molecule consists of two distorted tetrahedral B_2Fe_2 cages related by a noncrystallographic C_2 axis joined along an Fe–B edge such that the two Fe and two B bridgehead atoms define a butterfly structure with a dihedral angle of 162.7 (1)°. The positions of the hydrogen atoms, located and refined, agree with the NMR data obtained in solution. All bond distances and angles are normal based on previously characterized metallaboranes. Although $[B_2H_5Fe_2(CO)_6]^{n-}$, n = 0–2, have not been crystallographically characterized, the structures of closely related Ta[18] ($Cp^*{}_2Ta_2(\mu\text{-}Br)_2(B_2H_6)$) and Nb[19] ($Cp^*Nb_2(B_2H_6)_2$) analogues have been reported.

The observation of a coupled cage structure rather than a single cage reflects the isomeric possibilities for a given cage electron count.[20] As $[B_2H_4Fe_2(CO)_6]_2$ is a mixed main group–transition element cluster and a rare example of a cluster containing equal numbers of boron and iron atoms, one wonders if it will behave more like a metal or main-group cluster. Application of the counting rules developed by Mingos and co-workers for metal cluster coupling and fusion provides a test.[21] Considering total cluster valence electrons, $[B_2H_4Fe_2(CO)_6]_2$ possesses 76 while the rules predict 74.[22] On the other hand, if one formulates the $B_2H_4Fe_2(CO)_6$ fragment as shown in Chart I, part a, then the coupling of two such fragments can be viewed as taking place with the formation of two three-center two-electron bonds, each generated by the interaction of an empty orbital on the bare boron of one fragment with the electron-rich Fe–B edge of the other fragment as shown in Chart I, part b. Thus, a coupling scheme that is predicated on the 8–18 electron rules and the elimination of two-electron edge bonds fails.[23,24]

Although the oxidant remains to be identified, the apparent reaction

$$2[B_2H_4Fe_2(CO)_6]^{2-} + 4[\mathrm{ox}] \rightarrow [B_2H_4Fe_2(CO)_6]_2 + 4[\mathrm{red}] \quad (1)$$

constitutes oxidative coupling not unlike that known for $[B_{10}H_{10}]^{2-}$, i.e.,[9,25]

$$2[B_{10}H_{10}]^{2-} + 4[\mathrm{ox}] \rightarrow [B_{20}H_{18}]^{2-} + 4[\mathrm{red}] + 2H^+ \quad (2)$$

Indeed the cage–cage linkage in $[B_{20}H_{18}]^{2-}$ has been described as being composed of two three-center two-electron bonds as we now find in $[B_2H_4Fe_2(CO)_6]_2$. As each unit of $[B_2H_4Fe_2(CO)_6]_2$ has three bridging protons, two of which are FeHB bridges, deprotonation of the linked cluster product is possible, leading, in principle, to further condensation to higher linked species. Investigations along these lines are continuing.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

Supplementary Material Available: Tables of crystal data, atom coordinates, selected bond distances and angles, anisotropic thermal parameters, and H atom coordinates for $[B_2H_4Fe_2(CO)_6]_2$ (6 pages); tables of observed and calculated structure factors for $[B_2H_4Fe_2(CO)_6]_2$ (14 pages). Ordering information is given on any current masthead page.

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[17] Crystal data: $C_{12}H_8B_4O_{12}Fe_4$; orthorhombic, P_{bca}, a = 12.990 (4) Å, b = 12.279 (3) Å, c = 26.527 (10) Å, V = 4231.2 Å^3, Z = 8; D(calcd) = 3.30 g cm^{-3}; λ(Mo Kα) = 0.71073 Å; T = 123 ± 2 K; Enraf-Nonius CAD4 diffractometer. A total of 8410 reflections were collected in the $-h,-k,l$ and the $-h,-k,-l$ quadrants ($3.0° \leq 2\theta \leq 58.7°$), of which 5743 were unique and 4851 observed ($3\sigma(F_o)$). Lorentz, polarization and absorption corrections were applied. The structure was solved by direct methods, which revealed the positions of 24 non-hydrogen atoms. Subsequent difference electron density Fourier syntheses located the remaining atoms, including hydrogens. The structure was refined by a full-matrix least-squares process (anisotropic for non-hydrogen atoms with hydrogens at fixed isotropic displacement parameters); $R(F)$ = 3.4%, $R(\mathrm{w}F)$ = 4.4%, GOF = 2.01, $\Delta(\rho)$ = 0.55 e Å^{-3}.

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o-Phenylenemagnesium Tetramer: The First Organomagnesium Cluster

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The chemistry of di- and polymetalated aromatic compounds has been dominated by organolithiums;[1] illustrative examples are 1,8-dilithionaphthalene,[2] 2,2′-dilithiobiphenyl,[3] and 1,2-dilithiobenzene (**1**).[4] The corresponding bifunctional organomagnesium compounds have received little attention.[5] Because of our interest in divalent organomagnesiums,[6] we investigated the synthesis and structure of *o*-phenylenemagnesium (**2**).

1,2-Bis(bromomagnesio)benzene, the di-Grignard reagent corresponding to **2**, has been obtained from (trimeric) *o*-phenylenemercury (**3**) by reaction with lithium metal to give **1**, followed by addition of magnesium bromide.[4a] In analogy with the transformation **3** → **1**, we prepared **2** by stirring **3** in THF with magnesium (Scheme I).

The progress of the reaction was monitored by the disappearance of the sparingly soluble **3**; after 2 weeks of stirring at room temperature, the resulting clear, slightly brownish solution was carefully decanted from the amalgam. In spite of some loss of material in this process, **2** was obtained in 90% yield (titration after hydrolysis[7]). Compound **2** was further characterized by ^{1}H and ^{13}C NMR spectroscopy[8] and by its conversion to **4**[9] with chlorotrimethylstannane.

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[8] **2**: ^{1}H NMR (toluene-d_8; 250 MHz) δ 8.12 (dd, ^3J = 5.0 Hz, ^4J = 3.3 Hz, 2 H, H(3,6)), 7.23 (dd, ^3J = 5.0 Hz, ^4J = 3.3 Hz, 2 H, H(4,5)); ^{13}C NMR (THF-d_8; 92.6 MHz) δ 189.1 (br m, C(1,2)), 140.6 (dd, ^1J = 150.0 Hz, ^3J = 4.9 Hz, C(3,6)), 124.3 (dm, ^1J = 155.7 Hz, C(4,5)). A ^{13}C{^{1}H} NMR spectrum showed sharp singlets for all carbons.

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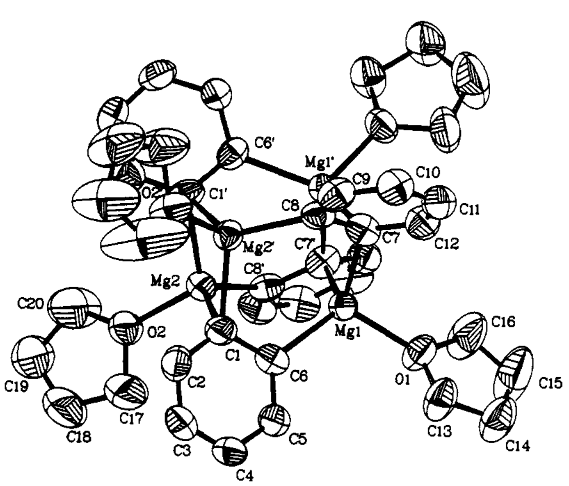
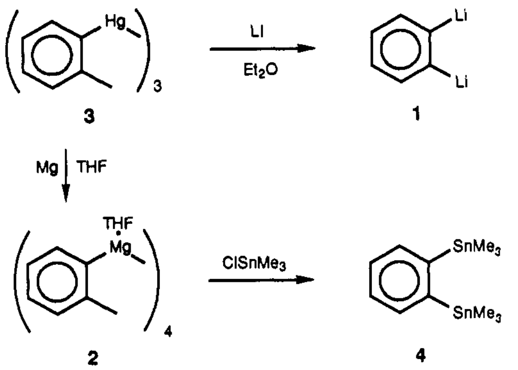


Figure 1. ORTEP drawing of **2**. Selected bond distances (Å) and angles (deg): Mg(1)–O(1), 2.041 (4); Mg(1)–C(6), 2.171 (5); Mg(1)–C(7), 2.273 (6); Mg(1)–C(7′), 2.291 (5); Mg(2)–O(2), 2.031 (4); Mg(2)–C(1), 2.314 (6); Mg(2)–C(1′), 2.237 (6); Mg(2)–C(8′), 2.139 (5); C(1)–C(6), 1.418 (8); O(1)–Mg(1)–C(6), 112.5 (2); O(1)–Mg(1)–C(7), 108.4 (4); O(1)–Mg(1)–C(7′), 106.3 (2); C(6)–Mg(1)–C(7), 109.8 (2); C(6)–Mg(1)–C(7′), 116.3 (2); C(7)–Mg(1)–C(7′), 102.9 (2); O(2)–Mg(2)–C(1), 102.3 (2); O(2)–Mg(2)–C(1′), 113.1 (2); O(2)–Mg(2)–C(8′), 111.0 (2); C(1)–Mg(2)–C(1′), 101.2 (2); C(1)–Mg(2)–C(8′), 120.0 (2); C(1′)–Mg(2)–C(8′), 108.9 (2); C(2)–C(1)–C(6), 118.4 (5); C(1)–C(6)–C(5), 116.5 (5); Mg(1)–C(7)–Mg(1′), 75.8 (2); Mg(2)–C(1)–Mg(2′), 77.2 (2).

Scheme I



Crystals of **2** were obtained by cooling a saturated solution in THF. The remarkable crystal structure[10] (Figure 1) shows a tetramer with C_2 symmetry; the core is a cluster of four magnesium atoms in a strongly distorted tetrahedral arrangement with four different magnesium–magnesium distances: Mg(1)–Mg(1′) 2.804 (2) Å, Mg(2)–Mg(2′) 2.841 (2) Å, Mg(1)–Mg(2) 3.305 (3) Å, Mg(1)–Mg(2′) 3.548 (3) Å. Tetrameric metal clusters are common in organolithium chemistry[1] but have to our knowledge not been encountered with diorganylmagnesiums.[5,11] Each face of the tetrahedron is saddeled by one *o*-phenylene unit, which is σ-bonded, e.g., via C(6), to one magnesium, with μ-bridging between two others via an unsymmetrical (!) three-center two-electron bond involving C(1). This lack of symmetry is caused by a slight difference in distance from a bridging carbon to its two magnesiums; two pairs of phenylenes can be distinguished which differ slightly in all three magnesium–carbon bond lengths. Correspondingly, each magnesium has three bonds: a σ-bond to one carbon and a bridging three-center two-electron relation to two different phenylene units. The normal tetrahedral coordination of each magnesium is completed by one THF oxygen. The short Mg(1)–Mg(1′) distance, resulting from μ-bridging by two phenylene carbons, is analogous to that observed in carbon-bridged dimers of ordinary diorganylmagnesiums.[11,12] It should be pointed out that while C(6) and C(1) are different in the solid state (σ- and μ-bonded, respectively), they are equivalent in solution according to the ^{13}C NMR spectrum;[8] apparently, the structure is fluxional in solution.

Why do metal clusters normally not occur in organomagnesiums, and why is **2** an exception to this rule? We feel that three factors may be responsible. In the first place, the difference in electronegativity is important; organomagnesiums are less polar, which generally reduces the tendency to form aggregates. Secondly, stoichiometry comes to mind: in tetrameric organolithiums, as in **2**, the faces of the tetrahedron of metals are capped by the organic group; this arrangement is apparently particularly stable if the charges on the metal and carbanion are the same: Li^+R^- or $Mg^{2+}R^{2-}$. The third factor is steric and probably the most important one. In tetrameric clusters, lithium may or may not carry an additional ether molecule;[1d] in the latter case, its electron demand is satisfied by *three* electron-deficient four-center two-electron bonds to carbon only. Magnesium is a stronger Lewis acid toward ethers and thus has a higher tendency to coordinate additional ether molecules. This is illustrated by the few known[11] cyclic organomagnesium structures that have two (or even three) molecules of THF/magnesium and show monomers,[13] dimers,[14] or trimers[15] with 5–15-membered rings. Models show that, for **2**, analogous oligomeric cyclic structures are overcrowded due to the close proximity of the two magnesiums bonded to the same benzene ring. Bridging as in **2** saves space while permitting magnesium to retain tetracoordination including *one* molecule of THF.

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Supplementary Material Available: Tables of fractional coordinates, anisotropic thermal parameters, bond distances and angles, and torsion angles for **2** (5 pages); listing of observed and calculated structure factors for **2** (22 pages). Ordering information is given on any current masthead page.

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(10) Crystal data for **2** ($C_{40}H_{48}O_4Mg_4$): hexagonal tablet shaped crystal (0.20 × 0.50 × 0.50 mm), monoclinic, space group $I2/a$, with $a = 17.071$ (3) Å, $b = 11.877$ (1) Å, $c = 18.809$ (1) Å, $\beta = 99.97$ (1)°, $V = 3756.0$ (6) Å^3, $Z = 4$, D(calcd) = 1.220 g cm^{-3}, $F(000) = 1472$, μ(Mo Kα) = 1.3 cm^{-1}; 3724 independent reflections (1.4° < θ < 26.5°); $\omega/2\theta$ scan; $T = 294$ K) were measured on an Enraf-Nonius CAD-4 diffractometer using Zr-filtered Mo Kα radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz polarization effects, absorption (DIFABS), and a linear decay (9%). The structure was solved by direct methods (SHELXS-86) and difference Fourier techniques and refined by full-matrix least squares (SHELX-76) to an R value of 0.066, $R_w = 0.074$, $w^{-1} = (\sigma^2(F) + 0.00130F^2)$, for 1990 reflections with $I > 2.5\sigma(I)$ and 220 parameters. The hydrogen atoms were added at calculated positions and refined riding on the respective carbon atoms. All non-H atoms were refined with anisotropic thermal parameters. A final difference Fourier map showed no residual density outside 0.48 and −0.28 e/Å^3 (near the disordered THF ring). The geometric details of the structure are provided as supplementary material.

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