

associated hydrogens,<sup>12,13</sup> 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<sub>10</sub>H<sub>13</sub><sup>-</sup> 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<sub>11</sub>H<sub>16</sub><sup>-</sup> 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 boride 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<sub>11</sub>H<sub>16</sub><sup>-</sup> model may be constructed with the 5 hydrogens in excess of 1 per boron distributed among both bridging and -BH<sub>2</sub> 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  
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RECEIVED MAY 16, 1963

## Chemistry of the Metal Carbonyls. XXIV.

### Bis-(pentacarbonylmanganese)-germane<sup>1,2</sup>

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<sup>3</sup> and 102.5 cc. (4.57 mmoles) of germane<sup>4</sup> 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<sup>-3</sup> mm.) of the crystals remaining in the reaction vessel afforded 600 mg. (95% yield based on Mn(CO)<sub>5</sub>H consumed) of very pale yellow H<sub>2</sub>Ge[Mn(CO)<sub>5</sub>]<sub>2</sub> (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<sub>10</sub>H<sub>2</sub>O<sub>10</sub>GeMn<sub>2</sub>: 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.,<sup>5</sup> 474.

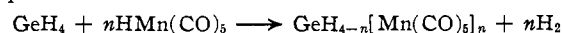
A sample (70.6 mg., 0.152 mmole) of bis-(pentacarbonylmanganese)-germane was heated at 180° (8 hr.) with iodine (2 g.). Combustion analysis of the

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<sub>2</sub>Ge[Mn(CO)<sub>5</sub>]<sub>2</sub> 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.<sup>6</sup> Under high resolution, the infrared spectrum of the new germanium-manganese compound (cyclohexane solution) shows a Ge-H stretching band at 2083 (s) cm.<sup>-1</sup>, and carbonyl bands at 2016 (vs), 2008 (s) and 1992 (s) cm.<sup>-1</sup>. Additional bands occur at 654 (s), 645 (s) and 633 (m) cm.<sup>-1</sup>.

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



since we have been unable to detect even a trace of H<sub>3</sub>GeMn(CO)<sub>5</sub> or HGe[Mn(CO)<sub>5</sub>]<sub>3</sub> among the products. Perhaps the first stage of the reaction is reduction, by the manganese pentacarbonyl hydride, of germane to GeH<sub>2</sub>, 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.

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

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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.<sup>1</sup> Such processes also have considerable biological importance.<sup>2</sup> 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).

(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. Starford 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.

2,4,6-trinitrotoluene (TNT), *sym*-trinitrobenzene (TNB) and 2,4,7-trinitro-9-fluorenone (TNF). The spectral effects are similar to those observed by Gouterman<sup>3</sup> for zinc tetraphenylporphyrin and are consistent with the formation of 1:1 complexes of the (predominantly) charge-transfer type. Neglecting solvent competition, the equilibrium constants,  $K_e$ , were found to be approximately 2.3, 10 and 345 l./mole at 25° for TNT, TNB and TNF, respectively, in acetone solution.<sup>4</sup>

A detailed study of the quenching of fluorescence of zinc phthalocyanine by a series of aryl nitro-compounds (A) has established the following: (a) the emission spectra of the quenched and unquenched solutions are identical; (b) the extent of quenching is greater than can be accounted for by ground state complex formation alone; (c) the ratio of fluorescence yields ( $\gamma^0/\gamma$ ) in the absence and presence of A varies linearly with the quencher concentration [A] for weaker quenchers; whereas, (d) for the strongest quenchers, the data are closely fitted by the expression

$$\gamma^0/\gamma = \{1 + k[A]\} \{1 + K_e[A]\} \quad (1)$$

where  $k$  is a constant and  $K_e$  is the ground state equilibrium constant determined independently from the absorption spectra. The sequence of values of the constant  $k$  appears to be that of the electron affinities of the quenchers. In Table I,  $k$  is correlated with the available positions of the charge transfer absorption bands of the corresponding hexamethylbenzene complexes.<sup>5</sup>

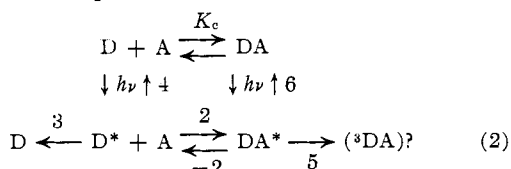
TABLE I

VALUE OF  $k$  IN ACETONE AT 25°

The last column gives the position of the corresponding hexamethylbenzene charge transfer complex absorption band in cyclohexane.

Quencher (acceptor)	Range of quencher concentrations, $M$	$k$ , l. mole <sup>-1</sup>	$\lambda$ (H.M.B. complex), $m\mu$
<i>p</i> -Nitrotoluene	0.05-0.40	1.6	...
Nitrobenzene	.05-0.40	3.0	...
2,4-Dinitrotoluene	.005-0.035	42	323
1,3-Dinitrobenzene	.005-0.035	47	343
2,4,6-Trinitrotoluene	.001-0.018	52	376
1,3,5-Trinitrobenzene	.001-0.018	75	387

The simplest interpretation of these observations is that in addition to forming ground state complexes, zinc phthalocyanine readily functions as an electron donor in the excited state with the result that the efficiencies of both the static and diffusional parts of the quenching mechanism are determined by the acceptor strengths of the quenchers. Thus we have



in which D, D\*, DA and DA\* represent ground state and excited fluor and complex, respectively. With  $k = k_2/(k_3 + k_4)$  this gives eq. 1, provided that  $k_5 \gg (k_6 + k_{-2})$  and is consistent with (a), (b) and (c). The absorption spectra show that D\* and DA\* have

(3) M. Gouterman, *J. Chem. Phys.*, **37**, 2266 (1962).

(4) The use of the unfavorable solvent acetone is due to the insolubility of zinc phthalocyanine in inert solvents. The surprisingly high  $K_e$  for the TNF complex does not rest on absorption data alone. Thus, the fluorescence of zinc phthalocyanine is quenched by TNF at a rate some fivefold greater than would be calculated on the basis of a diffusion controlled reaction and a reasonable estimate of the fluorescence lifetime.

(5) G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, West Berlin, 1961.

similar radiative lifetimes so that the absence of kinetic or spectroscopic evidence for DA\* emission implies an extremely fast radiationless deactivation of DA\*, probably by intersystem crossing as observed for the TNB complex of anthracene.<sup>6</sup> This suggestion cannot be tested readily since the phosphorescence of phthalocyanines occurs in the infrared.<sup>7</sup> Although we were able to populate the triplet state of zinc phthalocyanine by a flash photolytic method, the triplet yields could not be measured in the presence of the acceptors which were found to catalyze the triplet decay.

Picric acid was found to be exceptional in that its extremely strong complex with zinc phthalocyanine in acetone exhibits a new absorption band at 705  $m\mu$  and a new emission band at 714  $m\mu$ . These are not typical charge transfer transitions and probably represent a perturbation of the pigment molecule by formation of a strong hydrogen bond. The two moieties in this complex presumably are not coplanar with the result that process 5 is inhibited, the radiative step 6 is observed and the over-all effect is one of fluorescence enhancement. This type of behavior has been observed for numerous phthalocyanines and porphyrins and will be described in detail elsewhere.

(6) M. Kleinerman, L. Azarraga and S. P. McGlynn, in "Luminescence of Organic and Inorganic Systems," John Wiley and Sons, Inc., New York, N. Y., 1962.

(7) R. S. Becker and M. Kasha, *J. Am. Chem. Soc.*, **77**, 3669 (1955).

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### Carbon Orbital Hybridizations and Acidity of the Bicyclobutane System<sup>1,2</sup>

Sir:

As part of a program designed to correlate chemical reactivity with hybridizations of carbon atomic orbitals in small ring compounds,<sup>3</sup> we have examined the <sup>13</sup>C-H nuclear spin-spin coupling of tricyclo[4.1.0.0.2.7]heptane (I). The readily available tricyclic hydrocarbon I, recently reported by Moore and collaborators,<sup>4</sup> is thought to be a valid model for the bicyclobutane system, because the trimethylene bridge should be flexible enough not to introduce further strain into the system.

The following coupling constants were found for the carbon-13 satellites in the proton magnetic resonance spectrum of I

<sup>13</sup>C<sub>1</sub>-H, 200 ± 2; <sup>13</sup>C<sub>2</sub>-H, 146 ± 2; <sup>13</sup>C<sub>3</sub>-H, <sup>13</sup>C<sub>4</sub>-H, 125 ± 2 c.p.s.

(average of two indistinguishable coupling constants).<sup>5,6</sup>

Applying the well substantiated correlation of coupling constants with carbon atomic orbital hybridizations,<sup>7</sup> one arrives at 40 and 29% s-character for the exocyclic orbitals of carbon atoms 1 and 2, respectively. Normal sp<sup>3</sup> hybridization is found for the trimethylene bridge carbon atoms.

(1) Presented in part at the Carbanion Symposium of the American Chemical Society National Meeting, Los Angeles, Calif., April, 1963.

(2) This work was supported by NSF Grant G19927.

(3) Cf. G. L. Closs, *Proc. Chem. Soc.*, 152 (1962).

(4) W. R. Moore, H. R. Ward and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

(5) The carbon-13 satellite spectra were studied in natural abundance. To avoid errors in the assignment of the exceedingly weak signals, the spectra were run at 40 and 60 Mc.

(6) The vicinal proton-proton coupling constant,  $J_{R_1R_2}$ , was found to be 11.5 ± 0.5 c.p.s.

(7) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959); J. N. Shoolery, *ibid.*, **31**, 1427 (1959); C. Juan and H. S. Gutowsky, *ibid.*, **37**, 2198 (1962).