transfer *vs.* quenching of the excited oxygen;[16] 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_2 does not dimerize in the ground state,[17] our chemiluminescence spectra[2] for the emission from the $2[^1\Delta_g]$ 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.

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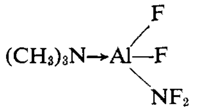
The Chemistry of Alane. VI. Preparation of an Aluminum Difluoramide from Trimethylamine Alane and Difluoramine

Sir:

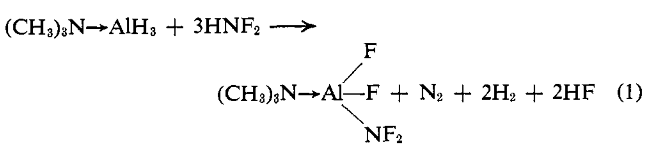
We wish to report the preparation of a new aluminum–fluorine compound (I) in which a difluoramino group is



$$(CH_3)_3N\rightarrow\overset{F}{\underset{NF_2}{Al}}-F$$

I

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[1] (2.4 mmoles) in 10 ml of dry tetrahydrofuran was added to a solution of 8 mmoles of difluoramine[2] 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_2, N_2F_2, or N_2F_4 were detected in the 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.

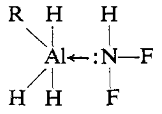


$$(CH_3)_3N\rightarrow AlH_3 + 3HNF_2 \longrightarrow (CH_3)_3N\rightarrow\overset{F}{\underset{NF_2}{Al}}-F + N_2 + 2H_2 + 2HF \quad (1)$$

I

Anal. Calcd for $C_3H_9AlF_4N_2$: C, 20.46; H, 5.15; N, 15.91; $(CH_3)_3N$, 33.57. Found: C, 20.62; H, 5.26; N, 15.60; $(CH_3)_3N$, 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^- or Me_3N), which then loses hydrogen to form the covalent Al–N bond. This initial intermediate cannot be formed in the case of tetracoordinate boron.

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(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).

(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 $[(NC)_5CoNC]^{3-}$,[1] $[(H_2O)_5CrNC]^{2+}$,[2] and $[(H_2O)_5CrSCN]^{2+}$.[3] 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^- and PF_6^- salts of $[(Et_4dien)PdSCN]^+$ and the kinetics and mechanism of isomerization of this complex.[4]

$$[(Et_4dien)PdSCN]^+ \longrightarrow [(Et_4dien)PdNCS]^+ \quad (1)$$

The reaction between $K_2[Pd(SCN)_4]$ and Et_4dien in the cold yields the unstable S-bonded isomer $[(Et_4dien)PdSCN]SCN$. To a solution containing 1 g of $K_2[Pd(SCN)_4]$ in 10 ml of acetone at $-10°$ was added 2 ml of

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(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) $Et_4dien = (C_2H_5)_2NC_2H_4NHC_2H_4N(C_2H_5)_2$.

Et_4dien. The reaction mixture changed color from deep red to bright yellow. The solvent was then largely removed (*ca.* 3 ml remaining), and the yellow crystals that separated were collected on a filter, washed with small amounts of cold water, alcohol, and ether, air-dried, and stored at 0°. *Anal.* Calcd for $[(Et_4dien)PdSCN]SCN$: Pd, 24.3; C, 38.40; H, 6.67; N, 15.99. Found: Pd, 24.5; C, 38.3; H, 6.67; N, 15.9.

The same reaction, but with different conditions, was used to prepare $[(Et_4dien)PdSCN]PF_6$. A cold solution of Et_4dien, 2 ml of amine in 10 ml of water, was added with rapid stirring to 40 ml of a water solution containing 1 g of $K_2[Pd(SCN)_4]$, in an ice–salt bath. After a few minutes a 10-ml water solution containing 1 g of NH_4PF_6 was added, and bright yellow flakes separated from solution. These were collected on a filter, washed with a small amount of cold water, alcohol, and ether, and then air-dried. *Anal.* Calcd for $[(Et_4dien)PdSCN]PF_6$: C, 29.75; H, 5.57; N, 10.68. Found: C, 29.20; H, 5.48; N, 10.57.

The infrared spectrum of this complex is in accord with its being the S-bonded isomer.[5] The hexafluorophosphate salt has only one band in the C–N stretching region at 2125 cm^{-1}. When it is dissolved in water and the solution heated for about an hour, the product isolated has a broad band at 2060 cm^{-1} and is the N-bonded isomer.[6] Since the hexafluorophosphate ion absorbs in part of the C–S stretching region, this region was examined using the thiocyanate salt. The S-bonded isomer has a very weak band at 710 cm^{-1}, and in the solid state at room temperature this converts to the N-bonded form with a slightly stronger band at 830 cm^{-1}.

The ultraviolet absorption spectra of the two isomers are markedly different, and the spectrum of an aqueous solution of the less stable isomer, PdSCN, gradually changes to that of the more stable form, PdNCS (Figure 1). That this isomerization occurs cleanly, with no side reactions such as aquation or chelate ring opening, is indicated by the well-defined isosbestic points at 365 and 308 mμ.

The rates of isomerization (eq 1) were measured at different temperatures by following the changes in optical density at 327 mμ of a solution containing initially the PdSCN isomer. The data gave excellent linear log plots, which were used to estimate the first-order rate constants shown in Table I. Also recorded in this table, at the same experimental conditions as for the isomerization studies, are the first-order rate constants for the reaction of PdSCN (eq 2) and of PdNCS (eq 3) with bromide ion. The rates of these reactions

$$[(Et_4dien)PdSCN]^+ + Br^- \longrightarrow [(Et_4dien)PdBr]^+ + SCN^- \quad (2)$$

$$[(Et_4dien)PdNCS]^+ + Br^- \longrightarrow [(Et_4dien)PdBr]^+ + SCN^- \quad (3)$$

are first order in substrate and zero order in reagent, the complex behaving like a pseudo-octahedral complex.[7]

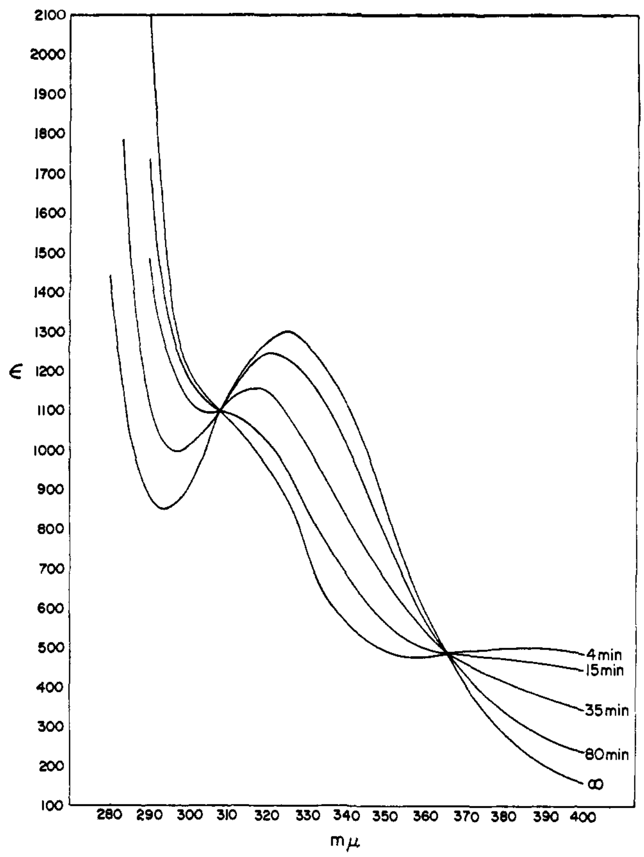


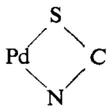
Figure 1. Changes in the absorption spectrum of a solution of $[(Et_4dien)PdSCN]PF_6$ at 25°. The final spectrum, ∞, is that known for $[(Et_4dien)PdNCS]PF_6$.

Table I. Kinetics of Isomerization and Reaction of Palladium(II) Complexes (Ionic Strength = 0.1 *M* $NaClO_4$)[a]

Reaction	Temp, °C	10^4k, sec^{-1}	ΔH^*, kcal/mole	ΔS^*, eu
Pd–SCN → Pd–NCS (1)	20	2.6		
Pd–SCN → Pd–NCS (1)	35	10.5	17.3 ± 0.5	−16.8 ± 1.0
Pd–SCN → Pd–Br (2)	35	10.8	17.3 ± 0.5	−16.8 ± 1.0
Pd–NCS → Pd–Br (3)	35	5.1	25.8 ± 0.5	+ 7.0 ± 1.0
Pd–SCN → Pd–NCS (1)	45	25.6		
Pd–SCN → Pd–Br (2)	45	25.6		
Pd–NCS → Pd–Br (3)	45	12.8		

[a] The concentration of complex was *ca.* 5 × 10^{-4} *M*, and the concentration of Br^- varied from 0.01 to 0.1 *M*.

Since the kinetic parameters for the isomerization (eq 1) and the reaction (eq 2) of PdSCN are identical (Table I), it follows that the two processes appear to take place by the same mechanism. That the rate of reaction does not depend on the concentration of the entering ligand suggests that it involves a dissociation, or a solvent-assisted ligand interchange process.[8] This means that isomerization (eq 1) takes place by an *intermolecular* and not an intramolecular process. The same type of mechanism has been proposed for the isomerization of $[Cr(H_2O)_5SCN]^{2+}$. Such a result is in contrast to that found[9] for the isomerization of $[(NH_3)_5CoONO]^{2+} \rightarrow [(NH_3)_5CoNO_2]^{2+}$. This is not surprising in view of the fact that NO_2^- is bent and SCN^- is linear. Thus, the energy required to bend the SCN^- ligand to give



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(5) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 1665 (1965).

(6) F. Basolo, W. H. Baddley, and J. L. Burmeister, *ibid.*, **3**, 1202 (1964).

(7) W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **86**, 2075 (1964).

(8) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964).

(9) R. G. Pearson, P. M. Henry, J. G. Bergman, and F. Basolo, *J. Am. Chem. Soc.*, **76**, 5920 (1954); R. K. Murmann and H. Taube, *ibid.*, **78**, 4886 (1956).

as a transition state for an intramolecular isomerization may be prohibitive. Finally, in further support of an intermolecular process is the observation that the stable isomer, PdNCS, reacts (eq 3) slower than does the less stable form.

Preliminary observations show that in the solid state at room temperature there is complete isomerization of $[(Et_4dien)PdSCN]SCN$ in 3 days, but under the same conditions there is no isomerization of $[(Et_4dien)PdSCN]PF_6$. Also the rate of isomerization of $[(Et_4dien)PdSCN]^+$ in nonpolar solvents such as benzene is slower than it is in water solution. These and other observations on systems of this type will be reported in detail later.

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The Isotopic and Phase Effects in Neutron-Irradiated Ethyl Bromide[1]

Sir:

The differences in the isotopic yields and the effects of phase on the relative yields of radiobromine produced by a nuclear process in organic bromides were repeatedly investigated and were the subject of many contradictory reports.[2] In a recent publication[3] Shaw and co-workers have shown that although the total organic yields of $^{80\mathrm{m}}$Br and ^{82}Br in neutron-irradiated ethyl bromide are quite similar, the repartition of their activity between the products is different. Current work in our laboratory seems to indicate that this isotopic effect could be correlated to the changes in the yields of different fractions upon irradiation in liquid and solid phase.

Carefully purified ethyl bromide[4] a containing 10^{-3} *M* fraction of bromine scavenger was irradiated for 1 to 3 sec in the pneumatic channels of EL 3 (CEA, Saclay), with a neutron flux about 10^{12} neutrons/cm²/sec. The solid-state irradiations were performed with polycrystalline material at approximately $-196°$. Samples were kept in liquid nitrogen before and after irradiation; since the irradiation time was very short, the samples were not cooled while exposed to the neutron flux.[5] Liquid-state irradiations were done at room temperature and the samples kept at 0° until extracted. Fifty minutes after irradiation the samples were extracted with a reducing wash. After the addition of carriers, the separation was made by gas chromatography.[4] The fractions were collected at the end of the column and counted three times: (1) 4 hr after extraction, (2) 20 hr later, and (3) 48 hr after extraction, when the remaining activity is due practically to ^{82}Br (35-hr half-life) only. This last measurement was used as a control. In this manner the yield of both bromine isotopes was determined from the same sample.

The results presented in Table I represent the mean ratios for at least three experiments; the mean deviations of the percentage yields did not exceed ±5 to 7% for the main fractions (about twice the value of the statistical counting error).

Table I. Isotope and Phase Effects in Neutron-Irradiated Ethyl Bromide

Products	Isotope effect[a]		Phase effect[b]	
	Liquid	Solid	$^{80\mathrm{m}}$Br	^{82}Br
Bromomethane	2.5	2.8	1.5	1.4
Dibromomethane	1.8	1.7	1.1	1.2
Tribromomethane	1.3	1.0	1.2	1.3
Ethyl bromide	1.0[c]	1.0[c]	2.2	2.4
Dibromoethane	0.8	0.6	12.5	16.0
Tribromoethane	0.7	0.7	4.7	4.0

[a] Yield for $^{80\mathrm{m}}$Br/yield for ^{82}Br. [b] Yield in solid phase/yield in liquid phase. [c] The ratio becomes >1 for heavily scavenged systems.[3]

The results obtained for the liquid-phase irradiations are in very good agreement with those of Shaw, although the neutron flux and irradiation times were completely different.[3,6] This was considered a confirmation of the purity of the material used, the separation method, and the absence of any parasite phenomenon.[7]

The complete analysis of the irradiation products in ethyl bromide shows that the activity is distributed between twelve separable products. In this communication we will only comment upon a few relevant features concerning the main fractions; work is currently done in our laboratory to obtain a more detailed understanding of this and similar systems.

An important point arising from Table I is the obviously "nonrandom" behavior of the two bromine isotopes; the isotopic yield ratio for a given product is remarkably constant when passing from the liquid to the solid phase despite the fact that the individual yields change by factors varying by as much as 1 to 16. The results in Table I also indicate that the products resulting from H-atom substitution show an isotope effect favoring ^{82}Br (yield for $^{80\mathrm{m}}$Br/yield for ^{82}Br < 1) and a very important phase effect, whereas those resulting from the scission of a C–C bond as well as the substitution of a Br atom (once diffusive reactions are eliminated at high scavenger concentrations[3]) present an isotope effect favoring $^{80\mathrm{m}}$Br (yield for $^{80\mathrm{m}}$Br/yield for ^{82}Br > 1), and show little or no difference in yield in the two phases.

The recent discovery[8a,b] that most ^{82}Br is produced through an isomeric transition from $^{82\mathrm{m}}$Br (6.2-min

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(1) This work was done under a research contract with the Commissariat á l'Energie Atomique.

(2) (a) For a recent review of the subject, see J. E. Willard, "Chemical Effects of Nuclear Transformations," Vol. 1, IAEA, Vienna, 1965, p 221; (b) R. M. A. Hahne and J. E. Willard, *J. Phys. Chem.*, **68**, 2582 (1964); (c) N. Nesmeyanov and E. S. Filatov, *Radiokhimiya*, **3**, 501 (1961); (d) J. E. Willard, ref 2a, 1961, p 215; (e) A. E. Richardson and A. F. Voigt, *J. Chem. Phys.*, **28**, 854 (1958); (f) M. Milman, *J. Am. Chem. Soc.*, **80**, 5592 (1958).

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(4) A detailed account of the experimental techniques will be published elsewhere; the chromatographic analysis and the calculation of the organic yields follow the same principles as those described in ref 3.

(5) The approximately estimated time the samples were out of liquid nitrogen is about 30–60 sec.

(6) P. F. D. Shaw, private communication.

(7) J. A. Merrigan and E. P. Rack, *J. Phys. Chem.*, **69**, 2795 (1965).

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