salts of II provide direct, high yield routes to the di- and trianions.

Treatment of the sodium salt of II with 1.2 equiv of butyllithium results in complete conversion (90% yield) to the lithium-sodium salt of $[Fe_4(CO)_{12}BH]^{2-}$, III.[8] Likewise, treatment of I with 2 equiv of butyllithium at −15 °C in THF for 45 min gives a 94% yield of the dilithium salt of the same dianion. Addition of another 1 equiv of butyllithium to the dianion results in the loss of the ^{11}B and ^{1}H signals due to the dianion with the production of no other signals. However, the solution remains homogeneous, and the infrared spectrum shows a shift in the CO bands to lower frequency suggesting the formation of $[Fe_4(CO)_{12}B]^{3-}$, IV (Figure 1). Although IV is ^{11}B silent, a fact we presently attribute to very rapid relaxation of the boron nucleus in the trianion,[9] protonation of a solution of IV with CF_3COOH results in the production of I in 80% yield. Indeed, the protonations/deprotonations are completely reversible. In going from I to IV there is a uniform shift of $\approx$50 cm^{-1} to lower energy as the three protons of I are sequentially removed (Figure 1). In addition, the infrared spectra suggest that the basic "butterfly" structure of I is retained on deprotonation. Note that IV is isoelectronic with $[Fe_4(CO)_{12}C]^{2-}$ which has been structurally characterized[10] and which has a very similar infrared spectrum. The ^{1}H NMR demonstrates the order of proton removal: FeHB followed by FeHFe followed by FeHB. The ^{11}B NMR chemical shifts corroborate this observation. Loss of the first proton from I creates an additional direct FeB interaction and a 34 ppm downfield shift occurs in going from I to II.[11] Loss of the FeHFe proton in going to III leaves the boron in virtually the same environment, and the chemical shifts of II and III are also nearly the same.

As the new anions are potentially significant precursors for cluster modification and expansion, we are beginning to explore the synthetic opportunities provided. For example, although II is unreactive with CH_3I at 60 °C for 4 h, reaction of III with CH_3I proceeds smoothly at 25 °C in THF to produce a quantitative (by NMR) yield of $[HFe_4(CO)_{12}BCH_3]^-$, V.[12] The spectroscopic data is consistent with V having a tetrahedral metal core similar to that found in the isoelectronic $[Fe_4(CO)_{12}CCH_3]^-$; however, confirmation awaits crystallographic characterization.[13,14] Clearly, there is considerable scope for cluster modification via these anions.

When a monoborane is placed in a metal-rich environment, its properties are dramatically changed from those of the free borane.[15] The ability to completely deprotonate a monoboron hydride must result from its interaction with the transition metals to which it is bound. The metal carbonyl fragments act as sinks to "absorb" the excess negative charge produced on deprotonation, and it is the multinuclear metal character of the cluster that permits multiple deprotonation.[16] This is another illustration of the potential usefulness of transition metals in systematically varying the properties and reactivity of main group species.

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[8] After metathesis of III with PPNCl [bis(triphenylphosphine)iminium chloride] the following spectroscopic data were observed: IR ν_{CO} (THF, cm^{-1}) 2020 w, 1960 vs, 1940 vs, 1910 sh, 1890 sh; $^{1}H\{^{11}B\}$ NMR (C_4D_8O, 25 °C) δ 7.48–7.76 (m, 30 H) PPN^+, −8.7 (br, 1 H) BHFe; ^{11}B NMR (THF, 25 °C) δ 153 (br, FWHM = 280 Hz, $\{^{1}H\}$ FWHM = 240 Hz; $J_{BH} \approx 80$ Hz).

[9] Note that the FWHM of the decoupled boron signals increases considerably as extent of deprotonation increases (100, 120, and 240 Hz for I, II, and III, respectively). Measurement of T_1 values (4.2, 2.6, and 0.2 ms for I, II, and III, respectively) suggests that the ^{11}B resonance of IV is not observed because of excessive broadness caused by rapid relaxation. Assuming a quadrupolar relaxation mechanism is dominant, the calculated trend in the electric field gradient at the boron nucleus as a function of extent of deprotonation supports this interpretation.

[10] Davis, J. H.; Beno, M. A.; Williams, J. M.; Zimmie, J.; Tachikawa, M.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 668.

[11] For metal-rich ferraboranes the correlation between chemical shift and the number of direct, unbridged FeB interactions is nearly independent of cluster charge and substituents on the metals. Rath, N. P.; Fehlner, T. P., unpublished observations.

[12] MS(FAB) $p^+ = 586.7$(obsd), 586.7(calcd); IR ν_{CO} (toluene, cm^{-1}) 2055 w, 2020 sh, 1995 sh, 1990 vs, 1950 w; ^{1}H NMR (C_6D_6, 25 °C) δ 7.01–7.15 (m, 30 H), 2.4 (s, 3 H), −18.4 (s, 1 H); ^{11}B NMR (THF, 25 °C) δ 122 (br, FWHM = 243 Hz, $\{^{1}H\}$ FWHM = 247 Hz).

[13] Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5621.

[14] As the methyl group is almost certainly terminal, a pair of electrons that were skeletal bonding in III become exocluster bonding in V. Hence, the reaction generates a 60-electron tetrahedral cluster from a 62-electron butterfly cluster. Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305. Alternatively, we have argued that I is a four-atom arachno cluster with an interstitial boron. Addition of a methyl group to the boron forces it into a cluster vertex thereby producing a five-atom closo cluster. Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organometallics* **1983**, *2*, 825.

[15] Fehlner, T. P. In *Boron Hydride Chemistry*; Muetterties, E. L.; Ed.; Academic: New York, 1975; p 175.

[16] Highly charged cluster anions have been synthesized previously. See, for example: Bhattacharyya, A. K.; Shore, S. G. *Organometallics* **1983**, *2*, 1252.

A New Synthetic Route to (α,β,γ,δ-Tetraphenylporphinato)iron(II)[1]

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Recent efforts in our laboratory have been directed toward the syntheses of new pyrrolyl and pyrrole complexes of the first row group VIII transition metals via the metal atom reactor.[2,3] We have previously reported a conceptually novel metalation reaction at the *N*-hydrogen of pyrrole and the pyrrole functionality with iron and cobalt.[1] This facile metalation reaction has proved to be synthetically useful in expanding the number of pyrrolyl-metal complexes available including the syntheses of new bis(η^1-pyrrolyl)iron(II) octahedral complexes and a synthetically useful Fe/pyrrolyl reagent.[4] We communicate here a new synthesis for (α,β,γ,δ-tetraphenylporphinato)iron(II) (abbreviated FeTPP), demonstrating that the reactivity of iron metal with pyrrole can be extended to the pyrrole functionality in larger molecules.

By using the metal vapor reaction outlined in Scheme I, FeTPP was synthesized in excellent yield as the metalloporphyrin excluding any axial ligands.

In many metal atom reactor syntheses it is desirable to simultaneously cocondense metal vapor with a reactive substrate vapor or a mixture of solvent and substrate vapors. The result is an efficient distribution of the reactive metal in a frozen matrix. This is necessary to minimize metal agglomeration upon meltdown and effect a greater product yield. In our previously reported reactions of iron and cobalt with pyrrole, we found the direct cocondensation of the metal and pyrrole vapors to be the most effective in product formation. Unfortunately, in extending the facile reaction of iron metal to the *N*-hydrogen of the pyrrole functionality in α,β,γ,δ-tetraphenylporphine (abbreviated H_2TPP), adequate sublimation of the porphyrin as a cocondensable solid is not experimentally feasible. Therefore, addition of a toluene solution of H_2TPP into a reactive iron/toluene slurry at low temperature was chosen as an alternate reaction pathway.

In step 1, we take advantage of the excellent solvating power of toluene toward metal atoms at low temperature.[5] A frozen iron/toluene matrix formed from the cocondensation of iron and toluene vapors at liquid nitrogen temperature is warmed to −94.6 °C by using an acetone/liquid nitrogen slush. At the slush temperature, the frozen matrix melts down as a reactive iron/toluene

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[1] Reagen, W. K.; Radonovich, L. J. *Synthetic Intermediates of Iron/Pyrrole and Cobalt/Pyrrole Produced via the Metal Vapor Cocondensation Technique*; 192nd National Meeting of the American Chemical Society, Anaheim, CA, Sept. 1986; Division of Inorganic Chemistry, abstract no. 215.

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[3] Klabunde, K. J. *Acc. Chem. Res.* **1975**, *8*, 393.

[4] Reagen, W. K.; Radonovich, L. J. *J. Am. Chem. Soc.* **1987**, *109*, 2193.

[5] (a) Groshens, T. G.; Henne, B.; Bartak, D.; Klabunde, K. J. *Inorg. Chem.* **1981**, *20*, 3629. (b) Radonovich, L. J.; Eyring, M. W., Groshens, T. J.; Klabunde, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 2816. (c) Henne, B. J.; Bartak, D. E. *Inorg. Chem.* **1984**, *23*, 369.

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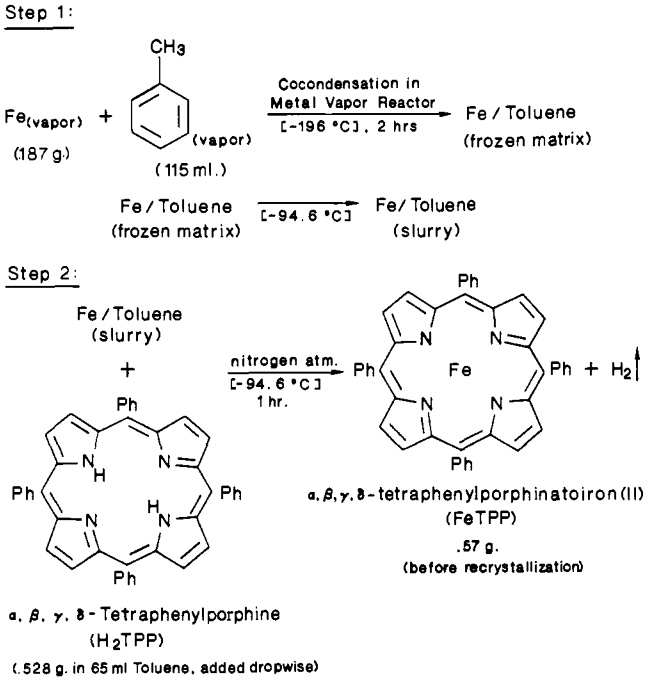
Scheme I



slurry. In step 2, a saturated solution (65 mL) of H_2TPP in toluene is added dropwise to the low-temperature (−94.6 °C) slurry. After addition of the H_2TPP to the slurry, the mixture is reevacuated and allowed to gradually warm to 0 °C. Upon warming, the evolution of gas is observed, indicating facile reactivity at the *N*-hydrogen of the H_2TPP. Filtration of the cold product mixture through a fine porosity frit removes unreacted metal and any insoluble material, resulting in a highly pure reaction product of the metalloporphyrin in toluene. After solvent removal, characterization of the solid reaction product using mass spectrometry, UV–vis spectroscopy, and infrared spectroscopy showed FeTPP, a trace of its oxygen degradation product, and no residual H_2TPP.

Mass spectrum (70 eV, 300 °C) showed 91 *m/e* as the base peak from residual toluene and a strong molecular ion peak at 668 *m/e* corresponding to FeTPP. No peak at 614 *m/e* corresponding to H_2TPP was detected. Except for a trace of its oxygen degradation product, the UV–vis spectrum in benzene showed a nearly clean spectrum of Fe/TPP with characteristic bands[6] at 419, 443, and 539 nm. No evidence for unreacted free H_2TPP was observed.

The overall reaction resulted in essentially 100% conversion of the H_2TPP used resulting in 0.57 grams (before recrystallization) of the ferrous porphyrin. The reaction requires an excess of iron in order to ensure the complete conversion of H_2TPP to FeTPP. We used a 4:1 molar ratio to ensure an excess of "reactive" metal, as metal agglomeration can be a competing process. The entire reaction can be completed in less than 5 h via this synthetic route. Advantages of this synthetic route vs. those previously reported[7] include a short reaction time, inexpensive reagents (H_2TPP and Fe metal), and a clean reaction yielding the ferrous porphyrin in quantitative yield.

Using cobalt in Scheme I has resulted in a low-yield synthesis (<2%) of CoTPP while nickel does not produce any detectable NiTPP. In metal atom reactions of pyrrole with the first row group VIII transition metals we have found the following general trend of reactivity: Fe ≫ Co > Ni (no reaction). Accordingly, α,β,γ,δ-tetraphenylporphine reactions with iron, cobalt, and nickel parallel the pyrrole reactivity pattern. It seems likely that the iron reactivity can be extended to a variety of porphyrins, phthalocyanines, polypyrrole, and other macrocycles incorporating the pyrrole functionality. Indeed, preliminary results using indole in a reaction analogous to the porphyrin reaction reported here has resulted in a reactive but stable iron/indole product. Exploration of this metalation reaction at the *N*-hydrogen of pyrrole and the pyrrole functionality with other transition metals on a preparative scale similar to that of iron is under investigation.

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Why Are π Bonds to Phosphorus More Stable toward Addition Reactions than π Bonds to Silicon?

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A clear example of the significant difference in stability toward addition reactions between compounds containing doubly-bonded silicon ($=SiR_2$)[1] and doubly-bonded phosphorus ($=PR$)[2] is found in the comparison of silabenzenes[3] with phosphabenzenes.[4] The former compounds dimerize so rapidly that they can only be isolated in inert matrices at very low temperatures.[5] In contrast, phosphabenzenes are perfectly stable toward dimerization at ambient temperatures and only react with hexafluoro-2-butyne, a potent Diels–Alder dienophile, on heating to 100 °C.[6]

In this communication we report the results of ab initio calculations, which show that π bonds in phosphenes are, in fact, substantially more thermodynamically stable toward addition reactions than π bonds in silenes. We show that two factors contribute to this difference—π bonds in phosphenes are stronger than π bonds in silenes, and σ bonds in silanes are stronger than σ bonds in phosphines. Both of these factors can be traced to the preference in the second row of the periodic table for orbitals containing unshared electrons to have large amounts of s character.

The calculations reported here were all performed with the 3-21G$^{(*)}$ basis set.[7] Geometries were optimized with RHF wave functions for closed-shell species[8] and with UHF wave functions for radicals. Electron correlation was included by using second-order Møller–Plesset (MP2) perturbation theory.[9,10] All calculations were carried out with GAUSSIAN 82.[12]

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