The sulfur atom of the 3-substituted compound is sterically incapable of coordination to the same metal atom that the oxygen coordinates. Thus, it is likely that the sulfur of 2-thenoyltrifluoroacetone does not coordinate.

Van Uitert[3] reported a value of 9.1 for the logarithm of the protonation constant for 2-thenoyltrifluoroacetone at 30° in 75 vol. % dioxane. He reported values of 9.5 and 8.0 for the average logarithm of the formation constants for both steps of the coordination reactions of copper(II) and nickel(II), respectively. The values reported in this study are lower in each case. In his pioneering work, Van Uitert based his calculations on only one point in each titration. He titrated with aqueous NaOH, using concentrated solutions of titrant so as not to deviate excessively from 75 vol. % dioxane. He could not determine the stepwise constants at the concentrations of reagents that he used, for the initial coordination in each formation constant titration was greater than $\bar{n} = 1$ before addition of any titrant.

In this work, many points were used in each titration to determine average values for each tabulated quantity. The titrant, tetramethylammonium hydroxide, was dissolved in 75 vol. % dioxane, so as not to change the solvent system during the titration. Use of dilute reagents and addition of perchloric acid together retarded the initial coordination enough to allow determination of stepwise formation constants.

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The Reaction of Iron Pentacarbonyl with Acetylacetone

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It has recently been reported that acetylacetone and iron pentacarbonyl react to form ferric acetylacetonate in low yield (8.5% based on iron pentacarbonyl).[1] The reaction was performed in the absence of a solvent and the isolation of the product involved its precipitation from acetone by the addition of water followed by subsequent recrystallization from benzene.

We have observed that iron pentacarbonyl reacts with acetylacetone in refluxing di-*n*-butyl ether to form, primarily, ferrous acetylacetonate (52% yield based on acetylacetone used), all manipulations being conducted in a nitrogen atmosphere. Isolation of the reaction product in air gives only ferric acetylacetonate in low yield.

Experimental

In a typical experiment acetylacetone (14.64 g., 0.1464 mole) and iron pentacarbonyl (28.60 g., 0.1460 mole) were dissolved together, under nitrogen, in 200 ml. of di-*n*-butyl ether. The mixture was refluxed for 15 hr. in the dark at 140°, after which time an orange precipitate had formed and the solution had turned dark red-brown. As the solution cooled under a slow stream of prepurified nitrogen more orange precipitate formed. The precipitate was filtered and washed twice with small portions of anhydrous diethyl ether and stored in a helium-filled drybox. The yield was 9.78 g. (52% based on acetylacetone used).

Anal. Calcd. for $FeC_{10}H_4O_4$: Fe, 21.98. Found: Fe, 22.07.

The magnetic susceptibility of the compound was determined with a Cheneveau balance and, after applying the diamagnetic correction, was found to correspond to 4.88 B.M. The spin-only moment for iron(II) is 4.90 B.M.[2]

The compound sinters at 177° and melts at 200–201° in an evacuated sealed capillary. Ferrous acetylacetonate is reported to sinter at 177° and to melt at 201°.[3] When determined in air, the compound melted at 178–181°, indicating that it had been converted into ferric acetylacetonate. Ferrous acetylacetonate is reported to be easily oxidized, especially when moist, to ferric acetylacetonate.[3]

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o-Carboranyl Derivatives of Boron Compounds

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The synthesis of many carborane derivatives has been accomplished by reaction of metallocarboranes with halo compounds.[1–3] In the present work, monolithio-*o*-carborane (I) was prepared from *o*-carborane and butyllithium in ether (eq. 1) and added to chlorobis(dimethylamino)borane (II) at 0° (eq. 2). The precipitate contained 84% of the theoretical amount of lithium chloride. Vacuum distillation of the solvent and recrystallization of the residue gave a 45% yield of the desired product, bis(dimethylamino)-*o*-carboranylborane (III). This compound

$$o\text{-}HCB_{10}H_{10}CH + LiC_4H_9 \longrightarrow \underset{\text{I}}{o\text{-}HCB_{10}H_{10}CLi} + C_4H_{10} \quad (1)$$

$$\underset{\text{I}}{o\text{-}HCB_{10}H_{10}CLi} + \underset{\text{II}}{ClB[N(CH_3)_2]_2} \longrightarrow \underset{\text{III}}{o\text{-}HCB_{10}H_{10}CB[N(CH_3)_2]_2} + LiCl \quad (2)$$

melted at 46 ± 2° and slowly distilled under vacuum at 100° in a molecular still. The infrared spectrum of

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(1) For nomenclature consult R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

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