

transfer vs. quenching of the excited oxygen;<sup>16</sup> vibrationally excited electronic states could be involved if the rate of energy transfer is greater than the vibrational relaxation rate.

Although there is now extensive evidence that O<sub>2</sub> does not dimerize in the ground state,<sup>17</sup> our chemiluminescence spectra<sup>2</sup> for the emission from the 2[<sup>1</sup>Δ<sub>g</sub>] state and the corresponding absorption data indicate probable dimer formation in the interaction of two excited singlet molecules, indicated by the highly abnormal Franck-Condon intensities in these spectra compared with the single molecule transitions.

A detailed presentation of our numerous types of spectral data and a more meticulous analysis of the interpretation will be submitted for publication shortly in another place.

(16) R. B. Kurtz, *Ann. N. Y. Acad. Sci.*, **16**, 399 (1954).

(17) Cf. B. R. Cairns and G. C. Pimentel, *J. Chem. Phys.*, **43**, 3432 (1965), and references therein.

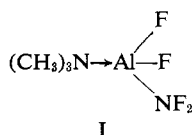
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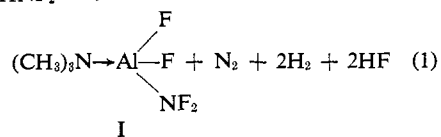
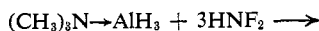
## The Chemistry of Alane. VI. Preparation of an Aluminum Difluoramide from Trimethylamine Alane and Difluoramine

Sir:

We wish to report the preparation of a new aluminum-fluorine compound (I) in which a difluoramino group is



attached to aluminum. To our knowledge this is the first example of a compound containing a difluoramino group bonded to a metal atom. The synthesis of I was accomplished by the reaction shown in eq 1. Trimethylamine alane<sup>1</sup> (2.4 mmoles) in 10 ml of dry tetrahydrofuran was added to a solution of 8 mmoles of difluoramine<sup>2</sup> in 20 ml of dry tetrahydrofuran kept at -23° under an argon atmosphere. The reaction media



became yellow and slowly precipitated a white, crystalline solid. The solid, which was isolated by filtration and dried *in vacuo*, weighed 0.35 g (95% yield). Gas evolution amounting to 5.8 mmoles (80% of theory) was observed during the reaction. The gas was collected in a buret over mercury and subjected to qualitative mass spectral analysis. Nitrogen and hydrogen were observed in addition to solvent and argon. No trace of HNF<sub>2</sub>, N<sub>2</sub>F<sub>2</sub>, or N<sub>2</sub>F<sub>4</sub> were detected in the

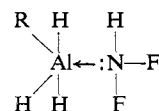
(1) E. Wiberg, H. Graf, and R. Uson, *Z. Anorg. Allgem. Chem.*, **272** (1953).

(2) A. Kennedy and C. B. Colburn, *J. Am. Chem. Soc.*, **81**, 2906 (1959); E. A. Lawton and J. Weber, *ibid.*, **81**, 4755 (1959).

evolved gas. The solid (I) dissolved readily in water without apparent gas evolution to yield a solution capable of oxidizing starch-iodide paper. The infrared spectrum of I displayed strong N-F absorptions at 10.25, 10.5-10.8, and 11.55 μ and was devoid of bands in the 5-6 μ region, indicating the absence of Al-H bonds. Treatment of I with sulfuric acid generated some difluoramine which was detected by mass spectrometry. Hot alkali quantitatively liberated trimethylamine from I.

*Anal.* Calcd for C<sub>3</sub>H<sub>9</sub>AlF<sub>4</sub>N<sub>2</sub>: C, 20.46; H, 5.15; N, 15.91; (CH<sub>3</sub>)<sub>3</sub>N, 33.57. Found: C, 20.62; H, 5.26; N, 15.60; (CH<sub>3</sub>)<sub>3</sub>N, 34.60.

A similar reaction was attempted between difluoramine and lithium aluminum hydride in dry 1,2-dimethoxyethane. However, this reaction proceeded with extreme vigor and could not be controlled so that no useful products were isolated. In contrast, lithium borohydride in dry 1,2-dimethoxyethane did not react with difluoramine. This marked difference in reactivity between the aluminum hydrides and lithium borohydride may be explained by the fact that aluminum can expand its octet, while boron cannot. Thus, reactions of tetracoordinate aluminum may involve the intermediate



(where R = H<sup>-</sup> or Me<sub>3</sub>N), which then loses hydrogen to form the covalent Al-N bond. This initial intermediate cannot be formed in the case of tetracoordinate boron.

(3) General Precision Aerospace, Little Falls, N. J.

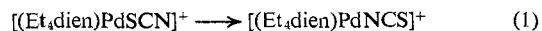
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January 8, 1966

## Intermolecular Isomerization of a Thiocyanatopalladium(II) Complex to Its Isothiocyanato Linkage Isomer

Sir:

Recent communications report the detection of the unstable linkage isomers [(NC)<sub>5</sub>CoNC]<sup>3-</sup>,<sup>1</sup> [(H<sub>2</sub>O)<sub>5</sub>CrNC]<sup>2+</sup>,<sup>2</sup> and [(H<sub>2</sub>O)<sub>5</sub>CrSCN]<sup>2+</sup>.<sup>3</sup> These complexes were prepared *in situ* and their solution chemistry was examined, but their salts were not isolated.

Because of this interest in linkage isomers of metal complexes, we wish to report the preparation of the SCN<sup>-</sup> and PF<sub>6</sub><sup>-</sup> salts of [(Et<sub>4</sub>dien)PdSCN]<sup>+</sup> and the kinetics and mechanism of isomerization of this complex.<sup>4</sup>



The reaction between K<sub>2</sub>[Pd(SCN)<sub>4</sub>] and Et<sub>4</sub>dien in the cold yields the unstable S-bonded isomer [(Et<sub>4</sub>dien)PdSCN]SCN. To a solution containing 1 g of K<sub>2</sub>[Pd(SCN)<sub>4</sub>] in 10 ml of acetone at -10° was added 2 ml of

(1) J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, **87**, 3002 (1965).

(2) J. H. Espenson and J. P. Birk, *ibid.*, **87**, 3280 (1965).

(3) A. Haim and N. Sutin, *ibid.*, **87**, 4210 (1965); **88**, 434 (1966).

(4) Et<sub>4</sub>dien = (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>NHC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>.