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Synthesis of metal-rich metallaborane clusters. Evidence for a mechanism involving fragment condensation *

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Abstract

A mechanistic hypothesis of metallaborane cluster build-up by the condensation of metal and boron containing fragments, which is supported by circumstantial evidence from previous work, suggests improved routes to the synthesis of ferraboranes. This work describes two new approaches consisting of the examination of two precursors with properties consistent with such a hypothesis. The first precursor, a neutral mononuclear dimethyl sulfide substituted iron tetracarbonyl, $Fe(CO)_4SMe_2$, is a new compound and the high yield synthesis and structural characterization of it are reported. This compound provides a better route to the ferraborane $Fe_2(CO)_6B_2H_6$ than those presently known and is an isolatable, alternate source of the $Fe(CO)_4$ fragment. The second precursor, $Fe(CO)_3(cco)_2$, where cco is η^2-*cis*-cyclooctene, is a known, ready source of the $Fe(CO)_3$ fragment. The reaction of $Fe(CO)_3(cco)_2$ with BH_3 sources at low temperatures results in good yields of known ferraboranes and a product distribution that depends primarily on the ratio of boron to iron in the reactants. Both of these results support a mechanism for metallaborane cluster formation involving rapid metal carbonyl fragment condensation as a principal mechanistic component.

Introduction

The large body of fascinating chemistry emanating from the laboratories of Gordon Stone over the past decade is based, in large part, on a simple, elegant idea. That is, molecules containing either unsaturated carbon–metal or metal–metal

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* Dedicated to Professor F.G.A. Stone.

bonds should be well suited for bonding to electron-rich transition metal fragments [1]. In this fashion, clusters containing a great variety of transition elements have been synthesized in a systematic, stepwise fashion [2]. We have admired his work for many years and we wish, in this contribution dedicated to Gordon on his birthday, it were possible to show that metallaborane clusters could be approached in a similarly elegant manner. Unfortunately, for our ferraborane and cobaltaborane systems, this is not possible at the present time. On the other hand, we think that what follows shows that, despite the apparently fortuitous nature and low yields of the original preparative routes, principles governing the synthesis of our cluster systems do exist but that they are of a significantly different type than the one exploited so forcefully by Gordon Stone and his co-workers. The search for such unifying principles has lead to substantial progress in both understanding the origin of compounds containing boron atoms in a highly metallic environment as well as in improving synthetic pathways to these species.

There are a very large number of compounds known containing direct transition element–boron bonds [3]. Most of these compounds contain many more boron atoms than metal atoms and the synthetic chemistry is dominated primarily by that associated with the relatively strongly bound main group element cage. We are not concerned with these interesting compounds here. Our recent work has been concentrated more on cluster systems made up predominantly of transition elements, i.e., metal-rich metallaboranes [4]. In these compounds the cluster framework is much more labile and the synthetic routes to these compounds have heretofore been less than straightforward. The following brief review of the various methods we have used in the past to obtain metal-rich metallaboranes suggests that there is in fact a common element connecting some ostensibly very different approaches. This, in turn, suggests some properties that an ideal cluster precursor should possess and, hence, a general approach to the synthesis of metal-rich metallaboranes. As discussed below, these ideas have now been tested experimentally in two cases with positive results.

Our initial entry to metal-rich ferraboranes was via the reaction shown in Fig. 1 [5]. This is an exceedingly complex system as it is well known that $[H]^-$ reacts with both B_5H_9 as well as $Fe(CO)_5$. In addition, $Fe_2(CO)_6B_2H_6$ was only one product of many and none is isolated in good yield. The formation of $Fe_2(CO)_6B_2H_6$ was

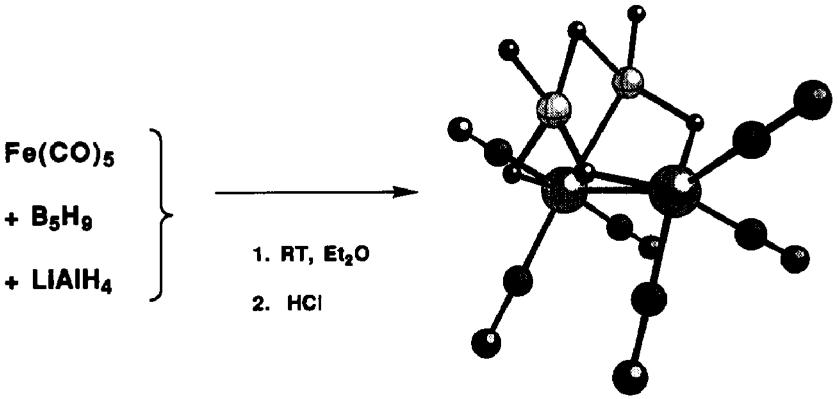

Fig. 1. Schematic representation of the original preparation of $Fe_2(CO)_6B_2H_6$.

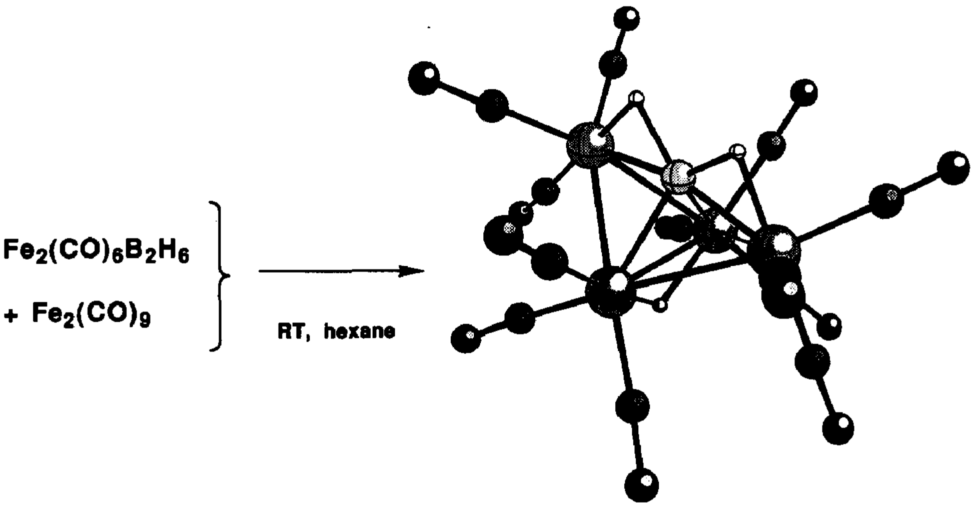

Fig. 2. Schematic representation of the original preparation of $HFe_4(CO)_{12}BH_2$.

further confused by the fact that not only were ferraboranes produced but also hydrocarbyl cluster compounds in which the hydrocarbyl fragment was derived from reduction of CO. Further, $Fe_2(CO)_6B_2H_6$ was found in low or trace yields in a variety of systems in which a BH_x source ($[BH_4]^-$, $BH_3 \cdot L$, B_2H_6, $[B_3H_8]^-$, or B_5H_9), a hydride source ($[BH_4]^-$, $[HBR_3]^-$, $[AlH_4]^-$, etc.) and a $Fe(CO)_y$ source ($Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$) were present. Despite the obscurity of its origins, $Fe_2(CO)_6B_2H_6$ can be converted in reasonable yield into a true metal-rich ferraborane, $HFe_4(CO)_{12}BH_2$, as shown in Fig. 2 [6]. This was a typical observation in that once a metallaborane was isolated it would undergo cluster degradation and expansion reactions relatively cleanly [7,8].

Significant insight into the origin of these ferraboranes was provided by the work of Jose Vites [9] when he found that the complexity of the reaction shown in Fig. 1 could be reduced. The ferraboranes in the reaction illustrated in Fig. 1 appear to result from the reaction of $[(CO)_4FeC(O)H]^-$ with boranes. Hence, he used stable salts of the $[(CO)_4FeC(O)Me]^-$ ion to produce the compounds plus a variety of new ferraboranes and hydrocarbyl iron clusters. For example, as indicated in Fig. 3 [9],

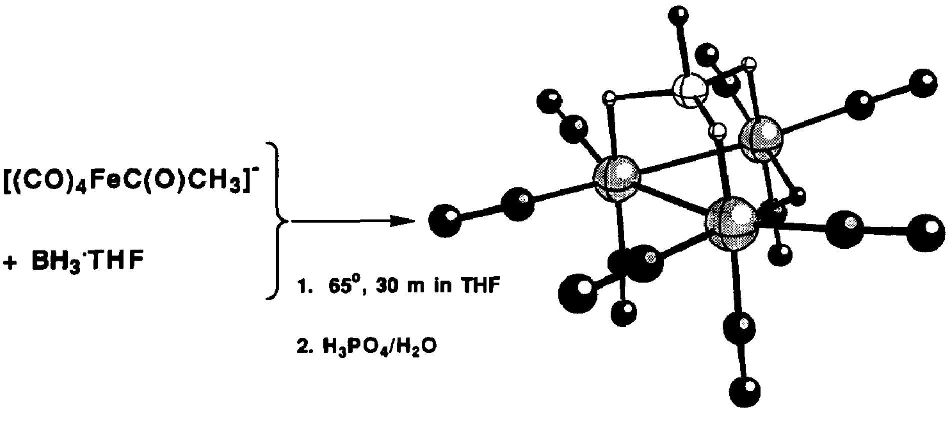

Fig. 3. Schematic representation of the original preparation of $HFe_3(CO)_9BH_4$.

another new ferraborane, $HFe_3(CO)_9BH_4$, was isolated and characterized via this synthetic route. Despite the change in source of iron carbonyl fragments, the qualitative product distribution is very similar to that from the reaction of $Fe(CO)_5$ and $[H]^-$ with $BH_3 \cdot THF$ at low temperatures. At the time, the only point clear to us was that the borane served two distinct roles. First it "activated" the metal carbonyl by reduction of the organic functionality and second it condensed in some fashion with the reactive metal fragments produced to yield the ferraborane products. The first suggestion was consistent with the fact that small amounts of $Fe_2(CO)_6B_2H_6$ are also produced in a thermal reaction of B_5H_9 with $Fe(CO)_5$ at temperatures where the borane is thermally stable but the metal carbonyl is not [10]. The second suggestion implied not only borane–metal fragment but also metal fragment–metal fragment condensation via multiple parallel and/or consecutive pathways. We have discussed these ideas in more detail elsewhere [11].

We anticipated that if the metal cluster building reaction were eliminated more selectivity and better yields of metallaboranes would result. Indeed, in more recent work we have used the $[Fe_4(CO)_{13}]^{2-}$ ion, in which the triply bridging carbonyl serves as the "organic" functionality, to prepare $HFe_3(CO)_9BH_4$ in $\approx 30\%$ yields [12]. Although mechanistic details are presently obscure, again the borane apparently "activates" metal carbonyls by reduction of the metal-bound bridging carbonyl ligand thereby leading to the formation of hydrocarbyl cluster complexes as well as metal-rich metallaboranes. However, just as a single ferraborane is the primary product so too a single organometallic cluster (in this case $CFe_5(CO)_{15}$) is formed in good yield.

At this stage we felt that further selectivity and enhancement of yield would result from adjustment of the available electron density on the active precursor CO ligand or from the utilization of sources of reactive metal carbonyl fragments. In the former case, "tuning" the "activation" reaction might allow selection of a single ferraborane product. In the latter case, elimination of the "activation" reaction completely would allow the existence of cluster formation by fragment condensation to be verified and, hopefully, manipulated.

Utilization of $Fe(CO)_4L$ as a ferraborane precursor

Presumably the "activation" of a metal carbonyl reagent by the Lewis acid takes place at the most negative CO site. Thus, in $[Fe(CO)_4C(O)Me]^-$ it is the acyl oxygen while in $[Fe_4(CO)_{13}]^{2-}$ it is the oxygen of the triply bridging carbonyl ligand. Now, the reactivity of the B–H bonds of the reagent $BH_3 \cdot L$ can be varied by changing L. Indeed, some complexes of borane, e.g., $BH_3 \cdot py$, are ineffective in the preparative reactions mentioned in the previous section. Likewise, the sensitivity of the carbonyls of $Fe(CO)_4L$ to electrophilic attack will depend on L. In order to employ mononuclear rather than polynuclear metal carbonyls in this synthetic approach as well as to improve selectivities, we have sought to change the reactivity of the carbonyls with respect to a given borane reagent, $BH_3 \cdot L$, by replacing one or more CO ligands with a better σ donor and/or poorer π acceptor ligand. For the system $Fe(CO)_4L$ we have already investigated $L = PPh_3$ [13] and THF [11]. The former compound yields only intractable products probably because the phosphine is too strongly bound to the metal. The latter, although effective for the preparation of $HFe_3(CO)_9BH_4$ [12,14] or $Fe_2(CO)_6B_2H_6$ [15] depending on solvent and borane adduct used, can only be produced in situ from the reaction of THF with $Fe_2(CO)_9$ [16]. Hence, we have sought to examine $Fe(CO)_4L$ containing loosely bound activating ligands L in an isolatable complex. A reasonable choice for L is SMe_2 as S is a somewhat more metal-compatible ligand atom than O but not as good as P.

The chemistry and properties of coordinated sulfur ligands are well established [17]; however, that of the complexes $Fe(CO)_4L$, L = thioethers, is not. Murray and Hartley expressed surprise about the paucity of compounds containing thioether ligands in 1981 and this probably reflects the poor coordinating ability of thioethers as simple monodentate ligands [18]. If so, then $Fe(CO)_4L$, L = thioethers, constitute potential precursors for ferraboranes of the type we desire. Some examples are known, however. The SMe_2 ligand is found as bridging ligand in polynuclear compounds (e.g., $[HRuRh_3(CO)_9]_2(\mu\text{-}SMe_2)_3)$ [19], as a terminal ligand in cationic mononuclear iron carbonyl compounds (e.g., $[Cp(CO)Fe(SMe_2)(PMe_3)]PF_6$, $\{Cp(CO)Fe(SMe_2)[=C(SMe)_2]\}PF_6$ [20] and $[CpRu(CO)(PPh_3)SMePh)]^+$ [21]) or, in one instance, $HRuCo_3(CO)_{11}(SMe_2)$ [19], as a terminal ligand in a cluster. Kuhn has effectively used $[CpFe(SMe_2)_3]^+$ as a source of the $[CpFe]^+$ fragment [22]. One example of a mononuclear complex of the type we were interested in, $Fe(CO)_4SC_4H_8$, was reported in 1962 [23] and some related compounds are known, e.g., $ReCl(CO)_3(SMe_2)_2$ [24]. Recently, Darensbourg has characterized a series of anionic complexes $[RSFe(CO)_4]^-$, R = Ph, Et, Me, H and examined the protonated and selected, methylated, labile neutral compounds [25]. Herein we report the convenient preparation of $Fe(CO)_4SMe_2$, an example of a neutral dimethyl sulfide substituted mononuclear iron carbonyl, and its utilization in the preparation of $Fe_2(CO)_6B_2H_6$ [26].

In a reaction presumably analogous to the formation of $Fe(CO)_4THF$ [16], the new compound can be synthesized in 50% yield from the direct combination of $Fe_2(CO)_9$ with SMe_2.

$$Fe_2(CO)_9 + SMe_2(\text{excess}) \rightarrow Fe(CO)_4SMe_2 + Fe(CO)_5 \qquad (1)$$

Further, it can be formed in even higher yield (80%) in the photochemical reaction of $Fe(CO)_5$ with SMe_2 at low temperature [11].

$$Fe(CO)_5 + SMe_2(\text{excess}) \xrightarrow[-CO]{h\nu} Fe(CO)_4SMe_2 \qquad (2)$$

In both cases $Fe(CO)_4SMe_2$ crystallizes from the reaction solution containing $Fe(CO)_5$ and SMe_2 as a pure yellow solid at low temperature and is separated by filtration.

Provided the SMe_2 ligand is viewed as a cylindrically symmetric ligand relative to the metal–sulfur axis, the spectroscopic data would be consistent with the formulation of $Fe(CO)_4SMe_2$ as a pentagonal bipyramidal $Fe(CO)_4L$ with an equatorial SMe_2 ligand and C_{2v} symmetry. Specifically the four absorptions observed in the CO stretching region of the IR spectrum distinguish it from the C_{3v} symmetry axial isomer for which three absorptions are expected [27]. However, crystallographic data obtained at low temperature in the solid state show that the SMe_2 ligand is, in fact, in an axial position (Fig. 4). Hence, the Me groups on the sulfur atom sufficiently perturb the metal center such that the symmetry at the iron atom is lower than C_{3v} with axial substitution [28]. Substitution in the axial position has been established for $(SCS)Fe(CO)_4$ [29] (three IR bands), $(c\text{-}1,3\text{-}C_4H_8S_2)Fe(CO)_4$

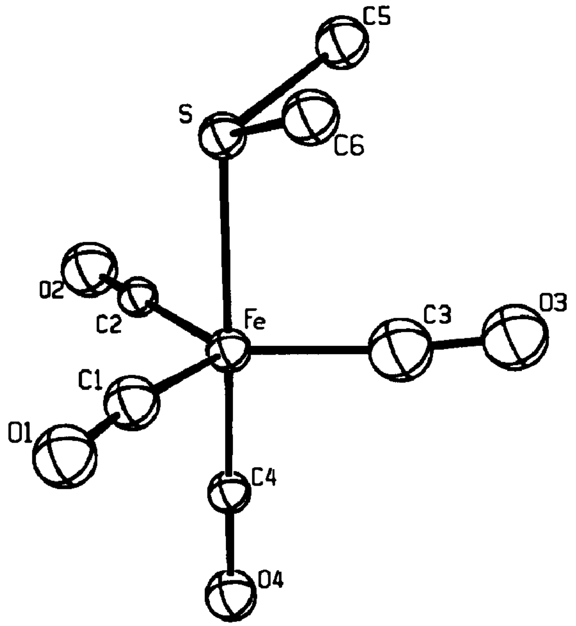

Fig. 4. The molecular structure of $Fe(CO)_4SMe_2$.

[30] (three IR bands) and $[PhSFe(CO)_4]^-$ (four IR bands) [25]. It is also consistent with the relative electronegativities of the CO and SMe_2 ligands.

The $Fe(CO)_4SMe_2$ complex is thermally labile. In the absence of excess dimethyl sulfide, solutions of $Fe(CO)_4SMe_2$ slowly decompose to $Fe(CO)_5$, free dimethyl sulfide and $Fe_3(CO)_{12}$. The formation of these decomposition products was observed by mass, infrared and ^{13}C-NMR spectrometric analysis of a pure sample held at room temperature. The addition of excess dimethyl sulfide stabilizes $Fe(CO)_4SMe_2$ in hexane solution. Under these conditions no decomposition (formation of $Fe(CO)_5$ in the IR) is observed after up to 5 h at room temperature.

The ready availability of $Fe(CO)_4SMe_2$ from inexpensive precursors and the lability of the dimethyl sulfide ligand makes this compound a potentially convenient source of the $Fe(CO)_4$ fragment just as $BH_3 \cdot SMe_2$, with which $Fe(CO)_4SMe_2$ is analogous (a C_{4v} $Fe(CO)_4$ fragment is isolobal with BH_3) [31], is a convenient, commercially available source of BH_3. Further, as SMe_2 is primarily a σ donating ligand, the carbonyl ligands on iron should be more negative and more reactive towards electrophilic reagents. The fact that the CO stretching vibrations of $Fe(CO)_4SMe_2$ appear at significantly lower energy than those of $Fe(CO)_5$ supports this contention. Hence, we have examined $Fe(CO)_4SMe_2$ as a potential precursor of ferraboranes.

The products of the reaction of $Fe(CO)_4SMe_2$ with $BH_3 \cdot SMe_2$ were observed by ^{11}B NMR and the spectra showed evidence of the formation of a triborane ($(B_3H_7)SMe_2$ [32]) and $Fe_2(CO)_6B_2H_6$. Further, signals observed in the δ 18–26 region are characteristic of the formation of compounds containing B–O bonds, e.g. $[RBO]_3$, and are typically observed in our systems when metal-bound CO ligands are reduced to hydrocarbyl fragments [33]. The $Fe_2(CO)_6B_2H_6$ ferraborane is produced in 25% yield (unoptimized NMR yield based on iron) as the only boron and metal containing product. This is approximately a ten-fold higher yield than that of the published route [26]. As both $Fe(CO)_4$ and BH_3 have low-lying empty valence orbitals, the formation of $Fe_2(CO)_6B_2H_6$ might be viewed as analogous to the build up of higher boranes from monoborane fragments [34]. Indeed $Fe_2(CO)_6B_2H_6$ is isolobal with B_4H_8, an unstable, but known borane [35]. However, we suspect that activation of $Fe(CO)_4SMe_2$ occurs via reductive loss of CO to yield an intermediate $[Fe(CO)_3SMe_2]$. This species can lose the weakly bound SMe_2 ligand either before or after condensation with additional BH_3 to form $Fe_2(CO)_6B_2H_6$. Thus, we conclude that the ferraboranes result from the formal condensation of $Fe(CO)_3$ fragments with borane.

Utilization of $Fe(CO)_3L_2$ as a precursor to ferraboranes

We have previously demonstrated that the reaction of $CpCo(PPh_3)_2$ with excess borane results in the formation of metal-rich cobaltaboranes [36]. The major product observed depends, among other factors, on the borane/cobalt ratio and all products can be simply related by the formal addition or substraction of CpCo, PPh_x, Ph or H fragments. These two observations suggest that the products originate from the condensation of transient CpCo (or $CpCoPPh_3$) fragments with themselves as well as with borane and that all products result from the same set of progenitor fragments. This system is simpler than those of the early ferraborane systems discussed above in that activation is by phosphine dissociation (and subsequent coordination of the free phosphine with borane). Thus, we wondered whether the iron system would exhibit an analogous dependence on relative concentration if the reaction of iron carbonyl fragments could be monitored with little perturbation by the fragment initiation reactions. That is, in the ferraborane syntheses reported thus far the rate controlling step appears to be the "activation" of the metal carbonyl reactant to produce the active metal carbonyl fragment. This is confirmed by the work on $Fe(CO)_4SMe_2$ reported above where we have suggested that activation (by reductive elimination of CO and dissociation of SMe_2) formally produced $Fe(CO)_3$ fragments which subsequently condensed with borane to yield the observed ferraboranes. Hence, a precursor that has the potential for the formal generation of $Fe(CO)_3$ fragments under mild conditions, preferably at low temperature, would test this conclusion and allow the nature of the cluster build-up process to be observed and, perhaps, controlled.

The photoreaction of $Fe(CO)_5$ at low temperature in the presence of *cis*-cyclooctene yields $Fe(CO)_3(cco)_2$, where cco is η^2-*cis*-cyclooctene [37]. The solid can be handled at room temperature but in solution at temperatures above $-35\,^\circ C$ $Fe(CO)_3(cco)_2$ serves as versatile source of the $Fe(CO)_3$ fragment. This, then appears to be an ideal compound to test whether or not $Fe(CO)_3$ fragments spontaneously condense with BH_3 to yield the set of known ferraboranes and whether the yields of these ferraboranes depend in a rational manner on the ratio of $[Fe(CO)_3]$ to $[BH_3]$ concentrations.

It was quickly demonstrated that the reaction of $Fe(CO)_3(cco)_2$ with borane at $-40\,^\circ C$ yielded known ferraboranes and that the identity of the major product depended on the $[Fe(CO)_3]/[BH]_3$ ratio. Clearly the reaction of $Fe(CO)_3$ with BH_3 is a very facile reaction in accord with our mechanistic postulates presented above. Further, these qualitative results were independent of whether $BH_3 \cdot THF$ or $BH_3 \cdot SMe_2$ were used and yields fell off rapidly at temperatures above $-20\,^\circ C$. Under the last conditions large amounts of a dark precipitate were produced, presumably

Table 1

NMR yields[a] of $Fe_2(CO)_6B_2H_6$, $HFe_3(CO)_9BH_4$, and $HFe_4(CO)_{12}BH_2$ from the reaction of $Fe(CO)_3(cco)_2$ with $BH_3 \cdot L$, L = THF, SMe_2, at −40 °C in hexane as a function of $[Fe(CO)_3]/[BH_3]$ ratio

$[Fe(CO)_3]/[BH_3]$	$Fe_2(CO)_6B_2H_6$	$HFe_3(CO)_9BH_4$	$HFe_4(CO)_{12}BH_2$	Total
$[Fe(CO)_3]$ = 23 m*M*, $BH_3 \cdot THF$				
4:3	0	0	8	8
1:3	2	19	6	27
1:10	4	38	2	44
1:30	9	50	0	59
$[Fe(CO)_3]$ = 23 m*M*, $BH_3 \cdot SMe_2$				
1:3	3	23	9	35

[a] Based on $Fe(CO)_3(cco)_2$.

by the decomposition of $Fe(CO)_3(cco)_2$. Following these initial studies, we carried out a systematic examination of the concentration dependence of the system using ^{11}B NMR to determine the yields of the principal ferraborane products ($Fe_2(CO)_6B_2H_6$, $HFe_3(CO)_9BH_4$, and $HFe_4(CO)_{12}BH_2$). The results are shown in Table 1 which contains the ferraborane yields (based on iron) as a function of $[Fe(CO)_3]/[BH_3]$ ratio for two borane sources. In order to verify these yields, selected systems were examined at higher scales and the major ferraborane products isolated and weighed. Under optimum conditions the isolated yield of $HFe_3(CO)_9BH_4$ approached 50%.

Two trends are immediately apparent in the data contained in Table 1. First, the compounds containing the higher Fe/B ratios are favored by high $[Fe(CO)_3]/[BH_3]$ ratios. Second, the total yield of ferraboranes increases and the amount of precipitate decreases with decreasing $[Fe(CO)_3]/[BH_3]$ ratio. Alkyl boranes were observed in the NMR spectrum, presumably produced from the reaction of the olefin with BH_3, but no other borane-containing products were observed in significant yield besides those given in Table 1. Changing from $BH_3 \cdot THF$ to $BH_3 \cdot SMe_2$ as borane source had no appreciable effect on the yields. However, for $BH_3 \cdot SMe_2$ three triplets were observed in the ^{11}B NMR in the δ 112–118 region rather than one. One of these triplets corresponds to $HFe_4(CO)_{12}BH_2$ and we suspect that the other two correspond to SMe_2-substituted analogues. The yield shown for $HFe_4(CO)_{12}BH_2$ in Table 1 is calculated on the basis of the sum of the three signals. There was no evidence for similar substitution of the other two products when $BH_3 \cdot SMe_2$ was used as the borane source.

These observations are in general accord with a mechanism in which the $Fe(CO)_3$ fragment condenses with itself and BH_3 via a complex set of concurrent and consecutive pathways. In the case of the cobaltaborane clusters we have suggested that reaction proceeds via ligand loss from $CpCoL_2$ to yield $(CpCo)_2L_3$, $(CpCo)_3L_3$ and $(CpCo)_4L_2$. For L = CO these reactions and all three polynuclear species have been characterized. We postulated that in the presence of BH_3, the polynuclear species were intercepted to yield cobaltaboranes with the efficiency of interception depending on the Co/BH_3 ratio. Hence, we propose a similar mechanism for the iron system. As shown in Fig. 5, an equilibrium involving $Fe(CO)_3(cco)_2$ and $[Fe(CO)_3(cco)]$ + free cco is postulated as the first step. This is in accord with the observation that $Fe(CO)_3(cco)_2$ decomposition is inhibited in the presence of excess

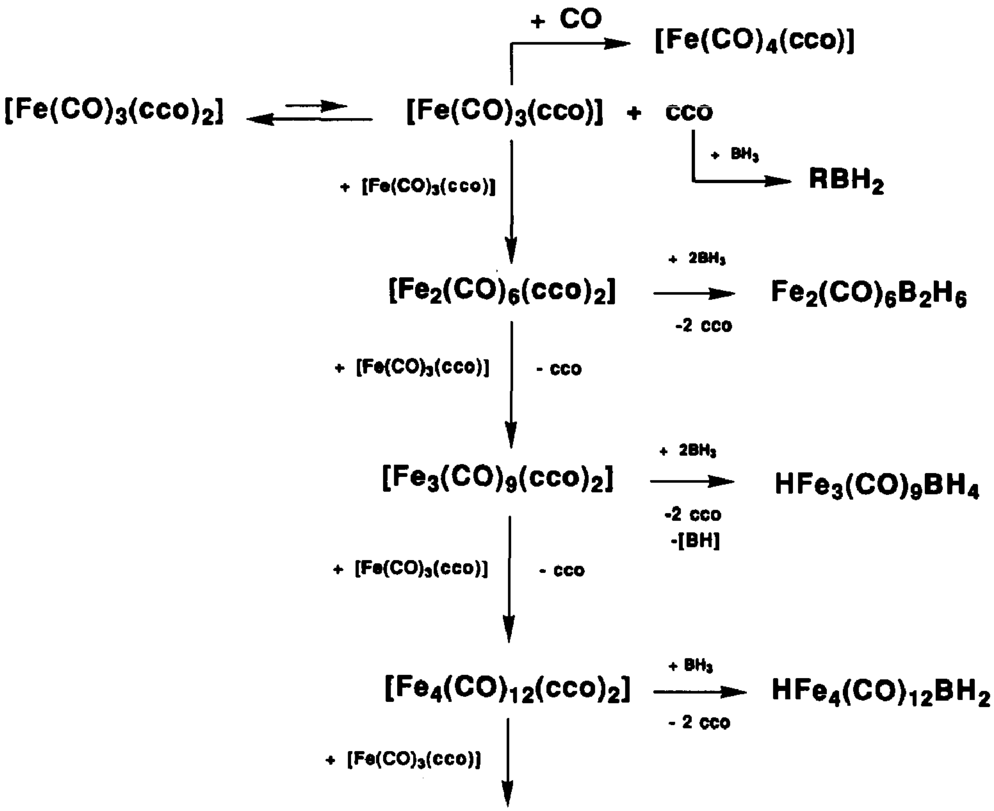

Fig. 5. Proposed mechanism for the reaction of $Fe(CO)_3(cco)_2$ with $BH_3 \cdot THF$. The compounds shown in brackets are suggested intermediates.

cco ligand and that in the presence of CO the solution of $Fe(CO)_3(cco)_2$ is immediately converted into $Fe(CCO)_4(cco)$. With $BH_3 \cdot L$ in the system the free olefin ligand will be consumed via a hydroboration reaction. In the absence of any trapping agent $Fe(CO)_3(cco)_2$ decomposes with the formation of $Fe(CO)_4(cco)$ as the predominant soluble product and with precipitation of an unidentified brown material. It is possible that this intractable material results from the condensation of iron fragments and one reasonable pathway is shown in Fig. 5. Hence, dimerization of $[Fe(CO)_3(cco)]$ leads to $[Fe_2(CO)_6(cco)_2]$, which would be a substituted analogue of the unbridged and unsaturated dinuclear species $Fe_2(CO)_8$ [38]. The analogous species $Os_2(CO)_8$ has been generated by photolysis of $Os_2(CO)_8(\mu\text{-}C_2H_4)$ and was observed in solution at ambient temperature by means of time-resolved IR spectroscopy on the microsecond time scale [39]. Trapping of $[Fe_2(CO)_6(cco)_2]$ by BH_3 with concurrent loss of cco follows with the ultimate formation of $Fe_2(CO)_6B_2H_6$. Similarly, $[Fe_3(CO)_9(cco)_2]$ (triangular structure) and $[Fe_4(CO)_{12}(cco)_2]$ ("butterfly" structure) are hypothetical, unsaturated tri- and tetra-nuclear iron clusters that could react in an analogous fashion with BH_3 to yield $HFe_3(CO)_9BH_4$ and $HFe_4(CO)_{12}BH_2$, respectively. Ferraborane cluster build-up reactions, e.g. $Fe_2(CO)_6B_2H_6 + [Fe(CO)_4] \rightarrow HFe_4(CO)_{12}BH_2$, are not included as the rates are slow at −40 °C.

Of course there are a number of mechanistic variations that could lead to the same set of products. For example, a possible intermediate in the formation of

$Fe_2(CO)_6B_2H_6$ might be $[Fe_2(CO)_6(cco)BH_3]$ which in turn could react with BH_3 or $[Fe(CO)_3(cco)]$ to yield the dinuclear and trinuclear ferraboranes respectively. Despite the variations possible, the important point is that the qualitative trends in Table 1 support a model of the general type as shown in Fig. 5. Thus, the increase in total yield of ferraboranes with increasing borane concentration is consistent with increased trapping efficiency of iron carbonyl intermediates on the way to intractable precipitates. The correlation of product Fe/B stoichiometry with $[Fe(CO)_3]/[BH_3]$ suggests a sequential iron cluster build-up with concurrent trapping of the intermediates as indicated in the proposed mechanism in Fig. 5.

Summary

Metal-rich metallaboranes formed from iron and cobalt appear to result from the facile condensation of very reactive metal and borane fragments in a complex mechanistic pathway in which metal framework build-up competes with ferraborane formation. The observed final products are those which are unreactive under the reaction conditions. Possibly this is a consequence of the fact that these products are thermodynamically stable relative to other potential ferraboranes, e.g., $Fe_3(CO)_9B_2H_6$, and kinetically stable with respect to metal carbonyl and borane, e.g., $Fe_3(CO)_{12}$ and B_2H_6. It is clear that although good yields of certain metallaboranes are accessible via this approach, e.g., $HFe_3(CO)_9BH_4$, others will only be found in modest yields utilizing reasonable $[Fe(CO)_3]/[BH_3]$ ratios, e.g., $HFe_4(CO)_{12}BH_2$.

Experimental

All reactions and manipulations were carried out with standard Schlenk-ware under a dry nitrogen atmosphere [40]. Solvents were dried (THF over KOH pellets, hexanes over molecular sieves), degassed and distilled before use. Methanol was degassed before use. $BH_3 \cdot THF$ (1 *M*, Aldrich), $BH_3 \cdot SMe_2$ (10 *M*, Aldrich), *cis*-cyclooctene (cco) (Aldrich) and SMe_2 (Aldrich) were used as received. Tricarbonylbis(η^2-*cis*-cyclooctene)iron, $Fe(CO)_3(cco)_2$, was prepared as described in the literature [37]. The mass spectral data were recorded on a Finnigan MAT 8450 high resolution mass spectrometer. IR spectra were recorded in a CaF_2 cell on a Perkin Elmer 1420 spectrophotometer and calibrated by using the polystyrene band at 1601 cm^{-1}. ^{11}B NMR spectra were obtained on a Nicolet NT 300 while ^1H spectra were obtained on Magnachem A 200 and GN 300 spectrometers. ^{11}B shifts are reported with respect to $BF_3 \cdot OEt_2$ ($\delta = 0$) and ^1H with respect to TMS ($\delta = 0$). ^{11}B NMR integrals were measured against an external standard of $[B_3H_8]NBu_4$ in acetone-d^6, which, in turn, was calibrated against a solution of $BH_3 \cdot THF$ of known concentration. Values of the integrals for resonances at δ -24.5 ($Fe_2(CO)_6B_2H_6$), 1.8 ($HFe_3(CO)_9BH_4$) and 114 ($HFe_4(CO)_{12}BH_2$) were used as quantitative measures of the concentrations of the respective ferraboranes.

Preparation of $Fe(CO)_4SMe_2$

A solution of $Fe(CO)_5$ (10 mL, 76 mmol) and $S(CH_3)_2$ (23 mL, 380 mmol) in hexane (370 mL) was irradiated at −10 °C using an immersion lamp reactor (solidex glass, $\lambda > 280$ nm) and a Philips HPK 125-W mercury lamp. During the irradiation the CO formed was removed by bubbling nitrogen through the solution.

After 24 hours a 90% yield of $Fe(CO)_4SMe_2$ was obtained. Specifically, it is found that about 60% $Fe(CO)_5$ reacts with SMe_2 to form the product in 5 hours. Although the yield of the product increases when the reaction is carried out for a longer time, e.g. 70–80% of the yield of the compound is observed in 9 hours, the reaction slows down considerably after 5 hours. Therefore the most efficient way to produce the compound is to stop the reaction after 5 hours, filter off the crystals of product and recycle the filtrate. MS: (EI) $P^+ = 230$ $(-4\ CO)$; $^{56}Fe_1{}^{12}C_6^{16}O_4{}^{32}S_1{}^1H_6^+$. IR (Hexane, cm^{-1}, CO): 2053s, 1978s, 1952vs, 1943vs. ^1H NMR: (tol.-d^8, −50 °C, δ), 1.12 (s, CH_3, 6 H). ^{13}C NMR: (tol.-d^8, 20 °C, δ), 214.4 (s, 4 CO), 28.5 (q, $J(C–H) = 140$ Hz, CH_3).

Solid state structure of $Fe(CO)_4SMe_2$

Space group, $P2_1/n$; $a = 6.404(13)$, $b = 10.726(4)$, $c = 13.333(16)$ Å, $\beta = 97.7(2)°$, $V = 907$ Å^3; $Z = 4$ (125 K); typical omega scan full-width half-heights, 0.48_0; 801 unique measured reflections of which 605 were considered observed ($F_o > 3\sigma(F_o)$); final agreement factors, $R_1 = 0.20$ and $R_2 = 0.23$, full-matrix isotropic least-squares refinement (49 variables). Standard reflections undergo anisotropic change during the data collection such that some intensities increase, some decrease, and some remain constant, presumably due to decomposition of the compound in the solid state.

Reaction of $Fe(CO)_4SMe_2$ with $BH_3 \cdot SMe_2$

The reaction was carried out in hexane (20 mL) under dry nitrogen in a 100 mL Schlenk flask equipped with a reflux condenser with a $[Fe(CO)_4SMe_2]:[BH_3 \cdot SMe_2]$ ratio of 1:30 (1.7 mmol of $Fe(CO)_4SMe_2$) at both 60 and 75 °C and the reaction progess was monitored by IR spectroscopy. After ca 24 h the solvent and unreacted $BH_3 \cdot SMe_2$ were removed under reduced pressure at 0 °C. Then 10 mL of hexane was added. The solution was kept at −78 °C for several hours in order to crystallize the unreacted $Fe(CO)_4SMe_2$. The yellow crystals of the latter were separated from the solution by filtration and the yield of essentially pure $B_2H_6Fe_2(CO)_6$ in the final solution determined by ^{11}B NMR. The production of $B_2H_6Fe_2(CO)_6$ corresponded to 18% and 25% at the two temperatures, respectively.

Reaction of $Fe(CO)_3(cco)_2$ with BH_3

In a Schlenk flask previously filled with dry nitrogen and containing a magnetic stirring bar, 90 mg (0.25 mmol) of $Fe(CO)_3(cco)_2$ was introduced and cooled to −40 °C. The solid compound was dissolved in a requisite amount of precooled hexanes. To this was added the appropriate amount of $BH_3 \cdot THF$ or $BH_3 \cdot SMe_2$ again precooled to −40 °C. The reaction mixture was stirred for 4–5 h at −40 °C and then warmed to −20 °C and the volatiles removed under vacuum (ca 4 h). The residue was dissolved in a known quantity of toluene and the filtered solution analysed by ^{11}B NMR. In a typical larger scale reaction, 380 mg (1.06 mmol) of $Fe(CO)_3(cco)_2$ in 10 mL hexane was reacted with a 30-fold excess of $BH_3 \cdot THF$ at −45 °C in the manner described above. After extracting the dry product ferraborane mixture into toluene (4 mL), the volume of the toluene extract was reduced to 2 mL and introduced onto a cold column (−15 °C) packed with silica gel. The products were separated as described earlier [7–9] and 63 mg (41% yield based on $Fe(CO)_3(cco)_2$) $HFe_3(CO)_9BH_4$ was obtained as the major product.

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