replacement of H_2O by CN^- in the heme coordination sphere reduces k_t by over 1 order of magnitude. Quantitation of I for M = Mg and Zn and with all the ligands studied here yielded the values for $k_t^{M}(L)$ shown in Table I.

The rate constant $k_b^{M}(L)$ is determined from the short-time absorbance rise of I. The kinetic traces in Figure 1 give $k_b^{Zn}(H_2O) = 345\ (30)\ s^{-1}$, minimally larger than $k_b^{Zn}(CN^-) = 243\ (25)\ s^{-1}$. For $L = H_2O$, reduction of the aquo-bound heme most likely yields the five-coordinate ferroheme, $Fe^{2+}P$.[10] However, ligand dissociation from $Fe^{2+}(CN^-)P$ is slow,[11] and the I → A process involves reoxidation of the CN^--bound species, $Fe^{2+}(CN^-)P$. Indeed, the data in Table I indicate that all the anionic ligands remain associated with iron throughout the electron-transfer cycle of eqs 1 and 2.[12] First, if ET-induced ligand loss were rapid compared to the I → A electron-transfer process, then one would expect that $k_b^{M}(X^-) = k_b^{M}(H_2O)$, contrary to observation. Second, for a given anion, $k_b^{Mg}(X^-) < k_b^{Zn}(X^-)$; this metal dependence indicates that $k_b^{M}(X^-)$ cannot represent rate-limiting ligand dissociation from the $Fe^{2+}(X^-)P$ redox partner of state I, followed by fast ET (i.e., ligand "gating"[3a,13] of I → A).[14]

The data presented in Table I show that (i) the $A^* \rightarrow I$ process is strongly reduced by anion binding to the heme, with $k_t^{M}(L^0) \geq 10 k_t^{M}(X^-)$, and (ii) in contrast, anion binding lowers the I → A rate constant k_b^{M} by less than 50%. These results can be interpreted as arising from changes in the activation free energy for ET, ΔG^*, that occur as the energetic consequence of persistent anion ligation on the ET time scale. Direct protein electrochemistry of $Mb^{3+}(CN^-)$ indicates that the $Fe^{3+}(X^-)P/Fe^{2+}(X^-)P$ redox potential is shifted negative by almost 500 mV relative to $Fe^{3+}(H_2O)P/Fe^{2+}P$;[15] this shift decreases the driving force for the $A^* \rightarrow I$ ET process for a hybrid with either M^{2a} from $-\Delta G^\circ \approx 1.0$–1.1 eV ($L = L^0$) to $-\Delta G^\circ \approx 0.5$–0.6 eV ($L = X^-$), and increases that for the I → A reaction from $-\Delta G^\circ \approx 0.7$–0.8 eV ($L = L^0$) to $-\Delta G^\circ \approx 1.2$–1.3 eV ($L = X^-$).[16] With these changes in driving force, both the 10-fold-lower values of $k_t^{M}(X^-)$ as compared to $k_t^{M}(L^0)$ and the small reduction in $k_b^{M}(L)$ upon anion binding can be accommodated by the classical Marcus expression, $\Delta G^* = (\lambda + \Delta G^\circ)^2/4\lambda$, with a single reorganization energy, $\lambda \sim 1$ eV, for both reactions of the protein complex.[17]

This value for λ places both the $A^* \rightarrow I$ and I → A processes near the peak of the Marcus free energy curve for $L = L^0$ and attributes the reduction in k_b for $L = X^-$ to an excursion into the inverted region of ET.[18] Within this context, the general result that $k_b^{M}(L) \gg k_t^{M}(L)$ appears to require that the preexponential factor for k_b^{M} is enhanced over that for k_t^{M}.[19] Measurement of ET in hybrids prepared from Hb mutants is addressing this issue.

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Registry No. Heme, 14875-96-8.

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[11] Holloway, M. R.; White, H. A. *Biochem. J.* **1975**, *149*, 221–231.

[12] In contrast, reduction of $Mb^{3+}(L)$ by exogenous $S_2O_4^{2-}$ requires ligand dissociation for most anionic ligands: (a) Cox, R. P.; Holloway, M. R. *Eur. J. Biochem.* **1977**, *74*, 575–587. (b) Olivas, E.; de Waal, D. J. A.; Wilkins, R. G. *J. Biol. Chem.* **1977**, *252*, 4038–4042.

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[14] Since $k_b^{Mg}(ImH) \approx k_b^{Mg}(H_2O)$ and $k_b^{Zn}(ImH) \approx k_b^{Zn}(H_2O)$, the fate of $Fe^{2+}(ImH)P$ is unclear.

[15] (a) We find that the reduction potential for the $Mb(Fe^{3+}L)/Mb(Fe^{2+}L)$ couple is +0.05 V vs NHE for $L = H_2O$, and −0.43 V vs NHE for $L = CN^-$ (to be submitted), as measured by cyclic voltammetry (ref 15b). (b) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706–723.

[16] Driving-force calculations utilize $E^{\circ\prime} = +0.95$ vs NHE for the half-reaction $(ZnP)^+ + e^- = ZnP$ (note the typographical error in ref 2a).

[17] We have taken the reorganization energies to be identical for reduction for all ligated hemes. This is likely a good approximation, even for $L = H_2O$, where ET is synchronous probably with ligand loss, because the inner-sphere contribution to the total reorganization energy is small.[4a] The λ reported here is slightly less than that reported in ref 4a. This is expected because that result includes a contribution from solvent reorganization about $[LRu(NH_3)_5]^{3+/2+}$.

[18] For an extensive observation of inverted-region ET, see: Fox, L. S.; Kozik, M.; Winkler, J. R.; Gray, H. B. *Science* **1990**, *247*, 1069–1071.

[19] This is true for both M considered separately. Despite very similar energetics, k_b and k_t for M = Zn are consistently larger than for M = Mg, indicative of a larger preexponential term in the former.

1,2-Dehydro-*o*-carborane[1]

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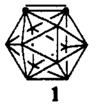
Though the similarity between benzene, the prototypal planar aromatic two-dimensional system of organic chemistry, and the icosahedral "super-aromatic" carboranes may at first seem remote, even forced, there is much the two have in common. Both owe their special stability to the presence of a fully filled system of bonding molecular orbitals, three for benzene, 13 for *o*-carborane.[2] Aromaticity is manifested in both cases by extraordinary thermal stability as well as unusual chemical reactivity. For instance, both species undergo aromatic substitution.[2c,3] There are many differences as well. Benzene requires ca. 1100 °C before two ring carbons move apart in a degenerate rearrangement,[4] but a mere 420 °C suffices to convert *o*-carborane to its meta isomer.[5] Connection between a benzene ring and an orbital on an α carbon dominates the chemistry of the benzyl system, yet the icosahedral frame and an α orbital are quite well insulated from each other.[6] We have been involved for some time in an exploration of the properties of carborane-based reactive intermediates.[7] Here we describe the first example of a dehydro-*o*-carborane (**1**) and make some comparisons to the related classically aromatic system, dehydrobenzene, or benzyne.[8]

The dots represent carbons - all other vertices are B–H.



1

In order to generate **1**, we have mimicked one of the earlier syntheses of benzyne in which an α-bromo anion is generated, only to suffer elimination of bromide.[9] After the failure of a number of direct routes from 1-bromo-*o*-carborane or 1,2-dibromo-*o*-carborane,[10] we proceeded by an indirect path in which the dianion **2** was treated with a single equivalent of bromine to generate the bromo anion, **3**. At 0 °C, this species is stable, unlike the corresponding α-bromo phenyl anion which requires temperatures as low as −100 °C to avoid rapid bromine loss.[11] Presumably,

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[1] Support for this work from the National Science Foundation (CHE 8800448) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[2] (a) Grimes, R. N. *Carboranes*; Academic: New York, 1970. (b) Onak, T. *Organoborane Chemistry*; Academic: New York, 1975. (c) Beall, H. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic: New York, 1975, Chapter 9. (d) Bohn, R. K.; Bohn, M. D. *Inorg. Chem.* **1971**, *10*, 350.

[3] Zakharkin, L. I.; Pisareva, I. V.; Bikkineev, R. K. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1977**, 577. Albagli, D.; Zheng, G.-x.; Jones, M., Jr. *Inorg. Chem.* **1986**, *25*, 129 and references therein.

[4] Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52. Scott, L. T.; Roelofs, N. H.; Tsang, T.-H. *J. Am. Chem. Soc.* **1987**, *109*, 5456.

[5] Wu, S.-h.; Jones, M., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 5373 and references therein.

[6] Hutton, R. S.; Roth, H. D.; Chari, S. L. *J. Phys. Chem.* **1981**, *85*, 753.

[7] Chari, S. L.; Chiang, S.-H.; Jones, M., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 3138. L'Esperance, R. L.; Li, Z.-h.; Van Engen, D.; Jones, M., Jr. *Inorg. Chem.* **1989**, *28*, 1823.

[8] Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic: New York, 1967.

[9] Reference 8, Chapter 1.

[10] Kam, C. K. A.B. Thesis, Princeton University, 1987.

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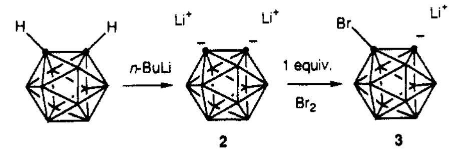
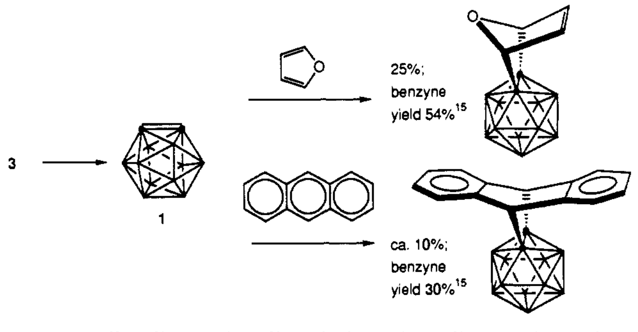
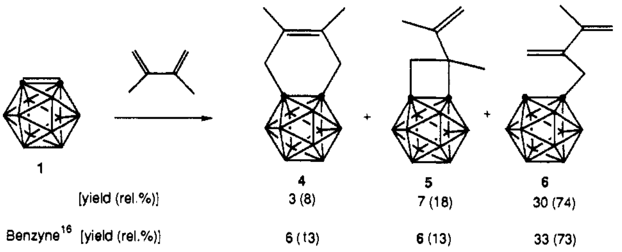
3 owes its relative stability to the presence of the negative charge on a carborane carbon (pK_a = 19–23)[12] and to the length of the carbon–carbon bond, estimated at 1.634 Å in *o*-carborane itself.[13]



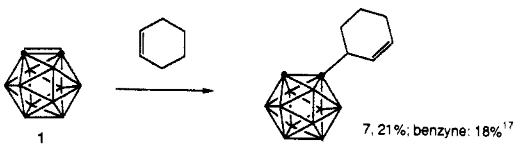
Warming **3** in the presence of dienes to 35 °C leads to products in which **1** has been trapped in Diels–Alder fashion.[14]



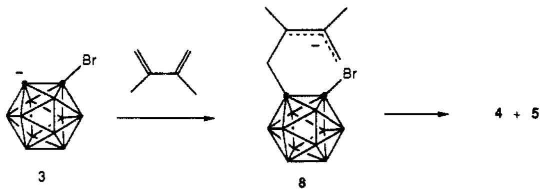
An acylic diene, 2,3-dimethyl-1,3-butadiene, gives three products, **4** (4 + 2 reaction), **5** (2 + 2 reaction), and **6** (ene reaction), all of which have equivalents in the related chemistry of benzyne.[16]



The relative yields of the three kinds of products are comparable for **1** and benzyne. Ene product dominates the reactions of both **1** and benzyne, although for **1** the 2 + 2 cycloaddition is favored somewhat over 2 + 4 addition. Simple alkenes do not give 2 + 2 addition, however. As for benzyne,[17] the product of the ene reaction, **7**, is the sole isolable product from reaction with cyclohexene.



We attribute all the reactions described here to **1**. Are there not other possible mechanistic explanations? Might not **2** or **3** be involved, for example? Dianion **2** can be eliminated by a simple control experiment. No products are isolated if the addition of bromine is eliminated from the reaction sequence. The bromo anion **3** poses a more difficult problem. One can imagine stepwise processes in which the 2 + 2 and 2 + 4 products are generated by an initial formation of an allyl anion (**8**), which then displaces bromine from the cage.[18]



This mechanism suffers a number of implausibilities. The first step must be substantially endothermic as the pK_a of *o*-carborane is 19–23[12] whereas pK_a's of simple allyl compounds are ca. 40.[19] Moreover, nucleophiles do not react with bromo carboranes to displace bromide and form an alkyl carborane. The formations of the ene products **6** and **7** are even harder to rationalize using **3** as the active ingredient. We think these reactions are best described in terms of the new reactive intermediate **1**.[20]

Supplementary Material Available: Experimental details of the trapping of 1,2-dehydro-*o*-carborane with furan and with anthracene, isolation of the Diels–Alder adduct in each case, and reaction of 1,2-dehydro-*o*-carborane with 2,3-dimethyl-1,3-butadiene and with cyclohexene (4 pages). Ordering information is given on any current masthead page.

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(11) Reference 8, pp 43–44.

(12) Shatenstein, A. I.; Zakharkin, L. I.; Petrov, E. S.; Yakovleva, E. A.; Yakoshin, F. S.; Vokmirovich, Z.; Isavera, G. G.; Kalinin, V. N. *J. Organomet. Chem.* **1970**, *23*, 313.

(13) Ott, J. J.; Gimarc, B. M. *J. Comput. Chem.* **1986**, *7*, 673.

(14) All new compounds reported here have been characterized spectroscopically. Elemental analyses have been obtained or precise masses determined by mass spectrometry.

(15) Wittig, G.; Hoffmann, R. W. *Chem. Ber.* **1962**, *95*, 2718.

(16) Wittig, G.; Dürr, H. *Justus Liebigs Ann. Chem.* **1964**, *672*, 55. For reactions of benzyne with other dienes, see: DeCamp, M. R.; Levin, R. H.; Jones, M., Jr. *Tetrahedron Lett.* **1974**, 3575. Jones, M., Jr.; Levin, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 6411.

(17) Reference 8 reports a personal communication from L. Friedman to the effect that cyclohexene does yield a 2 + 2 adduct (p 239, ref 20a), but neither earlier nor later workers find such a product. See ref 8 and, especially, the following reference, by Ahlgren and Åkerman, who explicitly discuss this problem: Ahlgren, G.; Åkerman, B. *Tetrahedron Lett.* **1970**, 3047.

(18) Of course direct, front-side displacement is out of the question, but a two-step process in which the allyl anion adds to the cage at the carbon bearing the bromine might give an intermediate that could later expel bromide. Such a process is not known.

(19) Vollhardt, K. P. C. *Organic Chemistry*; Freeman: New York, 1987.

(20) Two referees have suggested a sensible variant of the anion mechanism in which intermediates such as **8** first transfer bromine from the cage carbon to the allyl anion and then close. We have now found that norbornadiene reacts with "**1**" to give good yields of the product of the homo-Diels–Alder reaction.[21] If the bromo anion were active in this reaction, **3** would have to add to the diene to give, not an allyl anion, but a homoallyl anion. Moreover, the cage structure requires that the transferred bromine appear in an endo position. The final displacement of bromide is no longer possible! The case for **1** is strengthened.

(21) Ghosh, T., unpublished work.

Rearrangement of an Allyl Vinyl Rhenium Complex to a Rhenium Allyl Vinyl Ketone Complex via Two Consecutive Concerted Organometallic Rearrangements

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We recently discovered a new synthesis of rhenium carbene complexes $C_5H_5(CO)_2Re{=}CHR$ from the reaction of $(C_5H_5)_2Zr(\eta^2\text{-}COR)Cl$ and $K^+C_5H_5(CO)_2ReH^-$.[1] These rhenium carbene complexes display amphiphilic reactivity: both nucleophiles and electrophiles add to the carbene carbon.[2] Here we report that the vinylrhenium anions obtained by deprotonation of these carbene complexes are alkylated at rhenium by allyl halides to produce (σ-allyl)vinylrhenium intermediates that undergo facile rearrangement to allyl vinyl ketone complexes by two consecutive concerted organometallic rearrangements.

As reported earlier, deprotonation of $C_5H_5(CO)_2Re{=}CHCH_2CH_2CMe_3$ (**1**) with $KOC(CH_3)_3$ produced the vinyl-

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(1) Casey, C. P.; Nagashima, H. *J. Am. Chem. Soc.* **1989**, *111*, 2352.

(2) Casey, C. P.; Vosejpka, P. C.; Askham, F. R. *J. Am. Chem. Soc.*, in press.

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