, are summarized in Table 8. Data were collected at 128 K in the θ–2θ scan mode using Mo K_α radiation. Three intense reflections (1 0 5, 2 1 -2, 2 5 -4) were monitored every 97 reflections to check stability. Intensities of these reflections showed no decay during the course of the experiment (31.5 h). Of the 1581 unique reflections measured, 1152 were considered observed [$I > 3\sigma(I)$], and were used in the subsequent structure analysis.

Atoms were located by use of direct methods (MULTAN80), and calculations were performed on a VAX 11/750 computer. Only Ni, N, and methyl-C atoms were included with anisotropic thermal parameters. The hydrogen atoms of N,N-dimethylaniline were kept in calculated positions (C–H = 1.0 Å) with assigned B values based on the atoms to which they are attached. All carboranyl hydrogens were included in located positions in structure factor calculations. Parameters for hydrogen were not refined. Anomalous dispersion terms were applied to the scattering of Ni. The maximum on a final difference electron density map, near nickel, was 0.32 e Å^{-3}. Final position and thermal parameters for nonhydrogen atoms are provided in the supporting information.

Conclusions

The crystal structures of three nickelacarborane charge-transfer complexes were determined. In each case, the nickelacarborane is observed to be in a cisoid conformation. The long axis of the nickelacarborane is parallel to the plane of the aromatic donor. Contrary to intuition, the electron-deficient carbon atoms of the carborane cage are not pointed directly toward the donor molecule, but instead the dipole is rotated away from the normal of the aromatic hydrocarbon plane (Fig. 4). Based on frontier orbital calculations, there appears to be a strong correlation between the configuration of **1** with respect to the donor molecules. Additionally, the structure of the complexed **1** does not deviate significantly from that of uncomplexed **1**.

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