associated hydrogens,[12,13] there is, in the absence of an appreciable isotope effect, equal probability of loss of any of the top five borons as borane groups. After removal of one normal borane the labeled boron could be found in a 6(9) or 5(7,8,10) position in the resulting $B_{10}H_{13}^-$ fragment, and, after a second exchange, the label, if it remained in the molecule, could be found in any position. As yet there is no evidence for the existence of an isolable $B_{11}H_{16}^-$ salt but the model is useful in rationalizing this most unusual exchange reaction.

Irrespective of the precise mechanism of exchange, the fact that boron randomization occurs implies that interpretation of the results of isotopic tracer studies will have to be made with caution in this and related boron hydride systems.

Acknowledgments.—This work was supported by National Science Foundation Grant G-14595. We acknowledge the useful discussions of this work with Donald F. Gaines.

(12) From M.O. arguments it is not desirable to propose full 5-fold symmetry for both boron and hydrogen positions in a diamagnetic model of this form, as pointed out by W. N. Lipscomb (private communication). Thus a static form of the $B_{11}H_{16}^-$ model may be constructed with the 5 hydrogens in excess of 1 per boron distributed among both bridging and $-BH_2$ positions around the open top of the molecule.

(13) Hydrogen tautomerism in boron hydrides has been discussed by R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961).

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Chemistry of the Metal Carbonyls. XXIV.
Bis-(pentacarbonylmanganese)-germane[1,2]

Sir:

We wish to report air-stable bis-(pentacarbonylmanganese)-germane. This unusual compound was obtained by a new type of reaction involving treatment of a transition metal hydride with a volatile hydride of a main group element.

In a typical preparation 630 mg. (3.23 mmoles) of manganese pentacarbonyl hydride[3] and 102.5 cc. (4.57 mmoles) of germane[4] were sealed under vacuum with 390 mg. (3.19 mmoles) of tetrahydrofuran in a 100-cc. Pyrex bulb. After 8 days at room temperature (15°) the reaction vessel was opened to the vacuum system and hydrogen (64.8 cc., 2.89 mmoles) containing a trace of carbon monoxide was removed with a Toepler pump. Fractionation of the condensable gases showed that 1.61 mmoles of germane and 2.72 mmoles of manganese pentacarbonyl hydride had reacted. Sublimation (80° at 10^{-3} mm.) of the crystals remaining in the reaction vessel afforded 600 mg. (95% yield based on $Mn(CO)_5H$ consumed) of very pale yellow $H_2Ge[Mn(CO)_5]_2$ (m.p. 87–88°), moderately soluble in organic solvents. Analytical samples from this and other preparations were obtained by additional sublimations.

Anal. Calcd. for $C_{10}H_2O_{10}GeMn_2$: C, 25.8; H, 0.4; Mn, 23.6; mol. wt., 465. Found: C, 25.5, 25.5, 26.6; H, 0.3, 0.2, 0.4; Mn, 23.1; mol. wt.,[5] 474.

A sample (70.6 mg., 0.152 mmole) of bis-(pentacarbonylmanganese)-germane was heated at 180° (8 hr.) with iodine (2 g.). Combustion analysis of the

(1) Part XXIII: P. M. Treichel, M. A. Chaudhari and F. G. A. Stone, *J. Organometallic Chem.*, in press; part XXII: D. W. McBride, S. L. Stafford and F. G. A. Stone, *J. Chem. Soc.*, 723 (1963).

(2) The research reported herein has been sponsored by the U. S. Department of the Army, through its European Research Office.

(3) (a) W. Hieber and G. Wagner, *Z. Naturforsch.*, **13b**, 338 (1958); (b) R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 198 (1963).

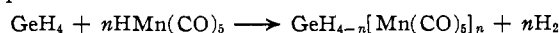(4) E. D. Macklen, *J. Chem. Soc.*, 1989 (1959).

(5) Determined in benzene, using a Mechrolab vapor pressure osmometer.

non-condensable gas formed gave 32.5 cc. (1.45 mmoles) of carbon monoxide and 3.25 cc. (0.145 mmole) of hydrogen. On the basis of a composition $H_2Ge[Mn(CO)_5]_2$ the volumes of carbon monoxide and hydrogen expected were 34.0 and 3.4 cc., respectively.

The proton n.m.r. spectrum (60 Mc.) of bis-(pentacarbonylmanganese)-germane in chloroform shows a single absorption at 6.67 τ. Proton resonances in germanes have been observed at 6.6–6.9 τ.[6] Under high resolution, the infrared spectrum of the new germanium–manganese compound (cyclohexane solution) shows a Ge–H stretching band at 2083 (s) cm.$^{-1}$, and carbonyl bands at 2016 (vs), 2008 (s) and 1992 (s) cm.$^{-1}$. Additional bands occur at 654 (s), 645 (s) and 633 (m) cm.$^{-1}$.

Bis-(pentacarbonylmanganese)-germane has been stored for months in air without apparent decomposition. It is also formed, but in small amount, by heating dimanganese decacarbonyl with germane at 140°, but the desired product is difficult to recover from unreacted manganese carbonyl, and the gas non-condensable at $-196°$ contains appreciable quantities of carbon monoxide. No manganese pentacarbonyl-substituted germanes were recovered from reactions between germane or potassium germyl and manganese pentacarbonyl chloride or bromide.

Apparently the reaction between germane and manganese pentacarbonyl hydride does not proceed *via* a simple substitution mechanism

$$GeH_4 + nHMn(CO)_5 \longrightarrow GeH_{4-n}[Mn(CO)_5]_n + nH_2$$

since we have been unable to detect even a trace of $H_3GeMn(CO)_5$ or $HGe[Mn(CO)_5]_3$ among the products. Perhaps the first stage of the reaction is reduction, by the manganese pentacarbonyl hydride, of germane to GeH_2, followed by addition of two manganese pentacarbonyl groups. Some support for this idea comes from preliminary observations on the effect of manganese pentacarbonyl hydride on silane. Reaction is slow and appears to follow a different course from that involving germane, forming very air-sensitive colored solids and manganese carbonyl. It is well known that the Si(II) state is not as easily attained as the Ge(II) state.

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(6) J. E. Drake and W. L. Jolly, *J. Chem. Soc.*, 2807 (1962).

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Electron-Donor Properties of Zinc Phthalocyanine

Sir:

It has been shown that electron transfer from phthalocyanine, in the ground and excited states, to chloranil is an efficient mechanism of charge carrier production in semiconducting films.[1] Such processes also have considerable biological importance.[2] Recent studies of the luminescence and associated properties of phthalocyanines in this Laboratory appear to demonstrate analogous electron-donor tendencies in fluid solution.

It was found that the absorption band of zinc phthalocyanine at 668 mμ is depressed and broadened in the presence of the strong acceptors (*i.e.*, Lewis acids)

(1) D. R. Kearns, G. Tollin and M. Calvin, *J. Chem. Phys.*, **32**, 1020 (1960).

(2) M. Calvin, *J. Theoret. Biol.*, **1**, 258 (1961).