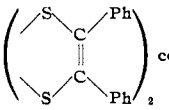
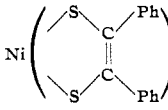
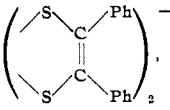
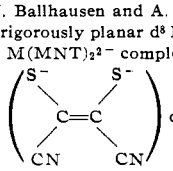
with its partner in the planar complex in one of the π-molecular orbitals of the complex.[5]

The $Co(TDT)_2^-$ anion is the first example of a high-spin, planar d^8 metal complex. The exceptionally weak field of the TDT ligand is indicated from the position of the first band in $Ni(TDT)_2^-$, which is tentatively assigned to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. For a Δ_1 ($xy \rightarrow x^2 - y^2$) in the neighborhood of 7000 cm.$^{-1}$, the planar Co^+ complex is predicted to be high-spin, even in the absence of axial interactions.[6] Since the electronic spectrum of $[(C_6H_5)_3As(CH_3)][Co(TDT)_2]$ is the same in acetone, acetonitrile and pyridine, axial effects probably are of no importance in this case

The $M(MNT)_2^{2-}$ complexes, which we reported earlier,[7] on oxidation give $M(MNT)_2^-$ complexes,[8] which apparently are composed of M^+ and MNT radical anion moieties.[9] Of interest is the reaction of Fe^{2+} and MNT, which gives $Fe(MNT)_2^-$ directly. The $Fe(MNT)_2^-$ complex has $S = {}^3/_2$, with d-d electronic bands at practically the same energies as planar, high-spin $Co(MNT)_2^{2-}$. Thus $Fe(MNT)_2^-$ and $Fe(TDT)_2^-$ are probably the first examples of high-spin Fe^+ in a planar situation. It is important to note that the ligand field strength of MNT is the same as a dianion with d^7 Co^{2+} and as a radical anion with d^7 Fe^+.

(5) Evidence has been presented that the Ni  complex is planar and contains Ni^{2+} and two radical anions. The two odd electrons are supposedly paired in the π-molecular system of the complex; see G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962). The Ni  complex can be reduced to Ni  , which has $S = {}^1/_2$ and shows a highly anisotropic e.s.r. spectrum; see ref. 8. The reduced complex may be electronically similar to $Ni(TDT)_2^-$.

(6) C. J. Ballhausen and A. D. Liehr, *ibid.*, **81**, 538 (1959), suggested that high-spin, rigorously planar d^8 Ni^{2+} is possible for a Δ_1 less than 10,000 cm.$^{-1}$.

(7) The $M(MNT)_2^{2-}$ complexes have been shown to consist of M^{2+} and two MNT  dianions. See ref. 1 and also H. B. Gray, R. Williams, I. Bernal and E. Billig, *ibid.*, **84**, 3596 (1962).

(8) For M = Ni, Pd and Pt, see A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *ibid.*, **85**, 2029 (1963). We thank Dr. R. H. Holm for allowing us to see a preprint of these results prior to publication.

(9) Thus for the coplanar ring system, *a stable electronic situation exists for either ten or twelve electrons* in the π-molecular orbitals composed of the nine p (π) valence orbitals. We are now carrying out a complete molecular orbital analysis of these systems.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK

HARRY B. GRAY
E. BILLIG

RECEIVED APRIL 23, 1963

An Unusual Boron Exchange Reaction[1]

Sir:

We wish to report an unprecedented type of exchange reaction involving complete isotopic substitution in a B_{10} framework. Previous studies of exchange and interconversion processes in boron hydrides and boron hydride ions containing ten or more boron atoms have concentrated almost exclusively[2] on exchange and tracer experiments using deuterium. Deuterated decaboranes have been prepared specifically labeled in a variety of positions by exchange of decaborane with diborane-d_6,[3] deuterium oxide,[4,5] or deuterium chloride,[6] and by reaction of the monosodium salt of decaborane, $NaB_{10}H_{13}$, with deuterium chloride.[4] Although within the limits of these experiments decaborane and the closely related salt $NaB_{10}H_{13}$ have appeared immune to framework disruptions, the initial results in the present study of skeletal rearrangements in the higher boron hydrides indicate that diborane undergoes *complete boron interchange* with $NaB_{10}H_{13}$ in ethereal solution.

A sample of $NaB_{10}H_{13}$ was prepared[4,7] by reaction of decaborane (0.778 mmole) of normal (20% ^{10}B) isotopic content with sodium hydride in diethyl ether solution. Hydrogen evolution according to the equation

$$B_{10}H_{14} + NaH \longrightarrow NaB_{10}H_{13} + H_2 \qquad (1)$$

was complete (97.3% of calculated) within 25 min. at room temperature. The solution was filtered under vacuum to give a pale yellow filtrate. Diborane, 96.4% ^{10}B (4.58 mmoles), was condensed into the flask and the contents were warmed to 0° and shaken for 1 hr., during which time no hydrogen formed. By mass spectrometric analysis the ^{10}B content of the recovered diborane was shown to have decreased to 62.7%, in close agreement with the value calculated (61.9% ^{10}B, taking into account the incomplete hydrogen evolution for (1)) for diborane exchange with all ten borons of the $NaB_{10}H_{13}$. Boron-10 enriched decaborane was recovered by treatment of the solution with hydrogen chloride[4,7] according to the equation

$$NaB_{10}H_{13} + HCl \longrightarrow B_{10}H_{14} + NaCl \qquad (2)$$

With suitable recorder amplitude variation, the ^{11}B n.m.r. spectrum of the ^{10}B enriched decaborane was nearly coincident with an isotopically normal decaborane spectrum, in agreement with the mass spectral determination of participation of all boron positions.

Although the $NaB_{10}H_{13}$ structure has not been determined, it is probable, from the n.m.r. spectrum[8] and the ready interconversion of decaborane and the salt by (1) and (2) (presumably involving primary removal and replacement of a bridge proton[4]), that the boron skeleton is similar to that of decaborane. With the implication that, in the absence of diborane, the boron framework of $NaB_{10}H_{13}$ undergoes neither dissociative nor internal rearrangement,[4] it therefore seems more probable that in ^{10}B exchange the borane-^{10}B ($^{10}BH_3$) adds to the normal $B_{10}H_{13}^-$, forming an exchange intermediate of over-all composition $B_{11}H_{16}^-$, capable of losing an isotopically normal borane to regenerate $B_{10}H_{13}^-$ containing the labeled boron in a position different from that originally occupied by the leaving boron. Considering only the boron framework, a model meeting these requirements can be formed by adding a boron to a decaborane-like cage between the 5 and 10 positions[9] to produce an icosahedral fragment with 11 of the 12 positions occupied, similar to the boron structure proposed[10] for the known[11] $B_{11}H_{14}^-$ ion. If the labeled boron is capable of losing its identity among the five top borons, perhaps by tautomerism of the ten

(1) Interconversion of Boranes. VII. For paper VI of this series see D. F. Gaines, R. Schaeffer and F. Tebbe, *Inorg. Chem.*, **2**, 526 (1963).

(2) Absence of boron exchange between ^{10}B labeled diborane, $^{10}B_2H_6$, and normal decaborane, $B_{10}H_{14}$, has been demonstrated: I. Shapiro and R. E. Williams, *J. Am. Chem. Soc.*, **81**, 4787 (1959).

(3) J. J. Kaufman and W. S. Koski, *ibid.*, **78**, 5774 (1956).

(4) J. J. Miller and M. F. Hawthorne, *ibid.*, **81**, 4501 (1959).

(5) I. Shapiro, M. Lustig and R. E. Williams, *ibid.*, **81**, 838 (1959).

(6) (a) M. F. Hawthorne and J. J. Miller, *ibid.*, **80**, 754 (1958); (b) J. A. Dupont and M. F. Hawthorne, *ibid.*, **84**, 1804 (1962).

(7) W. V. Hough and L. J. Edwards, Abstracts of Papers, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., 1958, p. 28-L.

(8) N. J. Blay, R. J. Pace and R. L. Williams, *J. Chem. Soc.*, 3416 (1962).

(9) The numbering system used is reproduced in ref. 5.

(10) E. B. Moore, L. L. Lohr and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961).

(11) V. D. Aftandilian, H. C. Miller, G. W. Parshall and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).

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).

CONTRIBUTION NO. 1113
DEPARTMENT OF CHEMISTRY
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA

RILEY SCHAEFFER
FRED TEBBE

RECEIVED MAY 16, 1963

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 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.

Acknowledgment.—We wish to thank the Germanium Research Committee for a gift of germanium dioxide.

(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.

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

DEPARTMENT OF CHEMISTRY
QUEEN MARY COLLEGE
UNIVERSITY OF LONDON
LONDON, E. 1., ENGLAND

A. G. MASSEY
A. J. PARK
F. G. A. STONE

RECEIVED MAY 13, 1963

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).