course, no such competition in the boron trichloride complex, which accounts for the greater π withdrawal.

Also of interest is the decrease in the phosphorus–o-fluorine coupling constant (J_{12}) when the phosphines form complexes, an effect that is especially marked in metal carbonyl complexes.[7]

Acknowledgment. We thank the National Research Council of Canada and the Defense Research Board of Canada (Grant No. 9530-49) for financial support.

(7) NOTE ADDED IN PROOF. We have now shown by double-irradiation techniques that J_{24} for $C_6F_5NH_2$ and C_6F_5COCl are of opposite sign. It appears most probable that, in general, the sign of J_{24} is opposite for π-withdrawing substituents and π-donating substituents. Figure 1 thus reduces to a single straight line, for which the least-squares equation is $J_{24} = -0.4706\delta_p + 74.64$. We have learned that Professor F. G. A. Stone (private communication; *J. Chem. Soc.*, in press) has attempted to relate $\delta_p - \delta_m$ in pentafluorophenylplatinum complexes to π-bonding effects.

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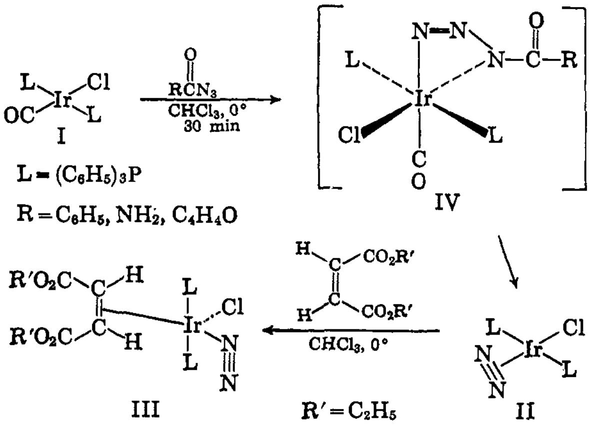
Iridium Complexes of Molecular Nitrogen

Sir:

In the course of our current exploration[1] of oxidative addition reactions of complexes having a d^8 configuration we have discovered two remarkable compounds in which molecular nitrogen is apparently bound to iridium. These compounds (II and III) represent the second reported instance of complexed nitrogen inasmuch as Allen and Senoff have recently described[2] the preparation of a cationic ruthenium(II) complex which is also thought to contain coordinated nitrogen.



Aside from the novel nature of these nitrogen compounds, their significance stems from the possibility that such complexes may lead to the development of homogeneous catalysts for the hydrogenation of nitrogen. Attempts to "fix" nitrogen are being made in laboratories throughout the world.

The discovery of the iridium–nitrogen complexes II and III ensued from our unsophisticated hypothesis that "unsaturated" d^8 complexes such as Vaska's[3] iridium(I) compound (I) are analogous to olefins in their chemical reactions. In an effort to prepare 1,3-dipolar adducts, the pseudo-olefinic complex I was treated with a series of acid azides. Whenever these reactions were carried out at 0°, the same golden yellow compound (II) was obtained (by precipitation with hexane) regardless of the azide employed. Structure II provisionally assigned to this complex is based on the following data. *Anal.* Calcd for $C_{36}H_{30}ClN_2P_2Ir$: C, 55.38; H, 3.84; N, 3.58; Cl, 4.61; P, 7.94. Found: C, 54.95; H, 3.98; N, 3.47; Cl, 5.06; P, 7.60. The infrared spectrum of II exhibits an intense absorption at 2095 cm^{-1} which is assigned to coordinated N_2. Other than a weak band[4] at 1970 cm^{-1}, no absorption bands are present in the region 3000–1600 cm^{-1}. The yellow complex II slowly decomposes in the solid state at room temperature evolving a gas and affording a green-gray, soluble solid of uncertain structure.[5] In a similar manner, solutions of II in chloroform or benzene decompose in 1–2 hr at room temperature evolving a gas. The intense infrared peak at 2095 cm^{-1} is lost during these decompositions. The yellow solid II was decomposed at 110° in a sealed flask under argon, and the evolved gas was found to be nearly pure nitrogen by analysis on a gas chromatographic column packed with a molecular sieve. Treatment of a $CHCl_3$ solution of II with a $CHCl_3$ solution of triphenylphosphine results in the immediate, vigorous evolution of nitrogen (gas chromatographic analysis) and the formation of a red solution. Presumably, chlorotris(triphenylphosphine)iridium(I) (analogous to the rhodium complex described by Wilkinson[6] as a homogeneous hydrogenation catalyst) is formed in this reaction. When solutions of the yellow solid are treated with carbon monoxide, a colorless intermediate is first formed[7] and subsequently decomposes to form Vaska's compound (I). Acetylenes, alkyl halides, hydrogen chloride, mercuric chloride, and carbon tetrachloride react with II, nitrogen is evolved, and new complexes are formed.

The formation of the nitrogen complex II from acid azides may involve a 1,3-dipolar intermediate such as IV which could form II by elimination of N-acyl isocyanate.[8] This speculation is supported by our inability to detect CO in the argon atmosphere over the mixture during the entire course of the reaction. Experiments in progress are designed to test further this hypothesis.

Treatment of the yellow complex II with diethyl maleate afforded a more stable pale yellow complex, which is thought to have the structure depicted for III. *Anal.* Calcd for $C_{44}H_{42}ClN_2O_4P_2Ir$: C, 55.46; H, 4.41; N, 2.94; Cl, 3.78; P, 6.51. Found: C, 55.32; H, 4.55; N, 3.05; Cl, 3.99; P, 6.57. The infrared spectrum (KBr) of III exhibits a single intense band at 2190 cm^{-1}, but no other absorption is found in the 2800–1800-cm^{-1} region. A strong doublet at 1735 and 1695 cm^{-1} is assigned to the ester groups. The shift of the coordinated nitrogen absorption from 2095 to 2190 cm^{-1} is surprising but can be rationalized in

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(1) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **87**, 4008 (1965); **88**, 180 (1966); **88**, 3504 (1966); *Chem. Commun.*, 244 (1966).

(2) A. D. Allen and C. V. Senoff, *ibid.*, 621 (1965).

(3) L. Vaska and J. W. Diluzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).

(4) We have no explanation for this absorption except that it may be an impurity.

(5) Molecular weight measurements suggest this is a trimer containing metal–metal bonds.

(6) J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun.*, 131 (1965).

(7) This is probably a five-coordinate complex containing two CO groups such as reported by L. Vaska, *Science*, **152**, 769 (1966).

(8) A reaction whereby a metal carbonyl reacts with azide ion to form N_2 and a metal N-isocyanate[9] may be related to our current observation.

(9) W. Beck and H. S. Smedal, *Angew. Chem.*, **78**, 267 (1966).

terms of decreased backbonding from the iridium in passing from an "unsaturated," four-coordinate iridium(I) complex to a "saturated," five-coordinate iridium(I) complex.[10] These absorption bands are similar to the strong band in the 2170–2115-cm^{-1} region found by Allen and Senoff in the spectra of the cationic ruthenium(II)–nitrogen complexes. The Raman band corresponding to the nitrogen triple-bond stretch is found at 2331 cm^{-1}.[2]

A solid sample of III was degraded by heating for 10 min at 165° under argon. The evolved gas was found to be nearly pure N_2 by gas chromatographic analysis. In another experiment a weighed sample of II was heated for 15 min at 200°, and the evolved gases were passed into a vacuum line through a trap cooled with liquid nitrogen. The volume of noncondensable gas was found to be 85% of the value calculated for evolution of 1 mole equiv of N_2. Mass spectral analysis demonstrated that the evolved gas was nitrogen of purity >99%.

The structures assigned to II and III must be considered tentative until X-ray diffraction studies have been completed. It seems possible that other nitrogen complexes can be prepared from organic azides and suitable four-coordinate complexes containing at least one carbonyl group. Experiments in progress are exploring the possibility of reducing coordinated nitrogen and of preparing homogeneous hydrogenation catalysts from II and III.[10a]

Acknowledgment. We are pleased to acknowledge the support of the National Science Foundation. We are also indebted to William Breckenridge, David Harrison, and Edward Weissberger for technical assistance with the gas analyses and to Professor Henry Taube for his encouragement.

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(10) Structures I and II depict the nitrogen bound edgewise to the metal. This conjecture stems from our hypothesis that nitrogen–metal π bonds should resemble acetylene–metal bonds. If this supposition is correct, one should seek nitrogen complexes in metal substrates which readily form stable complexes with acetylene or 2-butyne.

(10a) NOTE ADDED IN PROOF. The yellow compound II has been obtained in a crystalline form which is considerably more stable, melting at 151°. Water seems to be required for the formation of II inasmuch as a different product is formed when dry $CHCl_3$ is used as a solvent.

(11) Alfred P. Sloan Foundation Fellow; National Science Foundation Senior Postdoctoral Fellow.

(12) Correspondence concerning this paper should be sent to J. P. C. at the University of North Carolina.

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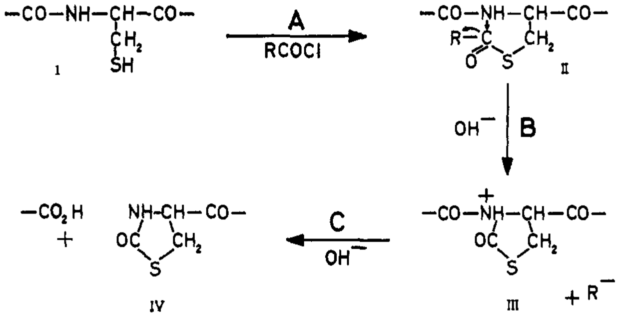
Specific Cleavage of Peptides at Cysteinyl Residues

Sir:

In studying the sequence of amino acid residues in a peptide chain it is an advantage to cleave the chain quantitatively at specific residues. This can be achieved in some cases by enzymes and by chemical modification of the side chains of amino acid residues.[1] Cysteinyl residues can be converted to S-2-aminoethylcysteinyl residues[2] and to dehydroalanyl residues,[3] and both of these modifications can be used to effect cleavage of the adjacent peptide bond. Recently the use of cyanide ion[4] and of cyanogen bromide[5] is reported to cleave cysteine peptides.

We wish to report a new approach to this problem based on the reaction series outlined below. In step A



the thiol group of I is acylated to form II. Step B involves the elimination of the anion R$^-$ from II and depends on the stability of R$^-$. In step C the acyl group of the 2-keto-3-acylthiazolidine (III) is hydrolyzed in analogy to the final step in the cyanide cleavage reaction,[4] where a 2-imino-3-acylthiazolidine is involved.

In the preliminary studies reported here we have used as model compounds various N-carbobenzyloxy tripeptides containing cysteine as the middle residue, and the cleavage has been followed quantitatively by converting the N-carbobenzyloxy amino acid into the corresponding free amino acid which is estimated by conventional methods. The acylating agents (RCOCl) used are 4-nitrophenyloxycarbonyl chloride[6] (R = $O_2NC_6H_4O$), phenylthiocarbonyl chloride[7] (R = C_6H_5S), and *n*-butylthiocarbonyl chloride[8] (R = C_4H_9S). The N-carbobenzyloxy tripeptides containing cysteine residues were prepared *in situ* from the corresponding N,S-dicarbobenzyloxy tripeptides[9] by sodium methoxide solution[10] and the thiol groups were then acylated by the appropriate acid chloride in phosphate buffer, pH 7. The liberation of thiol groups and their subsequent acylation were followed quantitatively by iodometric titration. The reaction product was then hydrolyzed in 1.0 *M* potassium hydrogen carbonate (pH 8.1) at 50° for 90 min. After acidification and vacuum evaporation the ether-soluble material was treated with hydrogen bromide in acetic acid[11] to remove quantitatively the N-carbobenzyloxy group; peptide bond cleavage was estimated using the Beckman–Spinco amino acid analyzer.

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(1) See review by B. Witkop, *Advan. Protein Chem.*, **16**, 221 (1961).

(2) H. Lindley, *Nature*, **178**, 647 (1956); M. A. Raftery and R. D. Cole, *Biochem. Biophys. Res. Commun.*, 10, 467 (1963).

(3) M. Sokolovsky, T. Sadeh, and A. Patchornik, *J. Am. Chem. Soc.*, **86**, 1212 (1964).

(4) J. L. Wood and N. Catsimpoolas, *J. Biol. Chem.*, **238**, PC 2887 (1963).

(5) E. Gross, C. H. Plato, J. L. Morell, and B. Witkop, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts, p 60C; W. Awad and P. E. Wilcox, *Biochem. Biophys. Res. Commun.*, 17, 709 (1964).

(6) G. W. Anderson and A. C. McGregor, *J. Am. Chem. Soc.*, **79**, 6180 (1957).

(7) H. Rivier, *Bull. Soc. Chim. France*, [4] **1**, 733 (1907).

(8) R. Riemschneider and O. Lorenz, *Monatsh. Chem.*, **84**, 518 (1953).

(9) A third crystalline modification of N,S-dicarbobenzyloxyglutathione has been obtained; mp 181–182° (uncor), plates from methanol–benzene $[\alpha]^{21}$D −34° (*c* 1, methanol). *Anal.* Calcd for $C_{26}H_{29}N_3O_{10}S$: C, 54.25; H, 5.08; N, 7.30; equiv wt, 287.8. Found: C, 53.87; H, 5.24; N, 7.52; equiv wt, 286. Two other crystalline modifications, mp 105–107° and 141–143°, $[\alpha]^{25}$D −32°, have been described previously.[10]

(10) M. Sokolovsky, M. Wilchek, and A. Patchornik, *J. Am. Chem. Soc.*, **86**, 1202 (1964).

(11) D. Ben-Ishai and A. Berger, *J. Org. Chem.*, **17**, 1564 (1952).