solution of the *o*-phenanthroline adduct of neodymium pentafluoropropionate. The adduct is prepared in two steps.[8] A solution of neodymium pentafluoropropionate in absolute alcohol is obtained by mixing stoichiometric amounts of a solution of neodymium chloride and a solution of sodium pentafluoropropionate, both saturated at room temperature, and filtering off the precipitated sodium chloride. On adding a solution of 1 equiv of *o*-phenanthroline in absolute alcohol, the alcoholate of the desired compound precipitates. Drying the solvate at 60° *in vacuo* removes the alcohol and yields the nonsolvated adduct. *Anal.* Calcd for $Nd(CF_3CF_2COO)_3 \cdot C_{12}H_8N_2$: Nd, 17.73. Found: Nd, 17.76. Solutions of the adduct in dimethyl sulfoxide have only a limited shelf life, presumably because of solvolysis of the adduct. For this reason, the spectra of absorption (Figure 1) and of emission (Figure 2) were run on freshly prepared solutions.

In the room-temperature laser experiment shown in Figure 3, we used a 5-cm long, 0.4-cm i.d. quartz cell, with flat and parallel windows having dielectric coatings of maximum reflectance at 1.06 μ[2]. The cell was filled through a side arm in which sufficient space was left for the expansion of the liquid. The light, from the pumping source, two E.G.&G. FX-51 flashlamps in series, was filtered through 1 cm of 10% potassium dichromate in water. This filter is opaque to light below 4800 A and above 11,500 A.[9] The lamps were fed by an 80-μf capacitor through a 300-μ Hz choke. The light reaching an RCA 7102 photomultiplier detector was filtered by a 1.06-μ interference filter with a 0.02-μ band width.

As might be expected from the low quantum yield of luminescence, the thresholds of the present solutions were higher than those in the Nd^{3+}–$SeOCl_2$–$SnCl_4$ system. The limited shelf life and the photodecomposition of dimethyl sulfoxide by ultraviolet radiation[10] make the organic system a less desirable laser material than the previously reported inorganic liquid.[1] Nevertheless, the present liquid laser does have the advantage that the active liquid is not corrosive and, presumably, not toxic. Furthermore, in comparison with previously reported organic laser systems, involving chelates of europium, the power or the energy output in this system is not inherently limited by excessive absorbance of an organic ligand,[11] since the pump bands originate exclusively in the ion itself. The fact that the insertion of the ultraviolet-absorbing aqueous dichromate filter causes an improvement in the performance of the organic laser proves that, unlike in the former chelates, pumping does not take place through the organic ligand.

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The Mechanism of the Formation of an Iridium Complex of Molecular Nitrogen *via* Organic Azides[1]

Sir:

Recent reports have described iridium[2] and ruthenium[3] complexes containing molecular nitrogen as a ligand. Aside from their novelty, interest in such complexes stems from the search for a catalyst to effect the hydrogenation of nitrogen under mild conditions. Stoichiometric fixation of nitrogen at atmospheric pressure through a presumably binuclear titanium complex has been partially elucidated.[4]

Herein are described the gross features of the mechanism (Figure 1) by which the iridium complex of nitrogen III is formed. The concepts inherent in this mechanism may be extended to the preparation of other nitrogen complexes and indeed to a wide range of π complexes.

Earlier it was reported[2] that Vaska's iridium complex I reacts with a series of acid azides to form the nitrogen complex III in high yield provided that the solvent $CHCl_3$ contained water or, as demonstrated herein, an alcohol. The following experimental observations lead us to propose the mechanism depicted in Figure 1.

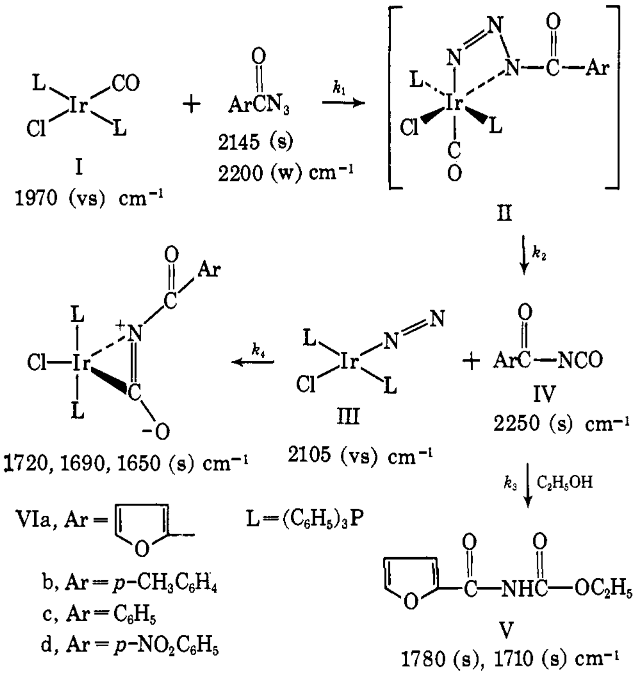

Figure 1.

When the reaction was carried out in reagent $CHCl_3$ (containing ethanol) using furoyl azide, the carbamic ester V was isolated from the reaction mixture as the major organic product and identified by complete elemental analyses, molecular weight, mass spectral pattern, and nmr and infrared spectra. Similarly, when the reaction was run in pure $CHCl_3$ to which other alcohols or water were added, the nitrogen com-

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[1] This work was supported by the National Science Foundation and the Advanced Research Projects Agency Contract SD-100.

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plex III was formed in high yield. However, in the absence of such a nucleophile using several acid azides, the nitrogen complex was not obtained, but instead a series of new complexes formulated as VI was isolated and characterized through elemental analyses and infrared and nmr spectra.

The mechanism was further clarified by examining the infrared spectrum during the course of the reaction.[5] Strong, sharp absorption bands were observed at the frequencies illustrated on Figure 1 for the starting carbonyl I, the nitrogen product III, the intermediate acyl isocyanate IV, the carbamate V, and the isocyanate complex VI, depending on the conditions under which the reaction was carried out. These assigned frequencies were independently confirmed by measuring the spectrum of each individual component.

A spectral study of the reaction between furoyl azide and Vaska's complex I in $CHCl_3$ containing ethanol revealed complete disappearance of the CO peak at 1970 cm^{-1} within 2 to 3 min and simultaneous reduction of the azide band at 2145 cm^{-1} (the azide was present in excess). Synchronous with the diminution of these two bands was the appearance of the nitrogen peak at 2105 cm^{-1} and the carbamate at 1780 and 1710 cm^{-1}. Repeated scans over the lifetime of the reaction revealed no other intermediate peaks in the range 1600–2400 cm^{-1}.

Examination of the same reaction in pure, dry $CHCl_3$ revealed the appearance of the acyl isocyanate peak at 2250 cm^{-1} along with that of the nitrogen peak at 2105 cm^{-1}. The rapid disappearance of the peak at 2250 cm^{-1} and enhancement of peaks at 1720 and 1690 cm^{-1}, characteristic of the acyl isocyanate complex VI, were observed. Intermediate peaks at 2065 and 1820 cm^{-1} were also observed and are considered to represent an intermediate in the formation of VI.

Further support for this scheme was obtained by examining the infrared spectrum during the course of the reaction between I and phenyl azide. Using $CHCl_3$ containing alcohol, a doublet at 2260 and 2280 cm^{-1}, characteristic of phenyl isocyanate, appeared at a rate commensurate with the appearance of the nitrogen complex (2105 cm^{-1}) and the disappearance of the carbonyl (1970 cm^{-1}) and the azide (2130 cm^{-1}). In this case the formation of nitrogen complex is slower than the reaction with the more electrophilic acyl azides. Further reaction between phenyl isocyanate and the nitrogen complex is very slow.

Finally, we have independently carried out the reaction between benzoyl isocyanate and the nitrogen complex III, observing the same spectral changes described above for the "dry" reaction and isolating the isocyanate complex VIc.

From these data we propose an initial attack on the acyl azide by the nucleophilic complex I (probably bimolecular) to form a presumed intermediate II (kinetically undetectable) which collapses to the nitrogen complex III and an acyl isocyanate IV. If an alcohol is present, IV is irreversibly intercepted; otherwise, it reacts with the nitrogen complex III to yield VI.

Our tentative formulation of VI as a π-bonded isocyanate is based on its infrared spectrum[6] (no absorption from 1720 to 2800 cm^{-1}) and its similarity to analogous acetylene complexes prepared from III.[7] The isocyanate group in VIa has been replaced by disubstituted acetylenes. Two of the isocyanate complexes have been shown to absorb 1 equiv of CO to form stable six-coordinate complexes.[8] The formulation of the complexes as depicted for VI is of interest inasmuch as heteronuclear multiple bonds transversely π bonded to metals are very unusual.[9a,b]

This mechanism suggests that other metal carbonyls can be converted to nitrogen complexes by reaction with organic azides. It may be anticipated that a bimolecular pathway involving a low activation energy will be required if the nitrogen complex is to be isolated. Kinetically labile but thermodynamically stable metal carbonyl complexes would be the most appropriate substrates. However, under more vigorous conditions the coordinated nitrogen could act as a reactive intermediate to trap other π-bonding ligands. This could be utilized as a method for preparing new catalyst systems. It is further anticipated that other ligands (such as tertiary phosphines) which react with organic azides can be replaced by nitrogen in this manner. Finally, systems electronically resembling azides, such as nitrous oxide, diazoalkanes, and carbodiimides, may be found to react by analogous pathways. Experiments in progress are testing these hypotheses.

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[5] A solution of azide (0.05 *M*) was slowly added and frozen on a solution (0.05 *M*) of Vaska's compound previously frozen. The mixture was allowed to partially melt, and samples removed by inverse filtration were rapidly introduced into a 1-mm calcium fluoride cell of special construction such that the solution is not in contact with any metal.

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New Structural and Stereochemical Aspects of the Cyclization of Olefinic Acetals

Sir:

Recently we reported on the stereospecific cyclization of an acyclic trienic acetal to give tricarbocyclic material of "natural" (*trans,anti,trans*) configuration.[1] Unanswered questions of immediate interest were (a) can this method be adapted to the production of fused-ring systems containing the angular methyl group, and (b) is the stereochemical course of the reaction dictated by the configuration of the olefinic bonds in the substrate?[2] The present study provides unequivocally affirmative answers to both of these questions. Thus the *trans* and *cis* dienic acetals I and III have been shown to undergo rapid stereospecific cyclization to give, in

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