

carbonyls, leading to the change of the shared hydrogen, could account for this.

As to the stereochemistry of **2**, the  $\delta$  value of the hydridic resonance, typical of the  $\text{Re}(\mu\text{-H})_2\text{Re}$  systems, could suggest a bridging location for the H ligands. However, the intensity ratio (2:1:1) of the carbonyl signals, in the low-temperature  $^{13}\text{C}$  NMR spectrum, clearly indicates that the hydrogen atoms are terminally bound. At higher temperatures, a dynamic behavior that equilibrates all CO ligands is observed, in contrast to **3**.

The different coordination mode of the H ligands in the two related species **2** and **4** (bridging in the unsaturated neutral **4** and terminal in the saturated anion **2**) is noteworthy. Although it is not unusual in organometallic chemistry to observe relevant stereochemical changes on varying the number of electrons, we think that in the present case this finding confirms that the  $\text{M}(\mu\text{-H})_2\text{M}$  system is intrinsically two electrons short.

Finally, we remark on the "amphoteric" behavior of compound **3**, whose H ligands (see Scheme I) can be supplied by both  $\text{H}^+$  and  $\text{H}^-$  and can be abstracted by both  $\text{OH}^-$  and  $\text{H}^+$ .<sup>11</sup>

**Registry No.** 1 [NEt<sub>4</sub>], 66745-33-3; 1 [NBu<sub>4</sub>], 87207-10-1; 2 [NEt<sub>4</sub>]<sub>2</sub>, 107890-40-4; 2 [NBu<sub>4</sub>]<sub>2</sub>, 107982-42-3; 3 [NEt<sub>4</sub>], 107890-38-0; 3 [NBu<sub>4</sub>], 107982-41-2; 4, 38887-05-7; Re<sub>2</sub>(CO)<sub>10</sub>, 14285-68-8; NEt<sub>4</sub>OH, 77-98-5; NBu<sub>4</sub>OH, 2052-49-5.

**Supplementary Material Available:** Tables of positional parameters, general temperature factor expressions, bond distances, and bond angles (5 pages); a listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

(11) A similar behavior was observed in  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^+$ : Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A. *Inorg. Chem.* 1985, 24, 2666.

## Synthesis and Reactivity of $(\eta^5\text{-C}_5\text{H}_7)\text{Fe}(\text{PMe}_3)_3^+\text{O}_3\text{SCF}_3^-$ . C-C Bond Formation via Nucleophilic Addition to C2 of an $\eta^5$ -Pentadienyl Ligand<sup>1</sup>

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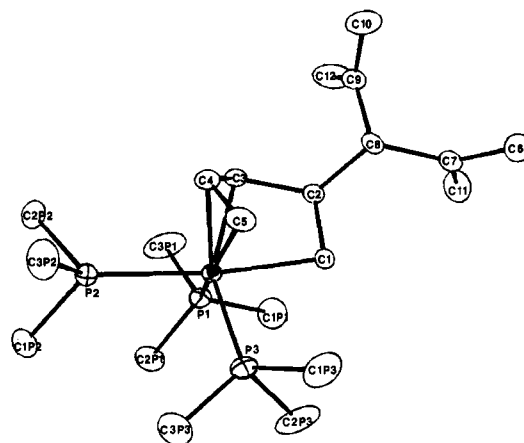
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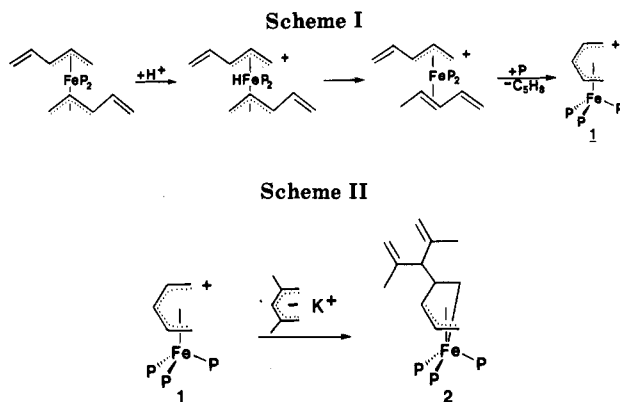
**Summary:** The electron-rich cationic complex  $(\eta^5\text{-C}_5\text{H}_7)\text{Fe}(\text{PMe}_3)_3^+\text{O}_3\text{SCF}_3^-$  (**1**) has been synthesized via the reaction of  $(\eta^3\text{-C}_5\text{H}_7)_2\text{Fe}(\text{PMe}_3)_2$  with  $\text{HPMe}_3^+\text{O}_3\text{SCF}_3^-$ . Treatment of **1** with 2,4-dimethylpentadienide ( $\text{C}_7\text{H}_{11}^-$ ) leads to nucleophilic attack at C2 of the  $\eta^5$ -pentadienyl ligand, producing the 1,3,4,5- $\eta$ -pentenediyl-iron complex  $[\text{Fe}-\text{CH}_2-\text{C}(\text{H})(\text{C}_7\text{H}_{11})-(\eta\text{-CH}^-\text{CH}^-\text{CH}_2)](\text{PMe}_3)_3$  (**2**), which has been structurally characterized. The attacking nucleophile 2,4-dimethylpentadienide bonds through its central carbon atom to the pentenediyl ligand.

The reactions of  $\eta^5$ -dienyl ligands with nucleophiles have been extensively investigated during the past decade.<sup>2</sup>

(1) Pentadienyl-Metal-Phosphine Chemistry. 11. For the previous paper in this series, see: Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* 1987, 109, 417.



**Figure 1.** ORTEP drawing of  $[\text{Fe}-\text{CH}_2-\text{C}(\text{H})(\text{C}_7\text{H}_{11})-(\eta\text{-CH}^-\text{CH}^-\text{CH}_2)](\text{PMe}_3)_3$  (**2**). Thermal ellipsoids are drawn to encompass 15% of the electron density.



However, the vast majority of these studies have involved complexes containing electron-poor  $\text{M}(\text{CO})_3^+$  ( $\text{M} = \text{Fe}, \text{Ru}$ ) moieties<sup>3</sup> and have resulted primarily in nucleophilic attack at a terminus (C1 or C5) of the  $\eta^5$ -dienyl ligand.<sup>4</sup> We now wish to report that the incorporation of strongly electron-donating  $\text{PMe}_3$  ligands into a  $(\eta^5\text{-C}_5\text{H}_7)\text{FeL}_3^+$  precursor leads to a clean reversal in the normally observed regiochemistry, i.e., nucleophilic attack at C2 of the dienyl ligand. This result is in accord with the prediction of Davies, Green, and Mingos<sup>5</sup> that nucleophilic attacks on odd open polyenyl ligands in *electron-rich* metal complexes will occur at even-numbered carbon atoms.

The electron-rich  $\eta^5$ -pentadienyl-metal complex  $(\eta^5\text{-C}_5\text{H}_7)\text{Fe}(\text{PMe}_3)_3^+\text{O}_3\text{SCF}_3^-$  (**1**) is produced in high yield from the reaction of  $(\eta^3\text{-C}_5\text{H}_7)_2\text{Fe}(\text{PMe}_3)_2$ <sup>6</sup> with

(2) See, for example: (a) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon: Oxford, 1982; Section 4.1.5. (b) Deeming, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 4, Chapter 31.3.4. (c) Pearson, A. J. *Acc. Chem. Res.* 1980, 13, 463.

(3) A variety of synthetic approaches to  $(\eta^5\text{-dienyl})\text{M}(\text{CO})_3^+$  complexes have been developed. See, for example: (a) Fischer, E. O.; Fischer, R. O. *Angew. Chem.* 1960, 72, 919. (b) Burton, R.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* 1961, 594. (c) Dauben, H. J., Jr.; Bertelli, D. J. *J. Am. Chem. Soc.* 1961, 83, 497. (d) Mahler, J. E.; Pettit, R. *Ibid.* 1963, 85, 3955. (e) Birch, A. J.; Chamberlain, K. B. *Org. Synth.* 1977, 57, 107. (f) Sosinsky, B. A.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1974, 2105.

(4) However, attack at C2 or C4 has been observed for several  $\eta^5$ -cycloheptadienyl-metal complexes. See, for example: (a) Edwards, R.; Howell, J. A. S.; Johnson, B. F. G.; Lewis, J. J. *J. Chem. Soc., Dalton Trans.* 1974, 2105. (b) Sosinsky, B. A.; Knox, S. A. R.; Stone, F. G. A. *Ibid.* 1975, 1633. (c) Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* 1984, 106, 6060.

(5) (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* 1978, 34, 3047. (b) This prediction is based on the charges of the carbon atoms in the polyenyl ligand.

Table I. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for 2

		Bond Distances			
Fe-P1	2.204 (2)	Fe-C5	2.130 (6)	C6-C7	1.429 (9)
Fe-P2	2.237 (2)	C1-C2	1.522 (8)	C7-C8	1.527 (9)
Fe-P3	2.176 (2)	C2-C3	1.514 (8)	C7-C11	1.41 (1)
Fe-C1	2.094 (5)	C2-C8	1.562 (8)	C8-C9	1.512 (8)
Fe-C3	2.157 (6)	C3-C4	1.390 (8)	C9-C10	1.39 (1)
Fe-C4	2.063 (6)	C4-C5	1.414 (9)	C9-C12	1.44 (1)
		Bond Angles			
P1-Fe-P2	94.56 (7)	P3-Fe-C3	151.1 (2)	C6-C7-C8	117.9 (6)
P1-Fe-P3	100.68 (7)	P3-Fe-C5	91.8 (2)	C6-C7-C11	121.0 (7)
P1-Fe-C1	89.2 (2)	C1-Fe-C3	68.1 (2)	C8-C7-C11	121.1 (6)
P1-Fe-C3	93.5 (2)	C1-Fe-C5	81.1 (3)	C2-C8-C7	112.9 (5)
P1-Fe-C5	163.8 (2)	C3-Fe-C5	70.8 (3)	C2-C8-C9	113.6 (5)
P2-Fe-P3	99.47 (8)	C1-C2-C3	103.3 (5)	C7-C8-C9	110.6 (5)
P2-Fe-C1	171.9 (2)	C1-C2-C8	115.5 (5)	C8-C9-C10	118.5 (7)
P2-Fe-C3	104.4 (2)	C3-C2-C8	113.1 (5)	C8-C9-C12	119.9 (6)
P2-Fe-C5	93.6 (2)	C2-C3-C4	122.3 (6)	C10-C9-C12	121.5 (7)
P3-Fe-C1	86.9 (2)	C3-C4-C5	124.8 (6)		

HPMe<sub>3</sub>+O<sub>3</sub>SCF<sub>5</sub>.<sup>7</sup> As shown in Scheme I, this reaction probably proceeds by initial protonation at the iron center,<sup>8</sup> followed by rapid migration of the hydride ligand to a terminal carbon atom of an η<sup>3</sup>-pentadienyl ligand.<sup>9</sup> The resulting η<sup>2</sup>-diene ligand is then displaced by an incoming PMe<sub>3</sub> molecule,<sup>10</sup> while the remaining pentadienyl ligand rearranges from η<sup>3</sup> to η<sup>5</sup>. The <sup>31</sup>P NMR spectrum of 1<sup>11</sup> is consistent with the octahedral coordination geometry shown in Scheme I, wherein one phosphine resides under the "mouth" and the other two reside in equivalent sites under the "edges" of the η<sup>5</sup>-pentadienyl ligand.<sup>12</sup> The mirror plane symmetry of 1 is also evident in its <sup>13</sup>C and <sup>1</sup>H NMR spectra: C1 and C2 are equivalent to C5 and C4, respectively, while H1<sub>a</sub>, H1<sub>s</sub>, and H2 are equivalent to H5<sub>a</sub>, H5<sub>s</sub>, and H4.<sup>11</sup>

The reaction of 1 with the carbon nucleophile 2,4-dimethylpentadienide (C<sub>7</sub>H<sub>11</sub>)<sup>-13</sup> cleanly produces [Fe-CH<sub>2</sub>-C(H)(C<sub>7</sub>H<sub>11</sub>)-(η-CH<sub>2</sub>-CH-CH<sub>2</sub>)](PMe<sub>3</sub>)<sub>3</sub> (2), as

shown in Scheme II.<sup>14</sup> To our knowledge, this is the first example of a nucleophilic attack at C2 of an acyclic pentadienyl ligand.<sup>15</sup> Compound 2 has been characterized by a single-crystal X-ray diffraction study,<sup>16</sup> and an ORTEP drawing of its structure is shown in Figure 1. Selected bond lengths and angles are given in Table I. As expected, the nucleophilic attack occurs exo to the Fe(PMe<sub>3</sub>)<sub>3</sub> moiety, displacing the attacked carbon C2 0.70 Å out of the C1/C3/C4/C5 plane and 2.69 Å away from the iron atom. Carbon atoms C1, C3, C4, and C5 retain strong interactions with the iron center. Within the 1,3,4,5-η<sup>4</sup>-pentadienyl ligand, carbon-carbon bonds C1-C2 and C2-C3 exhibit normal single bond lengths, while C3-C4 and C4-C5 exhibit typical allylic bond distances (see Table I).

The attacking nucleophile 2,4-dimethylpentadienide bonds through its central carbon atom C8 to the pent-

(14) Potassium 2,4-dimethylpentadienide-tetrahydrofuran<sup>13</sup> (0.21 g, 1.0 × 10<sup>-3</sup> mol) in 50 mL of tetrahydrofuran was added to a cold (-78 °C), stirred solution of (η<sup>5</sup>-C<sub>5</sub>H<sub>7</sub>)Fe(PMe<sub>3</sub>)<sub>3</sub><sup>+</sup>O<sub>3</sub>SCF<sub>5</sub><sup>-</sup> (0.50 g, 1.0 × 10<sup>-3</sup> mol) in 200 mL of tetrahydrofuran. This reaction solution was allowed to warm slowly to room temperature and then stirred for an additional 0.5 h. The tetrahydrofuran solvent was removed under vacuum, and pentane was added to extract the product 2. The resulting gold solution was filtered through a fine glass frit and cooled to -30 °C, producing amber crystals of 2, yield 0.37 g (83%). Anal. Calcd for C<sub>21</sub>H<sub>45</sub>FeP<sub>3</sub>: C, 56.50; H, 10.18. Found: C, 56.49; H, 9.91.

(15) Nucleophilic attack at C1 has been observed in the (η<sup>5</sup>-C<sub>5</sub>H<sub>7</sub>)Fe(CO)<sub>3</sub><sup>+</sup> system. See, for example: (a) Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* 1976, 954. (b) Bayoud, R. S.; Biehl, E. R.; Reeves, P. C. *J. Organomet. Chem.* 1979, 174, 297.

(16) Crystals of 2 were monoclinic, space group P2<sub>1</sub>/c, with a = 9.553 (3) Å, b = 16.803 (6) Å, c = 16.215 (6) Å, β = 100.11 (3)°, V = 2562 (2) Å<sup>3</sup>, and Z = 4. A single crystal (amber block) of dimensions 0.33 × 0.38 × 0.50 mm was grown from a saturated pentane/toluene (95/5) solution and sealed in a glass capillary under an inert atmosphere. Data were collected at 22 °C on a Nicolet P3 diffractometer using graphite-monochromated Mo Kα radiation. A total of 4141 independent reflections with 0° < 2θ < 50° were collected by using the θ/2θ scanning technique and a variable scan rate of 4-30°/min. All of the data and structure refinement were done with a modified Enraf-Nonius Structure Determination Package (modified by B. A. Frenz and Assoc., Inc., College Station, TX) on a VAX 11/780 computer. Only the 2209 independent reflections with intensities greater than 3 times their estimated standard deviations were used in the least-squares refinements. The structure was solved by standard Fourier techniques following the location of the iron atom from a Patterson map. All non-hydrogen atoms except for C3P3 were refined with anisotropic thermal parameters. Atom C3P3, when refined anisotropically, gave a badly elongated thermal ellipsoid and went nonpositive definite upon inclusion of hydrogen atoms at idealized positions. For this reason, C3P3 was refined isotropically. Furthermore, it was clear from the carbon-carbon bond distances that the methyl and methylene carbon atoms of the 2,4-dimethylpentadienyl substituent (C6, C11, C10, and C12) were disordered. Therefore, hydrogen atoms on C3P3, C6, C11, C10, and C12 were not included in the model. However, throughout the rest of the molecule, hydrogens were added at idealized positions by using the program HYDRO and included in the structure factor calculations, but not refined. The convergence values of the agreement indices were R<sub>w</sub> = 0.075 and R<sub>F</sub> = 0.056.

(6) Bleeke, J. R.; Hays, M. K. *Organometallics* 1984, 3, 506.

(7) (η<sup>3</sup>-C<sub>5</sub>H<sub>7</sub>)<sub>2</sub>Fe(PMe<sub>3</sub>)<sub>2</sub> (0.59 g, 1.7 × 10<sup>-3</sup> mol) and PMe<sub>3</sub>H<sup>+</sup>O<sub>3</sub>SCF<sub>5</sub><sup>-</sup> (0.33 g, 1.5 × 10<sup>-3</sup> mol) were stirred in 200 mL of tetrahydrofuran at room temperature for 1 h. The solution was then evaporated to dryness, and the residue was washed with pentane to remove a small quantity of unreacted 1. The product 2 was extracted into dichloromethane, and the resulting yellow solution was filtered through a fine glass frit. Evaporation of the solvent yielded the product as a yellow powder, yield 0.74 g (98%, based on limiting reagent). Anal. Calcd for C<sub>15</sub>H<sub>33</sub>FeP<sub>3</sub>PS: C, 36.01; H, 6.86. Found: C, 35.50; H, 6.89.

(8) (a) Rogers, W. N.; Baird, M. C. *J. Organomet. Chem.* 1979, 182, C65. (b) Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* 1979, 101, 619.

(9) (a) Nixon, J. F.; Wilkins, B. *J. Organomet. Chem.* 1974, 80, 129. (b) Bleeke, J. R.; Kotyk, J. J. *Organometallics* 1985, 4, 194. (c) Bleeke, J. R.; Hays, M. K. *Ibid.* 1987, 6, 486.

(10) *trans*-1,3-Pentadiene is the sole organic product of this reaction.

(11) <sup>1</sup>H NMR (20 °C, dichloromethane-d<sub>2</sub>, 300 MHz): δ -0.21 (br m, 2, H1<sub>a</sub>/H5<sub>a</sub>), 1.22 (virtual t, J<sub>H-P</sub> = 8 Hz, 18, "edge" phosphine Me's), 1.74 (d, J<sub>H-P</sub> = 8 Hz, 9, "mouth" phosphine Me's), 2.14 (br m, 2, H1<sub>s</sub>/H5<sub>s</sub>), 4.69 (br m, 2, H2/H4), 5.83 (t, J = 6 Hz, 1, H3). <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C, dichloromethane-d<sub>2</sub>, 75 MHz): δ 20.02 (virtual t, J<sub>C-P</sub> = 26 Hz, "edge" phosphine Me's), 24.35 (d, J<sub>C-P</sub> = 24 Hz, "mouth" phosphine Me's), 51.20 (d, J<sub>C-P</sub> = 10 Hz, C1/C5), 89.06 (s, C3), 97.69 (s, C2/C4), 122.1 (q, J<sub>C-F</sub> = 330 Hz, F<sub>3</sub>CSO<sub>3</sub><sup>-</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (20 °C, dichloromethane-d<sub>2</sub>, 121 Hz): δ 14.6 (J<sub>P-P</sub> = 53 Hz, "edge" P), 15.9 (J<sub>P-P</sub> = 53 Hz, "mouth" P) (second-order pattern with peaks at δ 14.4, 14.5, 14.8, 15.6, 15.9, 16.0, 16.3). IR (dichloromethane, selected peaks): 1423, 1422 (m, pentadienyl/PMe<sub>3</sub>), 1254 (s, pentadienyl/PMe<sub>3</sub>), 1154, 1030 (s, O<sub>3</sub>SCF<sub>5</sub><sup>-</sup>), 943 cm<sup>-1</sup> (s, PMe<sub>3</sub>).

(12) Exchange of "mouth" and "edge" phosphines (via rotation of the pentadienyl group with respect to the MP<sub>3</sub> fragment) can be observed by NMR spectroscopy when the sample is heated above 50 °C. Line-shape simulations of the variable-temperature NMR spectra yield a ΔG<sup>‡</sup> for exchange of 17.7 ± 0.4 kcal. For a more detailed discussion of this process in analogous compounds, see: (a) Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Organometallics* 1986, 5, 1642. (b) Bleeke, J. R.; Moore, D. A. *Inorg. Chem.* 1986, 25, 3522.

(13) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* 1979, 52, 2036.

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.<sup>17</sup>

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.<sup>18</sup> These rotations also drive atoms C11 and C12 apart, reducing steric contact between them.<sup>19</sup>

Perhaps the most characteristic spectral feature of **2**<sup>20</sup> is the strong shielding exhibited by the  $\sigma$ -bound carbon C1 in the <sup>13</sup>C NMR spectrum ( $\delta$  2.41). The protons associated with C1 (H<sub>1s</sub> and H<sub>1a</sub>) are also strongly shielded, appearing at  $\delta$  0.02 and -2.20, respectively, in the <sup>1</sup>H NMR spectrum. The <sup>31</sup>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.<sup>21</sup> 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,

(17) Bushby, R. J.; Patterson, A. S. *J. Organomet. Chem.* **1977**, *132*, 163.

(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. <sup>1</sup>H NMR (20 °C, benzene-*d*<sub>6</sub>, 300 MHz):  $\delta$  -2.20 (m, 1, H<sub>1a</sub>), 0.02 (m, 1, H<sub>1s</sub>), 0.68 (d,  $J_{H-P}$  = 4 Hz, 9, PMe<sub>3</sub>), 1.10 (d,  $J_{H-P}$  = 6 Hz, 9, PMe<sub>3</sub>), 1.35 (d,  $J_{H-P}$  = 6 Hz, 9, PMe<sub>3</sub>), 1.69, 1.83 (s's, 6, H<sub>11</sub>'s/H<sub>12</sub>'s), 2.41, 2.45 (overlapping s's, 2, H<sub>5</sub>/H<sub>8</sub>), 2.68 (m, 1, H<sub>2</sub>), 3.07 (m, 1, H<sub>3</sub>), 3.52 (m, 1, H<sub>4</sub>), 4.90, 5.05, 5.15 (s's, 4, H<sub>6</sub>'s/H<sub>10</sub>'s). One H<sub>5</sub> signal is obscured in the phosphine region. <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C, benzene-*d*<sub>6</sub>, 75 MHz):  $\delta$  2.41 (C1), 20.2 (d,  $J_{C-P}$  = 15 Hz, PMe<sub>3</sub>), 21.6, 21.7 (C11/C12), 23.0 (d,  $J_{C-P}$  = 19 Hz, PMe<sub>3</sub>), 24.2 (d,  $J_{C-P}$  = 17 Hz, PMe<sub>3</sub>), 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). <sup>31</sup>P{<sup>1</sup>H} NMR (20 °C, benzene-*d*<sub>6</sub>, 121 MHz):  $\delta$  17.9 (d of d,  $J_{P-P}$  = 24 Hz,  $J_{P-C}$  = 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<sup>-1</sup> (s, PMe<sub>3</sub>).

(21) We hope to exploit the electron-rich nature of the  $\eta^4$ -pentenediyl-iron-tris(trimethylphosphine) complexes in these functionalization reactions. One interesting possibility involves insertion of CO<sub>2</sub> into the Fe-C1 bond, followed by ring closure to yield the 7-membered lactone. CO<sub>2</sub> insertion into a M-C bond of electron-rich  $\eta^4$ -butadiene-iron-tris(trimethylphosphine) has recently been reported: Hoberg, H.; Jenni, K.; Krüger, C.; Raabe, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 810.

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.

## Reaction of Organoboranes with Hydrazoic Acid

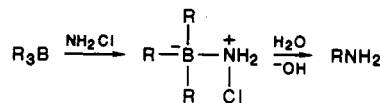
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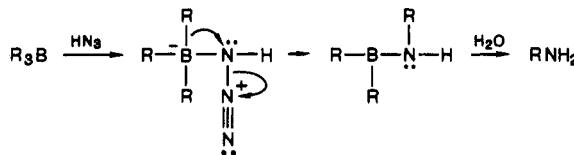
**Summary:** Organoboranes react with sodium azide in the presence of aqueous acid to yield primary amines. The reaction presumably proceeds via the anionotropic rearrangement of an organoborate complex.

Organoboranes have proven to be exceptionally versatile synthetic intermediates due to their ready availability and facile reactivity.<sup>1-3</sup> 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.<sup>4</sup> The reaction of chloramine with trialkylboranes, for example, provides for the synthesis of alkylamines.<sup>5,6</sup>



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 sulfonates.<sup>7-9</sup> Interestingly, no reaction of hydrazoic acid with organoboranes has been reported even though alkyl azides are known to react with borane reagents.<sup>10</sup>

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



(1) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1972.

(2) Pelter, A.; Smith, A. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: New York, 1979.

(3) Brown, H. C.; Zaidlewicz, M.; Negishi, E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982.

(4) Negishi, E.; Idacavage, M. *J. Org. React. (N.Y.)* **1985**, *33*, 1.

(5) Brown, H. C.; Heydkamp, W. R.; Breur, E.; Murphy, U. S. *J. Am. Chem. Soc.* **1964**, *86*, 3565.

(6) Kabalka, G. W.; Sastry, K. A. R.; McCollum, G. W.; Yoshioka, H. *J. Org. Chem.* **1981**, *46*, 4296.

(7) Rathke, M. W.; Inoue, N.; Varma, K. R.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 2870.

(8) Tamura, Y.; Minaimikawa, J.; Fujii, S.; Ikeda, M. *Synthesis* **1974**, 196.

(9) Jiganni, V. B.; Pelter, A.; Smith, K. *Tetrahedron Lett.* **1978**, 181.

(10) Suzuki, A.; Sono, S.; Itoh, M.; Brown, H. C.; Midland, M. M. *J. Am. Chem. Soc.* **1973**, *95*, 2394.