copper(II) distorts the site that adopts the usual 4 + 2 geometry with an apparent lengthening of the Cu–N(CS) apical bonds. Rao et al.[6] detected the HS ↔ LS transition with EPR spectroscopy on a guest ion, by preparing Mn-doped [Fe(phen)$_2$-(NCS)$_2$] and [Fe(pic)$_3$]Cl$_2$·EtOH (pic = 2-(aminomethyl)pyridine. However, only a broadening of the EPR resonance lines at the transition temperature was observed.

The present study surprisingly shows that it is quite possible to detect the HS ↔ LS transition in an iron compound by focussing on the EPR spectrum of a doped species, which acts as a "spy" to get information about the spin state of the host lattice. A copper(II) may be used in other systems. So, an effect comparable to that described above was observed for a Cu(II) doped [Fe(1-propyltetrazole)$_6$](BF$_4$)$_2$. Other EPR active ions may also be utilized. Preliminary results indicate that the EPR spectrum of a Mn(II) doped [Fe(NCS)$_2$(btr)$_2$](H$_2$O) also shows an abrupt change at T_c. The now described method of detecting spin crossover phenomena is not restricted to magnetically coupled systems. Detailed information on these two systems will be presented in later work.

Acknowledgment. The present investigations were carried out with support from the Netherlands Foundation for Chemical Research (SON) and with financial aid from the Netherlands Organization for Pure Research (ZWO) through project 11-28-17.

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(6) Rao, P. S.; Reuveni, A.; McGarvey, B. R.; Gangüli, P.; Gütlich, P. *Inorg. Chem.* **1981**, *20*, 204.

Multiple Deprotonation of a Ferraborane. Evidence for the Formation of a Discrete Transition-Metal Boride

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Received March 16, 1987

Discrete molecular clusters containing interstitial carbon atoms are now well known,[1] and the structural types observed mimic some of the solid state carbides. Although all clusters with interstitial atoms thus far identified contain electron precise, e.g., C, or electron rich, e.g., N, O,[2] atoms, there is no a priori reason why boron should not be found as an interstitial element in transition-metal clusters. Indeed metal borides are well known in the solid state[3] and exhibit a variety of structural types containing periodic units of one or more boron atoms. In the following, we present definitive evidence for the formation of a species containing a bare boron partially surrounded by metal atoms which is isoelectronic with an exposed iron carbide cluster.[4]

The exhaustive deprotonation of a metal-rich metallaborane provides an obvious route to a boride. However, small boranes are not known for ease of deprotonation.[5] The same is true of hydrocarbons, but the presence of a transition metal alters the situation considerably. For example, HFe$_4$(CO)$_{12}$CH yields a carbido cluster dianion on double deprotonation,[6] and we have already reported the facile single deprotonation of HFe$_4$(CO)$_{12}$BH$_2$, I, the isoelectronic analogue of HFe$_4$(CO)$_{12}$CH.[7] The PPN salt of [HFe$_4$(CO)$_{12}$BH]$^-$, II, resists further attempts at deprotonation, but we have now found that multiple deprotonation of I with butyllithium or further deprotonation of the alkali metal

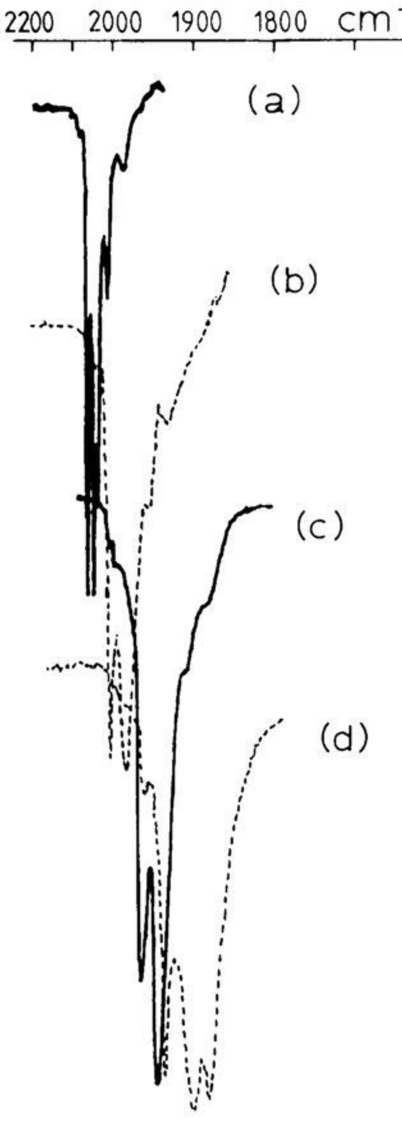
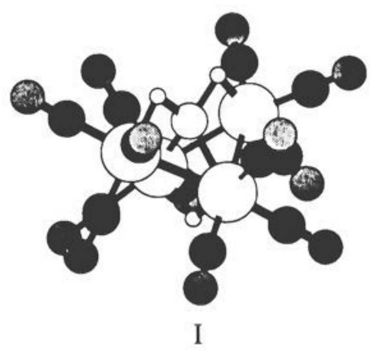
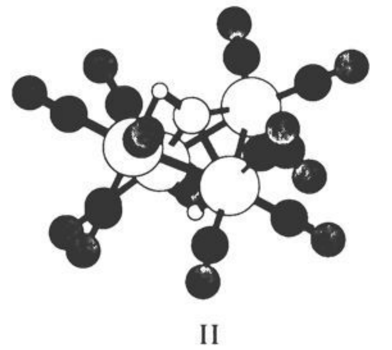


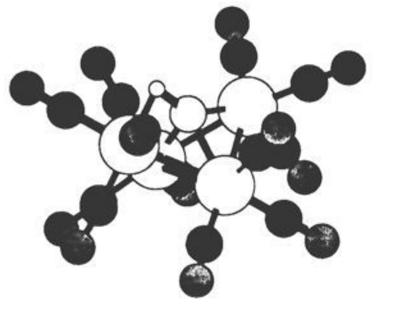
Figure 1. Infrared spectra of (a) I, (b) II, (c) III, and (d) IV (A small amount of III is present.).



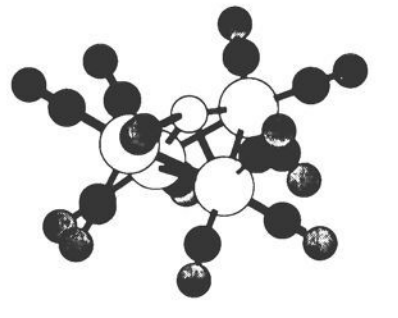
I



II



III



IV

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(1) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1.

(2) Fjare, D. E.; Gladfelter, W. L. *Inorg. Chem.* **1981**, *20*, 3533. Schauer, C. K.; Shriver, D. F., *Abstracts of Papers*, 193rd National Meeting of the American Chemical Society; American Chemical Society: Washington, DC, 1987; INORG 256.

(3) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984.

(4) The gold derivative, Au$_2$(PPh$_3$)$_2$Fe$_4$(CO)$_{12}$BH (Housecroft, C. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 6420), has been deprotonated thereby providing another example of a metal boride. Housecroft, C. E., private communication. Some evidence for a cobalt boride has been published. Schmid, G.; Bätzel, V.; Etzrodt, G.; Pfeil, R. *J. Organomet. Chem.* **1975**, *86*, 257.

(5) Although BHB hydrogens in polyhedral boranes have acidic character, only a few dianions have been reported. Shore, S. G. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; p 79. Wermer, J. R.; Shore, S. G. *Inorg. Chem.* **1987**, *26* 0000. Getman, T. D.; Wermer, J. R.; Shore, S. G. *Abstracts of Papers*, 193rd National Meeting of the American Chemical Society, American Chemical Society: Washington, DC, 1987; INORG 214.

(6) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541.

(7) Housecroft, C. E.; Buhl, M. L.; Long, G. J.; Fehlner, T. P. *J. Am. Chem. Soc.* **1987**, *109*, 3323.

0002-7863/87/1509-5273$01.50/0

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.

Acknowledgment. The support of the National Science Foundation under Grant CHE-8408251 is gratefully acknowledged.

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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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Received March 23, 1987

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.

(2) Klabunde, K. J.; Timms, P. L.; Skell, P. S.; Ittel, S. *Inorg. Synth.* **1979**, *19*, 59.

(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.