Communications to the Editor

Synthesis and Crystal Structure of [Et$_4$N]$_2$[Bi$_4$Fe$_4$(CO)$_{13}$]. Discovery of a Hybrid Zintl–Metal Carbonyl Cluster

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Received October 1, 1984

Zintl ions—anionic clusters of main-group elements—have been known for over half a century.[1] More recently, the discovery that sequestering the alkali metal cation with cryptands promotes cluster stability has enabled the structural characterization of a number of these materials.[2] Unlike their more famous main-group counterpart, the boranes, Zintl ions are naked clusters with no appended ligands. We wish to describe here the synthesis and characterization of the first hybrid Zintl–metal carbonyl, [Et$_4$N]$_2$[Bi$_4$Fe$_4$(CO)$_{13}$] (I).

The title compd. is prepared by treating [Et$_4$N][BiFe$_3$(CO)$_{10}$]^2 with pressures of CO (500–750 psi) or with triphenylphosphine in methylene chloride solution. A dark precipitate slowly develops, which has been shown to be [Et$_4$N]$_2$[Bi$_4$Fe$_4$(CO)$_{13}$] by X-ray and elemental analysis.[4] The infrared spectrum shows carbonyl bands at 2003 (m), 1960 (vs), 1908 (m), and 1880 cm^{-1} (CH$_3$CN). When CO is employed, Fe(CO)$_5$ is also produced. In the case of PPh$_3$, the formation of Fe(CO)$_4$PPh$_3$ and Fe(CO)$_3$(PPh$_3$)$_2$ (but no Fe(CO)$_5$) is detected.

The salt [Et$_4$N]$_2$[Bi$_4$Fe$_4$(CO)$_{13}$] crystallizes in the centrosymmetric orthorhombic space group $Pcab$ with $a = 14.128$ (3) Å, $b = 15.567$ (4) Å, $c = 39.816$ (18) Å, $V = 8756$ (5) Å^3, and D(calcd) = 2.55 g cm^{-3} for $Z = 8$ and $M_r = 1683.96$. There is no crystallographic symmetry imposed upon either the anion or cations. X-ray diffraction data (2θ 6.0–40.0°; Mo Kα radiation) were collected on a Syntex P2$_1$ automated four-circle diffractometer by using the ω-scan technique and were corrected for the effects of absorption ($\mu = 165.9$ cm^{-1}). The structure was solved by direct methods using the program MULTAN^5 and was refined by difference-Fourier and least-squares refinement techniques. The final discrepancy indices are $R_F = 7.8\%$ and $R_{wF} = 9.4\%$ for 2926 reflections with $|F_o| > 3\sigma(|F_o|)$ and $R_F = 6.1\%$ and $R_{wF} = 8.0\%$ for the 2343 reflections with $|F_o| > 6\sigma(|F_o|)$; as is apparent from these numbers, diffraction data were rather weak and of poor quality. The Et$_4$N$^+$ cations have the usual disordered configuration found previously in [Et$_4$N]$_2$[(μ-H)$_2$W$_2$(CO)$_8$]^6 and [Et$_4$N][BiFe$_3$(CO)$_9$(μ_3-CO)].^{3} The geometry of an isolated [Bi$_4$Fe$_4$(CO)$_{13}$]$^{2-}$ dianion is illustrated in Figure 1. The four bismuth atoms define a tetrahedron in which three faces are capped by Fe(CO)$_3$ units, while the fourth face is bare. Bi–Bi distances around the "bare" face (i.e., Bi(2)–Bi(3) = 3.162 (2), Bi(3)–Bi(4)

(1) Corbett, J. D. *Prog. Inorg. Chem.* 1976, *21*, 129.
(2) Corbett, J. D.; Critchlow, S. C.; Burns, R. C. *ACS Symp. Ser.* 1983, *No. 232*, 95–110.
(3) Whitmire, K. H.; Lagrone, C. B.; Churchill, M. R.; Fettinger, J. C.; Biondi, L. V. *Inorg. Chem.* 1984, *23*, 4227.
(4) Anal. Calcd for [Et$_4$N]$_2$[Bi$_4$Fe$_4$(CO)$_{13}$] (%): C, 20.68; H, 2.40; N, 1.66; Fe, 13.26; Bi, 49.64. Found: C, 18.62; H, 2.31; N, 1.70; Fe, 13.63; Bi, 50.12.
(5) (a) Germain, G.; Wolfson, M. M. *Acta Crystallogr., Sect. B* 1968, *B24*, 91. (b) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* 1971, *A27*, 368.
(6) Churchill, M. R.; Chang, S. W.-Y. *Inorg. Chem.* 1974, *13*, 2413.

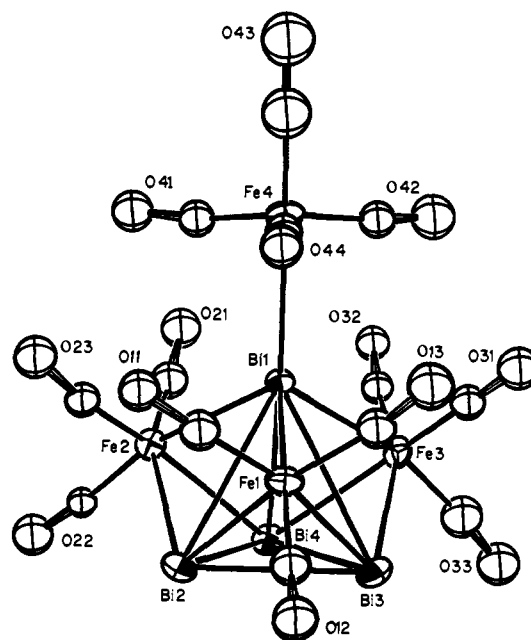**Figure 1.** Overall stereochemistry of the [Bi$_4$Fe$_4$(CO)$_{13}$]$^{2-}$ dianion. Note the approximate C_{3v} symmetry (ORTEP II diagram).

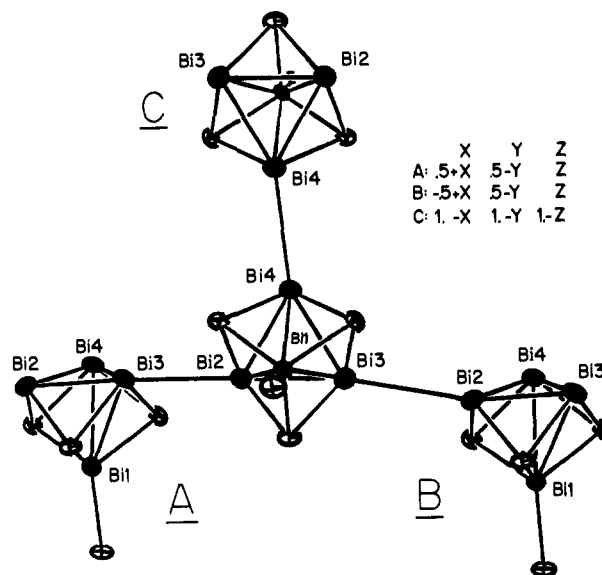**Figure 2.** Interactions between the central and surrounding [Bi$_4$Fe$_4$(CO)$_{13}$]$^{2-}$ dianions: Bi(2)–Bi(3; $^1/_2 + x$, $^1/_2 - y$, z) = 3.980 (2) Å, Bi(3)–Bi(2; $-^1/_2 + x$, $^1/_2 - y$, z) = 3.980 (2) Å, and Bi(4)–Bi(4; $1 - x$, $1 - y$, $1 - z$) = 3.981 (2) Å.

= 3.168 (2), Bi(4)–Bi(2) = 3.140 (2) Å) are substantially shorter than the other three Bi–Bi distances in the tetrahedral Bi$_4$ core of the anion (viz., Bi(1)–Bi(2) = 3.473 (2), Bi(1)–Bi(3) = 3.473 (2), Bi(1)–Bi(4) = 3.453 (2) Å). The μ_3-Fe(CO)$_3$ fragments are linked to the Bi$_4$ tetrahedron such that the Bi(1)–Fe linkages are slightly shorter than the other two Bi–Fe distances in each case (viz., Bi(1)–Fe(1) = 2.708 (5) vs. Bi(2)–Fe(1) = 2.753 (6) and Bi(3)–Fe(1) = 2.736 (6) Å; Bi(1)–Fe(2) = 2.699 (6) vs. Bi(2)–Fe(2) = 2.733 (5) and Bi(4)–Fe(2) = 2.729 (6) Å; Bi(1)–Fe(3) = 2.701 (6) vs. Bi(3)–Fe(3) = 2.714 (6) and Bi(4)–Fe(3) = 2.729 (6) Å). The fourth iron atom is the central atom of an

Fe(CO)$_4$ unit which is linked only to the apical Bi(1), with Bi-(1)–Fe(4) = 2.752 (6) Å. Atoms Fe(1), Fe(2), and Fe(3) are each in a distorted-octahedral coordination environment, whereas Fe(4) has a trigonal-bipyramidal geometry. The [Bi$_4$Fe$_4$(CO)$_{13}$]$^{2-}$ cluster as a whole has approximate C_{3v} symmetry.

As shown in Figure 2, there are weak Bi⋯Bi interactions between the dianions. These secondary contacts are reminiscent of the interactions observed in such solid state Zintl phases as Ca$_{11}$Bi$_{10}$.[7]

The two Bi–Bi distances observed for I (ca. 3.16 and 3.46 Å) are comparable with the two closest Bi–Bi contacts in the pure crystalline element (3.07 and 3.53 Å).[8] Compound I may be compared to the Bi$_4^{2-}$ anion, which has been crystallographically charterized.[9] In this molecule, a square-planar array of Bi atoms is observed with two unique Bi–Bi distances of 2.936 (2) and 2.941 (2) Å. These distances are noticeably shorter than for I, and this may arise via π interactions in the square-planar molecule since it is a 6π-electron system. Unfortunately, the Bi–Bi distance cannot be directly compared to that in tetrahedral Sn$_2$Bi$_2^{2-}$ since in that molecule the Sn and Bi atoms are equally disordered over all sites.[10] The bonding in this molecule will be discussed elsewhere.

Registry No. [Et$_4$N][BiFe$_3$(CO)$_{10}$], 92786-73-7; [Et$_4$N]$_2$[Bi$_4$Fe$_4$-(CO)$_{13}$], 94483-21-3; Fe(CO)$_4$PPh$_3$, 35679-07-3; Fe(CO)$_3$(PPh$_3$)$_2$, 21255-52-7; Fe(CO)$_5$, 13463-40-6; Bi, 7440-69-9; Fe, 7439-89-6.

Supplementary Material Available: Tables of fractional coordinates and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

(7) Deller, K.; Eisenmann, B. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1976**, *31B*, 29.

(8) Curka, P.; Barrett, C. S. *Acta Crystallogr.* **1962**, *15*, 865.

(9) Asai, A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 2482.

(10) Critchlow, S. C.; Corbett, J. D. *Inorg. Chem.* **1982**, *21*, 3286.

Kinetically Stable Conformers of 3,4,5,6-Tetramethyl-9,10-dihydroxy-9,10-dihydrophenanthrene as Probes of the Conformer Specificity of UDPglucuronosyltransferase

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Microsomal UDPglucuronosyltransferase (EC 2.4.1.17) participates in the mammalian metabolism of polycyclic aromatic hydrocarbons by catalyzing the glucuronidation of phenolic and *trans*-dihydro diol metabolites.[1] The enzyme has been shown to discriminate between stereochemically distinct carbinol groups of several dihydro diols, e.g., the 9,10-dihydroxy-9,10-dihydrophenanthrenes 1–3.[2] A salient feature of the stereochemical recognition of dihydro diols by UDPglucuronosyltransferase is the potential for conformer specificity (Scheme I). Unfortunately,

(1) (a) Nemoto, N.; Gelboin, H. V. *Biochem. Pharmacol.* **1976**, *25*, 1221. (b) Fahl, W. E.; Shen, A. L.; Jefcoate, C. R. *Biochem. Biophys. Res. Commun.* **1978**, *85*, 891. (c) Bansal, S. K.; Zaleski, J.; Gessner, T. *Ibid.* **1981**, *98*, 131. (d) Owens, I. S.; Mackenzie, P. I. *Ibid.* **1982**, *109*, 1075.

(2) Lewis, D. A.; Armstrong, R. N. *Biochemistry* **1983**, *22*, 6297.

Scheme I
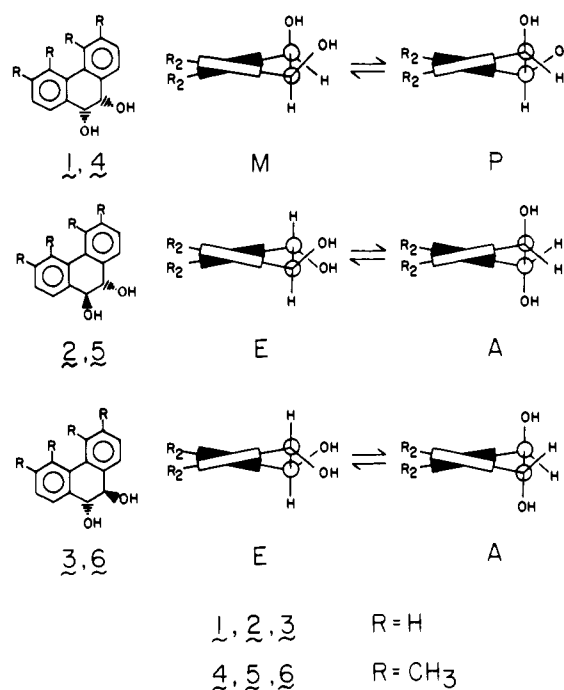
the kinetic lability of the conformers of 1–3 precludes their use in obtaining this information. In this paper we report the synthesis and use of the six kinetically stable, stereoisomeric conformers of 3,4,5,6-tetramethyl-9,10-dihydroxy-9,10-dihydrophenanthrene to ascertain the conformer specificity of UDPglucuronosyltransferase.

Oxidation of 3,4,5,6-tetramethylphenanthrene with OsO$_4$ followed by workup with NaHSO$_3$ gave the racemate **4**.[3] Further oxidation of **4** to the orthoquinone with DDQ[4] followed by the KBH$_4$ reduction in the presence of O$_2$[5] gave, stereoselectively, a mixture consisting of racemic trans diequatorial isomers **5E** + **6E** (98%) and cis isomers **4** (2%). Mutarotation of **5E** + **6E** (16 h, 90 °C, 25% CH$_3$OH, 75% H$_2$O) gave a 20% yield of **5A** + **6A** after separation of the equilibrium mixture by silica chromatography. Structures of the three racemates were based on proton NMR spectra of the corresponding diacetates, where vicinal coupling constants $^3J_{9,10}$ for the benzylic protons are particularly diagnostic of the relative configuration. Benzylic protons of diacetyl-**4** were magnetically nonequivalent, δ 5.81 (d, 1 H), 5.93 (d, 1 H), $^3J_{9,10}$ = 3.0 Hz. Coupling constants for the magnetically equivalent benzylic protons of the trans isomers were obtained from the natural-abundance ^{13}C-satellite resonances located 77 Hz upfield and downfield from the singlet resonance of the ^{12}C isotopomers.[6] Thus for diacetyl-(**5E** + **6E**) δ 5.91 (s, 2 H), $^1J_{^1H,^{13}C}$ = 155 Hz, $^3J_{9,10}$ = 11.2 Hz, and for diacetyl-(**5A** + **6A**) δ 5.80 (s, 2 H), $^1J_{^1H,^{13}C}$ = 155 Hz, $^3J_{9,10}$ = 3.1 Hz. Further confirmation of the structures of the *trans*-diacetates was obtained by X-ray crystallography as shown in Figure 1.

The *cis*-antipodes **4M** and **4P** were resolved on a preparative scale via synthesis, resolution, and hydrolysis of the diastereomeric bis[(−)-α-methoxy-α-(trifluoromethyl)phenylacetates.[7] Enantiomers **5A** and **6A** were readily resolved by HPLC using a chiral stationary phase.[8] The diequatorial isomers **5E** and **6E** were

(3) Armstrong, R. N.; Lewis, D. A. *J. Org. Chem.*, in press.

(4) Lehr, R. E.; Taylor, C. W.; Subdh, K.; Mah, H. D.; Jerina, D. M. *J. Org. Chem.* **1978**, *43*, 3462.

(5) Platt, K. L.; Oesch, F. *Synthesis* **1982**, 459.

(6) Cobb, D. I.; Lewis, D. A.; Armstrong, R. N. *J. Org. Chem.* **1983**, *48*, 4139.

(7) (a) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543. (b) Armstrong, R. N.; Kedzierski, R.; Levin, W.; Jerina, D. M. *J. Biol. Chem.* **1981**, *256*, 4726.

(8) Pirkle, W. H.; Finn, J. M.; Schreiner, J. L.; Hamper, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 3964.