

can be determined at various  $R$  values by measuring the decrease in optical rotation as a function of time (Table II).

If the proposed mechanism is operating, the rate of racemization should vary with  $R$  (inversely proportional to concentration of metal ion) according to the function:  $k' = 3ka(1/R - 3/R^2)$ . This function is zero at  $R = 3$ , has a maximum at  $R = 6$ , and slowly tapers off at higher  $R$  values. A plot of  $k'/ka$  against  $R$  for the various runs shows excellent agreement with the theoretically constructed curve (Figure 1).

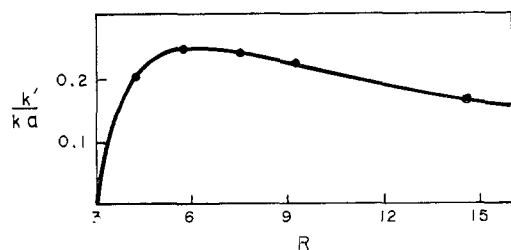


Figure 1.—Effect of ligand to metal ratio,  $R$ , on the rate of racemization of 1. The points represent experimental runs, and the curve is constructed theoretically from  $k'/ka = 3(1/R - 3/R^2)$ .

This strongly supports our proposed mechanism and the reaction is an interesting example of a racemization path, where the action of the metal ion is truly catalytic and where the substrate itself acts as the basic racemization agent.

**Acknowledgments.**—We are indebted to Dr. J. Sibilja, Mr. G. Babbit, and Mrs. Komarowski for ir and nmr analyses. Thanks are also due to Professor M. Goodman for the CD measurements, to R. H. Miller for the computer analyses of the rate constants, and to Mr. F. Koff for technical assistance.

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## Dimethylmercury and Tetraborane(10)

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Received November 12, 1969

Dimethylmercury<sup>2</sup> will alkylate tetraborane(10)<sup>3</sup> to give 2-methyltetraborane(10).<sup>4</sup> The best yield (68%) at optimum conversion (27%) was obtained after 5 min at 50° in a volume of 200 ml when the ratio of dimethylmercury to tetraborane was 2.50:0.42 (in mmol).<sup>5</sup> From this was recovered by glpc tetraborane (0.25), 2-methyltetraborane (0.12), methylboranes

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(0.09), and trimethylborane (0.01). Reactants in the ratio 2.38:0.78 underwent a 10% conversion at 25° after 1.6 hr with a 62% yield of 2-methyltetraborane. After 5 hr at 25° reactants in the ratio 3.78:1.37 gave a 42% conversion and a 56% yield. About the same amount of dimethylmercury and larger proportions of tetraborane gave approximately the same conversion, but the yield of methyltetraborane diminished. The reaction appeared to proceed in the dimethylmercury as solvent, and the more dilute the solution, the better was the yield. When all substances were present as vapor only, there was no reaction.

Under similar conditions trimethylbismuth<sup>6</sup> gave 5% conversion to 2-methyltetraborane. Trimethylgallium<sup>7</sup> converted 50% of tetraborane to trimethylborane.

Pentaborane(11) with dimethylmercury after 1 hr gave pentaborane(9), tetraborane(10), and the products expected from the latter. In 12 hr diborane(6) was 16% converted to methylboranes.

The results reported here are reminiscent of the cases where trimethylgallium and diborane(6) gave gallium metal and methylboranes<sup>8</sup> and where bis(trifluoromethylmercury) and diborane in dimethyl sulfide solvent gave the dimethyl sulfide adduct of trifluoromethylborane.<sup>9</sup>

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## Protonic Complexes of Oxo Ligands with Tetrachloroauric Acid

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Received December 1, 1969

At the turn of the century Pickard and Kenyon<sup>1</sup> prepared a series of compounds of tertiary phosphine oxides with acids and salts. Complexes of phosphine oxides with various metal ions<sup>2-4</sup> and nonmetals (halogens)<sup>5</sup> have now been widely studied. Pickard and Kenyon's complexes with acids, however, have received less attention. Collamati<sup>6</sup> studied the compound tetrachloroauric acid-bis(triphenylphosphine oxide),  $\text{HAuCl}_4 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ , and found that the phosphine oxide molecules are not coordinated to the gold(III) but are bonded to the hydrogen ion as in the

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