manganese compound. Bromine reacts with the manganese compound to produce HBr and traces of $BrMn(CO)_5$, $Br_2Mn_2(CO)_8$, and $2\text{-}BrB_5H_8$, the only tractable products. Both the rhenium and manganese compounds survive short exposure to the atmosphere.

Experimental Section

All experiments were carried out in a nitrogen atmosphere or in a high-vacuum system. Ether solvents were dried over $LiAlH_4$. The ^1H nmr spectra were obtained at 60 and 100 Mc using Varian A-60A and HA-100 spectrometers. The ^{11}B nmr spectra were obtained at 32.1 Mc using the HA-100 spectrometer. Infrared spectra were obtained in carbon disulfide and cyclohexane solutions using a Beckman IR-10 spectrometer. The carbonyl stretching regions were examined more closely using cyclohexane solutions in a Perkin-Elmer 421 spectrometer.

$2\text{-}[Re(CO)_5]B_5H_8$.—Sodium pentacarbonylrhenate(−1) was prepared by stirring overnight a mixture of 5 ml of 1% sodium amalgam with 0.837 g (1.28 mmol) of $Re_2(CO)_{10}$ dissolved in about 10 ml of tetrahydrofuran (THF). The resulting solution was decanted from the excess amalgam and the THF evaporated under vacuum. Diethyl ether was then distilled onto the salt, and after warming to room temperature, the ether was evaporated and the salt heated to about 50° for 0.5 hr under high vacuum in order to remove as much of the THF as possible. About 30 ml of ether and 0.455 g (4.66 mmol) of $2\text{-}ClB_5H_8$[7] were then condensed onto the reddish orange salt. The reaction flask was warmed to ambient temperature and stirred for 2 hr, during which a brown precipitate was formed. The reaction products were separated by fractional condensation. In the fractionation, 0.150 g (1.54 mmol) of $2\text{-}ClB_5H_8$ was recovered along with 0.265 g (0.68 mmol) of $2\text{-}[Re(CO)_5]B_5H_8$, a yield of 27%, which was purified by repeated condensations at −16°. The melting range of $2\text{-}[Re(CO)_5]B_5H_8$ is 10–11°. A significant, though unmeasured, amount of $HRe(CO)_5$ (identified by its volatility and infrared spectrum)[8] was produced in the reaction.

The analysis of $2\text{-}[Re(CO)_5]B_5H_8$ for hydrogen and carbon monoxide was accomplished by allowing a weighed sample of the material to distil slowly through a Vycor tube heated with two Meeker burners.[9] The liberated CO and H_2 were continuously removed by an automatic Toepler pump. The quantity of the $CO\text{–}H_2$ mixture was determined volumetrically. The mixture was then oxidized to CO_2 and H_2O by circulation over CuO at 300–320° until no materials volatile at −196° remained. The H_2O was separated from the CO_2 by fractional condensation of the H_2O at −78°. The CO_2 was determined volumetrically, and the H_2O was obtained by difference. *Anal.* Calcd for $2\text{-}[Re(CO)_5]B_5H_8$: CO, 36.0; H, 2.08. Found: CO, 36.6; H, 2.05.

$2\text{-}[Mn(CO)_5]B_5H_8$.—Sodium pentacarbonylmanganate(−1) was prepared by stirring an ether solution of 1.03 g (2.64 mmol) of $Mn_2(CO)_{10}$ with excess 1% sodium amalgam. Then 0.620 g (6.35 mmol) of $2\text{-}ClB_5H_8$ was condensed onto the $NaMn(CO)_5$ solution at −196°. The reaction flask was warmed to room temperature and stirred for 1 hr, during which the solution turned deep red and a brown precipitate formed. The product, $2\text{-}[Mn(CO)_5]B_5H_8$, was separated by high-vacuum distillation through a U tube cooled to −8° and by condensation in a U tube at −22°. The melting range of carefully purified samples of $2\text{-}[Mn(CO)_5]B_5H_8$ is −11 to −10°. The yield was 0.93 g (3.6 mmol), or 69%.

A number of attempts to obtain CO and H analyses using the same procedure as for the $2\text{-}[Re(CO)_5]B_5H_8$ gave variable results for no apparent reasons. The characterization is therefore based entirely on the infrared and nmr data. The similarities observed in these data leave little doubt that the compound is correctly formulated as $2\text{-}[Mn(CO)_5]B_5H_8$.

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Boron-11 Decoupling Studies on the Proton Nuclear Magnetic Resonance of $C_2B_4H_8$

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The proton nmr of $C_2B_4H_8$ has been recorded and consists of a single peak (τ 3.68), a 1:1:1:1 quartet (τ 6.56), another 1:1:1:1 quartet (τ 10.13), and a broad peak (τ 12.6) which have been assigned to the H–C, $H_{\text{terminal}}\text{–}B_{4,5,6}$, $H_{\text{terminal}}\text{–}B_1$, and H_{bridge} hydrogen nuclei, respectively.[1] The assignment of the high-field quartet to $H_t\text{–}B_1$, however, was based more on analogy[2] than on direct evidence. On this assumption it was necessary, from area considerations, to assign the low-field quartet to two overlapping resonances, $H_t\text{–}B_{4,6}$ and the chemically unique $H_t\text{–}B_5$. Without direct evidence available there still remained the ambiguity of the $H_t\text{–}B_1$ and $H_t\text{–}B_5$ assignments. With this in mind the present study was undertaken.

The structure of $C_2B_4H_8$ has been verified by X-ray studies[3] and it is clear that each of the basal boron atoms (4,6 and 5) of the pentagonal-pyramidal framework has, in addition to a terminal hydrogen, an attached bridge hydrogen(s) whereas the apex boron has an attached terminal hydrogen only. With boron-11 decoupling experiments carried out at 19.2 Mc it is possible to irradiate selectively the high- and low-field proton nmr quartets. When the high-field quartet is collapsed, the rest of the spectrum remains unchanged. In striking contrast, collapse of the low-field quartet is accompanied by a markedly sharpened bridge hydrogen region. Such observations are consistent only with the original $H_t\text{–}B_1$ (no bridge hydrogens) assignment to the high-field quartet.

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