**Table I. Reaction of Hydrazoic Acid with Trialkylboranes**

alkene[a]	product	isol yield,[b] %	mp picrate,[c] °C (lit. mp, °C)
		79	111 (112)[11]
		80	116 (118)[11]
		87	312[d] (314)[12]
		70	158 (158)[13]
		72	172 (174)[14]

[a] The alkenes were converted to the corresponding organoboranes by reaction with $BH_3 \cdot THF$. [b] Yields are based on generation of 1 mol of alkylamine/mol of organoborane. [c] Melting points are uncorrected. [d] Melting point of the hydrochloride salt.

In preliminary experiments, we observed that trialkylboranes slowly reacted with hydrazoic acid in a gently refluxing THF/water mixture.

$$[CH_3(CH_2)_6CH_2]_3B + HN_3 \xrightarrow{\Delta} CH_3(CH_2)_6CH_2NH_2$$
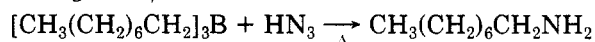
The reaction yields generally exceeded 50% after a period of 12–24 h. Nitrogen evolution was monitored, and it coincided with the formation of the product amine.

The modest reaction rate could be a consequence of either an unfavorable coordination between the boron atom and the hydrazoic acid or a slow migration of an alkyl group to the electron-deficient nitrogen atom. In an effort to enhance the rate of the rearrangement reaction, hydrochloric acid was added to the reaction mixture. The extra acid did not significantly affect the reaction rate but did result in slightly greater yields of product. This fact, plus the observation that the ^{11}B resonance of trioctylborane (85 ppm downfield from $BF_3 \cdot OEt_2$) does not shift upon addition of HN_3, leads us to conclude that the observed reaction rate is a consequence of an unfavorable complexation between the borane and hydrazoic acid.

We then investigated the feasibility of generating the hydrazoic acid in situ, thereby avoiding the synthesis of potentially hazardous hydrazoic acid. We found that trialkylboranes do react with sodium azide in the presence of hydrochloric acid to yield alkylamines. The results of our study are summarized in Table I.

$$R_3B \xrightarrow[HCl, \Delta]{NaN_3} RNH_3{}^+Cl^- \xrightarrow{NaOH} RNH_2$$
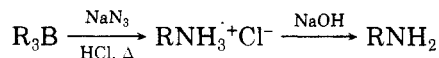
Amination: General Procedure. 1-Octene (12 mmol, 1.34 g) was hydroborated with $BH_3 \cdot THF$ (4 mmol, 4 mL of a 1.0 M solution in THF) at 0 °C for 1 h, in a 50-mL round-bottomed flask fitted with a reflux condenser and a magnetic stirring bar. Sodium azide (8 mmol, 0.52 g) was then added to the solution followed by 10 mL of aqueous 10% HCl. The reaction was gently refluxed overnight and then diluted with aqueous HCl (20 mL, 10%). The mixture was extracted with 2 × 50 mL of ether, the aqueous layer made basic (aqueous NaOH), and the product extracted into ether. The ether layer was dried over potassium hydroxide and filtered and the solvent removed to yield 0.41 g (79%) of 1-aminooctane (picrate, mp 111 °C (lit.[11] mp 112 °C)).

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A Chiral Mononuclear Complex of eHTP. Structure and Paramagnetically Decoupled ^{31}P NMR of FeCl(CO)(η⁴-eHTP)⁺ (eHTP = $(Et_2CH_2CH_2P)_2PCH_2P(CH_2CH_2PEt_2)_2$)

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Summary: The reaction of 1 or 2 equiv of $FeCl_2$ with the hexaphosphine ligand eHTP, $(Et_2CH_2CH_2P)_2PCH_2P(CH_2CH_2PEt_2)_2$, in the presence of CO produces the mononuclear species $[FeCl(CO)(\eta^4\text{-eHTP})][Cl]$ (2) in high yields. The single-crystal X-ray structure of 2 reveals that the Fe(II) atom is octahedrally coordinated with the eHTP ligand acting as a tetradentate ligand with two dangling phosphine groups. The addition of small amounts of $FeCl_2$ to solutions of 2 results in labile coordination of $FeCl_2$ to the free phosphine groups causing the disappearance of their ^{31}P NMR signals from paramagnetic broadening, while further addition of $FeCl_2$ increases the coordinated residence time on the dangling phosphorus atoms and effectively decouples them from the internal phosphorus atoms.

The hexatertiary phosphine $(Et_2CH_2CH_2P)_2PCH_2P(CH_2CH_2PEt_2)_2$, eHTP, was designed to act as a binucleating ligand system and the coordination chemistry of this ligand has so far produced only dimer complexes when 2 equiv of mononuclear metal compounds have been added to it.[1-3] It was not unusual, therefore, when the the reaction of 2 equiv of $FeCl_2$ with eHTP yielded a binuclear species, $Fe_2Cl_2(eHTP)^{2+}$. It was surprising, however, when this dimer complex reacted with carbon monoxide to produce a mononuclear complex. We report here the synthesis and structure of this novel mononuclear eHTP complex as well as its inusual ^{31}P NMR behavior in the presence of $FeCl_2$.

The reaction of 2 equivs. of $FeCl_2$ with eHTP[1] in ethanol under inert atmosphere conditions produces a light red precipitate of $[Fe_2Cl_2(eHTP)][Cl]_2$ (1) in high yields. This paramagnetic complex in soluble in methanol, acetonitrile, or water, yielding red solutions. The magnetic susceptibility in acetonitrile solution at room temperature gave an effective magnetic moment of 5.0 μ_B/iron atom. This fits well with a tetrahedral type structure and compares favorably with values of 4.9–5.2 μ_B found in mononuclear

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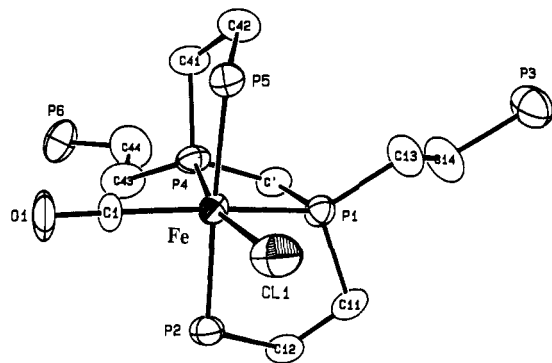
Figure 1. ORTEP plot of FeCl(CO)(η^4-eHTP)$^+$ (2) with probability elipsoids shown at the 33% level. The ethyl groups on the terminal phosphorus atoms have been ommited for clarity. Relevent bond distances (Å) are Fe-Cl1 = 2.362 (2), Fe-P1 = 2.2500 (9), Fe-P2 = 2.2753 (9), Fe-P4 = 2.213 (1), Fe-P5 = 2.2461 (9), and Fe-C1 = 1.798 (7). Selected bond angles: Cl1-Fe-P1 = 94.58 (5)°, Cl1-Fe-P2 = 89.00 (4)°, Cl1-Fe-P4 = 164.83 (5)°, Cl1-Fe-P5 = 86.55 (5)°, Cl1-Fe-Cl = 99.1 (4)°, P1-Fe-P4 = 73.31 (4)°, P1-Fe-P2 = 83.82 (3)°, P1-Fe-Cl = 163.9 (4)°, P2-Fe-P5 = 175.47 (4)°, P1-C'-P4 = 93.8 (2)°.

FeCl(P$_3$)$^+$ complexes prepared by King and co-workers.[4] The absence of any unusual deviations in the magnetic moment points to an open-mode structure where the iron atoms are well-separated and magnetically noninteracting.[1] It is interesting to note that the formulation of 1 implies that a considerable amount of coordinative unsaturation is present with a 14-electron count for each iron atom. The maintenance of unsaturation in the presence of potentially coordinating ligands (chloride counteranion) is probably a consequence of the strongly Lewis basic donor ligand set. The three alkylphosphines supply enough electron density to the metal center to cause expulsion of the weaker σ-donating chloride anion. We were interested, therefore, in examining the reaction of a π acceptor ligand, such as carbon monoxide, with 1.

A methanol solution of [Fe$_2$Cl$_2$(eHTP)][Cl]$_2$ was exposed to an atomsphere of CO causing the initial red color to lighten to orange. A diamagnetic light yellow material may be isolated from this mixture by column chromatography followed by recrystallization from acetonitrile (30% yield). Higher yields of the yellow material can be obtained by reacting 1 equiv of FeCl$_2$ with eHTP followed by the addition of CO, chromatographing on neutral alumina, and recrystallization from acetonitrile (66% isolated yield). The IR spectrum of the complex shows a single strong absorption at 1945 cm^{-1} corresponding to a terminal CO. The X-ray structure on this material reveals a mononuclear Fe(II) complex [FeCl(CO)η^4-eHTP)][Cl] (2) (an ORTEP plot is shown in Figure 1 with selected bond distances and angles).[5]

(4) King, R. B.; Bibber, J. W. *Inorg. Chim. Acta* **1982**, *59*, 197.

(5) Compound 2 crystallizes in the space group *C2/c* with *a* = 36.975 (6) Å, *b* = 10.471 (2) Å, *c* = 26.159 (5) Å, β = 134.02 (3)°, *V* = 7283 (5) Å^3, and *Z* = 8. Intensity data was collected at 25 °C by using Mo Kα and the ω-scan technique in the range 3° < 2θ < 45° on a Nicolet P3 diffractometer. A total of 6967 reflections were collected skipping over the systematically absent reflections due to C-centering. The structure was solved by using the direct methods program series in the SHELXTL program package and refined by using the Enraf-Nonius SDP program package using 4685 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ and 334 parameters. There was a 70:30 disording of the coordinated chloride and carbonyl ligands which could only be modeled for the 70% sites and the one 30% chloride site. Hydrogen atoms were calculated into place and included in the final structure factor calculation. The final discrepany indices are *R* = 0.064 and *R*$_w$ = 0.095 with a GOF = 2.43. Tables including a summary of crystal and data collection information, positional parameters, complete bond distance and angle listings, anisotropic thermal parameters, and calculated and observed structure factor tables are included in supplementary information.
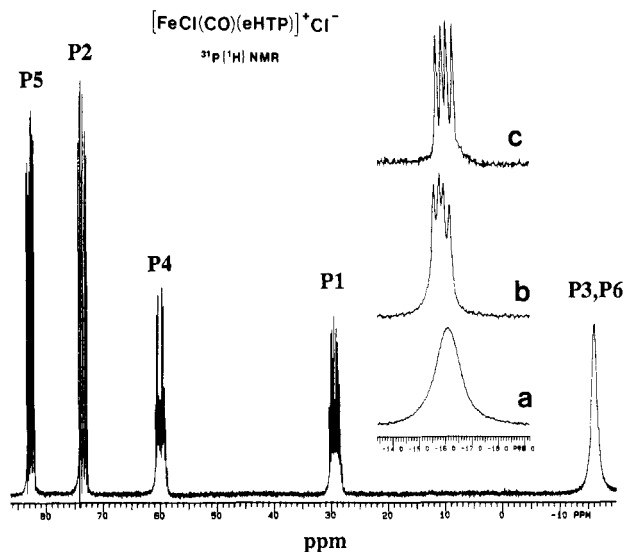

Figure 2. ^{31}P{^{1}H} NMR of 2 in methanol-d_4 at room temperature. The labeling scheme for the phosphorus atoms corresponds to that used in the crystal structure. The inset illustrates the effects of diluting the sample with methanol-d_4 on the ^{31}P NMR signal for the dangling phosphorus atoms: spectrum a, most concentrated; spectrum c, least concentrated.

The iron atom is in a substantially distorted octahedral environment with cis carbonyl and chloride ligands. The eHTP ligand occupies the other four coordination sites about the iron center and this represents the first example of an η^4-mode for eHTP. The two internal phosphorus atoms are participating in a four-membered chelate ring located trans to the CO and Cl$^-$ ligands. This ring is planar and has a P-CH$_2$-P bond angle of 93.8 (2)°, which is in marked contrast to the extraordinarily large P-CH$_2$-P angle of 129.8 (9)° seen in the platinum dimer complex Pt$_2$Cl$_2$(eHTP)$^{2+}$.[3] The four-membered chelate ring also has a very compressed P1-Fe-P4 angle of 73.31 (4)°, while the transoidal OC-Fe-Cl bond angle is expanded to 99.1 (4)°. Each of the internal phosphorus atoms also participates in a five-membered chelate ring involving one of its (diethylphosphino)ethyl substituents. These terminal phosphines are trans to each other while the two remaining terminal phosphines are dangling. An interesting aspect of this η^4-eHTP coordination mode is the chirality it endows on the complex. This results from the propeller-like arrangement of the five-membered chelate rings. Since no effort was made at resolution, both enantiomers are present in the crystal structure. Interestingly, there are only two other iron complexes with similar geometries, namely, FeCl(CO)[P(OMe)$_3$]$_4^+$ and FeI(CO)(depe)$^{2+}$ (depe = Et$_2$PCH$_2$CH$_2$PEt$_2$), neither of which has been crystallographically characterized.[6,7]

The solid-state structure is fully consistent with the solution ^{31}P{^{1}H} NMR data for the recrystallized material (Figure 2). The ^{31}P spectra shows six different phosphorus signals: four downfield resonances correspond to the four coordinated phosphines, while the two upfield bands corresponds to the dangling phosphorus atoms. Concentrated samples have a single broad, poorly resolved band, while dilution of the solution with pure solvent causes the signal to sharpen and resolve into the two doublets expected for the dangling phosphines (Figure 2). Dilution with a solution of tetraethylammonium chloride, however,

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P4   P1

ppm   ppm
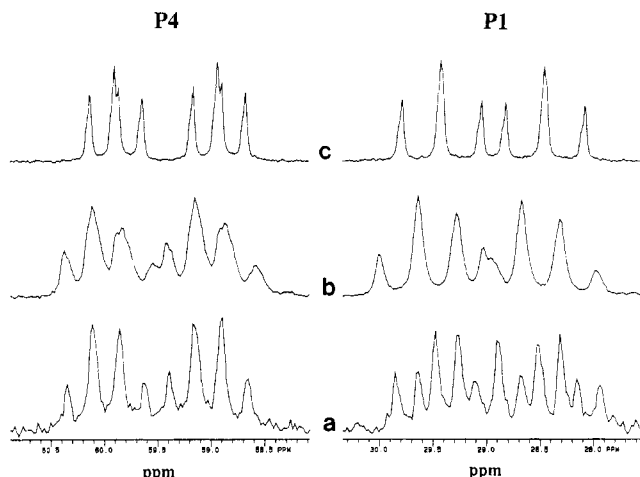
Figure 3. Expanded $^{31}P\{^{1}H\}$ NMR spectrum for phosphorus atoms P2 and P4. Spectra b and c show the effects of adding 4 and 8 equiv of $FeCl_2$ to the solution, with spectrum c illustrating the complete decoupling of the dangling phosphorus atoms from the internal phosphine resonances.

does *not* cause sharpening of the band but rather maintains the unresolved signal seen for concentrated samples. The broadness of the signals due to the free phosphine groups is, therefore, related to the halide ionic strength of the solvent since the PF_6^- salt of **2** has a resolved set of two doublets for the free phosphine groups that are not affected by concentration changes. It would appear that part of the positive charge on the complex is distributed out onto the dangling phosphorus atoms, and this is causing a weak ion pairing effect with the chloride counteranions.

The ^{31}P NMR of **2** from the reaction of Fe_2Cl_2-(eHTP)$^{2+}\cdot 2Cl^-$ with CO *after* column chromatography but *prior* to recrystallization is missing the signal due to the two free phosphine groups at −16 ppm. The disappearance of the dangling phosphorus resonances is caused by the presence of $FeCl_2$ resulting from the breakup the dimer species **1**. Recrystallization gives pure **2** and the recurrence of the ^{31}P NMR signal of the uncoordinated phosphines. Addition of even a small amount (<0.1 equivs) of $FeCl_2$ to **2** causes immediate loss of the signal at −16 ppm. The addition of substitutionally inert, paramagnetic chromium trisacetylacetonate, on the other hand, has no effect on the ^{31}P NMR. This implies two important features about the $2/FeCl_2$ system: there is direct bonding between the dangling phosphines and the added $FeCl_2$ and that the bonding between the free phosphines and $FeCl_2$ is very labile. The paramagnetic $FeCl_2$ moiety rapidly hops among the uncoordinated phosphorus atoms causing them to have fast relaxation rates which broadens their signals into the base line. The four coordinated phosphines are not labile and cannot participate in this process so their resonances are not lost. It is most probable that the $FeCl_2$ is actually bound to the dangling phosphines as a $FeCl_3^-$ unit. This has been previously observed by Bleeke and Hays in one of their cationic iron pentadienyl phosphine complexes which was found to have a tetrahedral $FeCl_3(PR_3)^-$ counteranion, the first such species crystallographically characterized.[8]

The $FeCl_2$ does, however, have an unusual and most interesting effect on the internal phosphorus signals. The observed coupling to the respective dangling phosphine is dependent on the amount of $FeCl_2$ present in solution. This paramagnetic decoupling can be clearly seen in Figure

3 which shows the effect of adding 4 and 8 equiv of $FeCl_2$ on the ^{31}P NMR signals for the internal phosphorus atoms P1 and P4. This progressive chemical decoupling can be understood when time averaging of different coupling values is considered. When bound to the paramagnetic center, phosphorus spin-state interconversion is rapid leading to an average constant of zero.[9] However, while the phosphorus atom is dangling free, the coupling has its full value. The observed coupling, therefore, is proportional to the time the phosphine is unbound. As more $FeCl_2$ is added, the average time the dangling phosphorus atoms are uncoordinated decreases causing a lessening in the observed coupling to the internal phosphine groups. While paramagnetic decoupling has been previously observed primarily for $^{1}H-^{31}P$ coupling constants,[9,10] this is the first example of $^{31}P-^{31}P$ decoupling induced by a paramagnetic center and should prove quite useful in studying compounds with dangling phosphine or other spin-labeled coordinating groups,[11] particularly when traditional heteronuclear decoupling techniques are not available.

2 could represent an important starting material for the clean, high-yield preparation of mixed-metal dimers, particularly if the strained four-member chelate ring can be broken open on coordination of a second electrophilic metal center.[12] We also plan to resolve **2** by crystallization with a chiral anion and study the reaction chemistry of this chiral mononuclear species. An especially interesting reaction we plan to probe is the reduction to Fe(0) and the possibility of C–H bond activation and functionalizations.[13]

Supplementary Material Available: Tables of crystal data and collection, positional parameters, full bond distance and angle listing, and anisotropic thermal parameters (10 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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