(broad and featureless), 19 200, and 25 300 cm^{-1} where the latter two bands occur as shoulders on an intense high-energy band. There was no discernible structure of the low-energy side of the low-energy band, nor were there any low-energy bands in the 4000–6000-cm^{-1} region.

The EPR spectrum consisted of a broad symmetrical signal centered at $g = 2.094$ with a peak-to-peak width of 656 ± 5 G.

Discussion

Although several materials with the empirical formula A$^+$CuCl$_3^-$ (or A^{2+}Cu$_2$Cl$_6^{2-}$) are known, only a few have been shown to contain discrete Cu$_2$Cl$_6^{2-}$ ions. Both tetraphenyl-arsonium[8] and tetraphenylphosphonium[9] trichlorocuprate have been examined crystallographically and shown to contain dimeric Cu$_2$Cl$_6^{2-}$ ions in which copper adopts a distorted tetrahedral geometry and the dimer comes about by two distorted tetrahedra showing an edge. In contrast, potassium trichlorocuprate forms dimeric Cu$_2$Cl$_6^{2-}$ ions in which copper adopts a square-planar geometry.[3] The coplanar dimers are stacked in the following manner
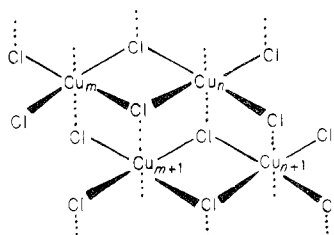
The magnetic behavior of these materials is distinctly different. The first two materials have been shown to exhibit intradimer ferromagnetic interactions and have triplet ground states with $2J = +46$ cm^{-1} [10] and $2J = +85$ cm^{-1},[11] respectively. The magnetic properties of KCuCl$_3$ have been the subject of several studies.[3,12,13] The careful work by the Japanese showed conclusively that there is a strong antiferromagnetic intradimer interaction ($2J = -35$ cm^{-1}) with a sizable interdimer interaction as expected from the structural results.

The physical appearance of tetramethylethylenedi-ammonium hexachlorodicuprate, (tmenH$_2$)Cu$_2$Cl$_6$, is striking, the material crystallizing as shiny bronze-colored needles. By way of contrast, tetramethylethylenediammonium tetra-chlorocuprate, which may be precipitated from the same solutions used to form (tmenH$_2$)Cu$_2$Cl$_6$ by addition to acetone, is bright yellow.[4] A red or red-brown color has been claimed[14] to be characteristic of chloride-bridged copper dimers, and on this basis (tmenH$_2$)Cu$_2$Cl$_6$ is undoubtedly similar to those materials which have been established as containing the di-μ-chloro-tetrachlorodicuprate(II) anion. However, both the planar[14] and tetrahedral[8] Cu$_2$Cl$_6^{2-}$ exhibit a band near 20 000 cm^{-1}, hence the reddish color. It has been claimed that crystals of planar Cu$_2$Cl$_6^{2-}$ exhibit pleochroism when examined with a polarizing microscope, whereas those of tetrahedral Cu$_2$Cl$_6^{2-}$ do not, and on that basis (tmenH$_2$)Cu$_2$Cl$_6$ is expected to be planar, since it exhibits pleochroism similar to that of KCuCl$_3$. However, (C$_6$H$_5$)$_4$PCuCl$_3$, which contains tetrahedral Cu$_2$Cl$_6^{2-}$, also exhibits this pleochroism,[9] so that existence of pleochroism is not an adequate demonstration of planarity. The most convenient method of distinguishing geometries comes from near-infrared spectra, since planar Cu$_2$Cl$_6^{2-}$ has d–d absorptions at 12 900 cm^{-1} (broad) and 10 500 cm^{-1} (shoulder)[14] whereas tetrahedral Cu$_2$Cl$_6^{2-}$ exhibits well-resolved absorptions at 12 200 and 8930 cm^{-1}.[8] On this basis (tmenH$_2$)Cu$_2$Cl$_6$, which exhibits an extremely broad absorption band centered about 11 400 cm^{-1} with no low-energy band, may be assigned a square-planar geometry.

Hara et al.[13] were able to describe the magnetic properties of KCuCl$_3$ in terms of the Hamiltonian

$$H = -2J_a\vec{S}_m\cdot\vec{S}_n - g\beta(\vec{S}_m + \vec{S}_n)\cdot H$$
$$- g\beta(\vec{S}_m\cdot\vec{H}_m{}^M + \vec{S}_n\cdot\vec{H}_n{}^M)$$

where $\vec{H}$ is the external magnetic field and $\vec{H}_m{}^M$ is the molecular field. Using this Hamiltonian the susceptibility may be written as

$$X_m = \frac{Ng^2\beta^2}{kT[3 + \exp(-2J_a/kT)] - 4zJ_b}$$

with the term $4zJ_b$ arising from the Weiss coefficient in the molecular field model, where z is the number of nearest neighbors to a copper ion being considered and J_b is the exchange integral between copper ions in adjacent dimers.[15] For KCuCl$_3$ J_b/J_a was found to be 0.05.

If this formulation for magnetic susceptibility is applied to the data for [tmenH$_2$]Cu$_2$Cl$_6$, there is no improvement to the fit with finite values of J_b, thus leading to the conclusion that there are no significant intermolecular interactions. The similarity in magnetic properties of KCuCl$_3$ and [tmenH$_2$]-Cu$_2$Cl$_6$ indicates that the chlorocuprate complex in the latter compound is very similar to the Cu$_2$Cl$_6^{4-}$ unit in KCuCl$_3$ but that the stacking arrangement may not exist.

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Thallium Derivatives of *closo*-Carboranes. 1. Pyrolysis of Tl$_2$R^{1}R^{2}C$_2$B$_9$H$_9$ Species

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Heterocarboranes derived from main-group elements have received relatively little attention in comparison to those derived from transition metals.[1] However, the reported examples of non-transition-metal heterocarborane syntheses and

Table I. Characterization Data

	Yield, % (via pyrolysis)	Mp (dec), °C	Elemental anal. (theory), %				Mol wt (calcd for monomer)		Mass spec cutoff (m/e at 34 and 70 eV)
			B	C	H	Tl	Benzene	Ethyl acetate	
TlC$_2$B$_9$H$_{12}$^{a}	14	260							340
Tl(CH$_3$)C$_2$B$_9$H$_{11}$	28	295	27.51 (27.73)	10.41 (10.27)	3.89 (3.73)		697 (351.67)	374 (351.67)	354
Tl(CH$_3$)$_2$C$_2$B$_9$H$_{10}$	20	290	25.00 (26.61)	13.54 (13.13)	5.00 (4.38)	55.72 (55.88)	534 (365.67)	362 (365.67)	368

^{a} Elemental analysis reported previously.[4]

Table II. Infrared Spectra,^{a} cm^{-1} (Intensity)

TlC$_2$B$_9$H$_{12}$^{b} 2900 s, 2600–2380 s, mult, 1470 s, 1377 s, 1265 m, 1180 m, 1090 m, 1040 s, 1030 s, 985 m, 955 w, 912 m, 889 m, 880 w, 858 w, 820 w, 777 m, 746 m, 730 m, 723 m, 695 m

Tl(CH$_3$)C$_2$B$_9$H$_{11}$^{c} 2960 m, 2940 m, 2915 m, 2880 m, 2855 m, 2540–2470 s, mult, 1457 m, 1488 m, 1377 w, 1273 w, 1155 w, 1125 w, 1087 w, 1060 w, 1030 s, 995 s, 960 w, 920 w, 898 w, 775 vs

Tl(CH$_3$)$_2$C$_2$B$_9$H$_{10}$^{c} 2975 m, 2940 m, 2880 m, 2580–2620 s, mult, 1455 s, 1390 m, 1380 m, 1260 w, 1205 m, 1110 m, 1070 m, 1027 s, 955 w, 922 m, 900 m, 890 m, 830 m, 775 vs, 685 w, 660 m, 630 m

^{a} Key: s, strong; m, medium; w, weak; v, very; mult, multiplet. ^{b} Nujol mull. ^{c} Carbon tetrachloride mull.

reactions allow one to envision the development of an area of boron chemistry possibly as vast as the still growing "metallo" carborane area.

Stone et al. reported the preparation and examples of the synthetic utility of Tl$_2$R^{1}R^{2}C$_2$B$_9$H$_9$ species.[2] We were intrigued by the suggestion that Tl might be covalently bound to the pentagonal face of the dicarbollide (R^{1}R^{2}C$_2$B$_9$H$_9$) moiety and have undertaken an investigation of thallium derivatives of carboranes. The subject of this report is the synthesis and characterization of thallium-containing heterocarboranes formed via the vacuum pyrolysis of Tl$_2$R^{1}R^{2}C$_2$B$_9$H$_9$.

Experimental Section

Physical Measurements. Mass spectral data were obtained on a Perkin-Elmer Model RMU-7 spectrometer. Proton magnetic resonance data were obtained on a Jeolco Model JNM-PS-100 MHz spectrometer. The 80.5-MHz ^{11}B NMR spectra were obtained on an instrument designed and built by Professor F. A. L. Anet and his research group at UCLA. The infrared spectra were recorded on a Beckman IR 20A-X spectrometer.

Apparatus and Materials. The reactor was constructed from Pyrex glass and resembled a standard vacuum sublimator with the cold finger extending to approximately 1.25 in. above a flat bottom. The total volume of the reactor was approximately 125 mL. The top and bottom portions of the reactor were connected via a ground-glass flat surface. Attachment to the vacuum line was through a 2-mm vacuum stopcock with a standard ground-glass joint.

Tl$_2$R^{1}R^{2}C$_2$B$_9$H$_9$ reactants were prepared according to the method of Stone et al.[2]

General Procedure for Pyrolyses. Approximately 10 mmol of the appropriate Tl$_2$R^{1}R^{2}C$_2$B$_9$H$_9$[2] species was placed in the reactor (described above). The reactor was attached to the high-vacuum line and slowly heated to 100 °C at 10^{-6} Torr. After approximately 1 h at 100 °C the cold finger was filled with a dry ice–acetone slush (−80 °C) and the reactor was quickly heated to between 200 and 300 °C depending on the dithallium reactant (220 °C when R^1 = R^2 = CH$_3$; 230 °C when R^1 = CH$_3$, R^2 = H; 300 °C when R^1 = R^2 = H). A vigorous reaction ensued, accompanied by bubbling of the melt. During the reaction the materials volatile enough to pass the −80 °C cold finger were passed into a −196 °C trap. The materials caught at −80 °C were subsequently identified, by comparing their mass spectra, melting points, and infrared spectra with published data,[3] as R^{1}R^{2}C$_2$B$_9$H$_9$ species. The reactions required approximately 2 h to go to completion, after which the reactor was cooled to room temperature and the sublimate was extracted into dry, hot benzene (from which it crystallized on addition of hexane and cooling). Analytical data are given in Tables I and II.

General Procedure for Metatheses. Approximately 10 mmol of the appropriate Tl$_2$R^{1}R^{2}C$_2$B$_9$H$_9$ species was dissolved in a benzene

solution containing a slight excess (over equimolar quantity) of either acetic, benzoic, or propionic acid. The mixture was heated at reflux for at least 1 h. The thallium carboxylate by-product was insoluble in benzene and was recovered via filtration. The benzene filtrate was evaporated to dryness and the residue recrystallized from a benzene–hexane mixture giving, in general, a 90% plus yield of the desired TlR^{1}R^{2}C$_2$B$_9$H$_{10}$.

Reaction of Tl$_2$(CH$_3$)C$_2$B$_9$H$_{10}$ with HCl. Approximately 0.5 g of Tl$_2$(CH$_3$)C$_2$B$_9$H$_{10}$ was suspended in 10 mL of dry benzene. Anhydrous HCl gas was bubbled through the suspension. After approximately 10 min the yellow Tl$_2$(CH$_3$)C$_2$B$_9$H$_{10}$ had been replaced by an off-white solid. The mixture was filtered under a nitrogen atmosphere and the benzene solvent was removed under vacuum at 30–40 °C. The residue was a colorless, moisture-sensitive semisolid identified by its mass spectrum as B$_9$C$_2$H$_{12}$(CH$_3$) (m/e cutoff at 148 corresponding to the parent minus two hydrogen atoms).

Reaction of Tl$_2$(CH$_3$)$_2$C$_2$B$_9$H$_9$ and Tl$_2$C$_2$B$_9$H$_{11}$ with HCl. The procedure was similar to that described above for Tl$_2$(CH$_3$)C$_2$B$_9$H$_{10}$. The dimethyl product, B$_9$C$_2$H$_{11}$(CH$_3$)$_2$, was a white crystalline solid, mp 62–64 °C. The presence of bridge hydrogen was indicated by a weak band at 2030 cm^{-1} in the infrared spectrum. The mass spectrum exhibited a cutoff at m/e 162. When a 0.1-g sample of B$_9$C$_2$H$_{11}$(CH$_3$)$_2$ was heated in benzene under reflux conditions, hydrogen was evolved and B$_9$C$_2$H$_9$(CH$_3$)$_2$ (mp 54–56 °C) was recovered.

Analogous results were obtained with the Tl$_2$C$_2$B$_9$H$_{11}$–HCl system. The product was identified by mass spectroscopy (cutoff at m/e 144).

Results and Discussion

The pyrolysis reaction yields thallium metal and TlR^{1}R^{2}C$_2$B$_9$H$_{10}$ as the major products. Some H$_2$ and the corresponding *closo*-carborane R^{1}R^{2}C$_2$B$_9$H$_9$ are also produced, and the thallium metal is contaminated with approximately 3% boron, 0.3% hydrogen, and 0.7% C. The thallacarboranes, TlR^{1}R^{2}C$_2$B$_9$H$_{10}$, are all white, crystalline, relatively volatile, air-stable compounds, soluble in benzene, other aromatic solvents, THF, and diethyl ether (slightly) and insoluble in hydrocarbons, CS$_2$, CCl$_4$, etc. We originally suggested[5] that the thallacarborane be formulated TlR^{1}R^{2}C$_2$B$_9$H$_9$ and that the reaction was a disproportionation.

$$Tl_2R^1R^2C_2B_9H_9 \rightarrow Tl + TlR^1R^2C_2B_9H_9 \qquad (1)$$
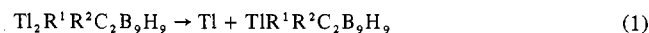
It is quite possible that reaction 1 does in fact occur as an intermediate step. However, the thallacarborane, TlR^{1}R^{2}C$_2$B$_9$H$_9$, would be an odd-electron species and one might expect it to be very reactive, conceivably reacting with hydrogen in the high-temperature melt.

$$TlR^1R^2C_2B_9H_9 + {}^1\!/_2H_2 \rightarrow TlR^1R^2C_2B_9H_{10}$$
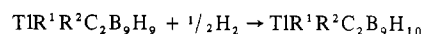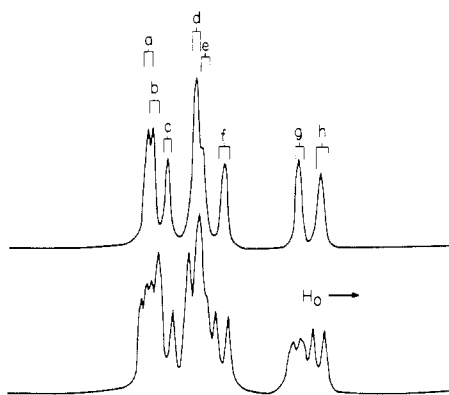
Figure 1. The 80-MHz ^{11}B NMR spectrum of [Tl(CH$_3$)C$_2$B$_9$H$_{10}$]$_2$ in THF. Chemical shifts, ppm (BF$_3$·O(C$_2$H$_5$)$_2$ = 0), and coupling constants (Hz) are (a) 10.3 (128), (b) 11.1 (128), (c) 13.5 (138), (d) 17.8 (128), (e) 18.7 (112), (f) 22.0 (152), (g) 33.4 (112), and (h) 37 (144). Top spectrum is proton decoupled.

Alternatively, Tl$_2$R^{1}R^{2}C$_2$B$_9$H$_9$ might react directly with hydrogen at high temperatures.

$$\text{Tl}_2\text{R}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_9 + \text{H}_2 \rightarrow \text{TlH} + \text{TlR}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_{10} \tag{3}$$
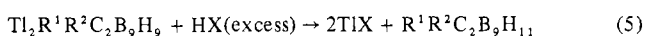
The presence of C, H, and B in the residue suggests that the hydrogen is produced via initial decomposition of some of the starting material. The presence of small amounts of the *closo*-carboranes R^{1}R^{2}C$_2$B$_9$H$_9$ is undoubtedly the result of further decomposition of TlR^{1}R^{2}C$_2$B$_9$H$_{10}$ via an oxidative closure reaction.

$$\text{TlR}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_{10} \rightarrow \text{Tl} + \text{R}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_9 + \frac{1}{2}\text{H}_2 \tag{4}$$
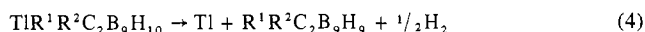
Although not strictly analogous, this reaction appears to be similar to the pyrolytic oxidative closure of 3-Sn-1,2-B$_9$C$_2$H$_{11}$ reported by Rudolph et al.[6]

All of the thallacarboranes, though volatile at low pressures, readily dissociate at moderate temperatures according to eq 4. Since the overall pyrolysis reaction requires temperatures no higher than 325 °C (see Experimental Section), the pyrolysis of Tl$_2$R^{1}R^{2}C$_2$B$_9$H$_9$ species provides a convenient route to the *closo*-carboranes R^{1}R^{2}C$_2$B$_9$H$_9$.

The action of strong protic acids (HX, where X$^-$ = Cl$^-$, SO$_4^-$, H$_2$PO$_4^-$, etc.) on Tl$_2$R^{1}R^{2}C$_2$B$_9$H$_9$ proceeds as shown in eq 5. The *nido*-carboranes were readily identified by melting

$$\text{Tl}_2\text{R}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_9 + \text{HX(excess)} \rightarrow 2\text{TlX} + \text{R}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_{11} \tag{5}$$

point and IR and mass spectroscopy. In contrast, the action of weak acids such as acetic and benzoic acids proceeds as shown in eq 6. The thallacarboranes produced via reaction

$$\text{Tl}_2\text{R}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_9 + \text{RCOOH} \rightarrow \text{TlR}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_{10} + \text{RCOOTl} \tag{6}$$

6 are identical with those produced via pyrolysis.

In benzene solution the monomethyl derivative, Tl(CH$_3$)(H)C$_2$B$_9$H$_{10}$, exists principally as the dimer (mol wt found 695; calcd 701.59). The dimethyl derivative, Tl(CH$_3$)$_2$C$_2$-B$_9$H$_{10}$, shows appreciable association while the unsubstituted thallacarborane, TlC$_2$B$_9$H$_{12}$, was not sufficiently soluble in benzene to obtain molecular weight data. In ethyl acetate, all three of the thallacarboranes studied in this research were monomeric.

The mass spectrum of the thallacarboranes showed the expected cutoff clusters corresponding to the TlR^{1}R^{2}C$_2$B$_9$H$_{10}^+$ ions. In the Tl(CH$_3$)C$_2$B$_9$H$_{11}$ spectrum we observed a strong 18 boron atom cluster with a cutoff at m/e 294 corresponding to the [(^{12}C^{1}H$_3$)^{12}C$_2$^{11}B$_9$^{1}H$_9$]$_2^+$ ion. This, coupled with the observed molecular weight in benzene, suggests that Tl(CH$_3$)C$_2$B$_9$H$_{11}$ is a dimeric species in which the carborane
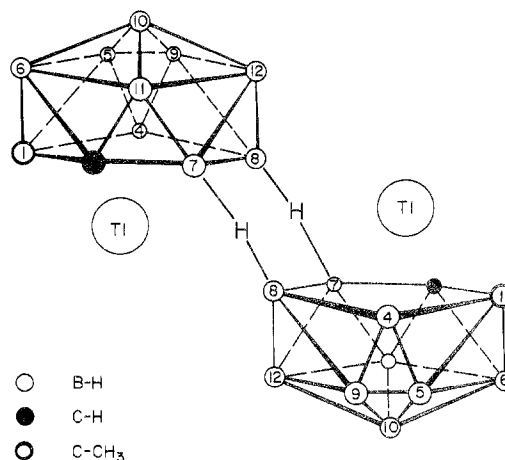
Figure 2. Proposed static structure of [Tl(CH$_3$)C$_2$B$_9$H$_{11}$]$_2$.

portions are attached to each other (i.e., as opposed to a Tl–Tl bond) and the thallium atoms are easily removed in the ionization process.

Preliminary x-ray diffraction data indicate that Tl(CH$_3$)C$_2$B$_9$H$_{11}$ crystallizes in an orthorombic space group consistent with a dimer of C_2 or σ symmetry or monomers having no symmetry. The measured density of the crystalline product (2.25 g/cm^3) provides a calculated molecular weight of 701.6 for the dimer or 350.8 for the monomer. A distance of approximately 5.3 Å separates the Tl atoms.

The ^{1}H NMR spectrum of Tl(CH$_3$)C$_2$B$_9$H$_{11}$ showed the expected carborane C–H and C-attached methyl resonances (τ 7.74 (1) and τ 8.26 (3), respectively). The 80-MHz ^{11}B NMR spectrum, shown in Figure 1, indicates eight distinct boron resonances, seven of unit area and one of area 2. The fine structure on the doublet at 33.4 ppm suggests a B–H–B bridge. The spectrum is consistent with that expected for an asymmetrically substituted ortho C$_2$B$_9$ icosahedral fragment with accidental equivalence of two resonances. The spectrum measured in benzene was nearly identical with the spectrum in THF but not as clearly resolved.

The 80-MHz ^{11}B NMR spectrum Tl(CH$_3$)$_2$C$_2$B$_9$H$_{10}$ showed three clusters of peaks (in either benzene or ethyl acetate) which on proton decoupling yielded four distinct resonances with integrated areas of 3:4:1:1. This is consistent with that expected for a symmetrically substituted C$_2$B$_9$ icosahedral fragment (assuming two pairs of accidental overlaps). Evidence for bridge hydrogen bonding was not definitive due to extensive overlapping of signals.

The 80-MHz ^{11}B NMR spectrum of TlC$_2$B$_9$H$_{12}$ in benzene (poorly resolved) and in acetic acid was identical with the spectrum of (3)-1,2-C$_2$B$_9$H$_{12}^-$ discussed in some detail by Hawthorne et al.[7]

Our proposed static structure for [Tl(CH$_3$)C$_2$B$_9$H$_{11}$]$_2$, shown in Figure 2, is consistent with the data reported herein although not proven by the data. The fine structure on the doublet at 33.4 ppm, which we attribute to bridge hydrogen coupling, can be rationalized using a model similar to the one suggested by Hawthorne et al.[7] in which tautomerization of the bridge hydrogens between the boron atoms of the pentagonal face occurs.

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Iron(0) Oxidation by Hydrogen Chloride in Tetrahydrofuran: a Simple Way to Anhydrous Iron(II) Chloride

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Anhydrous iron(II) chloride is prepared by reaction of iron powder with dry HCl at high temperature.[1] Its preparation under milder conditions has received considerable attention; e.g., attempts to obtain $FeCl_2$ by heating the tetrahydrate under nitrogen[2] or in vacuo afforded a product often contaminated with Fe(III). Azeotropic distillation of the water from the tetrahydrate using benzene–methanol (or other mixtures) gave the dihydrate.[3] Recently Winter[4] reported that the reaction of HCl with Fe(0) in hot methanol affords $FeCl_2 \cdot 6CH_3OH$. Subsequent prolonged heating in vacuo of the methanol-solvated species affords $FeCl_2$.

We have carried out the reaction of iron powder with anhydrous HCl in tetrahydrofuran (THF) at low temperature (5 °C) and we have obtained a pearly microcrystalline compound which analyzes for $FeCl_2 \cdot 1.5THF$ (I).

It is sparingly soluble in THF and in nonpolar solvents but soluble in coordinating solvents such as alcohols, dimethylformamide, and dimethyl sulfoxide and very soluble in water. Compound I suspended in THF readily undergoes replacement of the coordinated THF by a number of ligands (phosphines, amines, sulfides); therefore I represents a convenient starting material for the preparation of iron(II) compounds where acidic species such as water and alcohols must be excluded.

The IR spectrum of I (4000–200 cm^{-1}, Nujol mull) shows bands at 1071 (vs), 918 (w), and 886 (vs) cm^{-1} attributable to coordinated THF and bands at 345 (s), 288 (m), 279(s), and 238 (s) cm^{-1} due to ν(Fe–Cl) and diagnostic of a polymeric structure.

Careful heating of I in vacuo (or under nitrogen) at 80–85 °C for 1 h gives off THF leaving colorless $FeCl_2$.

We have investigated the influence of the temperature on the reaction of Fe with HCl in THF and we have found that when the reaction was carried in a thermostated bath at 5 °C no other products were formed beside I, even with excess HCl. When the reaction was run at room temperature (20 °C) without temperature control, as long as iron powder was present in the system, the temperature increased only moderately (up to 25 °C). After Fe(0) completed oxidation, an increase in the temperature was recorded (up to 45 °C), while the solid $FeCl_2 \cdot 1.5THF$ passed into solution, which assumed a syrupy consistency. From this solution 4-chloro-1-butanol

(cb) (80% yield based on the starting THF) and $FeCl_2 \cdot cb$ (96% based on iron) were isolated.

It is known that THF can undergo nucleophilic and acid-catalyzed ring-opening reactions. Examples of the former reaction are provided by the cleavage by tritylmagnesium bromide,[5] by lithium aluminum hydride with $AlCl_3$,[6] and by diborane[7] or diborane in the presence of iodine[8] to give 4-R-1-butanol.

The acid-catalyzed ring-opening reaction in the presence of $TiCl_4$[9] and the reaction with HCl in the presence of $ZnCl_2$, under reflux,[10] afford 1,4-dichlorobutane.

In our case it can be inferred that iron(0) oxidation by the tetrahydrofuranium ion is energetically favored with respect to the ring-opening reaction which can take place only when all of the iron has been oxidized.

Experimental Section

All of the reactions were carried out in the absence of air and moisture. THF was dried and distilled under nitrogen. Anhydrous HCl was prepared as reported in ref 11. IR spectra were recorded with a Perkin-Elmer 557 spectrometer and ^1H NMR spectra with a Varian HA 100 spectrometer.

Preparation of $FeCl_2 \cdot 1.5THF$. Anhydrous HCl was bubbled slowly (30 drops/min) through a stirred suspension of hydrogen-reduced iron powder (1.0 g) in THF (50 cm^3) at 5 °C. A white microcrystalline solid began to separate after 30 min and the reaction was complete in 2 h. Dry nitrogen was bubbled through the slurry cooled at 0 °C in order to eliminate the excess HCl and the solid filtered by vacuum-line technique, washed with anhydrous THF, and dried in vacuo at room temperature.

This compound is very sensitive to moisture and must be stored under dry nitrogen.

Anal. Calcd for $FeCl_2 \cdot 1.5C_4H_8O$: C, 30.7; H, 5.15; Cl, 30.2; Fe, 23.8. Found: C, 30.5; H, 5.1; Cl, 30.4; Fe, 23.7.

Preparation of $FeCl_2$. Compound I was heated under vacuum at 80–85 °C for 1 h with absolute exclusion of oxygen and moisture. It converted to a light, white compound. The THF could be eliminated as well by heating I at the same temperature in a pure, dry nitrogen flow.

Anal. Calcd for $FeCl_2$: Cl, 55.94; Fe, 44.06. Found: Cl, 56.1; Fe, 43.8.

Identification of the Ring-Opening Reaction Products. (i) Isolation of $FeCl_2 \cdot HO(CH_2)_4Cl$. The reaction of HCl with iron powder was allowed to run without temperature control starting from 20 °C. A moderate temperature increase was recorded during the iron oxidation process (up to 25 °C). When this reaction was complete, compound I separated.[12] The temperature began to rise reaching a maximum of 45 °C in 1 h, while I passed slowly into solution which assumed a syrupy consistency. HCl was bubbled for a further 30 min and then nitrogen was passed through the solution cooled at 0 °C until excess HCl was eliminated. The residual THF was evaporated, in vacuo, at room temperature and addition of toluene–pentane (1:1) caused precipitation of a white solid which was filtered out, washed with toluene and pentane, and dried in vacuo; yield 96% based on iron.

Anal. Calcd for $FeCl_2 \cdot HO(CH_2)_4Cl$: C, 20.3; H, 3.85; Cl, 45.4; Fe, 23.6. Found: C, 20.4; H, 3.90; Cl, 45.4; Fe, 23.5.

(ii) Isolation of 4-Chloro-1-butanol. The reaction syrup was distilled in vacuo to give 35 g of a colorless, fruit-smelling liquid boiling at 52.5 °C (1.5 mmHg); $n^{20}D$ 1.4519 (lit.[13] $n^{20}D$ 1.4518). ^1H NMR (in C_6D_6, TMS as internal standard):[14] τ 6.65 (2 H, H^1, triplet, J_{1-2} = 6.0 Hz), 6.78 (3 H, H^4 + OH, broadened triplet, J_{3-4} = 6.0 Hz; OH proton masked by the central peak of the triplet), 8.48 (4 H, H^2 + H^3, multiplet).

Anal. Calcd for C_4H_9ClO: C, 44.25; H, 8.36; Cl, 32.65. Found: C, 44.3; H, 8.37; Cl, 32.63.

References and Notes

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