UV Irradiation of $Cp(PMe_3)Re(\eta^2\text{-}CH_2PMe_2)H$ (10) with $P(CD_3)_3$. A solution of **10** (2 mg, 0.005 mmol, 0.01 M) and $P(CD_3)_3$ (0.005 mmol, 0.01 M) in 0.41 mL of cyclohexane-d_{12} was prepared in a sealed NMR tube. $^{31}P\{^1H\}$ NMR analysis revealed the ratio $\mathbf{10}/P(CD_3)_3 = 1.4$. Irradiation for 1 h followed by ^1H NMR analysis showed that no reaction had occurred (<5% conversion).

The NMR tube was reopened[41] under high vacuum, and an additional 0.44 mmol of $P(CD_3)_3$ added. The tube was resealed by flame and irradiated 1 h. ^1H NMR spectroscopy showed that a small amount of pentane interfered with integration. The tube was quickly opened under nitrogen in the drybox, and the solution was evaporated and then redissolved in benzene-d_6. ^1H NMR analysis revealed 4.0 H (vs. 5.0 H for the Cp resonance) at the PMe_2 site (δ 1.13) of **11**. The following relative product ratio was observed: **1** (48%), **10** (10%), **11** (42%).

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Registry No. 1, 96760-24-6; **3**, 102733-96-0; **4**, 102733-97-1; **5**, 97577-92-9; **6**, 97577-92-9; **7**, 102648-85-1; **8**, 102733-98-2; **9**, 102648-86-2; **10**, 102733-99-3; **11**, 102648-87-3; **12**, 102734-00-9; **13**, 102648-88-4; **14**, 102734-94-1; **15**, 102648-89-5; **16**, 102648-90-8; $KReO_4$, 10466-65-6; Re, 7440-15-5; cyclopentadiene, 542-92-7; trimethylphosphine-d_9, 22529-57-3; methyl-d_3 iodide, 865-50-9; triphenyl phosphite, 101-02-0.

Supplementary Material Available: Crystal packing diagram, molecular geometry and labeling scheme for **16**, hydrogen positional parameters and their esd's, and listings of F_o and F_c (24 pages). Ordering information is given on any current masthead page.

Main Group Chemistry on a Metal Framework: Reactions of $[(\mu\text{-}H)Fe_3(CO)_9BH_2R]^-$ (R = H, CH_3) with Lewis Bases

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Abstract: The reactions of $[(\mu\text{-}H)Fe_3(CO)_9BH_2R]^-$ (R = H, CH_3) with Lewis bases (L = CO, $PhMe_2P$, NEt_3, and H_2O) are explored. For R = H and L = $PhMe_2P$, substitution via H_2 rather than CO elimination to yield $[(\mu\text{-}H)Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH_2]^-$ competes with cluster fragmentation to yield $PhMe_2P{\cdot}BH_3$, $[(\mu\text{-}H)Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)_2]^-$, $Fe(CO)_3(PhMe_2P)_2$, and a ferraborane anion spectroscopically characterized in situ. The fragmentation pathway predominates in the presence of excess Lewis base, whereas H_2 elimination is favored by low ligand levels. For L = $PhMe_2P$ the H_2 displacement pathway is promoted with R = CH_3. A kinetic study for L = $PhMe_2P$ reveals a first-order rate dependence on both substrate and ligand for fragmentation, suggesting associative activation. The dual-fragmentation path observed illustrates competitive base displacement of isolobal fragments from a single cluster. An analysis at intermediate ligand levels results in the definition of base-promoted cluster substitution via H_2 elimination. Under the conditions explored here, CO yields only H_2 displacement, H_2O only fragmentation, and NEt_3 adduct formation with slow fragmentation but no H_2 displacement.

The chemistry of trigonal BH_3 as well as tetrahedral adducts with Lewis bases, BH_3L, has been well documented.[1,2] Both the high reactivity of free BH_3 and the varied reactivity of borane adducts with ordinary Lewis bases are expressions of fundamental bonding concepts.[3] However, the effects of the coordination of BH_3 to a transition metal on the reactivity of the main group fragment is not well explored. One would say unexplored except that one of the most interesting and versatile base adducts of BH_3, that with H^- (BH_4^-), forms numerous mononuclear transition-metal complexes of varying hydride hapticity.[4,5] The fact that BH_3 can be displaced from these borohydride complexes[6] suggests that they might well be described as BH_3 metal hydride complexes. We have recently characterized the first example of what can formally be described as a tridentate cluster bound tetrahydroborate ligand spanning three metal atoms, i.e., $(\mu\text{-}H)Fe_3(CO)_9BH_4$ (I′).[7,8] This compound can act as a protonic acid, and with bases I′ initially loses a proton from a B–Fe edge to give I which in turn constitutes an example of a metal cluster bound monoborane.[8,9] Hence, I provides an opportunity to explore the reactivity of an important main group hydride when bound in an unusual fashion to a multinuclear metal framework. In this report we consider reactivity of I with respect to selected Lewis bases.

When attack on exo-cluster CO ligands is ignored, I contains two potential sites of base attack, viz., metal or main group center. There is a considerable body of information on ligand substitution in metal carbonyls although mechanistic studies on cluster systems

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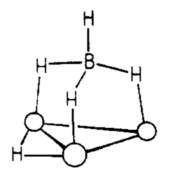
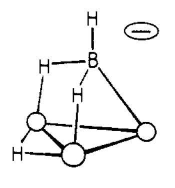


I′



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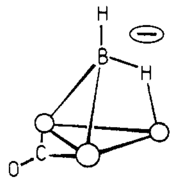

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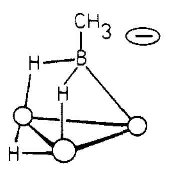

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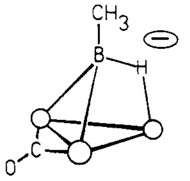

IV

are farily limited.[10] It is known that transition-metal clusters tend to fragment in the presence of nucleophiles, a problem Pöe has called the "Achilles' heel" of cluster substitution.[11] When substitution is observed, the replacement of the first CO by a good nucleophilic ligand can take place by an associative mechanism[10,12-14] contrasting with the widely observed dissociative processes of mononuclear transition-metal carbonyl substitution reactions.[10] However, Keister et al. have recently demonstrated that initial ligand substitution on the cluster $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-CX})$ (X = CMe, NR_2) is not ligand dependent.[15] Also Atwood et al. have demonstrated a dissociative mechanism for the reaction of $M_3(CO)_{12}$(M = Fe, Os) with phosphine bases,[16] and Geoffroy et al. see a ligand-independent path for $H_2FeRu_3(CO)_{13}$ reacting with PPh_3.[17] It has been suggested that a dissociative mechanism applies to transition-metal cluster substitution for ligands of low nucleophilicity and, in general, to subsequent CO substitutions on clusters that already possess a non-CO ligand.[10]

Ligand substitution for CO attached to boron has been reported for the cluster $(\mu\text{-H})_3Os_3(CO)_9B(CO)$ which reacts with PMe_3. Substitution is quantitative under mild conditions, yielding $(\mu\text{-H})_3Os_3(CO)_9B(PMe_3)$,[18] and there was no report that the phosphorus donor induces cluster fragmentation. With respect to substitution on boranes themselves, processes of the type in eq 1 have been studied kinetically. Associative, dissociative, and

$$L' + L\cdot BH_3 \rightarrow L'\cdot BH_3 + L \qquad (1)$$

ligand interchange mechanisms are operative, the balance between them depending on reaction conditions, relative Lewis basicities of L and L′, and steric factors.[1] Herein we explore some of the reactions of I with Lewis bases to define the effect of the trimetal framework on the reactivity of the capping monoborane. In addition we present some mechanistic information on the reaction of I with $PhMe_2P$, thereby demonstrating the consequences of competition between main group and metal sites for the incoming ligand.

Experimental Section

General Procedures. All reactions were carried out with standard Schlenk techniques.[19] Solvents were dried (toluene over anhydrous $MgSO_4$, THF over KOH pellets, hexane over molecular sieve), degassed, and distilled before use, methanol and dichloromethane were dried over molecular sieves and degassed before use, and anhydrous diethyl ether was distilled before use. The following reagents were used as received: PPNCl (PPN = bis(triphenylphosphine)iminium chloride) (Aldrich), CF_3COOH (Aldrich), CO (Linde, CP grade), and $PhMe_2P$ (Aldrich). H_3PO_4 (Fisher) was degassed before use. NEt_3 (Eastman) was fractionated in vacuo before use. $BH_3\cdot THF$ and $Li[Et_3BH]$ (1.0 M, Aldrich) were titrated[20] prior to use. Column chromatographic separations were performed on 60–200-mesh silica gel (Baker).

^{11}B, ^{31}P, and ^{1}H FT NMR spectra were obtained on a Nicolet 300-MHz instrument, infrared spectra were recorded on a Perkin-Elmer 983 spectrometer, and mass spectra were obtained on an AEI-MS 9 spectrometer. ^{11}B NMR chemical shifts are reported with respect to δ ($BF_3\cdot OEt_2$) 0; ^{31}P shifts with respect of δ (H_3PO_4) 0; ^{1}H shifts with respect to δ (Me_4Si) 0. H_2 and CO were measured with a Carle Model 311 gas chromatograph equipped with 80% Porapak N + 20% Porapak 0 (50/80 mesh) and molecular sieve (5A) columns in series.

Due to the micromolar scale of reactions, weighing by difference was not found to be an accurate method of determining the quantity of material. Thus, we adopted a procedure of measuring the ^{11}B NMR integrals against an external standard ($Bu_4N[B_3H_8]$ in acetone-d_6) which itself was calibrated against a solution of $BH_3\cdot THF$ of known concentration. We have found this procedure to be precise and of sufficient accuracy for our needs. Relative NMR yields are reported as uncorrected integrals of appropriate measured resonances.

[I]PPN and [III]PPN were prepared as previously described.[8]

Preparation of $[Fe_3(CO)_9(\mu\text{-CO})BH_2]$PPN, II: Reaction of I with CO. CO (1 atm) was bubbled slowly through a solution of the PPN salt of I (0.03 mmol) in toluene (3 mL) at 45 °C for 40 h. During this time, the reaction solution turned from red-orange to red-brown. The progress of the reaction was followed by ^{11}B NMR. $[Fe_3(CO)_9(\mu\text{-CO})BH_2]^-$ was obtained in 80% yield. IR: ν_{CO} (toluene, cm^{-1}) 2051 w, 1989 vs, 1963 s, 1935 m, 1790 w. ^{1}H NMR ($CD_3C(O)CD_3$, 20 °C): δ 7.73–7.56 (m, 30 H, PPN^+ cation), 6.0 (br, 1 H), −11.1 (br m, 1 H). ^{11}B NMR ($CD_3C(O)CD_3$, 20 °C): δ 57.4 (br, dd); $\{^1H\}$ J_{BH} = 130 (terminal), J_{BH} = 50 Hz (bridge).

Preparation of $[Fe_3(CO)_8(\mu\text{-CO})(PhMe_2P)BH_2]$PPN from [II]PPN. In a typical reaction, $PhMe_2P$ (0.0011 mL, 0.008 mmol) was added to the PPN salt of II (0.008 mmol) in acetone (1.5 mL) at room temperature. The reaction was monitored by using ^{31}P NMR and was complete within 17 h. During this time the solution turned from red-brown to dark brown. IR ν_{CO} (toluene, cm^{-1}): 2052 w, 1990 vs. 1963 s, 1934 m, 1872 m. ^{31}P NMR ($CD_3C(O)CD_3$, 20 °C): δ 30.2 (m, 1 P), 21.7 (m, 2 P, PPN^+ cation). ^{11}B NMR ($CD_3C(O)CD_3$, 20 °C): δ 56.8 (br, dd); $\{^1H\}$ (−20 °C) J_{BH}(terminal) ≈ 140,[21] J_{BH}(bridge) ≈ 40 Hz.[21] ^{1}H NMR ($CD_3C(O)CD_3$, −20 °C): δ 7.73–7.56 (m, 30 H, PPN^+ cation), 7.49–7.37 (m, 5 H, *Ph*Me_2P), 1.25 (m, 6 H, Ph*Me*$_2$P), 6.0 (br, 1 H), −11.6 (br, 1 H).

Preparation of $[Fe_3(CO)_8(\mu\text{-CO})(PhMe_2P)BH_2]$PPN from [I]PPN. A stock solution of $PhMe_2P$ (0.008 mL, 0.056 mmol) in acetone (0.072 mL) was prepared. An aliquot of the solution (0.01 mL, 0.007 mmol of $PhMe_2P$) was added to a solution of [I]PPN (0.028 mmol) in acetone (1.5 mL) at room temperature. The reaction was monitored by multinuclear NMR for 24 h, further 0.01 mL aliquots of the phosphine solution being added after 6½, 11, and 23½ h. The products of the reactions were characterized in situ by ^{31}P, ^{11}B, and ^{1}H NMR. After 30 h, 70% (by ^{11}B NMR) of I had reacted, giving 67% yield of $[Fe_3(CO)_9(\mu\text{-CO})(PhMe_2P)BH_2]$PPN and 33% fragmentation (see Results).

Preparation of $(\mu\text{-H})Fe_3(CO)_9(\mu\text{-CO})BH(CH_3)$. $(\mu\text{-H})Fe_3(CO)_9(\mu\text{-CO})BH(CH_3)$ is formed as a byproduct in the preparation of $(\mu\text{-H})Fe_3(CO)_9BH_3(CH_3)$.[16] The brown neutral ferraborane is characterized as follows. ^{11}B NMR ($CD_3C(O)CD_3$, 20 °C: δ 76.4 (d); $\{^1H\}$ J_{BH} = 40 Hz, ^{1}H NMR: δ 1.09 (s, 3 H, CH_3), −13.2 (br, 1 H), −25.6 (s, 1 H); MS calcd for $^{56}Fe_3{}^{10}B^{12}C_{11}{}^{16}O_{10}{}^{1}H_5$ 474.806 amu, obsd 474.801 amu. Sequential loss of 10 CO molecules was observed from the parent ion. A close correlation is noted between the NMR parameters for this molecule and those of $(\mu\text{-H})Fe_3(CO)_9(\mu\text{-CO})BH_2$.[9]

Preparation of [IV]PPN. $(\mu\text{-H})Fe_3(CO)_9(\mu\text{-CO})BH(CH_3)$ was dissolved in hexane (5.0 mL) and the solution stirred for 15 min with a solution of PPNCl (0.29 g, 0.5 mmol) dissolved in methanol (5 mL). After the hexane solution was removed and the methanol solution was pumped dry, the ferraborane anion formed by the deprotonation of $(\mu\text{-H})Fe_3(CO)_9(\mu\text{-CO})BH(CH_3)$ was obtained as a brown residue. It was

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characterized as [IV]PPN as follows. ^{11}B NMR ($CD_3C(O)CD_3$, 20 °C): δ 74.5 (d); {^1H} J_{BH} = 40 Hz. ^1H NMR: δ 7.7–7.5 (m, 30 H, PPN^+ cation), 1.10 (s, 3 H, CH_3), –10.3 (br, 1 H). These spectral parameters are similar to those of the related [II]PPN in which the terminal boron-bound CH_3 of IV is replaced by a terminal hydrogen.

Preparation of $[Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH(CH_3)]PPN$ from [III]PPN. $PhMe_2P$ (0.0048 mL, 0.034 mmol) was added to a solution of [III]PPN (0.011 mmol) in acetone (1.5 mL) at room temperature and was stirred. The reaction was followed by ^{11}B NMR. The head gas was sampled (GLC) periodically, demonstrating that H_2 was evolved as the reaction progressed. After 2 h, III had completely reacted, and the major product characterized in situ was $[Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH(CH_3)]PPN$. ^{11}B NMR ($CD_3C(O)CD_3$, 20 °C): δ 72.7 (br, m); ^{31}P NMR ($CD_3C(O)CD_3$, 20 °C): δ 32.2 (m, 1 P), 21.7 (m, 2 P, PPN^+ cation). ^1H NMR ($CD_3C(O)CD_3$, 20 °C): δ 7.7–7.5 (m, 30 H, PPN^+ cation), 7.4–7.2 (m, $PhMe_2P$), 1.28 (m, $PhMe_2P$), 1.10 (s, CH_3), –10.3 (br, 1 H).

Reaction of [I]PPN with H_2O. An excess of distilled water (ca. 10 mmol) was added to a solution of [I]PPN (0.03 mmol) in acetone (2 mL) at room temperature. After 30 min, ^1H and ^{11}B NMR showed the formation of $[HFe_3(CO)_{11}]^-$ ($\delta(^1H)$ –14.75) and $B(OH)_3$($\delta(^{11}B)$ 18.8) and the loss of 15% of I.

Reaction of [I]PPN with NEt_3. NEt_3 (0.028 mL, 0.2 mmol) was added to [I]PPN (0.04 mmol) in acetone (1.5 mL) and stirred at room temperature. The reaction was monitored over a period of 8 h by ^1H and ^{11}B NMR. No gas production was observed by volumentric analysis. Gas analysis (GLC) of the head gas above the reaction solution showed no trace of H_2 during the 8 h period. The major product (80%) reverted to I during attempts to chromatographically isolate it and, therefore, could only be spectroscopically characterized in situ. ^{11}B NMR ($CD_3C(O)CD_3$, 20 °C): δ 5.1 (s, fwhm = 110 Hz). ^1H NMR ($CD_3C(O)CD_3$, –65 °C): δ 2.62 (q, 6 H, J_{HH} = 6 Hz, $N(CH_2CH_3)_3$), 0.97 (t, 9 H J_{HH} = 6 Hz, $N(CH_2CH_3)_3$). Two products, accounting for ≈20% of the total reaction products, grew in together. One was characterized as $H_3B{\cdot}NEt_3$. ^{11}B NMR ($CD_3C(O)CD_3$, 20 °C): δ –12.2[22] (q, J_{BH} = 98 Hz). ^1H NMR ($CD_3C(O)CD_3$, 20 °C): δ 2.75 (q, J_{HH} = 7 Hz, $N(CH_2CH_3)_3$), 1.13 (t, J_{HH} = 7 Hz, $N(CH_2CH_3)_3$). The other had a narrow ^1H NMR resonance at –15.3 ppm and no correpsponding ^{11}B resonance. The material has the characteristics of an amine-substituted $[HFe_3(CO)_{11-x}(NEt_3)_x]^-$ (see Discussion).

Determination of Reaction Order for the Reaction of [I]PPN with $PhMe_2P$. A stock solution of [I]PPN (0.192 mmol) in acetone (6.0 mL) was prepared, and 1.5 mL aliquots were used in reactions with $PhMe_2P$ in which the phosphine concentration was varied. In a typical reaction, $PhMe_2P$ (0.068 mL, 0.48 mmol) was added to [I]PPN (0.048 mmol) in acetone (1.5 mL). The reaction was followed by ^{11}B NMR at a spectrometer temperature of ≈30 °C until 2–3 half-lives had elapsed. The reaction was repeated using 0.96 and 1.68 mmol $PhMe_2P$, respectively, each with 0.048 mmol of [I]PPN. The reproducibility of the data was checked by repeating the run with 1.44 mmol of $PhMe_2P$. During the reaction period, the solution changed from orange-red (characteristic of I) to brown. Four products were characterized in situ by multinuclear NMR ($CD_3C(O)CD_3$, 20 °C) and by comparison with authentic samples: Data for $PhMe_2P{\cdot}BH_3$.[23] ^{31}P NMR: δ 3.90 (dq); {^1H} J_{PB} = 60 Hz. Data for $[(\mu\text{-}H)Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)_2]PPN$. ^{31}P NMR: δ 34.0 (m, 2 P), 21.7 (m, 2 P, PPN^+ cation). ^1H NMR: δ 7.7–7.5 (m, PPN^+ cation), –14.3 (s). Data for $Fe(CO)_3(PhMe_2P)_2$. ^{31}P NMR: δ 50.3 (doublet of heptets, 2 P); {^1H} $J_{PH(Me)}$ = 9, $J_{PH(Me')}$ = 7 Hz.[24] Data for [V]. ^{31}P NMR: δ 36.0 (m, fwhm = 29 Hz, 1 P); {^1H} $J_{PH(Me)}$ = 10, $J_{PH(Fe\text{-}H\text{-}B)} \leq 6$ Hz. ^{11}B NMR: δ 20.3 (br, m); {^1H} J_{BH}(terminal) ≈ 90,[21] $J_{BH(Fe\text{-}H\text{-}B)} \approx 40$ Hz.[21] ^1H NMR ($CD_3C(O)CD_3$, –80 °C): $\delta \approx 3.0$ (br, 1 H), –11.7 (br, 3 H). It was not possible to assign ligand phenyl and methyl ^1H resonances to individual species.

Results

Reaction of I with CO. Although at higher temperatures decomposition is extensive and more rapid than reaction with CO,[9] at 45 °C in the presence of CO I slowly converts exclusively to II via the elimination of H_2 and the addition of a basally bridging CO (eq 2). Hence, the reaction is parallel to, if much slower than, that of $(\mu\text{-}H)_3Fe_3(CO)_9(\mu_3\text{-}CCH_3)$ with CO at 60 °C that we have previously reported.[25]

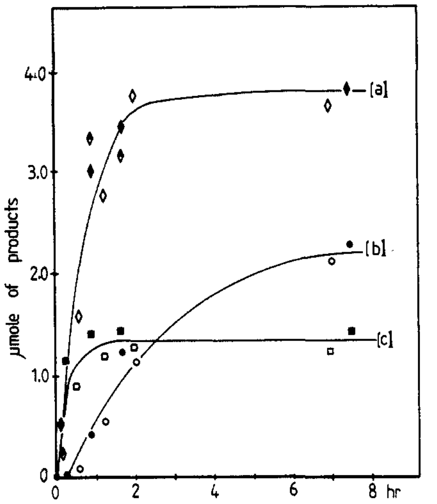

Figure 1. Correlation of ^{31}P and ^{11}B NMR product data for the reaction of [I]PPN (14 μmol) with $PhMe_2P$ (16 μmol). Lines a and c are fragmentation pathways; line b is the H_2 elimination pathway: (♦) ^{31}P $Fe(CO)_3(PhMe_2P)_2$, (◊) ^{11}B V, (◊) ^{31}P V; (●) ^{31}P and (○) ^{11}B $[Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH_2]^-$; (■) ^{31}P $[(\mu\text{-}H)Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)_2]^-$, (□) ^{11}B $PhMe_2P{\cdot}BH_3$. After 8 h, 55% of I has reacted and, based on the products observed, 15 μmol of $PhMe_2P$ has been consumed.

$$[HFe_3(CO)_9BH_3]^- + CO \rightarrow [Fe_3(CO)_9(\mu\text{-}CO)BH_2]^- + H_2 \qquad (2)$$

During the conversion of I to II, the changing environment of the boron is reflected in the ^{11}B NMR shift from δ 6.1 (I) to 57.4 (II), a change that we have attributed to loss of FeHB interactions.[8] At 1 atm of pressure the concentration of CO[26] is less than the initial concentration of I (0.01 mmol/mL), and cluster integrity is retained (vide infra). As a consequence of the incoming ligand's association with the metal base, the BH_3 moiety in I is converted into a BH_2 unit by H_2 elimination.

Reaction of I with H_2O. In the presence of excess H_2O, I fragments as shown in eq 3. Since water is a poor Lewis base with respect to iron(0), it is not surprizing that we observe products

$$[HFe_3(CO)_9BH_3]^- + H_2O \rightarrow [HFe_3(CO)_{11}]^- + B(OH)_3 \qquad (3)$$

that evidence attack at the boron apex of I. However, it is noteworthy that the reaction is very slow, showing that in its cluster environment, the monoborane of I exhibits little hydridic character. (Note that reaction with strong acid leads to I′.[8,9]) Formally, the removal of the "borane cap" from I leaves an unsaturated metal triangle that apparently scavanges adventitious CO to form the well-characterized iron hydride cluster $[(\mu\text{-}H)Fe_3(CO)_{10}(\mu\text{-}CO)]^-$.[3] This behavior contrasts to that with CO, and clearly, whether substitution via H_2 displacement or cluster fragmentation is observed depends on the nature of the Lewis base.

Reaction of I with $PhMe_2P$. $PhMe_2P$ is a strong Lewis base for both transition metals and boranes. Hence it provides an opportunity to explore competition between the qualitatively different routes defined above. In doing so, we demonstrate a reaction pathway concentration dependence as well as an additional fragmentation pathway.

Under conditions of 10-fold excess $PhMe_2P$ or greater, four reaction products are observed (see below). The three of certain identity can only arise by fragmentation of I. By following the reaction using ^{31}P, ^{11}B, and ^1H NMR, we demonstrated that during the course of the reaction these four products arise from

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[22] Heitsch, C. W. *Inorg. Chem.* **1965**, *4*, 1019.

[23] ^{11}B and ^1H NMR resonances were consistent with published data: Mathur, M. A.; Myers, W. H.; Sisler, H. H.; Ryschkewitsch, G. E. *Inorg. Synth.* **1974**, *15*, 128.

[24] $Fe(CO)_3(PhMe_2P)_2$ was identified by synthesizing a mixture of $Fe(CO)_3(PhMe_2P)_2$ and $Fe(CO)_4(PhMe_2P)$ following the method described for related complexes: Braterman, P. S.; Wallace, W. J. *J. Organometal. Chem.* **1971**, *30*, C17. $Fe(CO)_4(PhMe_2P)$ was then prepared by an independent route: Siegl, W. O. *J. Organometal. Chem.* **1975**, *92*, 321. ^{31}P NMR ($CD_3C(O)CD_3$, 20 °C) δ 50.3 (m, $Fe(CO)_3(PhMe_2P)_2$) 42.4 (heptet, J_{PH} = 10 Hz, $Fe(CO)_4(PhMe_2P)$).

[25] Vites, J. C.; Fehlner, T. P. *Organometallics* **1984**, *3*, 491.

[26] Gjaldbaek, J. C. *Acta Chem. Scand.* **1952**, *6*, 623.

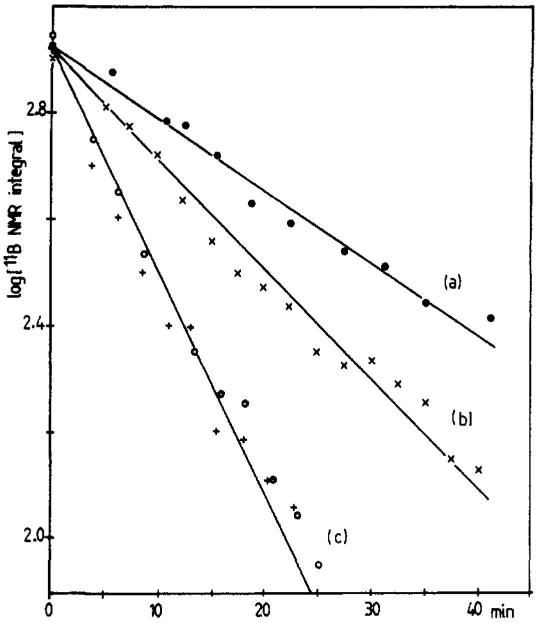

Figure 2. First-order rate plot for the disappearance of I during reactions with $PhMe_2P$ at 30 °C in acetone: (a) 10-fold $PhMe_2P$; (b) 20-fold $PhMe_2P$; (c) two independent runs for 30-fold $PhMe_2P$.

two parallel pathways. This is illustrated by curves a and c in Figure 1 which contains data for a reaction with a 1:1 ratio of I to ligand. Correlation of the data using PPN^+ as an internal ^{31}P standard and $B_3H_8^-$ as an external ^{11}B standard allows Figure 1 to be constructed in terms of product yields.

Pathway c is well defined in terms of products: $PhMe_2P{\cdot}BH_3$ is known,[23] and although the phosphine-substituted derivative of $[(\mu\text{-H})Fe_3(CO)_{10}(\mu\text{-CO})]^-$ observed has not, to our knowledge, been reported, the appearance of a hydride resonance at δ −14.3 in the ^1H NMR (i.e., close to δ −14.75 for $[(\mu\text{-H})Fe_3(CO)_{10}(\mu\text{-CO})]^-$ itself) along with the ^{31}P NMR behavior allows us to identify the product as $[(\mu\text{-H})Fe_3(CO)_8(\mu\text{-CO})(PhMe_2P)_2]^-$. As the two phosphine ligands are equivalent this reaction constitutes a route to a specific disubstituted cluster. This is significant because direct reaction of closely related clusters with phosphine base can lead to complete cluster fragmentation.[27] In our own attempts to directly substitute $[(\mu\text{-H})Fe_3(CO)_{10}(\mu\text{-CO})]^-$ with $PhMe_2P$, we observe the hydride resonance at δ −14.3, but in the ^{31}P NMR we see the substituted product as well as resonances that can be attributed to other isomers or products of fragmentation. The products of path c, then, involve interaction of the base with both boron and iron.

Table I. Rate Constants for the Reaction of I with Excess PMe_2Ph

$[I]_0$, M	$[PMe_2Ph]_0$, M	k', min^{-1} [a]	k_a, min^{-1} [b]	k_c, min^{-1} [c]
0.032	0.31	0.030 (0.98)	0.016 (0.98)	0.012 (0.99)
0.032	0.60	0.044 (0.98)	0.031 (0.98)	0.023 (0.99)
0.032	0.99	0.088 (0.99)	0.052 (0.91)	0.040 (0.99)
0.032	0.99	0.086 (0.97)	0.050 (0.94)	0.032 (0.98)

[a] Defined in eq 5. The number in parentheses is the correlation coefficient for the linear fit. [b] Pseudo-first-order rate constants for the formation of V, eq 4. [c] Pseudo-first-order rate constant for the formation of $PhMe_2PBH_3$, eq 4.

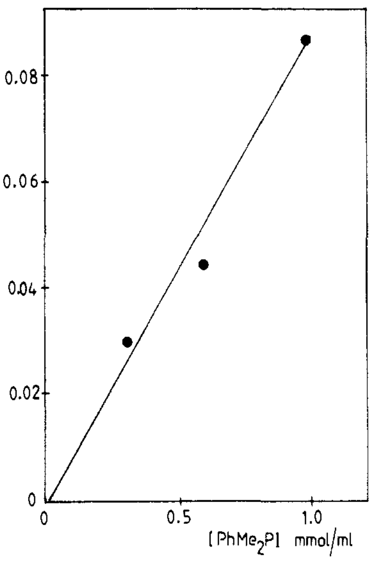

Figure 3. Plot of pseudo-first-order rate constants (k') against concentration of $PhMe_2P$ (eq 4).

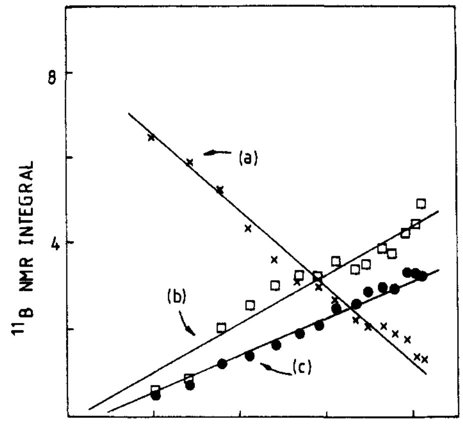

Figure 4. Plot of disappearance of I (a) and appearance of V (b) and $PhMe_2BH_3$ (c) (relative ^{11}B integrals vs. $(1 - e^{-k't})$, where k' is defined in eq 5) for $[I]_0 = 0.1[PMe_2Ph]_0$.

The second fragmentation, pathway a, is defined by the formation of $Fe(CO)_3(PhMe_2P)_2$ and a new ferraborane, V. It is important to note that we do not see the formation of $Fe(CO)_4(PhMe_2P)$ during the reaction of I with $PhMe_2P$. The formation of mono- without disubstituted $Fe(CO)_5$ is not readily accomplished,[24] and therefore, the observed specificity is mechanistically significant (see below). As we could not isolate V nor, as yet, prepare it independently, it has only been characterized in situ. (See Experimental Section.) The number of iron atoms in V is known to be one or greater. The observed ^{31}P NMR resonance at δ 36.0 (one P by integration) suggests metal-bound phosphorus which is corroborated by the lack of boron–phosphorus coupling both in the ^{31}P and ^{11}B NMR. The ^{11}B and ^1H NMR spectra of V show two types of proton attached to boron: viz., one terminal and three Fe–H–B bridge protons. We postulate that V results from I by the displacement of an $Fe(CO)_3$ fragment (lost as $Fe(CO)_3(PhMe_2P)_2$) by $PhMe_2P$. This would suggest that formulation of V as $[Fe_2(CO)_6(PhMe_2P)BH_4]^-$, an isolobal analogue of $[(\mu\text{-H})Fe_3(CO)_{10}(\mu\text{-CO})]^-$. Although V is not unambiguously defined, it is clear that the products result from a fragmentation similar to that of path c. However, here the products result from interaction of the base only with iron. This is summarized in eq 4. Note that $BH_3{\cdot}L$ is isolobal with $Fe(CO)_3L_2$.

$$[HFe_3(CO)_9BH_3]^- + PhMe_2P \xrightarrow{a} Fe(CO)_3(PhMe_2P)_2 + [Fe_2(CO)_6(PhMe_2P)BH_4]^-$$

$$[HFe_3(CO)_9BH_3]^- + PhMe_2P \xrightarrow{c} PhMe_2P{\cdot}BH_3 + [HFe_3(CO)_9(PhMe_2P)_2]^- \quad (4)$$

Competition between the two paths consistently favors the formation of $Fe(CO)_3(PhMe_2P)_2$ and V (see Figure 1), and it is doubtful (see below) that conditions that exclusively yield

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[27] Louidichi, M.; Pince, R.; Dahan, F.; Mathieu, R. *Organometallics* **1983**, *2*, 1417.

Table II. Initial Rates for the Formation of $[Fe_3(CO)_9(PhMe_2P)BH_2]^-$

run	$[I]_0$, M[a]	$[L]_0$, M[a]	R_0, M h^{-1} × 10^3[b]	$R_0/[I]_0$, h^{-1}	$R_0/[L]_0$, h^{-1}
1a[c]	0.019	0.006	0.33	0.017	0.054
1b[c]	0.017	0.007	0.34	0.020	0.055
1c[c]	0.009	0.010	0.57	0.063	0.057
2	0.009	0.011	0.47	0.050	
3	0.016	0.050	0.96	0.060	
4	0.031	0.155	2.20	0.056	

[a] Initial concentrations of I and $PhMe_2P$. [b] Initial rate based on formation of $[Fe_3(CO)_9(PhMe_2P)BH_2]^-$ observed by ^{11}B or ^{31}P NMR at 25 °C in acetone. [c] $^1/_4$ mol equiv L added at 8-h intervals.

V and $Fe(CO)_3(PhMe_2P)_2$ can be found.

The reaction of I with ≥10-fold excess $PhMe_2P$ was found to be first order in I over several half-lives and dependent on $PhMe_2P$ (Figure 2). The rate constants, k' (eq 5), determined from the data shown in Figure 2 and contained in Table I, show a linear relationship with phosphine concentration (Figure 3), proving a first-order dependence on $PhMe_2P$. The overall second-order rate

$$\frac{-d[I]}{dt} = k[I][PhMe_2P] = k'[I] \qquad (5)$$

constant, k, is 1.5×10^{-3} M^{-1} s^{-1}. Figure 4 illustrates the pseudo-first-order behavior observed for the formation of V and $PhMe_2P\cdot BH_3$.[28] Although the scatter is higher, the plots are linear. The sum of the two rate constants equals k' consistent with the parallel paths postulated (Figure 4a and 4c). Table I contains similar k's at the other ligand levels.

A reduction in the level of $PhMe_2P$ relative to I causes another reaction pathway to appear. This is illustrated in Figure 1 by curve b which corresponds to the formation of $[Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH_2]^-$. This product was identified by comparing its spectroscopic properties with those of the CO substitution product of II with $PhMe_2P$. The ^{31}P NMR shift (δ 30.2) and lack of BP coupling indicate substitution at Fe rather than at B. This is confirmed by noting that the ^{11}B and ^1H NMR characteristics of II and its monophosphine-substituted analogue are very similar, indicating that neither boron nor proton environment undergoes large perturbation upon cluster substitution at an iron site. However, the terminal and bridge protons that in II are individually observed at 20 °C (if somewhat broadened) are not observed in $[Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH_2]^-$ at room temperature. Thus, the substitution of $PhMe_2P$ for a CO lowers the barrier for proton scrambling. Finally, the reaction of I with lower concentrations of ligand is accomplished by the evolution of H_2 as shown in eq 6.

$$[HFe_3(CO)_9BH_3]^- + PhMe_2P \xrightarrow{b} [Fe_3(CO)_9(PhMe_2P)BH_2]^- + H_2 \qquad (6)$$

To be able to understand the difference between the H_2 displacement and cluster fragmentation pathways, it is necessary to investigate the ligand dependence of path b (Figure 1 and eq 6). Observation of path b exclusively at low ligand levels implies a lower order in phosphine. However, because of the complexity of the system, a kinetic analysis cannot be done explicitly. Some insight can be gained by examining initial rate data for the formation of $[Fe_3(CO)_9(PhMe_2P)BH_2]^-$ for four reactions with significantly different phosphine levels (Table II). For runs 2–4, where $[PhMe_2P]_0/[I]_0 \geq 1$, the initial rates are proportional to $[I]_0$ and independent of $[PhMe_2P]_0$. Run 1, corresponding to a 1:1 $PhMe_2P$:I reaction, is carried out by adding aliquots of $^1/_4$ mol equiv of $PhMe_2P$ at intervals of ca. 6–8 h; 70% reaction was observed after 30 h, yielding 33% fragmentation and 67% H_2 displacement. The normal 1:1 reaction yields 67% fragmentation and 33% H_2 displacement. In this case the initial rate of H_2 displacement product is considerably lower than expected on the basis of $[I]_0$. However, if one assumes that a 1:1 adduct of I and $PhMe_2P$ precedes H_2 elimination, the $[PhMe_2P]_0$ determines the initial rate. As demonstrated in Table II, initial rate/$[PhMe_2P]_0$ is constant for run 1 and equal to the value obtained in runs 2–4. This suggests association between I and phosphine preceding H_2 elimination.

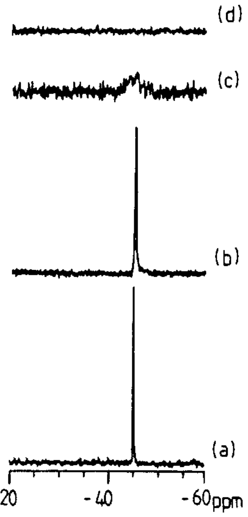

Figure 5. $^{31}P\{^1H\}$ NMR (121.4 MHz) in acetone-d_6 at 30 °C for (a) free $PhMe_2P$ (δ −45.6) at a concentration equivalent to the lowest used in reaction with I. (b) Reaction of 3:1 $PhMe_2P$:I with 3-fold excess at $t \approx$ 10 min (δ −45.2). (c) Reaction of 1:1 $PhMe_2P$:I at $t \approx$ 10 min (δ −44.1). (d) Reaction of 0.25:1 $PhMe_2P$:I at $t \approx$ 10 min (no signal).

In accord with this conclusion based on initial rates, we observe a marked broadening of the free-ligand $^{31}P\{^1H\}$ NMR resonance as the level of $PhMe_2P$ is reduced relative to I (Figure 5). Free $PhMe_2P$ (not in the presence of I) exhibits a sharp signal at δ −45.6 (fwhm $\{^1H\}$ = 18 Hz). In the presence of a significantly greater than 3-fold ligand excess with respect to I, the ^{31}P NMR resonance for the unreacted $PhMe_2P$ after 10 min reaction time is virtually identical in shift and line width with that of the control free-ligand signal. For a 3-fold ligand excess (Figure 5b) the signal is shifted 0.4 ppm to lower field, and the fwhm of the proton-decoupled signal is 30 Hz. At a $PhMe_2P$:I ratio of 1:1, a further broadened free phosphine signal at δ −44.1 is observed (Figure 5c), while at lower concentrations, no ^{31}P resonances are observed at all until product signals are resolved (Figure 5d). These observations are consistent with an exchange process involving the free ligand.[29] There is no evidence that any of the phosphine-substituted products is involved in such an exchange process except for $[(\mu\text{-}H)Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)_2]^-$, but since this species is present at largest concentrations when little free-ligand line broadening is observed, it is unlikely to cause the observed phenomenon. Thus, a reasonable explanation is an exchange of free ligand with an intermediate, an adduct of I with $PhMe_2P$, that is rapid on the NMR time scale.

In summary, these observations are consistent with the formation of an adduct between I and $PhMe_2P$ as expressed in eq 7.[30] The extent to which path b is observed will depend on the level to which the adduct builds up during the course of the reaction. It is postulated that in the presence of high ligand levels,

$$I + PhMe_2P \rightarrow [I\cdot PMe_2Ph] \xrightarrow{+PhMe_2P} \text{paths a and c}$$

$$I + PhMe_2P \rightarrow [I\cdot PMe_2Ph] \rightarrow \text{path b} \qquad (7)$$

loss of $[I\cdot PMe_2Ph]$ via fragmentation keeps the concentration of the intermediate at very low levels; i.e., the association reaction

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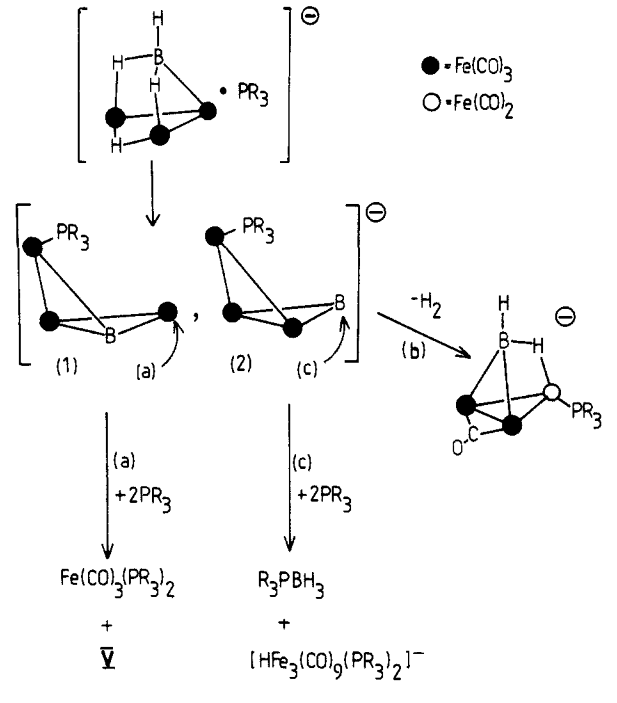
(28) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed.; Wiley: New York, 1961; p 162.

(29) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982.

(30) Wilkins, R. G. *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*; Allyn and Bacon: Boston, 1974.

Scheme I

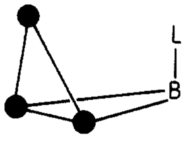


of I + PMe_2Ph is rate controlling. At low ligand levels [$I\cdot PMe_2Ph$] builds up and unimolecular decay [path b] can compete effectively with fragmentation.

The structure of the $PhMe_2P$ adduct of I (eq 7) is not known, but it can be envisioned as leading to more than one reaction (Scheme I). Ignoring bridging hydrogens which we know are mobile,[8] I has three Fe–Fe and three B–Fe edges. We postulate that [$I\cdot PR_3$] is predisposed toward edge bond cleavage and that either edge type can rupture, yielding the two "butterfly" structures shown in Scheme I. Note that cluster opening on base attack has been suggested as mechanistically significant in similar systems[31] and is consistent with electron counting rules.[32] We suggest that the phosphine ligand ends up on a "wing-tip" iron and subsequent rapid attack by additional phosphine takes place on the other "wing-tip" atom, thereby leading to the observed fragmentation products.

At low levels of phosphine, H_2 elimination competes effectively with fragmentation. This unimolecular path should be sensitive to substituents particularly on boron, and thus, we have examined the reaction of III with $PhMe_2P$. I and III differ by the replacement of a boron-bound terminal H by a methyl group. In the presence of a 3-fold excess of $PhMe_2P$, III reacts more rapidly than I to yield H_2 and the phosphine-substituted ferraborane anion $[Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH(CH_3)]^-$. Indeed the methyl substituent on boron promotes H_2 elimination to such an extent that it constitutes the predominant pathway. We know that methyl substitution for H on I′ increases the hydrogen mobility of the cluster,[8] and therefore, this mobility may be an important factor in the H_2 elimination process. In any case, the balance between H_2 elimination and fragmentation must be a delicate one and must depend on the nature of the "butterfly" intermediates[33] as well as concentration and nature of the base.

Note that in the cleavage of a BFe edge, the phosphine could have ended up on boron, yielding an intermediate of type 3. To explore whether such a species might also be a participant in the reaction scheme, we examined a base with a high affinity for boron and a low affinity for iron, i.e., an amine.



(3)

When NEt_3 is added to a solution of I, the disappearance of the ^1H NMR resonance at δ −13.1 associated with the endo hydrogens of I demonstrates reaction. In the presence of ≤5-fold equiv of NEt_3, I exhibits a ^{11}B NMR signal that gradually shifts upfield from δ 6.2 to 5.1 during the course of the reaction defined by the loss of the δ −13.1 ^1H signal. The new resonance shows no clear coupling to protons (fwhm ≈ 110 Hz, proton coupled and decoupled), suggesting attachment of the NEt_3 ligand to boron. Three types of amine environment are evidenced in the ^1H NMR spectrum during the reaction of I with NEt_3, and these can be assigned to free NEt_3, $Et_3N\cdot BH_3$, and coordinated amine in the cluster adduct product. At the same time as these ligand ^1H signals are observed, the ^{11}B NMR confirms the presence of only two products containing boron, viz., $Et_3N\cdot BH_3$ and the product at δ 5.1. In the high-field region of the ^1H NMR spectrum, however, we fail to observe (even at −80 °C) proton resonances for skeletally bound or terminal hydrogens. These types of hydrogens should be present in the adduct product as no H_2 evolution is observed during the reaction. We conclude that NEt_3 interacts with I but is not able to activate the cluster toward H_2 elimination. The adduct formed is stable enough to exist in situ but loses amine quite readily during attempts to isolate it. We suggest that here the adduct of I has the amine coordinated to boron, i.e., 3. By difference, we conclude that H_2 elimination in the case of CO and phosphine results from coordination of the incoming ligand to iron (Scheme I).

An additional reaction pathway, that becomes increasingly important as NEt_3 concentration increases, results in the formation of $Et_3N\cdot BH_3$. Although paralleling the formation of $PhMe_2P\cdot BH_3$ described above, this reaction is very much slower. By analogy with the phosphine reaction, Scheme I, the second product of this fragmentation path should be a substituted derivative of $[(\mu\text{-}H)Fe_3(CO)_{10}(\mu\text{-}CO)]^-$. In fact, a weak proton resonance at δ −15.3 grows in at the same time as the ^{11}B signal for $Et_3N\cdot BH_3$ but gradually decays again, being replaced by one at δ −14.75. Since the latter is due to $[(\mu\text{-}H)Fe_3(CO)_{10}(\mu\text{-}CO)]^-$, it is reasonable that the former is due to an amine-substituted derivative thereof that loses NEt_3 and picks up adventitious CO to form the more favored unsubstituted metal carbonyl hydride anion. Again we suggest that the intermediate has form 3 and that coordination to boron combined with the small affinity of NEt_3 for iron makes fragmentation sluggish.

Conclusions

The results reported here demonstrate that in the presence of Lewis bases, I is subject to a delicately balanced competition between cluster retention (substitution via H_2 displacement) and cluster fragmentation that depends on the nature of the base, upon base concentration, and substituents on boron. In the case of the phosphine ligand, low ligand concentrations and alkyl substitution enhance H_2 displacement relative to cluster fragmentation. Just as we have previously shown that H_2 elimination provides a low-energy path for cluster expansion,[34] so too does H_2 displacement provide a low-energy route to phosphine-substituted II. The fact that hydrogen can be a better leaving group than CO is demonstrated by the fact that the substitution of CO from II by PR_3 is slower than the displacement of H_2 from I by PR_3. The two fragmentation paths observed demonstrate the displacement of isolobal fragments (BH_3L and $Fe(CO)_3L_2$) from the cluster. In

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(31) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985.

(32) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(33) An open intermediate has also been postulated for the reaction of $(\mu\text{-}H)_3Os_3(CO)_9B(CO)$ with PMe_3: Jan, D.-Y.; Hsu, L.-Y.; Shore, S. G. Presented at the 188th National Meeting of the American Chemical Society, Philadelphia, Aug 1984; paper INORG 180.

(34) Housecroft, C. E.; Fehlner, T. P. *Organometallics* **1986**, *5*, 379.

a homonuclear tetrahedral metal cluster, these would constitute degenerate paths. Finally, just as with the conventional base adducts of BH_3, the reactions of I with Lewis bases are a sensitive function of reaction parameters.

Acknowledgment. The support of the National Science Foundation (CHE-84-08251) is gratefully acknowledged.

Registry No. [I]PPN, 102233-76-1; [II]PPN, 102233-78-3; [III]PPN, 102233-85-2; [IV]PPN, 102339-50-4; $[Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH_2]PPN$, 102233-80-7; $(\mu\text{-}H)Fe_3(CO)_9(\mu\text{-}CO)BH(CH_3)$, 102233-81-8; $[Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH(CH_3)]PPN$, 102233-84-1; H_2O, 7732-18-5; NEt_3, 121-44-8; $PhMe_2P$, 672-66-2; CO, 630-08-0; $[HFe_3(CO)_{11}]^-$, 55188-22-2; $PhMe_2 \cdot BH_3$, 35512-87-9; $Fe(CO)_3(PhMe_2P)_2$, 52253-91-5; $[(\mu\text{-}H)Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)_2]PPN$, 102233-87-4; Fe, 7439-89-6.

Enantiomeric Purity Determination of 1,2-Diols through NMR Spectroscopy without Chiral Auxiliaries[1]

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Abstract: The use of optically active chiral auxiliaries for enantiomeric purity determinations by NMR can be avoided if the appropriate conditions for the "self-discrimination" of enantiomers are met. Molecular aggregation under fast-exchange conditions is shown to potentially render self-discriminating chiral molecules in nonracemic mixtures through the generation of diastereomeric relationships among groups. This phenomenon should not a priori be considered exceptional. The general principles of self-discrimination are analyzed in detail and conveniently applied in the case of dioxastannolanes, which are known to be strongly associated in solution. 1,2-Propanediol (**1**) and 1-phenyl-1,2-ethanediol (**2**) have been chosen as representative examples of the class of 1,2-diols, and are converted to the corresponding 2,2-dibutyl-1,3,2-dioxastannolanes (**3** and **4**) by means of achiral dibutyltin reagents. Mixtures of various enantiomeric excess of **3** and **4**, respectively, have been studied by ^{13}C NMR spectroscopy in concentrated solutions in $CDCl_3$, where they show the phenomenon of self-discrimination. The fractional intensities of the signals from the *R* and *S* enantiomers can be used for measurements of enantiomeric excess with an estimated accuracy of ±2%.

The determination of enantiomeric purity of chiral compounds is usually accomplished by exploiting their interaction with a different, optically active species. Based on this principle, many methods and techniques have been developed:[2,3] for instance, in NMR, excellent results are often achieved by using chiral solvents or auxiliaries to resolve signals from the two enantiomers in diastereomeric adducts.[2,3f-i]

When stable compounds are formed, or the parent enantiomeric species exchange slowly among the adducts, each diastereomeric adduct gives rise to a different NMR spectrum; when the exchange is fast, each parent enantiomer gives rise to a different spectrum, because the enantiomers spend at least fractions of time in diastereotopic environments. In the latter case adduct formation need not be complete nor the complexing agent (chiral auxiliary) need be enantiomerically pure.

Chiral auxiliaries are not an absolute requirement. It has been recently shown[4,5] that, when a compound, present as two enantiomers, *d* and *l*, forms kinetically inert dimers, the difference between the *dd* (*ll*) and *dl* (*ld*) diastereoisomers is detectable by NMR. Here the applicability of the method depends on the knowledge of the relative tendency to form homo- or heterodimeric aggregates.

The next logical step in the exploitation of achiral reagents for enantiomeric purity determinations would be to induce the formation of dimers, among which the interchange of monomeric units can be fast on the NMR time scale. As long as the enantiomeric composition differs from that of the racemic mixture, different signals from the *d* and *l* units are expected, with intensities directly proportional to [*d*] and [*l*]. The mixture would thus exhibit self-discrimination.

Although a few examples of self-discrimination under fast-exchange conditions have appeared in the literature,[6] this phenomenon is still considered exceptional.[2d] The purpose of the present paper is to investigate the potentiality of this phenomenon and to provide criteria for its general application. We show that self-discrimination can be conveniently used for the enantiomeric purity determination of chiral 1,2-diols, whose difficulty has been already pointed out.[3f] Diols are easily converted into dioxastan-

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[†] Università di Firenze.

[‡] Centro di Studio sulla Chimica e la Struttura dei Composti Eterociclici e loro Applicazioni.

(1) Group 4 Organometallic Reagents. 2. For part 1 see: Roelens, S.; Taddei, M. *J. Chem. Soc., Perkin Trans. 2* **1985**, 799–804.

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