J. Am. Chem. Soc. 1984, 106, 2723-2725

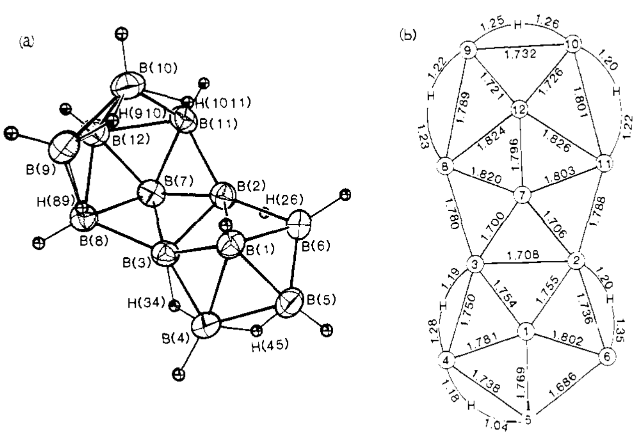

Figure 1. (a) ORTEP drawing of molecular structure. (b) Connectivity diagram showing bond distances. Estimated standard deviations are ≤0.01 and ≤0.06 Å for B-B and B-H distances, respectively.

tivities thus deduced indicate open B_8 and B_6 units joined at a common B-B edge, with B-H-B bridges located on the perimeter.[9b] The proton NMR spectrum exhibits three broad B-H-B resonances that convey little structural information.

An X-ray structural analysis[10] has confirmed the boron connectivity pattern implied by the 2D NMR evidence and reveals that the two borane units are oriented with their open faces directed away from each other, as depicted in Figure 1. The molecule contains six B-H-B bridges, two of which [H(26) and H(34)] can be regarded as quasi-terminal H atoms since B(2) and B(3) have no other attached hydrogens. While the molecule has no solid-state symmetry, tautomerism of H(45) in solution between equivalent B-B edges would produce mirror symmetry on the NMR time scale, in agreement with the ^{11}B NMR data. The compound is structurally related to several other boranes having 13-18 boron atoms, in which two borane cages share a common edge; perhaps most similar to $B_{12}H_{16}$ are $B_{16}H_{20}$,[11] $B_{18}H_{22}$,[12] and i-$B_{18}H_{22}$,[13] in which the open sides of the respective cage fragments face in opposite directions. The $B_{12}H_{16}$ geometry clearly reflects its synthesis from $B_6H_9^-$, as shown by the presence of two pyramidal B_6 fragments whose apex borons are B(1) and B(12). The merger of these hexaborane units is related, in a formal sense, to the metal-induced fusion of $R_2C_2B_4H_4^{2-}$ (a cage-isoelectronic counterpart of $B_6H_9^-$) to form $R_4C_4B_8H_8$;[2a] however, the structure of the latter carborane indicates that fusion of the two C_2B_4 units occurs face to face. As a possible rationale for the different conformation observed in $B_{12}H_{16}$, we note that steric crowding of the B-H-B bridges is minimized during the fusion process if the two pyramidal B_6 units bond in "trans" fashion. It is, however, conceivable that other isomers of $B_{12}H_{16}$ (as yet unobserved) can form during metal-promoted fusion or perhaps via rearrangement of the compound described here.

From the observation that $FeCl_2$ is required in the fusion of both $B_5H_8^-$ and $B_6H_9^-$, taken together with the earlier work on carborane fusion (in which metallacarborane intermediates have been isolated and characterized[2a,3]), we infer that the reactions described here involve intermediate metal-borane complexes such as $Fe(B_5H_x)_2$, $Ru(B_5H_x)_2$, and $Fe(B_6H_x)_2$; however, no such complexes have been isolated. The $FeCl_3$ functions as an oxidizer and is convenient although other oxidants (e.g., I_2) can be employed. In the $RuCl_3$-$B_5H_8^-$ reaction, Ru^{3+} evidently serves as both complexing agent and oxidant.

It seems clear that metal-promoted fusion of boranes offers a useful approach to the controlled synthesis of designed cage species, in which the metal ion mediates low-energy conjoining of separate polyhedral fragments. Our efforts are now directed to determining the scope of this reaction as applied to boranes and to the optimization of certain syntheses, including that of $B_{10}H_{14}$ where the attainment of high yields from $B_5H_8^-$ salts appears a reasonable goal.

Acknowledgment. This work was supported by the U.S. Army Research Office. The Nicolet NMC-360 FT NMR spectrometer was obtained in part through a grant to the Department of Chemistry from the National Science Foundation.

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

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Catalysis of the Exchange of Hydrogen and Carbon Isotopes in the Water/Hydrogen and Bicarbonate/Formate Redox Couples: A Comparison of the Exchange Current Densities on Palladium

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We wish to report that the exchange of hydrogen and carbon isotopes in the CO_3H^-/HCO_2^- aqueous redox couple occurs at a rate that is of the same order of magnitude as the hydrogen isotope exchange in the H_2O/H_2 aqueous redox system at 298 K using a Pd-based heterogeneous catalyst when the various species are at about unit activity and near the thermodynamic composition. Recent research results from this laboratory[1] have established that various forms of supported Pd are capable of effecting the equilibration of the $H_2O/H_2/CO_3H^-/HCO_2^-$ redox system at 298 K and 1 atm H_2, eq 1. Results from the equilibration using the Pd-based catalysts accord well with earlier findings[2] using an enzyme for the reduction of CO_3H^- to HCO_2^- that establish the equilibrium ratio CO_3H^-/HCO_2^- to be approximately one at 298 K and 1 atm H_2 in H_2O solvent. Since CO_3H^- is an aqueous equivalent of CO_2, the findings with the Pd-based catalysts establish that molecules having a C-H bond can be made under mild conditions from H_2 and CO_2. Like several other noble metals, Pd is known to be an excellent electrode surface from which to evolve H_2 from aqueous electrolyte solution.[3] However, there are no known electrode surfaces that are similarly highly regarded with respect to the reduction of CO_2 in aqueous electrolyte solution. Since we have found that supported Pd will effect the reduction of CO_3H^- under mild conditions, we have undertaken a study of the exchange of hydrogen (^1H = H, ^2H = D) and carbon (^{12}C, ^{13}C) isotopes in the system represented by eq 1 in order to establish the efficacy of Pd electrode surfaces for the reduction of aqueous CO_2 near the thermodynamic potential.

$$H_2 + CO_3H^- \xrightleftharpoons{\text{supported Pd}} HCO_2^- + H_2O \qquad (1)$$

Various compositions (concentration, ratio, and isotopic distribution) of CO_3H^-/HCO_2^- have been dissolved in H_2O solvent

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Table I. Catalyzed Isotope Exchange in $H_2O/H_2/CO_3H^-/HCO_2^-$ [a]

starting solution	run	catalyst[b]	rxn time, h	[formate], M $H^{12}C$	[formate], M $D^{12}C$	[formate], M $H^{13}C$	[formate], M $D^{13}C$	[DOH], M	[bicarbonate], M ^{12}C	[bicarbonate], M ^{13}C
1.0 M $Na[^{13}CO_3H]$	1	Pd/C	0.75			0.10	0.01_4	0.31		0.89
			2.2			0.18	0.04_1	1.4		0.78
			21			0.37	0.06_8	4.9		0.57
	2	Pt/C	0.75			0.00	0.00_0	0.43		1.0
			21			0.00	0.00_0	5.7		1.0
	3	Pd/C	0.8			0.08	0.00_7	0.49		0.91
	4		0.8			0.12	0.02_2	0.54		0.86
	5	Pt/C	0.8			0.00	0.00_0	0.62		1.00
	6		0.8			0.00	0.00_0	0.60		1.00
	7	Pd/PQ	20			0.16	0.02_9	1.6		0.81
	8		20			0.15	0.04_0	2.4		0.81
	9	Pt/PQ	19			0.01_5	0.00_0	2.8		0.98
	10		20			0.01_6	0.00_0	2.7		0.98
1.0 M $Na[H^{13}CO_2]$	11	Pd/C	1.0			0.83	0.04_5	0.51		0.12
	12	Pt/C	1.0			0.97_8	0.00_0	0.81		0.02_2
0.47 M $Na[^{13}CO_3H]$ + 0.53 M $Na[H^{12}CO_2]$	13	Pd/C	1.0	0.31	0.02_1	0.06_9	0.01_5	0.81	0.20	0.39
	14		1.0	0.32	0.04_3	0.06_1	0.01_1	0.84	0.17	0.40
	15	Pt/C	1.0	0.53	0.00_0	0.00_0	0.00_0	0.82	0.00	0.47
	16		1.0	0.53	0.00_0	0.00_0	0.00_0	0.63	0.00	0.47
0.47 M $Na[^{13}CO_3H]$ + 0.53 M $Na[H^{13}CO_2]$	17	Pd/C	1.0			0.49	0.03_6	0.83		0.48
	18		1.0			0.48	0.02_8	0.63		0.49

[a] All results are for stirred 1.0 mL of H_2O samples held at 298 K and under 1.7 atm D_2. All analyses were done by NMR spectroscopy using CD_3CN and 2-pyrazinecarboxylate as internal standards for ^2H and ^1H NMR, respectively. [b] The catalysts are Pd/C, Johnson-Matthey type 2, 5% Pd on C, 22 m² of Pd/g; Pt/C, Johnson-Matthey 5% Pt on C; Pd/PQ, high surface area (400 m²/g) SiO_2 derivatized with *N,N'*-bis[3-(trimethoxysilyl)propyl]-4,4'-bipyridinium dibromide followed by ion exchange with $PdCl_4^{2-}$ and subsequently reduced with H_2 in H_2O, as described in ref 4, to give 0.1 g of Pd per gram of derivatized powder; Pt/PQ, same as Pd/PQ except $PtCl_4^{2-}$ was used. For Pd or Pt/C, 10 mg/mL of solution was used; for Pd or Pt/PQ, 20 mg/mL of solution was used.

and exposed to 1.7 atm D_2 gas and 10 mg/mL of 5% Pd or Pt on C catalyst. A few experiments have been carried out using $[SiO_2]-[(PQ^{2+}\cdot M)_n]$ where M = Pd or Pt; $[SiO_2]-$ is high surface area (~400 m²/g) silica; and the $[(PQ^{2+}\cdot M)_n]$ is a polymer anchored onto the surface of SiO_2 as previously reported.[4] The isotopic composition of the solvent and the CO_3H^-/HCO_2^- system was measured by ^1H, ^2H, and ^{13}C NMR after reaction at 298 K.[1] Results from the experiments are given in Table I.

The data in Table I show two important results. First, the Pd-based catalysts give significant activity toward the CO_3H^-/HCO_2^- redox couple, whereas the Pt-based catalysts give little or no activity under the same conditions. Second, the exchange rate of the CO_3H^-/HCO_2^- redox couple is within 1 order of magnitude of the exchange rate of the H_2O/H_2 redox couple measured in the same medium using the Pd-based catalysts. Further, the H_2O/H_2 exchange rate is about the same for the Pd- and Pt-based catalysts. These results lead to the conclusion that Pd is about as effective in equilibrating the CO_3H^-/HCO_2^- redox couple as in equilibrating the H_2O/H_2 redox couple under nearly standard conditions. The second conclusion from the work is that the ability to effect equilibration of the H_2O/H_2 couple does not ensure the ability to equilibrate the CO_3H^-/HCO_2^- couple. There does seem to be a small yield of formate from $[SiO_2]-[(PQ^{2+}\cdot Pt)_n]$ catalysis that is not found with the Pt on C. This may be due to a change in the nature of the Pt in the $(PQ^{2+})_n$ polymer compared to that of Pt on C.[5] In any event, the Pt-based catalysts give a much smaller reponse to the CO_3H^-/HCO_2^- redox couple than the Pd-based catalysts under the same conditions where the response to the H_2O/H_2 redox couple is similar. The reasons for the differences in Pd- and Pt-based catalysts are currently under study.

Since $E°(CO_3H^-/HCO_2^-) \cong E°(H_2O/H_2)$[1,2] and we have used substances close to unit activity at 298 K, the data in Table I can be useful in estimating the exchange current density for both the CO_3H^-/HCO_2^- and the H_2O/H_2 redox couples at Pt or Pd in the medium used. Much mechanistic work has been done on the H_2O/H_2 redox couple in acidic solution,[6] and the exchange current density[3] is typically about $10^{-3.1}$ A/cm² for Pt and $10^{-3.0}$ A/cm² for Pd in ~1 M H_2SO_4, though the value can be much larger for very clean surfaces.[6d,f] An issue here is whether the CO_3H^- medium seriously alters this high exchange current density. If isotope effects[7] are ignored and it is assumed that the Pd on C catalysts have ~22 m² of Pd per gram of catalyst, the exchange current density for the H_2O/H_2 in experiments 13 and 14 is ~$10^{-4.7}$ A/cm² near the equilibrium situation for the $H_2O/H_2/CO_3H^-/HCO_2^-$ system. This is only about 50 times less than the typical exchange current density in acidic solution. Interestingly, the incorporation of deuterium into formate is only 10–20 times slower than the incorporation of deuterium into water when the formate concentration is 50–100 times lower than that of water. Preliminary results show that when the CO_3H^- concentration is higher the amount of deuterated formate produced does increase compared to the amount of deuterated water. Further, the initial yield of deuterated formate compared to deuterated water, and the initial rate of formate formation, improves by about a factor of 2 when 1.0 M $Cs[CO_3H]$ is used rather than $Na[CO_3H]$. A study of exchange rates in various media is in progress.

In summary, Pd-based catalysts are about as effective in equilibrating the CO_3H^-/HCO_2^- couple as in equilibrating the H_2O/H_2 couple. These results suggest that formate formation from aqueous CO_3H^- could occur at Pd electrodes with reasonable efficiency compared to H_2 formation near the thermodynamic potential. Finally, the results illustrate that formation of C–H

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(7) Conway, B. E. *Proc. R. Soc. London, Ser. A* **1960**, *256*, 128. Preliminary results show that formate formation from 1.0 M $Na[CO_3H]$ in H_2O under 1.7 atm H_2 compared to 1.7 atm D_2 occurs with a rate difference of less than a factor of ~2.

bonds from H_2 and a CO_2 equivalent can occur under mild conditions at a rate that can be regarded as fast as measured against the catalyzed H_2O/H_2 exchange process taken as a benchmark.

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Registry No. Pd, 7440-05-3; CO_3H^-, 71-52-3; HCO_2^-, 71-47-6; H_2, 1333-74-0; C, 7440-44-0; H_2O, 7732-18-5.

Electroreduction of Oxygen by Pillared Cobalt Cofacial Diporphyrin Catalysts

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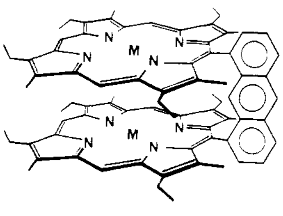
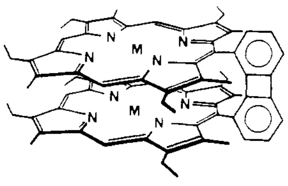
It has been shown that a graphite surface coated with a binuclear CoCo cofacial diporphyrin enables the reduction of dioxygen to occur via a 4-e pathway at potential near that of a platinum electrode.[2-4] Until now, the only macrocyclic complex capable of mediating the direct 4-e path of dioxygen reduction is a binuclear cobalt diporphyrin linked via two diametrically positioned four-atom amide chains (Co–Co–4 or Co_2FTF4).[3,4] Under identical experimental conditions, the majority of other similar compounds with different linking chains yielded predominantly H_2O_2. Collman and Anson[3] have attributed this unique reactivity to the ability of the dicobalt porphyrin to form a μ-peroxo complex as well as proper matching of formal redox potentials between metal and O_2. Work in our laboratory emphasized the fact that other dicobalt porphyrins can form the μ-peroxo species just as well and that the conformation of the O_2-intercalated complex may be critical.[4,5] Since it is difficult to test any theory with only one working datum point, the search for other electrocatalytically effective systems becomes a necessity. Ideally, one needs a wide range of diporphyrins whose redox potentials, interplanar distance, and conformation can be manipulated under strict control. This turns out to be practically impossible for the amide-linked dimers owing to the tendency for them to adopt a "slipped" conformation, i.e., the two rings are laterally displaced.[6-8] Changing the length or the constituents of the linkage would inevitably introduce variation in the degree of slippage, in addition to the vertical ring separation. We have therefore sought other designs to circumvent this problem.



1a, M = 2H
b, M = Co^{II}



2a, M = 2H
b, M = Co^{II}

1,8-Anthryldiporphyrin **1a** and 1,8-biphenylenediporphyrin **2a** were synthesized in a rational and stepwise manner.[9] The best method we now use affords diporphyrins in nearly 20% yield from readily obtainable dipyrrylmethanes.[10] The unique feature of this system is that the two porphyrin rings are anchored onto a rigid pillar such that the steric confines built into the system would prevent the two rings from rocking sideways to create a large lateral slippage. However, the two rings are still capable of bending back and forth along the ridge of the spacer groups.[9] Such flexibility presumably would make these two diporphyrins ideal binuclear systems for trapping substrate between the metals. Indeed, the Co^{II}Co^{II} dimers readily form the μ-peroxo species[5] with dioxygen. Figure 1 shows the highly symmetric patterns of the EPR spectra of the oxidized μ-superoxo dimers. Previously, we have noticed a curious correlation[4] between the shape of the Co–O_2–Co EPR signal and the electrocatalytical ability to mediate the 4-e reduction of O_2 on graphite surface; the well-resolved hyperfine lines would suggest these two dicobalt diporphyrins to be very good catalysts.

Rotating ring–disk voltammograms have been obtained at a graphite electrode coated with **1b** and **2b** in an oxygen-saturated 0.5 M aqueous trifluoroacetic acid solution.[11] As shown by Figure 2 and the compiled data in Table I, the result of O_2 reduction obtained in the present study is comparable to those of Co–Co–4 or Co_2FTF4. These four compounds clearly distinguish themselves as a special group from all other porphyrins and diporphyrins in terms of $E_{1/2}$ for O_2 reduction as well as the ring current. Furthermore, the rotating disk voltammograms of **1b** and **2b** exhibit a maximum ($\sim$+0.4 V) in the limiting current. This has been observed previously only with Co–Co–4 or Co_2FTF4. In the present systems the disk current decreases and then rises as the potential is scanned to more negative regions. The ring current follows the disk current, although not quantitatively. A possible explanation for this phenomenon is that the pillard dimers lose some of their activity toward the 4-e reduction of O_2 at more negative potentials but have significant catalytic activity toward the reduction of H_2O_2 at these potentials.[12]

The redox potentials of the surface-adsorbed dicobalt porphyrins consist of two well-separated waves (Table I), believed to be the Co^{II}/Co^{III} couple for the first and the second ring, respectively. Although the reduction of O_2 seems to begin near the foot of the second wave (less positive one),[3] a comparison of E_f^s for all porphyrins in Table I and previously published data failed to show any apparent correlation between the catalytic behavior and the redox potential. The metal–metal distance as well as the overall dimer conformation is likely more important in determining the catalytic response. The enigma as pointed out earlier is that there are many CoCo diporphyrins, including Co–Co–5 and "slipped" Co–Co–4,[4] all capable of forming intercalated peroxo and superoxo complexes, but only Co–Co–4 or Co_2FTF4 with a certain distance can bring about the 4-e process. To add to this puzzle, we now

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(10) In addition to the (dimethoxymethyldipyrryl)methene condensation described in ref 11, we also discovered that the MacDonald-style 2 + 2 dipyrrylmethane coupling can be successful if the reaction is conducted with 0.4% $HClO_4$ in methanol (Chang, C. K.; Abdalmuhdi, I. *Angew. Chem.* **1984**, *96*, 154).

(11) The ring–disk electrode (Pine Instrument Co. model AFDT06 PG/Pt) used for all measurements reported here is identical with those used previously in our laboratories and in Pasadena. Before coating, the electrode was first polished briefly on a wheel using silicon carbide paper (Sears 320) and cleansed with water and methylene chloride in an ultrasonic bath. The electrode was then soaked in a methylene chloride solution containing the dicobalt complex ($\sim$2 mM) for 15 min to effect adsorption. This method yielded superior results and was very reproducible.

(12) By use of 1 mM H_2O_2, **1b** catalyzes the reduction of H_2O_2 at ca. +0.13 V (Liu, H. Y.; Anson, F. C.; Chang, C. K.; Abdalmuhdi, I., manuscript submitted).

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