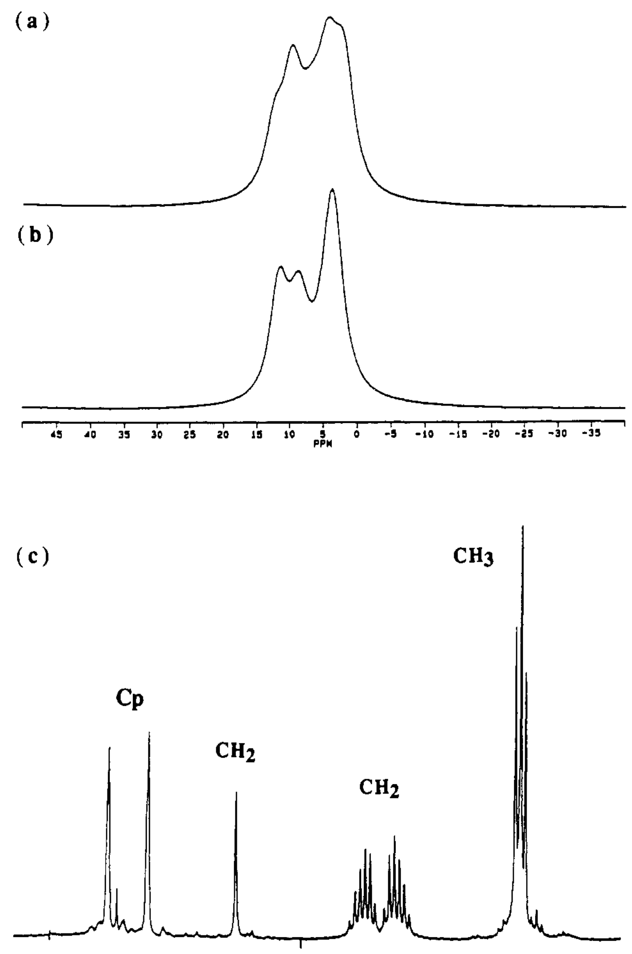

Figure 2. (a) 64.1-MHz ^{11}B NMR spectrum, (b) proton-decoupled ^{11}B NMR spectrum, and (c) 200-MHz ^1H NMR spectrum of CH_2[*closo*-1-(η-C_5H_4)Co(2,3-$Et_2C_2B_4H_4$)$]_2$.

removal of either one or two of the apical boron atoms of the carborane cages occurred during the TLC separation. Such decapitation reactions are well-known[3] for metal-2,3-$Et_2C_2B_4H_4$ complexes. Likewise, several of the minor products of the reaction gave mass spectra consistent with these formulas, but they were isolated in amounts insufficient to allow complete characterization.

Pure samples of **1** were obtained by vacuum sublimation of the crude material isolated by TLC. A single crystal X-ray determination of **1** established the structure shown in the ORTEP diagram in Figure 1. The compound is seen to be composed of two *closo*-1-(η-C_5H_4)Co(2,3-$Et_2C_2B_4H_4$) metallacarborane fragments joined by a cyclopentadienyl-bridging methylene group. The bond distances and angles within each cobaltacarborane fragment are normal and within the ranges observed in *closo*-1-(η-C_5H_5)Co-(2,3-$Me_2C_2B_4H_4$).[9] The cobalt to cyclopentadienyl ring bonding appears normal, but with slightly longer cobalt to ring carbon distances being observed to the carbons atoms located on the same side of the complex as the carborane ethyl groups (i.e. Co1-Cp3, Co1-Cp4 and Co1′-Cp1′, Co1′-Cp5′). The carborane and cyclopentadienyl rings in both fragments adopt approximately eclipsed configurations with respect to each other.

In many organometallic complexes containing the dicyclopentadienylmethane group, the metal bonding faces of the two rings are located cis to each other, such that metal-metal bonded complexes are observed. Owing to the coordinative saturation of the cobalt atoms in CH_2[*closo*-1-(η-C_5H_4)Co(2,3-$Et_2C_2B_4H_4$)$]_2$, cobalt-cobalt bonding is not possible, and the complex adopts a configuration that minimizes the steric interactions in the molecule. Thus, the two cobaltacarborane fragments are oriented at nearly a right angle, as evidenced by the 83.6 (2)° dihedral angle between the planes of the two cyclopentadienyl rings and the 89.1 (2)° dihedral angle between the planes of the two carborane faces. The closest interaction between the two fragments occurs at B5-Cp2′ (3.65 Å) and HB5-HCp2′ (2.75 Å). Similar types of *transoid* configurations have been observed in $CH_2[(\eta\text{-}C_5H_4)Cr(CO)_2(NO)][(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4C_2H_3)]$,[2q] $C(Me)R[(\eta\text{-}C_5H_4)Mn(CO)_3]_2$ (R = $OSiMe_3$, OH or H),[2s-u] and $SiMe_2[(\eta\text{-}C_5H_4)ZrCl_2(\eta\text{-}C_5Me_5)]_2$.[2r]

The 112.6 (9)° Cp1-Cc-Cp2 angle observed at the bridging methylene carbon is similar to comparable angles in both metal-metal-bonded dicyclopentadienylmethane complexes where the metals are by necessity oriented in a cis fashion—$CH_2[C_5H_4Rh(CO)]_2\text{-}\mu\text{-}CH_2$, 112.5 (5)°,[2a] $CH_2[C_5H_4Rh(CO)]_2\text{-}\mu\text{-}CO$, 112.3 (4)°,[2k] $CH_2[C_5H_4Ru(CO)_2]_2$, 114.5 (7)°,[2k] and $CH_2[C_5H_4Ru(CO)(\mu\text{-}CHMe)]_2$, 115.7 (5)°[2n]—and other non metal-metal-bonded bridged dicyclopentadienylmethane complexes where the metals are oriented in the *transoid* configuration such as $CH_2[(\eta\text{-}C_5H_4)Cr(CO)_2(NO)][(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4\text{-}C_2H_3)]$ (114.1 (4)°)[2q] or $C(Me)R[(\eta\text{-}C_5H_4)Mn(CO)_3]_2$ (R = $OSiMe_3$, 108.7 (6)°, OH, 110.2 (3)°, or H, 111.0 (3)°).[2s-u]

The NMR data for **1** are consistent with the observed structure. As shown in Figure 2, the ^{11}B NMR spectrum consists of three resonances in a 1:1:2 ratio at shifts characteristic of *closo*-1-(η-C_5H_5)Co(2,3-$R_2C_2B_4H_4$) complexes.[3] The ^1H NMR spectrum shows, in addition to the resonances from the carborane ethyl groups, two triplet resonances arising from the two sets of cyclopentadienyl ring protons and a singlet resonance of intensity 2 at 3.36 ppm which is assigned to the two bridging methylene protons. The observation of a singlet bridging methylene resonance is consistent with the spectra observed for other non metal-metal-bonded dicyclopentadienylmethane-bridged complexes[2b,q,s] and suggests the free rotation of the cyclopentadienyl rings about the bridging methylene in solution. Equivalent bridging-methylene protons have also been observed[10] in other methylene-bridged metallacarborane complexes derived from the benzyltetramethylcyclopentadienyl ligand.

Acknowledgment. We thank the National Science Foundation for the support of this research. We also thank Ms. Beverly Barum for assistance with the spectral data and Dr. Henry Bryndza for information concerning the synthesis of the dicyclopentadienylmethane dianion.

Registry No. **1**, 136676-20-5; CH_2Cl_2, 75-09-2; $(C_5H_6)_2CH_2$, 31196-70-0; 2,3-$Et_2C_2B_4H_6$, 80583-48-8; $CoCl_2$, 7646-79-9; 2,3-$Et_2C_2B_4H_4CoH$-2,3-$Et_2C_2B_3H_5$, 80593-36-8; $Et_4C_4B_8H_8$, 115796-00-4; $CH_2[(\eta\text{-}C_5H_4)Co(Et_2C_2B_3H_5)]_2$, 136676-21-6; $CH_2[(\eta\text{-}C_5H_4)Co(Et_2C_2B_4H_4)][(\eta\text{-}C_5H_4)Co(Et_2C_2B_3H_5)]$, 136676-22-7; cyclopentadiene, 542-92-7.

Supplementary Material Available: Tables of thermal parameters, bond angles, hydrogen atom coordinates, and least-squares planes (10 pages); a table of observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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X-ray Crystal Structure of $[Bi(NMe_2)_3]$

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Much of the current interest in the chemistry of bismuth derives from its importance as a constituent in the copper oxide based superconducting materials with high critical temperatures.[1]

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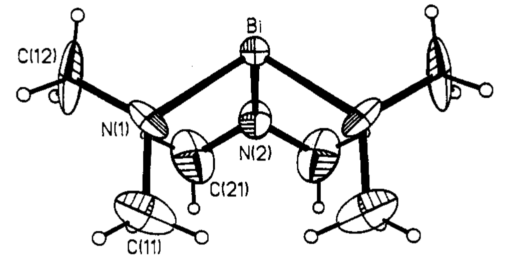

Figure 1. View of the molecular structure of **1** showing the atom-numbering scheme. Ellipsoids are drawn at the 40% probability level.

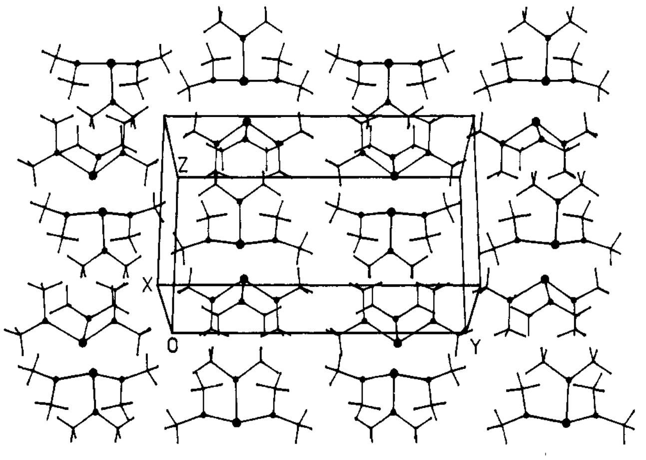

Figure 2. Crystal packing diagram of **1**.

Potential precursors for these materials are bismuth alkoxides[2] and bismuth amides,[3] although only in recent years have compounds of this type been studied in any detail. In ref 3 we reported the synthesis and X-ray crystal structure of $[\text{Bi}(\text{NPh}_2)_3]$, the first homoleptic bismuth amide to be structurally characterized. Herein we report details of the crystal and molecular structure of $[\text{Bi}(\text{NMe}_2)_3]$ (**1**) and of a slightly improved synthesis.

Results and Discussion

Compound **1** was first described by Ando et al.[4] These workers prepared **1** from the reaction between 3 equiv of $\text{Li}[\text{NMe}_2]$ and BiCl_3 in THF and isolated the complex as yellow crystals in 20% yield, but a slight modification of this procedure affords **1** with typical yields of ca. 60%. We note also that, apart from its potential usefulness as a precursor to bismuth chemistry in general, **1** is extremely volatile[4] and thus potentially valuable for chemical vapor deposition work.

The above-mentioned volatility of **1** indicated that strong intermolecular bonding was unlikely in the solid state, and this was confirmed by an X-ray crystallographic study. Compound **1**, which resides on a crystallographic mirror plane, is monomeric (Figures 1 and 2) and comprises a bismuth atom in a trigonal pyramidal coordination environment bonded to three NMe_2 groups. The Bi–N distances of 2.189 (18) and 2.180 (21) Å are comparable to those in $[\text{Bi}(\text{NPh}_2)_3]$ (**2**), 2.12 (2)–2.28 (2) Å,[3] but substantially shorter than most other structurally characterized Bi–N bonds, e.g. $[\text{BiCl}_5(\text{pyridine})]^{2-}$ (2.615 (8) Å),[5] $[\text{BiX}_2(\text{pyridine})_3(\text{S}_2\text{CNEt}_2)]$ (X = Cl, 2.668 (7), 2.698 (8), 2.794 (8) Å; X = I, 2.86 (1), 2.71 (1), 2.72 (1) Å),[6] $[\text{BiI}_2(\text{bpy})(\text{S}_2\text{CNEt}_2)]$ (2.61 (1), 2.56 (1) Å),[7] $[\text{BiI}_2(\text{terpy})(\text{S}_2\text{CNEt}_2)]$ (2.61 (2), 2.61 (2), 2.63 (2) Å),[7] $[\text{Bi}\{\text{N(Ph)=NC(S)=NN(H)Ph}\}_3]$ (2.678 (9), 2.706 (8), 2.746 (10) Å),[8] although it should be noted that the coordination numbers in the various compounds are quite different, being three in **1** and **2** and six or seven in the other examples.[9] We note also the bismuth azide complex $[\{\text{BiMe}_2(\text{N}_3)\}_n]$ with bridging μ-η^1-N_3 ligands (Bi–N 2.49 (6), 2.50 (6) Å)[10] but more particularly, the cyclic amide derivative $[\text{BiN}(\text{Bu}^t)\text{Si}(\text{Me})_2\text{N}(\text{Bu}^t)\{\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}]$ (**3**) recently reported by Veith and Malisch and co-workers.[11] In complex **3**, the Bi–N distances (2.17 (1), 2.18 (1) Å) are comparable to those in **1** and **2**.

Table I. Bond Lengths (Å) and Angles (deg) for **1**

Bi–N(1)	2.189 (18)	Bi–N(2)	2.180 (21)
N(1)–C(11)	1.457 (26)	N(1)–C(12)	1.381 (34)
N(2)–C(21)	1.409 (34)		
N(1)–Bi–N(2)	98.3 (5)	N(1)–Bi–N(1′)	96.2 (9)
Bi–N(1)–C(11)	120.9 (16)	Bi–N(1)–C(12)	111.3 (16)
C(11)–N(1)–C(12)	115.4 (23)	Bi–N(2)–C(21)	123.4 (15)
C(21)–N(2)–C(21′)	106.8 (26)		

Table II. Atomic Coordinates ($\times 10^4$) for **1**

	x	*y*	*z*
Bi	1300 (2)	7500	7244 (1)
N(1)	2986 (21)	6422 (13)	6455 (15)
C(11)	3566 (36)	6376 (22)	4866 (24)
C(12)	2506 (42)	5625 (18)	7104 (40)
N(2)	−557 (33)	7500	5348 (19)
C(21)	−900 (39)	6751 (24)	4434 (27)

The shortest intermolecular Bi–N contacts in crystals of **1** are 3.192 Å, considerably outside the normal bonding range (vide supra). The shortest Bi–Bi contacts are 3.849 Å, which may also be considered as nonbonding.

The angles around the bismuth center in **1** (N(1)–Bi–N(2) = 98.3 (5)°, N(1)–Bi–N(1′) = 96.2 (9)°, sum of angles 292.8°) define a trigonal center which is slightly more pyramidal than that found in **2** (sum of angles 296 and 297° for two independent molecules),[3] but whereas for **2**, all nitrogen centers are trigonal planar, in **1** they are slightly pyramidal (sum of angles at N(1) 347.6; sum at N(2) 353.6°). In complex **3** the relevant angles at bismuth are W–Bi–N(1) = 104.4 (3)°, W–Bi–N(2) = 103.1 (4)°, and N(1)–Bi–N(2) = 71.4 (4)°, with sum of angles 278.9°, i.e. slightly more pyramidal than either **1** or **2** although this is to be expected as a result of the four-membered BiN_2Si ring. A full listing of bond lengths and angles for **1** is given in Table I, atomic positional parameters are presented in Table II.

Ando et al.[4] reported ^{1}H NMR data for **1** (δ 3.45 reported as τ 6.55) although the solvent used was not given. We observed a signal at δ 3.72 for **1** in toluene-d_8 at 295 K (500 MHz) which was significantly broadened at 183 K and shifted to 3.85 ppm. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1**, in the same solvent, a signal was observed at δ 48.4 which had broadened considerably at 203

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K and was unobservable at 183 K. These data are consistent with hindered rotation about the Bi–N bond at low temperature although we have not been able to obtain limiting spectra. In ref 3 we reported that the ^{1}H NMR spectrum of [Bi{N(SiMe$_3$)$_2$}$_3$] (**4**) was also significantly broadened at 190 K. We have now obtained better data on this complex, which give an activation energy for Bi–N bond rotation of 41 (2) kJ mol^{-1} (see Experimental Section).

Experimental Section

Preparation. A solution of Li[NMe$_2$] (1.20 g, 24.0 mmol) in THF (15 mL) was added to a stirred solution of BiCl$_3$ (2.47 g, 7.8 mmol) in THF (15 mL) cooled to −78 °C (dry ice/ethanol bath), which resulted in the appearance of a yellow coloration. The mixture was stirred for 1 h and allowed to warm to room temperature after which time all volatiles were removed by vacuum, resulting in a yellow-green oily residue. Extraction with hexane (20 mL) followed by filtration through Celite afforded a yellow solution. Removal of all volatiles by vacuum from this yellow filtrate and sublimation onto a cold finger at dry ice temperature afforded **1** as a yellow crystalline solid (1.66 g, 62%). The best conditions for sublimation are using a pressure of about 10^{-2} Torr and warming the flask to 30 °C. X-ray quality crystals were obtained in the same way although it is better to use smaller quantities of material and to crystallize them directly onto the sides of the flask. In contrast to the report of Ando et al.,[4] we did not find it necessary to reflux the reaction mixture, which factor may be responsible for the higher yields obtained. Moreover, lower temperature sublimation is preferable to a higher temperature distillation as a means of purifying **1**. Bismuth analysis for the sublimed material (by EDTA titration): Calcd for $C_6H_{18}N_3Bi$, 61.3; found, 60.4%.

We have observed that **1** is rather light sensitive, especially in bright sunlight, turning black on exposure, although it can be handled under normal laboratory conditions for short periods without noticeable decomposition. It is best stored in a freezer in the dark, under which conditions it is stable for months.

X-ray Crystallography. Crystal data for **1** at 240 K: crystal dimensions 0.62 × 0.27 × 0.19 mm, M_r = 170.60; orthorhombic, a = 7.646 (2), b = 15.114 (4), c = 8.726 (2) Å, V = 1008.3 Å^3; space group *Pnma*, Z = 4; D_c = 2.247 g cm^{-3}; μ (Mo Kα) = 17.38 mm^{-1}. Data were measured on a Stoe–Siemens diffractometer using Mo Kα radiation (λ = 0.71073 Å) (graphite monochromated), ω/θ scan mode, with $2\theta_{max}$ = 50°, *hkl* ranges 0–9, 0–18, and 0–10, respectively. Due to rapid linear decay of intensity, only one unique set of 926 reflections were used, of which 683 had $F > 4\sigma_c(F)$. Data were corrected for Lorentz/polarization effects and absorption (empirically; ratio of maximum:minimum transmission = 3.40), using DIFABS[12] after all non H atoms were found and refined isotropically. The structure was solved by direct methods[13] with atomic scattering factors taken from ref 14. Anisotropic thermal motion parameters for all non H atoms were refined to minimize $\sum w\Delta^2$, $\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 109 - 72G + 1324G^2 - 336S + 350S^2 - 652GS$ ($G = F_o/F_{max}$, $S = (\sin\theta)/(\sin\theta_{max})$).[15] H atoms were refined at idealized positions with C–H = 0.96 Å, H–C–H = 109.5°, and U(H) = 1.2U_{eq}(C). For 50 refined parameters, R = 0.061, R' = 0.048, and goodness of fit = 1.26. An isotropic secondary extinction coefficient x was refined to 6 (3) × 10^{-7}, whereby $F'_c = F_c/(1 + xF_c^2/(\sin 2\theta))^{1/4}$. Largest features in final difference synthesis were next to the Bi atom.

NMR Data for 4 Obtained in Toluene-d_8. 500-MHz data (Bruker AMX 500): ^{1}H (293 K) 0.55, (190 K) 0.74, 0.53, T_c = 210 K, ΔG^* = 41.3 kJ mol^{-1}; ^{13}C{^{1}H} (293 K) 7.51, (190 K) 8.24, 6.13, T_c = 215 K, ΔG^* = 40.7 kJ mol^{-1}. 300-MHz data (Bruker WM 300): ^{1}H (297 K) 0.54, (185 K) 0.70, 0.54, T_c = 208 K, ΔG^* = 42.2 kJ mol^{-1}; ^{13}C{^{1}H} (290 K) 7.48, (195 K) 8.07, 6.00, T_c = 210 K, ΔG^* = 40.6 kJ mol^{-1}. ΔG^* was calculated from $\Delta G^* = RT_c\,(22.96 + (\ln T_c)/\Delta\nu)$. R = 8.314 J K^{-1} mol^{-1}.

Acknowledgment. We thank the SERC for financial support and BP Research (Sunbury, U.K.) for CASE awards (N.A.C. and G.A.F.). N.C.N. and W.C. also thank the Royal Society for additional supporting funds.

Registry No. **1**, 57403-58-4; **4**, 76505-24-3; Li[NMe$_2$], 3585-33-9; BiCl$_3$, 7787-60-2.

Supplementary Material Available: Tables of hydrogen positional parameters and anisotropic thermal parameters (1 page); a table of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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Additions and Corrections

1991, Volume 30

Habib Nasri, Yaning Wang, Boi Hanh Huynh,* F. Ann Walker,* and W. Robert Scheidt*: Reactions of Bis(nitro)($\alpha,\alpha,\alpha,\alpha$-tetrakis(*o*-pivalamidophenyl)porphinato)iron(III) with Pyridine and Imidazole. EPR and Mössbauer Spectra and Molecular Structures of the Mixed-Ligand Species.

Page 1486. Footnote *b* of Table V is incorrectly printed. The footnote should have read as follows: $\Delta/\lambda = E_{xz} - E_{xy} - (1/2)V/\lambda = g_x/(g_z + g_y) + g_z/(g_y - g_x) - (1/2)V/\lambda$ = tetragonality of Blumberg and Peisach. Nonetheless, all values in the table were calculated correctly.—W. Robert Scheidt