

molecule but we confidently assign this ionization to that from an exo-polyhedral molecular orbital.

The spectrum of a large *closo*-carborane, 1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, is presented in Figure 4 and the data are shown in Table I. At the top of the figure a band showing obscure, but reproducible, structure is shown in more detail. One possible assignment of this structure, indicated in the figure, is in terms of progressions in a frequency of 2300 cm<sup>-1</sup>. Although SCF calculations have not been done for this species, we again suggest that this band, or part of it, may be assigned to ionization from an exo-polyhedral orbital.

Finally, we wish to point out that exo-polyhedral orbitals present evidence for themselves in the photoelectron spectra of boranes as well. We have measured the spectrum of pentaborane(9) and the results are reported in Table I. Our results agree with those reported previously<sup>19</sup> with the exception of the band at highest ionization potential. In the previous study,<sup>19</sup> the real band at 18.65 eV is obscured by a large tail which is probably caused by scattered electrons. The point of interest to this study is the band between 14 and 15 eV which is presented in Figure 5. There is reproducible structure which can only be reasonably assigned to a boron-hydrogen stretch. The SCF calculations<sup>20</sup> (Table I) indicate that this band may result from ionization from three molecular orbitals, two of which involve boron and terminal hydrogens and which would be defined as exo-polyhedral molecular orbitals. The third involves bridge hydrogens and is endo-polyhedral. This is the only band in the spectrum that shows fine structure, and even though it is indistinct, we feel that the structure would suffice to identify the band as exo-polyhedral.

In summary, it has been shown that the validity of the exo-endo separation of the molecular orbitals of boranes and heteroboranes is substantiated by the photoelectron spectra of these species. In particular, certain exo orbitals exhibit characteristic empirical features that should enable them to be identified even in the absence of good calculations. This appears particularly true of those orbitals that may be crudely considered as the in phase combination of terminal boron-hydrogen interactions. It is possible that an examination of these bands as a function of chemical environment may well

lead to a better understanding of the electronic structure of these species.

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**Registry No.** 1,5-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, 20693-66-7; 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, 20693-67-8; 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub>, 20693-69-0; 1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, 16986-24-6; B<sub>5</sub>H<sub>9</sub>, 19624-22-7.

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# Notes

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## Fixation of Molecular Nitrogen in Aqueous Solution. Catalysis by Platinum Group Metal Ions

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Nitrogen fixation is a subject of very active research interest in many laboratories in recent years. Much of the work on nitrogen fixation is centered on the use of titanium catalysts, in the presence of strong reducing agents like metallic aluminum,<sup>1</sup> metallic potassium,<sup>2</sup> or sodium naphthalide,<sup>3,4</sup> or electrolytic reduction in the presence of aluminum isopropoxide.<sup>5</sup> In all these cases the yield of ammonia varies from a fraction of 1 mol of ammonia/mol of the catalyst to a stoichiometric yield. While many stable dinitrogen complexes of various platinum group metal ions are known, none of them were previously used as catalysts in nitrogen fixation studies.

We report in this note the fixation of nitrogen at atmospheric temperature and pressure in aqueous solution catalyzed by Ru(II)-, Ru(III)-, Rh(III)-, Ir(III)-, Os(II)-, and Os(III)-chloro complexes.

## Experimental Section

**Materials.** Commercial samples of ruthenium(III) chloride, rhodium(III) chloride, iridium(III) chloride, osmium(III) chloride, titanium(III) chloride, and dimethyltin dichloride were obtained from Alfa Inorganics. Stannous chloride, triphenylphosphine, and hydrazine were Fischer AR grade reagents. <sup>15</sup>N<sub>2</sub> (25% enrichment) was obtained from Volk Radiochemicals, Inc.

**Procedure.** A mixture of 1 vol. of nitrogen and 3 vol. of hydrogen at room temperature (25°) and 1 atm pressure was passed through a catalyst solution of the above-mentioned metal ions (10<sup>-3</sup>-10<sup>-4</sup> M) in 3 M hydrochloric acid. The catalytic solutions were obtained by adding a suitable reducing agent (TiCl<sub>3</sub>, SnCl<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>SnCl<sub>2</sub>) to the requisite transition metal ion in a 10:1 molar ratio. The resulting solution has the characteristic absorption spectrum of the transition metal ion. After circulation of nitrogen and hydrogen for about 24 hr, a sample of the solution was withdrawn from the reaction mixture and the amount of ammonia formed estimated with a micro-Kjeldahl apparatus.

**Table I.** Fixation of Nitrogen in Aqueous Solution at 25° and 1 Atm (N<sub>2</sub> + 3H<sub>2</sub>) Catalyzed by Platinum Group Metal Ions

No.	Catalyst	Reducing agent	[Catalyst], M	Yield of NH <sub>3</sub> , mol/mol of catalyst
1	Ru(II)	TiCl <sub>3</sub>	1.6 × 10 <sup>-3</sup>	0.40
2	Ru(III)	SnCl <sub>2</sub>	1.6 × 10 <sup>-3</sup>	0.07
3	Ru(III)	(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub>	4.0 × 10 <sup>-4</sup>	0.05
4	Rh(III)	TiCl <sub>3</sub>	1.0 × 10 <sup>-3</sup>	0.36
5	Rh(III)	SnCl <sub>2</sub>	5.0 × 10 <sup>-4</sup>	0.40
6	Rh(III)	SnCl <sub>2</sub> + PPh <sub>3</sub>	5.0 × 10 <sup>-4</sup>	0.06
7	Rh(III)	SnCl <sub>2</sub> + TiCl <sub>3</sub>	1.0 × 10 <sup>-3</sup>	0.36
8	Ir(III)	SnCl <sub>2</sub>	2.7 × 10 <sup>-3</sup>	0.10
9	Ir(III)	TiCl <sub>3</sub>	2.7 × 10 <sup>-3</sup>	0.20
10	Os(II)	TiCl <sub>3</sub>	2.7 × 10 <sup>-3</sup>	0.10
11	Os(III)	SnCl <sub>2</sub>	2.7 × 10 <sup>-3</sup>	0.12

In the above solutions the active reducing agent seems to be molecular hydrogen since no ammonia was obtained when gaseous nitrogen alone was passed through the catalytic solution.

**Isotopic Analysis.** An isotopic mixture of <sup>15</sup>N<sub>2</sub> (25% enrichment) and H<sub>2</sub> in the ratio of 1:3 was circulated through a catalyst solution containing Ru(II) + TiCl<sub>3</sub> or Rh(III) + SnCl<sub>2</sub>. The liberated ammonia was absorbed in the Kjeldahl apparatus and the resulting NH<sub>4</sub>NO<sub>3</sub> and <sup>15</sup>NH<sub>4</sub>NO<sub>3</sub> solution was carefully dried and examined with a mass spectrometer. The mass spectrograms of N<sub>2</sub>O obtained by the decomposition of NH<sub>4</sub>NO<sub>3</sub> and <sup>15</sup>NH<sub>4</sub>NO<sub>3</sub> gave relative peak intensities of 4:1 for mass 44 and 45, respectively, indicating enrichment of <sup>15</sup>N in the reaction product.

## Results

The yield of ammonia obtained in the catalytic runs varied from 0.05 to 0.4 mol/mol of catalyst, as indicated in Table I. The best catalysts were found to be Ru(II) + TiCl<sub>3</sub> and Rh(III) + SnCl<sub>2</sub>. TiCl<sub>3</sub> and SnCl<sub>2</sub> alone or combined were inactive in the fixation of nitrogen under the same experimental conditions.

Fixation of nitrogen from the reaction mixture consisting of nitrogen and hydrogen was further established by isotopic analysis. Prominent peaks of N<sub>2</sub>O at mass numbers 44 and 45 (<sup>14</sup>N<sub>2</sub>O and <sup>14</sup>N<sup>15</sup>NO) established nitrogen fixation in catalyst systems no. 1 and 5 of Table I (Ru(II) + TiCl<sub>3</sub> and Rh(III) + SnCl<sub>2</sub>). These were the systems which gave the highest yields of ammonia. The ratio of the intensities obtained for N<sub>2</sub>O of mass numbers 44 and 45 confirm that the nitrogen fixed was produced from the nitrogen gas circulated through the catalytic solution.

## Discussion

Fixation of molecular nitrogen in aqueous solution containing molybdenum,<sup>7</sup> molybdenum and iron,<sup>8</sup> and iron compounds<sup>9</sup> in the presence of thiol groups and a reducing agent like borohydride or dithionite had been previously reported. In all these cases, the maximum yield of ammonia reported<sup>2-9</sup> varied from 0.05 to 0.15 mol/mol of the catalyst. These systems are of some theoretical interest because they serve as models of nitrogenase.

Although a truly catalytic system for the fixation of molecular nitrogen at ambient conditions is yet to be developed,<sup>6</sup> the reactions carried out in the present investigation are significant as the first catalysis by platinum group metal ions in aqueous solution. Of the nitrogen fixation systems tabulated in Table I, the maximum yield of ammonia was obtained with solutions of the metal ions ruthenium(II) and rhodium(III) having the 4d<sup>6</sup> electronic configuration. The metal ions iridium(III) and osmium(II) with the 5d<sup>6</sup> configuration were far less reactive than the 4d<sup>6</sup> systems. The observed catalytic reactivity of these metal ions is thus in accord with the reported stability<sup>6</sup> of their stable dinitrogen complexes which decreases in the order 5d > 3d > 4d. The ruthenium(II) and rhodi-

um(III) solutions employed in the present investigation are expected to form reactive dinitrogen complexes in the absence of stabilizing ligands such as ammonia or tertiary phosphines. These complexes are thus readily reduced to ammonia. It is interesting to note that no stable dinitrogen complex of rhodium(III) has been reported thus far.

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**Registry No.** N<sub>2</sub>, 7727-37-9; Ru(II), 22541-59-9; Ru(III), 22541-88-4; Ir(III), 22555-00-6; Os(II), 22542-07-0; Os(III), 22542-06-9; TiCl<sub>3</sub>, 7705-07-9; SnCl<sub>2</sub>, 7772-99-8; (CH<sub>3</sub>)<sub>2</sub>SnCl<sub>2</sub>, 753-73-1.

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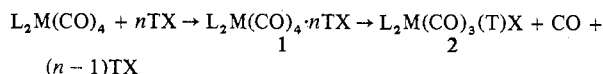
## Preparation of [diphosMo(CO)<sub>4</sub>SnCl<sub>3</sub>]<sup>+</sup>[SnCl<sub>5</sub>OH<sub>2</sub>]<sup>-</sup> and Related Derivatives

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There is kinetic<sup>1-3</sup> and synthetic<sup>4,5</sup> evidence that the reaction of metal carbonyl complexes with SnX<sub>4</sub> or HgX<sub>2</sub> (X = halogen) proceeds in a stepwise fashion. The first step (or steps) involves donor-adduct formation, and the second, oxidation, e.g.



L<sub>2</sub> = for example (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (diphos) or 2,2'-dipyridyl; TX = HgX<sub>2</sub> or SnX<sub>4</sub>.

Depending on the nature of the metal carbonyl compounds of either type 1 or type 2 may be isolated. However, the SnCl<sub>4</sub> derivatives of type 1 have not been fully characterized because of their air-sensitive nature.<sup>6</sup>

Herein we report the characterization of the products of the reaction of 2 mol of SnCl<sub>4</sub> with L<sub>2</sub>M(CO)<sub>4</sub> (L<sub>2</sub> = diphos or diars [1,2-((CH<sub>3</sub>)<sub>2</sub>As)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]; M = Mo or W). An X-ray crystallographic study<sup>7</sup> of one of these has shown that it should be formulated as [diphosMo(CO)<sub>4</sub>SnCl<sub>3</sub>]<sup>+</sup>[SnCl<sub>5</sub>OH<sub>2</sub>]<sup>-</sup>.