replacement of H₂O 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 $k_1^{M}(L)$ 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 $k_b^{2n}(H_2O)$ = 345 (30) s⁻¹, minimally larger than $k_b^{2n}(CN^-) = 243$ (25) s⁻¹. For $L = H_2O$, reduction of the aquo-bound heme most likely yields the five-coordinate ferroheme, Fe²⁺P.¹⁰ However, ligand dissociation from $Fe^{2+}(CN^{-})P$ is slow,¹¹ and the I \rightarrow 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 $I \rightarrow A$ 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 \rightarrow 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 $k_t^{M}(L^0) \ge 10k_t^{M}(X^-)$, and (ii) in contrast, anion binding lowers the I \rightarrow 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 Mb³⁺(CN⁻) indicates that the Fe³⁺(X^-)P/Fe²⁺(X^-)P redox potential is shifted negative by almost 500 mV relative to $Fe^{3+}(\dot{H}_2O)P/Fe^{2+}P$;¹⁵ this shift decreases the driving force for the A^{*} \rightarrow I ET process for a hybrid with either M^{2a} from $-\Delta G^{\circ}$ $\approx 1.0-1.1 \text{ eV}$ (L = L⁰) to $-\Delta G^{\circ} \approx 0.5-0.6 \text{ eV}$ (L = X⁻), and increases that for the I \rightarrow A reaction from $-\Delta G^{\circ} \approx 0.7 - 0.8 \text{ eV}$ $(L = L^0)$ 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 $k_1^{M}(X^{-})$ as compared to $k_1^{M}(L^0)$ 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, λ \sim 1 eV, for both reactions of the protein complex.¹⁷

This value for λ places both the $\bar{A}^* \rightarrow I$ and $\bar{I} \rightarrow A$ 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

(13) (a) Hoffman, B. M.; Ratner, M. A. J. Am. Chem. Soc. 1987, 109, (13) (a) Hoffman, B. M.; Ratner, M. A. J. Am. Chem. Soc. 1987, 109, (237-6243. (b) McLendon, G.; Pardue, K.; Bak, P. J. Am. Chem. Soc. 1987, 109, 7540-7541. (c) Hoffman, B. M.; Ratner, M. A.; Wallin, S. A. Adv. Chem. Series, in press. (d) Brunschwig, B. S.; Sutin, N. J. Am. Chem. Soc. 1989, 111, 7454-7465. (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 Fe²⁺(ImH)P is unclear. (15) (a) We find that the reduction potential for the Mb(Fe³⁺L)/Mb

(15) (a) We find that the reduction potential for the Mb(Fe³⁺L)/Mb-(Fe²⁺L) couple is ± 0.05 V vs NHE for L = H₂O, and ± 0.43 V vs NHE for = 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 $E^{\circ} = +0.95$ 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.⁴⁴ 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_i for M = Zn are consistently larger than for M = Mg,

indicative of a larger preexponential term in the former.

ET in hybrids prepared from Hb mutants is addressing this issue.

Acknowledgment. This research has been supported by NIH Grants HL 13531 and HL 40453 and by NSF Grant DMB 8907559 to B.M.H. and by NIH NRSA Postdoctoral Fellowship HL07531 to M.J.N. We thank Professor H. B. Gray for fruitful discussions.

Registry No. Heme, 14875-96-8.

1,2-Dehydro-o-carborane¹

Henry L. Gingrich,* Tirthankar Ghosh, Qiurong Huang, and Maitland Jones, Jr.*

> Department of Chemistry, Princeton University Princeton, New Jersey 08544 Received December 14, 1989

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



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-ocarborane,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,

(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.;

(4) Scott, L. T. Acc. 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.

© 1990 American Chemical Society

⁽¹⁰⁾ Koening, S. H.; Brown, R. D.; Lindstrom, T. R. Biophys. J. 1981, 34, 397-408

⁽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.

⁽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.

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 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 + 42 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

(14) All new compounds reported here have been characterized spectroscopically. Elemental analyses have been obtained or precise masses deter-

(15) Wittig, G.; Hoffmann, R. W. Chem. Ber. 1962, 95, 2718.
(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. dm. Chem. Soc. 1969, 01, 6411 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 Akerman, who explicitly discuss this problem: Ahlgren, G.; Akerman, B. Tetrahedron Lett. 1970, 3047.

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.

(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**

Charles P. Casey,* Paul C. Vosejpka, and James A. Gavney, Jr.

> Department of Chemistry, University of Wisconsin Madison, Wisconsin 53706

Received January 2, 1990

We recently discovered a new synthesis of rhenium carbene complexes $C_5H_5(CO)_2Re=CHR$ from the reaction of $(C_5H_5)_2Zr(\eta^2-COR)Cl$ 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 $(\sigma$ -allyl)vinylrhenium intermediates that undergo facile rearrangement to allyl vinyl ketone complexes by two consecutive concerted organometallic rearrangements.

As reported earlier, deprotonation of $C_5H_5(CO)_2Re=$ CHCH₂CH₂CMe₃ (1) with KOC(CH₃)₃ produced the vinyl-

0002-7863/90/1512-4083\$02.50/0 © 1990 American Chemical Society

⁽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.

⁽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.

Casey, C. P.; Nagashima, H. J. Am. Chem. Soc. 1989, 111, 2352.
 Casey, C. P.; Vosejpka, P. C.; Askham, F. R. J. Am. Chem. Soc., in press.