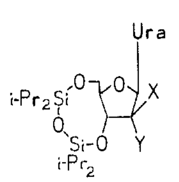
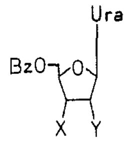


9 X = H, Y = $OCOC_6H_4$-*m*-CF_3

10 X = Y = H

11 X = H(D), Y = D(H) (~86%)



12 X = Y = OBz

13 X = Y = H

suggest the intervention of a planer sp^2 radical on the C2′ which abstracts hydrogen on the less hindered α (ribo) face.

A more convenient deoxygenation method is to use less expensive benzoyl esters. Photoreaction of tri-*O*-benzoyluridine **12** (1.4 mM) and MCZ (1 equiv) in isopropyl alcohol–water proceeded only slowly to give a poor yield of **13** even after a 24- h irradiation. Interestingly, addition of magnesium perchlorate (1.4 mM)[14] to the reaction system remarkably accelerated the photoreduction to produce a high yield (85%) of **13** at 18 h of irradiation with the recovery of MCZ (78%).[15]

The present method provides access to the generation of free radicals selectively from secondary hydroxyl groups of complex molecules under mild aqueous conditions, thus broadening the application of free radical reactions in organic synthesis. Further applications of this photosensitized electron-transfer reaction as well as the mechanistic study are under investigation.

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(14) Mizuno, K.; Ichinose, N.; Otsuji, Y. *Chem. Lett.* **1985**, 455.

(15) Throughout this photosensitized irradiation, sensitizer MCZ was mostly recovered, indicating a recycling of the sensitizer probably via electron transfer from solvent radical (X·) to the sensitizer radical cation ($D^{\cdot+}$) as depicted in Scheme I.

The Least Coordinating Anion

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Attention has been drawn recently to the myth of the noncoordinating anion.[1-4] The common spectator anions of polar solution (ClO_4^-, PF_6^-, BF_4^-, $CF_3SO_3^-$, etc.) frequently become coordinated ligands in low dielectric media, particularly when attempting to synthesize coordinatively unsaturated cations. While there is probably no such thing as a truly noncoordinating anion, the search for the *least* coordinating anion has as its reward the opportunity to synthesize the most reactive, coordinatively unsaturated cations. It has also been pointed out recently that the structural parameters of complexes with so-called weakly binding anions may in fact reflect quite strong binding.[1,2,5] Short metal–anion bond distances are frequently observed. A relatively unperturbed structure of the coordinated vs. uncoordinated anion is taken to reflect ionicity in the bonding.[1] In such complexes it is often the kinetic criterion of substitutional lability that earns the anion its designation as weakly coordinating.[6,7] These observations prompt us to report the use of the carborane anion $B_{11}CH_{12}^-$ as a novel candidate for the least coordinating anion. The structure of the complex formed by pairing $B_{11}CH_{12}^-$ with the formal cation $[Fe^{III}(TPP)]^+$ (TPP = tetraphenylporphyrinate) provides ready structural criteria for illustrating weak coordinative binding.

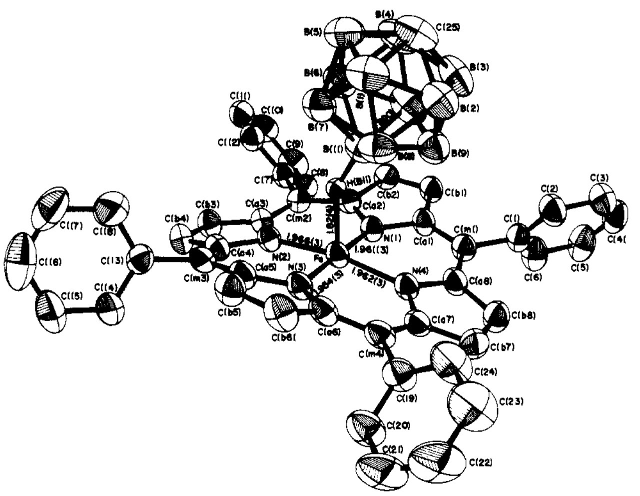

Figure 1. ORTEP drawing of the $Fe(TPP)(B_{11}CH_{12})$ molecule. Individual bond distances in the coordination group are displayed. Vibrational ellipsoids are contoured to enclose 50% of the electron density. For clarity, the only hydrogen atom shown is that involved in the Fe–H–B bonding.

In our search for the most weakly coordinating anion we have chosen $B_{11}CH_{12}^-$ for its large size, nearly spherical shape, and surprising chemical stability.[8] An unusual, η^1 mode of benzene coordination observed in the X-ray crystal structure of its silver salt[9] gave the first indication that $B_{11}CH_{12}^-$ is an unusually poor electron donor.[10] We have chosen $[Fe(TPP)]^+$ as the test case cation for several reasons. The square-planar cation with two vacant coordination sites is sterically wide open for coordination and thus offers a severe test of the coordinative passivity of an anion. In fact, this cation has never been isolated. The perchlorate "salt" has a notably short Fe–O bond[4] and, contrary to an earlier suggestion,[11] hexafluoroantimonate is also a coordinating anion.[3] The structural parameters in Fe(TPP)X systems are particularly sensitive to the nature of X^- and offer a number of criteria for measuring the strength of the cation/anion interaction. Large out-of-plane displacements of the iron atom toward the axial ligand X are observed for strongly binding halides (~0.5 Å) but these displacements progressively decrease $I^- > ClO_4^- > SbF_6^-$ as the interaction weakens.[12] Similarly, as the axial anion interaction decreases the equatorial charge attraction of the iron atom for the porphyrinato nitrogen atoms should increase. Thus, the complex with the least coordinating anion is expected to have the shortest Fe-N bond lengths.

$Fe(TPP)(B_{11}CH_{12})$ is conveniently prepared by stoichiometric reaction of Fe(TPP)Br with $AgB_{11}CH_{12}$[9] in dry toluene.[13] Coordination of the carborane anion is indicated[9] by splitting of the strong B–H absorption in the IR spectrum (2550 (s), 2380 (m) cm^{-1}, KBr disk). Consistent with weak coordination of the anion,

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(1) Humphrey, M. B.; Lamanna, W. M.; Brookhart, M.; Husk, G. R. *Inorg. Chem.* **1983**, *22*, 3355.

(2) Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599.

(3) Shelly, K.; Bartczak, T.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1985**, *24*, 4325.

(4) Reed, C. A.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 2948.

(5) Strauss, S. H.; Abney, K. D.; Long, K.; Anderson, O. P. *Inorg. Chem.* **1984**, *23*, 1994.

(6) Nitschke, J.; Schmidt, S. P.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 1972.

(7) Harrowfield, J. M.; Sargeson, A. M.; Singh, B.; Sullivan, J. C. *Inorg. Chem.* **1975**, *14*, 2864.

(8) (a) Knoth, W. H. *J. Am. Chem. Soc.* **1967**, *89*, 1274. (b) Knoth, W. H. *Inorg. Chem.* **1971**, *10*, 598.

(9) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955.

(10) η^1-benzene coordination in $Ag(B_{11}CH_{12})\cdot(C_6H_6)_2$ reflects arene-to-silver σ donation rather than silver-to-arene π back-donation which in turn reflects poor σ donation from the carborane anion.[9]

(11) Baldwin, J. E.; Haraldsson, G. G.; Jones, J. G. *Inorg. Chim. Acta* **1981**, *51*, 29.

(12) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543.

(13) λ_{max}(toluene) 406, 500, 675 nm.

0002-7863/86/1508-3117$01.50/0

Table I. Porphyrin Core Coordination Parameters (Å) of Five-Coordinate Ferric Porphyrins[a]

complex	Fe–N	Ct···N	Fe···CT	ref
Fe(TPP)I	2.066 (11)	2.014	0.53	19
Fe(TPP)(OClO$_3$)	2.001 (5)	1.981	0.30	4
Fe(TPP)(FSbF$_5$)	1.978 (3)	1.974	0.15	3
Fe(TPP)(B$_{11}$CH$_{12}$)	1.961 (5)	1.955	0.10	this work

[a] Ct = center of the mean plane of the 24-atom porphyrin core; N = porphinato nitrogen atom (average of four values).

this species is very sensitive to traces of moisture (or other ligands) in both the solid state and solution. It crystallizes from toluene as a monosolvate.[14]

The molecular stereochemistry and bond parameters of the coordination group of Fe(TPP)(B$_{11}$CH$_{12}$)·C$_7$H$_8$ are displayed in Figure 1. Interestingly, the carborane anion coordinates to the iron through an unsupported Fe–H–B bridge bond. As we have noted elsewhere,[9] this is a rare form of M–H–B interaction, particularly for large boron clusters.[15] There is no significant distortion of the cage atoms relative to an uncoordinated carborane anion.[16] The coordinated B–H bond (1.25 (4) Å) is ca. 0.2 Å longer than the average of the 10 other B–H bonds. The Fe–H distance is found to be 1.82 (4) Å but the uncertainty in this number may be greater than is implied by the formal error owing to the inherent problems of using X-ray data to position a hydrogen atom in a three-center two-electron bond.[17] Nevertheless, it is longer than the corresponding distances found in ferraboranes with Fe–H–B interactions.[18] This is consistent with a higher oxidation state of iron and weak coordination of the carborane anion.

The coordination of a B–H bond makes it difficult to evaluate the metal–anion bond length as a criterion of interaction strength. However, the iron–porphyrin bond parameters are an unusually sensitive guide to the nature of the interaction with the anion and they indicate an extremely weak interaction. Table I compares the core coordination parameters of a series of isostructural complexes where X = I$^-$, ClO$_4^-$, SbF$_6^-$, and B$_{11}$CH$_{12}^-$. Fe(TPP)I is representative of high-spin five-coordinate ferric porphyrins[12] and has a long average Fe–N bond length (2.066 (11) Å) and a large out-of-plane iron displacement (0.53 Å).[19] These parameters decrease along the series with Fe(TPP)(B$_{11}$CH$_{12}$) having the shortest average Fe–N bond (1.961 (5) Å) and the smallest iron atom displacement (0.10 Å) of any known five-coordinate ferric porphyrin complex. The central hole size of the porphyrin (Ct--N) also follows the same trend.

The core parameters of Table I are the results of two properties of the coordinating anion, its binding strength, and its ligand field strength. Both effects can work in concert thereby amplifying the changes observed along the series. The binding strength is the usual combination of electronic and steric effects that control bond formation. The ligand field effect has been discussed at length: the weaker the axial ligand field, the lower the population of the $d_{x^2-y^2}$ orbital.[4] The gradual lowering of the spin multiplicity is accompanied by a contraction of the coordination core.[20] The end position of the carborane anion in the series must result from it being the weakest binding anion. We note that the carborane anion cannot engage in pπ donation, a factor that could give rise to weak field characteristics despite strong binding. Since O and F atom ligands may act as pπ donors their weak field character must not necessarily be taken to indicate weak binding. The carborane anion is clearly the weakest σ-donor in the series.

In summary, the core coordination parameters of five-coordinate M(III) metalloporphyrins appear to provide a generally useful structural criterion for the strength of anion binding. The present results lead to the suggestion that B$_{11}$CH$_{12}^-$ is the least coordinating anion known to date, at least for the [Fe(TPP)]$^+$ moiety. We are currently extending these studies to other coordinatively unsaturated cations and to related carborane anions of even lower coordinating potential.

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Supplementary Material Available: Tables of fractional atomic coordinates, anisotropic thermal parameters, and isotropic thermal parameters for the hydrogen atoms (5 pages). Ordering information is given on any current masthead page.

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(14) Crystal data: Fe(N$_4$C$_{44}$H$_{28}$)(B$_{11}$CH$_{12}$)·C$_7$H$_8$: triclinic, a = 13.660 (2) Å, b = 14.656 (3) Å, c = 13.142 (2) Å, α = 94.85 (1)°, β = 109.63 (1)°, γ = 75.81 (1)°; space group $P\bar{1}$; z = 2; ρ_{calcd} = 1.25, ρ_{obsd} = 1.24 g/cm^3; R_1 = 0.079, R_2 = 0.092; 7446 unique observed data ($F_o > 3\sigma(F_o)$, $2\Theta < 54.9°$). Intensity data were collected at 293 K on a Nicolet P$\bar{1}$ diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using θ–2θ scanning.

(15) (a) Grimes, R. N. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum Press: New York, 1982; Chapter 7. (b) Teller, R. G.; Bau, R. *Struct. Bonding* (*Berlin*) **1981**, *44*, 1.

(16) In comparison to [Fe(TPP)(THF)][B$_{11}$CH$_{12}$]; complete details of this and the present structure will be published: Shelly, K.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A., manuscript in preparation.

(17) (a) Takusagawa, F.; Fumagalli, A.; Koetzle, T.; Shore, S. G.; Schmitkons, T.; Fratini, A. V.; Morse, K. W.; CWei, C.-Y.; Bau, R. *J. Am. Chem. Soc.* **1981**, *103*, 5165. (b) Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *Ibid.* **1981**, *103*, 1485.

(18) Fe–H distances range from 1.56 to 1.61 Å; see: (a) Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organometallics* **1983**, *2*, 825. (b) Haller, K. J.; Anderson, E. L.; Fehlner, T. P. *Inorg. Chem.* **1981**, *20*, 309. (c) Mangion, M.; Ragaini, J. D.; Schnitkons, T. A.; Shore, S. G. *J. Am. Chem. Soc.* **1979**, *101*, 754.

(19) Hatano, K.; Scheidt, W. R. *Inorg. Chem.* **1979**, *18*, 877.

(20) Along the series X = I$^-$, ClO$_4^-$, SbF$_6^-$, B$_{11}$CH$_{12}^-$ the spin state changes from $S = {}^5/_2$ (d$_{x^2-y^2}$ populated), through admixed $S = {}^3/_2, {}^5/_2$ to essentially pure $S = {}^3/_2$ (d$_{x^2-y^2}$ unpopulated). Both the SbF$_6^-$ and B$_{11}$CH$_{12}^-$ complexes have nearly identical magnetic and Mössbauer characteristics that are indicative of an essentially pure $S = {}^3/_2$ spin state.

Microporous Aluminum Oxide Films at Electrodes. 3. Lateral Electron Transport in Self-Assembled Monolayers of *N*-Methyl-*N'*-octadecyl-4,4'-bipyridinium Chloride

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Widespread interest in organized, synthetic monolayers is largely due to their resemblance to biological membranes.[1] They can also be used as subcomponents of multilayer, molecularly organized microstructures.[2] We report here on the direct electrochemical measurement of the lateral electron transport in a monolayer assembly of electroactive amphiphilic molecules. Porous aluminum oxide films at gold electrodes[3] were used as substrates for self-organization of the assembly.

Assembly of amphiphilic monolayers can be accomplished by well-developed Langmuir–Blodgett techniques[4] and by the molecular self-organization process.[5] Both methods are capable of producing films equivalent in structure and in the degree of molecular organization.[5,6a–c] As demonstrated recently by Sagiv, adsorption and self-assembly of alkyltrichlorosilanes on polar surfaces lead, in addition, to the formation of chemically bonded monolayers of remarkable stability.[6b,7a–c] Also, molecular self-

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(1) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley: New York, 1982.

(2) See for example: Kuhn, H. *Thin Solid Films* **1983**, *99*, 1.

(3) (a) Miller, C. J.; Majda, M. *J. Am. Chem. Soc.* **1985**, *107*, 1419. (b) Miller, C. J.; Majda, M. *J. Electroanal. Chem.*, in press.

(4) Kuhn, H.; Möbius, D.; Bücher, H. In *Physical Methods of Chemistry*, Weissberger, A.; Rossiter, B. W., Eds.; Wiley: New York, 1972; Vol. 1, Part III, p 577.

(5) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45 and references therein.

(6) (a) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 52. (b) Maoz, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *100*, 465. (c) Gun, J.; Iscovici, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *101*, 201.