enediyl ligand. This result is consistent with SCF-MO calculations on the pentadienyl anion, which indicate that the central carbon atom is slightly more negative than the terminal carbons.[17]

Several structural features of the dimethylpentadienyl substituent are noteworthy. First, the methyl and methylene groups on each side of the dimethylpentadienyl group (C6/C11 and C10/C12) are disordered in the solid state; hence, bond distances C6–C7, C7–C11, C9–C10, and C9–C12 are all intermediate between normal carbon–carbon single and double bonds (1.39–1.44 Å). Second, the dimethylpentadienyl substituent is symmetrically oriented with respect to the Fe–C2–C8 plane. As a result, C6 and C10 are essentially equidistant from this plane, as are C7/C9 and C11/C12. Furthermore, torsional angles C1–C2–C8–C9 and C3–C2–C8–C7 are very close to 180°. Third, rotations about carbon–carbon bonds C7–C8 and C8–C9 push carbon atoms C6 and C10 (which are endo to the pentenediyl ligand) away from the C1/C3/C4/C5 plane to relieve steric strain.[18] These rotations also drive atoms C11 and C12 apart, reducing steric contact between them.[19]

Perhaps the most characteristic spectral feature of **2**[20] is the strong shielding exhibited by the σ-bound carbon C1 in the ^{13}C NMR spectrum (δ 2.41). The protons associated with C1 ($H1_s$ and $H1_a$) are also strongly shielded, appearing at δ 0.02 and −2.20, respectively, in the ^{1}H NMR spectrum. The ^{31}P NMR spectrum of **2** exhibits the expected AMX pattern.

Work currently underway in our laboratories is directed toward (a) establishing the scope of **1**'s reactivity toward nucleophiles and (b) effecting further functionalizations of the pentenediyl ligand.[21] Results of these studies will be reported in future communications.

Acknowledgment. Support from the National Science Foundation (Grant CHE-8520680) is gratefully acknowledged. Washington University's High Resolution NMR Service Facility was funded in part by National Institutes of Health Biomedical Research Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co. M.K.H. thanks the AAUW Educational Foundation for providing a Dissertation Fellowship.

Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, significant least-squares planes, and torsional angles for **2** (7 pages); a listing of observed and calculated structure factor amplitudes for **2** (9 pages). Ordering information is given on any current masthead page.

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[18] C6 and C10 lie 3.98 and 3.89 Å from the C1/C3/C4/C5 plane, while C11 and C12 lie 2.51 and 2.56 Å from this plane, respectively.

[19] A preliminary conformational analysis using program SYBIL (TRIPOS Assoc., Inc., St. Louis, MO) has shown that the solid-state structure of **2** closely correlates with a calculated minimum-energy conformation for the molecule.

[20] For the following NMR data, refer to numbering scheme in Figure 1. ^{1}H NMR (20 °C, benzene-d_6, 300 MHz): δ −2.20 (m, 1, $H1_a$), 0.02 (m, 1, $H1_s$), 0.68 (d, J_{H-P} = 4 Hz, 9, PMe_3), 1.10 (d, J_{H-P} = 6 Hz, 9, PMe_3), 1.35 (d, J_{H-P} = 6 Hz, 9, PMe_3), 1.69, 1.83 (s's, 6, H11's/H12's), 2.41, 2.45 (overlapping s's, 2, H5/H8), 2.68 (m, 1, H2), 3.07 (m, 1, H3), 3.52 (m, 1, H4), 4.90, 5.05, 5.15 (s's, 4, H6's/H10's). One H5 signal is obscured in the phosphine region. $^{13}C\{^{1}H\}$ NMR (20 °C, benzene-d_6, 75 MHz): δ 2.41 (C1), 20.2 (d, J_{C-P} = 15 Hz, PMe_3), 21.6, 21.7 (C11/C12), 23.0 (d, J_{C-P} = 19 Hz, PMe_3), 24.2 (d, J_{C-P} = 17 Hz, PMe_3), 42.0 (C2), 46.0 (C5), 50.4 (C3), 66.5 (C8), 91.8 (C4), 111.5 (C6, C10), 145.8, 145.0 (C7, C9). $^{31}P\{^{1}H\}$ NMR (20 °C, benzene-d_6, 121 MHz): δ 17.9 (d of d, J_{P-P} = 24 Hz, J_{P-P} = 28 Hz), 25.4 (d of d, J_{P-P} = 17 Hz, J_{P-P} = 28 Hz), 27.8 (d of d, J_{P-P} = 17 Hz, J_{P-P} = 24 Hz). IR (pentane, selected peaks): 1638 (m, C=C stretch of dimethylpentadienyl), 935, 930 cm^{-1} (s, PMe_3).

[21] We hope to exploit the electron-rich nature of the η^4-pentenediyl–iron–tris(trimethylphosphine) complexes in these functionalization reactions. One interesting possibility involves insertion of CO_2 into the Fe–C1 bond, followed by ring closure to yield the 7-membered lactone. CO_2 insertion into a M–C bond of electron-rich η^4-butadiene–iron–tris(trimethylphosphine) has recently been reported: Hoberg, H.; Jenni, K.; Krüger, C.; Raabe, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 810.

Reaction of Organoboranes with Hydrazoic Acid

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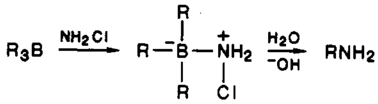
Summary: Organoboranes react with sodium azide in the presence of aqueous acid to yield primary amines. The reaction presumably proceeds via the anionotropic rearrangement of an organoborate complex.

Organoboranes have proven to be exceptionally versatile synthetic intermediates due to their ready availability and facile reactivity.[1-3] The boranes complex with a variety of functionalized Lewis bases and undergo synthetically useful anionotropic rearrangement reactions involving the migration of an alkyl group from the electron-rich boron to a neighboring electron-deficient center.[4] The reaction of chloramine with trialkylboranes, for example, provides for the synthesis of alkylamines.[5,6]



A number of permutations of this reaction have been developed in which the electron deficiency on the nitrogen atom is induced by leaving groups such as sulfonates and sulfinates.[7-9] Interestingly, no reaction of hydrazoic acid with organoboranes has been reported even though alkyl azides are known to react with borane reagents.[10]

We wish to report that trialkylboranes react with hydrazoic acid to produce alkylamines. The reaction presumably proceeds via the rearrangement of an organoborate complex.

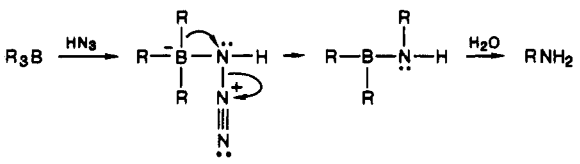


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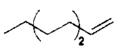
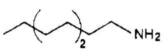
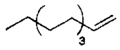
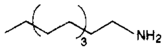
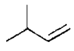
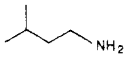
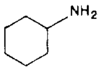
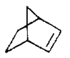
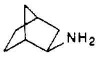
Table I. Reaction of Hydrazoic Acid with Trialkylboranes

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·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·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·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 $FeCl(CO)(\eta^4\text{-eHTP})^+$ (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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