reaction was kept below 45° by external cooling. Two layers formed and the top organic layer was removed and dried over $CaSO_4$. The product (*ca.* 25 g, 60% yield based on formaldehyde) distilled at 162.5–165° (743 mm). Henry reported a boiling point of 168°.[3]

N,N'-Dimethylimidazolidine. An aqueous (*ca.* 37%) formaldehyde solution (0.19 mole) was added slowly to a solution of N,N'-dimethylethylenediamine (0.19 mole) in 200 ml of chloroform. After stirring for several hours, the water layer was removed and the chloroform layer was dried over $MgSO_4$. Atmospheric pressure distillation served to remove the solvent; the product (26% yield) distilled at 110–112° (collected as a cloudy material). After several days a red oil separated and the clear liquid was distilled trap to trap *in vacuo*. The product must be refrigerated to prevent decomposition. Krässig reports a boiling point of 114°.[15]

N,N'-Diethylimidazolidine. The procedure of Donia, *et al.*,[16] was followed except that the reaction mixture were merely dried thoroughly over $CaSO_4$ and then distilled at atmospheric pressure to give the product boiling at 152–155° in 35% yield. Donia, *et al.*, report a boiling point of 65.6° (35 mm).[16]

Acknowledgments. This investigation was supported by Public Health Service Research Grant CA-07064-03 from the National Cancer Institute and by the Advanced Research Projects Agency. We are indebted to the National Science Foundation for a Predoctoral Fellowship to C. H. Yoder. A gift of elemental germanium from Texas Instruments, Inc., is gratefully acknowledged.

The Reaction between Metal Carbonyls and Amines. II. Iron Carbonyl with Pyrrolidine. Initial Stages of the Reaction[1-3]

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Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana 47907. Received May 16, 1966

Abstract: The reaction between $Fe(CO)_5$ and pyrrolidine has been investigated, using infrared and nmr spectra, conductance measurements, and stoichiometry; attention is focused on the first species (I) formed in this reaction. The over-all reaction path is similar to that of the reaction between $Fe(CO)_5$ and piperidine or *n*-butylamine; however, certain differences occur which have permitted further elucidation of the structure and nature of I. Additional conductance data on $Fe(CO)_5$–piperidine reactions are also presented. The data reported here put the more tentative proposals of the earlier paper regarding the nature of I on a firmer basis.

When iron pentacarbonyl, $Fe(CO)_5$, and piperidine or *n*-butylamine are mixed at room temperature, a reaction ensues at once which yields a compound (I) in which considerable modification of the metal carbonyl and amine moieties has taken place.[3] In water, this compound hydrolyzes to form $HFe(CO)_4^-$ (II) and the carbamate of the amine, $>NCOO^-$, both as the $>NH_2^+$ salts. After some time at room temperature, but more rapidly at 60°, I reacts to form another metal carbonyl containing species III in which there is evidence for formylation of the amine at the nitrogen, *i.e.*, a carbon monoxide insertion reaction has taken place. We have now investigated the reaction of $Fe(CO)_5$ with pyrrolidine, and extended the studies of the reaction between $Fe(CO)_5$ and piperidine. These investigations have yielded a body of evidence concerning the structure and nature of I, a compound which is the important first intermediate in the CO insertion reaction which has taken place.

The general reaction path in the pyrrolidine case parallels that of piperidine and *n*-butylamine,[3] but certain differences in I for pyrrolidine allow more detailed structural and chemical evidence to be obtained.

The hydrolysis products of I in pyrrolidine reaction mixtures were again found to be $HFe(CO)_4^-$ and pyrrolidine carbamate. It was these hydrolysis products in the other amines which first led to a proposed structure for I containing the linkage $>NCOFe-$.

Although spectral evidence was interpreted to mean that I was probably an $LFe(CO)_4$ compound with the amide ligand, L, located at the axial position of a trigonal bipyramid, two other structures were also possible.[3] These were both trigonal bipyramidal $L_2Fe(CO)_3$ compounds, either with both ligands on planar sites or with one axial and one planar. Each of these could give the observed 5-μ region CO stretching frequency pattern of 2010 (w–m), 1918 (m), and 1895 (s) which I shows, when the amine is piperidine or *n*-butylamine. The 5-μ region spectrum of an $Fe(CO)_5$–pyrrolidine reaction mixture taken within 2 min after mixing is shown in Figure 1. This spectrum shows the same basic pattern found in the piperidine and *n*-butylamine cases. As can be seen in the pyrrolidine case, however, the strong band is split into a doublet with components at 1898 and 1885 cm^{-1}. These bands are due to $C{\equiv}O$ stretching vibrations of the metal carbonyl moiety in I. Since the number of metal carbonyl CO groups in the molecule must be equal or greater than the number of bands due to fundamental modes in the 5-μ region ($C{\equiv}O$ stretching vibrations), the presence of four fundamental bands for I in pyrrolidine solutions clearly eliminates the $L_2Fe(CO)_3$ structures as possibilities for I.

The spectrum of I in the pyrrolidine case is readily understood in terms of the proposed $LFe(CO)_4$ struc-

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[1] Abstracted in part from the Ph.D. Thesis of B. J. Bulkin, Purdue University, June 1966.

[2] Supported by a contract with the Atomic Energy Commission.

[3] Paper I of this series: W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer, and N. Koizumi, *J. Am. Chem. Soc.*, **87**, 3080 (1965).

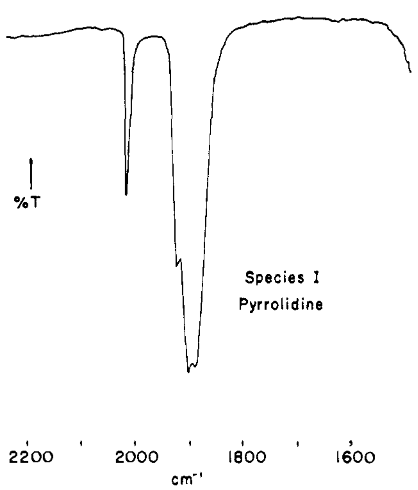

Figure 1. Infrared spectrum of $Fe(CO)_5$–pyrrolidine reaction mixture at species I stage, 5-μ region.

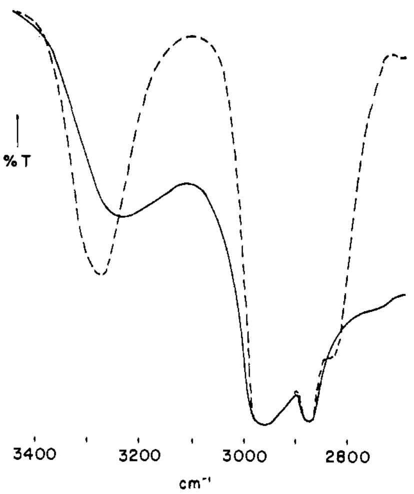

Figure 2. N–H and C–H stretching regions; $Fe(CO)_5$–pyrrolidine reaction mixture; ———, reaction mixture; ......, pyrrolidine.

ture. For the idealization of this structure as a trigonal bipyramid with L equivalent to a mass point, one expects two medium intense bands arising from the two A_1 fundamentals and an intense band due to the degenerate E fundamentals. However, L may be sufficiently bulky or asymmetric in actuality to perturb the above picture, with the primary observable result being the splitting of the strong band due to the removal of the exact degeneracy of the two E modes.[4] Thus, the band near 2010 cm^{-1} is assigned to the A_1 vibration in which the "planar" and "axial" CO groups are vibrating in phase (probably more "planar" than "axial"), the band near 1918 cm^{-1} to the A_1 vibration in which the "planar" and "axial" CO groups vibrate out of phase with each other (probably more "axial" than "planar"), and the doublet at 1898 and 1885 cm^{-1} to the two, nearly degenerate, perturbed E modes.

As in the case of piperidine,[3] solutions of I formed from $Fe(CO)_5$ and pyrrolidine show a weak band at 1640 cm^{-1} which is assigned to the C=O stretching frequency of the amide group (L) in I. While this band is weak compared with the intense metal carbonyl C=O stretching vibrations, its intensity is nonetheless consistent with previous observations[5] of systems of this kind. It should be noted that water has a band in this region. That the observation is not due to water is shown by two facts. First, the more intense, high frequency water bands are missing in these spectra. Second, the amount of water corresponding to the observed absorption would result in the formation of sufficient $HFe(CO)_4^-$ (species II)[3] to make its bands prominent in the spectrum; no such bands were found.

Turn now to the question of the position of the proton which originally was on the nitrogen atom of the amine. Several possibilities exist for its location in species I, including remaining on the nitrogen (thereby giving the nitrogen a formal positive charge), transfer to the amide oxygen or to the iron atom, or loss to another amine molecule, resulting in an ionic structure of the type $(>NH_2)^+(>NCOFe(CO)_4)^-$. Infrared spectra of concentrated solutions of I in pyrrolidine (Figure 2) provide important information on this question. First, they show a band at 3230 cm^{-1} definitely assignable as an N–H stretching mode. Second, the spectra show a broad, intense, multiple absorption centered at about 2700 cm^{-1} with half-band width of *ca.* 600 cm^{-1}. The broad absorption is characteristic of strongly hydrogen-bonded systems, and the multiple absorptions superimposed on it are similar to those found in secondary amine salts in this region. In these compounds, a lowering of the N–H stretching frequencies results in a coupling of these with the C–H stretches giving rise to multiple absorption. Thus the observed pattern was similar to that found in the spectrum of a Nujol mull of pyrrolidinium chloride which was prepared and examined for comparison purposes. However, it should be noted that spectra of I did not show the characteristic NH_2^+ deformation mode which generally occurs between 1500 and 1650 cm^{-1} and which appears as a weak band at 1600 cm^{-1} in a pyrrolidine hydrochloride mull. The absence of this band, however, cannot be taken as proof that I does not have a pyrrolidinium ion because of the differences in environment between I in solution (ion pairs, etc., see below) and that in the pyrrolidinium chloride mull. Nevertheless, these spectra of I can be said to demonstrate that there is at least one proton on nitrogen in this compound, and that they (it) seem(s) to be in a positively charged environment.

Species I is isolable as a white to pale-yellow solid in the pyrrolidine case, and this solid is moderately stable at room temperature for a few days in absence of air and light. Beer's law analysis[6] confirms that this compound has the formula $Fe(CO)_5(C_4H_9N)_2$, as shown by Hieber.[7] The properties of this solid were studied in some detail in connection with the question of the nature of I and position of the proton.

As the solid I has a substantial vapor pressure at room temperature, a spectrum was taken in the gas phase. This spectrum showed the bands of unmodified $Fe(CO)_5$ and amine, as was asserted by Hieber.[7] Thus, although the solution and solid-state spectra are identical,[3] and both show considerable modification of the

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[4] That this, in fact, is often found experimentally is documented by D. K. Huggins and H. D. Kaesz, *Progr. Solid State Chem.*, **1**, 444 (1964), and others.

[5] W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, **94**, 862 (1961); Professor R. Pearson, private communications.

[6] The authors wish to thank Dr. M. T. Yang for kindly making these measurements.

[7] W. Hieber and N. Kahlen, *Chem. Ber.*, **91**, 2223 (1958).

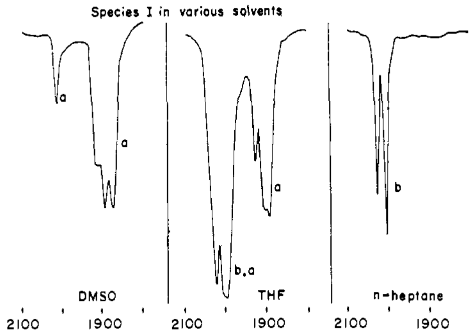

Figure 3. Infrared spectra of solid species I (pyrrolidine) in various solvents, 5-μ region; a, bands due to species I; b, bands due to $Fe(CO)_5$.

amine and metal carbonyl moieties, in the gas phase the compound comes apart into the reactants.

Although solid species I is soluble in both polar and nonpolar solvents, infrared spectra showed that in the pyrrolidine case, as for the piperidine case reported earlier,[3] I is completely dissociated in normal heptane to $Fe(CO)_5$ and amine. However, unlike the piperidine case, no spectroscopically detectable amount of $Fe(CO)_5$ was found in pyrrolidine solutions of I. Furthermore, it was found that as the polarity of solvents in which solid I was dissolved was increased, the equilibrium between reactants ($Fe(CO)_5$ and pyrrolidine) and products (species I) was driven further to the product side. This is strikingly shown in Figure 3. Thus in DMSO only species I was observed in solution, no free $Fe(CO)_5$ was found. In THF, of intermediate polarity, both unreacted $Fe(CO)_5$ and species I were found to exist in equilibrium. It is felt that this experiment bears heavily on the nature of species I, pointing up its ionic character in a rather unique way.

In investigating the possible ionicity of species I, two lines of conductance measurements have been pursued. The first of these is the conductance *vs.* time behavior of species I solutions which are reacting to form species III. This behavior, in the pyrrolidine case, paralleled that for piperidine[3] in that the conductance was constant when only I was present and a decrease occurred as III formed in the reaction mixture. The actual values of the molar conductance in pyrrolidine solutions is considerably higher than that for piperidine, however. It is found, for example, that a 0.08 *M* solution of $Fe(CO)_5$ in pyrrolidine shows a molar conductance of 1.45 mho cm^2/mole whereas a solution of $Fe(CO)_5$ in piperidine of the same concentration showed a molar conductance of only 0.025 mho cm^2/mole. The decrease in conductance accompanying the formation of III (from 2.42 to 0.59 mho cm^2/mole for 0.118 *M* $Fe(CO)_5$ in pyrrolidine at 60°) is strong evidence for the presence of ions when species I is dissolved in an amine, despite the fact that the actual molar conductances are low. Indeed, it was these low molar conductance values which led to an investigation of the concentration behavior of the conductance. A typical result of these studies is shown for pyrrolidine in Figure 4. Similar results are obtained when the amine is piperidine. This is the characteristic curve which Fouss[8] has shown to be due to ion association to pairs and triple ions. It is observed with salts in solvents of dielectric constant less than 10; indeed we have found that piperidine and pyrrolidine have dielectric constants of 5.9 and 6.3, respectively.

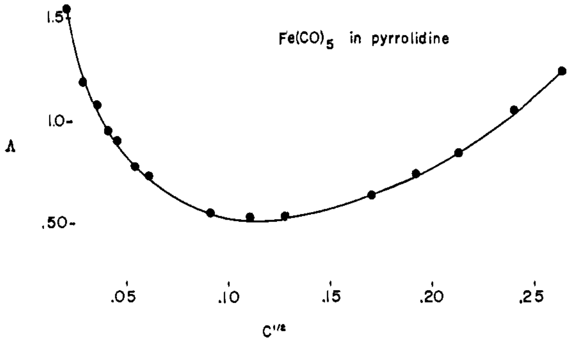

Figure 4. Molar conductance *vs.* (concentration)$^{1/2}$; $Fe(CO)_5$ in pyrrolidine.

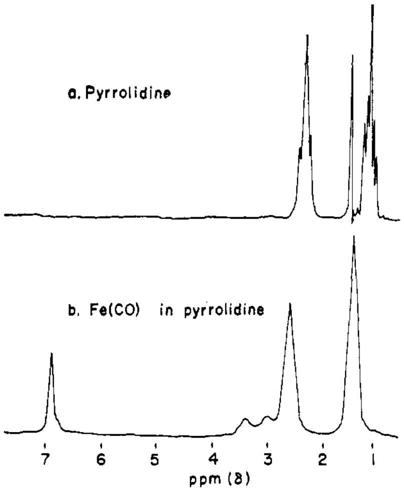

Figure 5. Nmr spectrum of pyrrolidine, a; nmr spectrum of $Fe(CO)_5$ in pyrrolidine, b.

Nuclear magnetic resonance spectra of I in DMSO and of concentrated solutions of $Fe(CO)_5$ in pyrrolidine show essentially the same spectrum, Figure 5b. The region of hydrogen on iron resonances (10–25 ppm upfield from tetramethylsilane) was searched thoroughly in solutions of I, but no line was found. It was therefore concluded that this could not be the position of the proton.

The nmr spectrum of pyrrolidine (Figure 5a) shows three sets of peaks, centered at δ values of 1.2, 1.8, and 2.5 ppm and with intensity ratios of 4:1:4, respectively. The peak at 1.8 can therefore be readily assigned to the proton on nitrogen in the amine, and Gutowsky, *et al.*,[9] have shown that the resonance at 2.5 ppm is assignable to the α protons and that at 1.2 ppm to the β protons.

The striking change observed in comparing the nmr spectrum of pyrrolidine with the nmr spectrum of solutions of species I (Figure 5b) is the shift of more than 5 ppm downfield of the N–H proton from its position in free pyrrolidine. Its intensity relationship to the

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[8] R. M. Fouss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 18.

[9] H. S. Gutowsky, R. L. Rutledge, M. Tamres, and S. Searles, *J. Am. Chem. Soc.*, 76, 4242 (1954).

other two sets of resonances (1:4:4) remained constant, however. This shift must mean that there has been substantial deshielding of the proton on the nitrogen atom, or it has moved to a different site, which is similarly electron deficient. We can understand this draining off of charge from the nitrogen atom when we recall that the infrared evidence indicated a substantial gain in negative charge on the metal carbonyl moiety in I. The fact that a single peak was observed for this proton means that despite the 2:1 ratio of amine to metal carbonyl in pyrrolidine species I, the protons are equivalent, or that some rapid exchange phenomenon is taking place in solution.

The resonance of the protons α to the nitrogen atom is virtually unshifted in position in spectra of I. However it is split into several components. Two reasonable interpretations exist for this observation, and both of them may be true simultaneously. First, the structure of I in solution may be such as to make these protons nonequivalent with respect to the nmr spectrum. Second, we may have two slightly different types of pyrrolidine molecules present in I, which have somewhat different environments about the protons. In the case of the N–H proton resonance, this would be washed out by exchange, but in the case of the α protons, it may be precisely what we are seeing here. No change in the resonance due to the protons β to the nitrogen atom in the pyrrolidine ring was observed, and it seems unlikely that any complex would affect this resonance substantially.

Once again, the ionic nature of I is driven home by the nmr experiments. It can be seen that the charge which infrared data showed to be transferred to the metal carbonyl moiety has come from the nitrogen atom. This was already tentatively indicated by the infrared spectra of concentrated solutions of I in pyrrolidine.

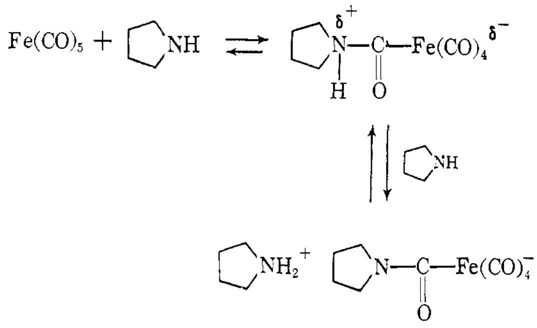
It is useful to point out some of the differences which exist between species I in piperidine and pyrrolidine. In considering these differences, one should note that these amines have virtually the same base strengths, dielectric constants, CNC angles, and compositions, differing only by the presence of one additional methylene group. Yet piperidine appears in species I at a 3:1 ratio of amine to $Fe(CO)_5$, whereas the ratio of pyrrolidine to $Fe(CO)_5$ in I is 2:1. The conductances of both piperidine and pyrrolidine solutions show the same sort of time, temperature, and concentration dependencies, however the absolute values of the molar conductances are nearly 100 times greater in pyrrolidine than in piperidine. Despite these differences, the overall reaction product, species I, appears to be the same type compound in both cases. Just what the explanation is for these differences between amines must await the result of current work in this laboratory concerned with the specific effects of varying properties of the amines on the reaction products.

What then, is our current picture of species I? Infrared structural evidence shows that it has four metal carbonyl CO groups, arranged in the trigonal bipyramidal configuration about an iron atom, with one axial position in the structure occupied by a ligand. This ligand, according to present chemical and spectroscopic evidence, is an amide linkage, >NCO–. This means that species I is a compound in which the amine has come in and attacked the electron-deficient carbon atom of the metal carbonyl in agreement with calculations[10] which show that the C atoms are the most electron-deficient atoms in metal carbonyls.

How can such an attack take place? It may be pictured as being either direct or indirect. In the latter case, the amine first attacks the iron atom, then undergoes a rearrangement in which the amine migrates to a carbon site to yield the amide-substituted metal carbonyl. Previous workers[11,12] have cited evidence for a solvent-assisted migration of the methyl group of $CH_3Mn(CO)_5$ in the presence of other ligands to give $CH_3COMn(CO)_4L$. In the case of species I, we may thus have a case where the first intermediate, $Fe(CO)_5$-(amine), is not observed, but rearranges to form the CO-inserted product. We thereby have the interesting case where the migrating group and the solvent assisting the migration are the same.

The position of the proton on the amine ligand is perhaps best viewed, according to the available evidence, as being in mobile equilibrium in solution between the ligand amine nitrogen and the nitrogen atom of another amine molecule, though we should expect that it would spend most of its time on the nitrogen of the amine which is not bonded to the carbonyl. In solid species I this proton might be forming a bridge between the two nitrogens.

This portion of the reaction picture is summarized in the following scheme.



Thus, the data reported here put the more tentative proposals of the earlier paper[3] regarding the nature of species I on a firmer basis.

Experimental Section

Chemicals. The $Fe(CO)_5$ used was a product of Antara Chemicals and was specified as better than 99.5% $Fe(CO)_5$. Impurities in this reagent have been found to be negligible,[13] and it was used without further purification. Purified or reagent grade piperidine and pyrrolidine were used. They were purified according to the method described in detail earlier.[3] THF and *n*-heptane were distilled from CaH_2 in a current of nitrogen. DMSO was freshly distilled from molecular sieves immediately prior to use in experiments, as it is very hygroscopic. All preparations and handing of iron carbonyl compounds were carried out with the rigorous exclusion of air and moisture. Samples were protected from light during storage.

Spectra. Infrared spectra were taken with the Perkin-Elmer Model 421 dual grating spectrophotometer, calibrated in the 5-μ region with DCl gas. Demountable KBr cells were used, or varying thickness, except that very concentrated solutions of Nujol mulls were taken as thin films between KBr plates.

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[10] W. C. Nieuwpoort, D.Sc. Thesis, University of Amsterdam, 1964.

[11] T. H. Coffield, R. D. Closson, and J. Kozikowski, *J. Org. Chem.*, 22, 598 (1957).

[12] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964).

[13] R. Summitt, Ph.D. Thesis, Purdue University, 1961.

Nmr spectra were obtained on the Varian A-60 nmr spectrometer, except for the high-field measurements which were made on the Varian HR-56.4, nmr spectrometer. Nmr tubes were sealed under N_2 to prevent contamination from air and moisture.

Spectrum of $Fe(CO)_5$ in Pyrrolidine (5-μ Region). $Fe(CO)_5$ (0.2 ml) was added to 10 ml of pyrrolidine and a spectrum taken within 2 min after mixing in a 0.015-mm cell. The results are shown in Figure 1.

Concentrated Solutions of $Fe(CO)_5$ and Pyrrolidine. $Fe(CO)_5$ (1.0 ml) was mixed with 3.0 ml of pyrrolidine and spectra taken between KBr plates within 2 min after mixing. An intense N–H stretching mode distinct from that of free pyrrolidine was found in these spectra (Figure 2). Nmr spectra were also obtained from these solutions, with the results shown in Figure 5.

Hydrolysis of Species I. Pyrrolidine Case. To a solution of 0.2 ml of $Fe(CO)_5$ in pyrrolidine was added 0.5 ml of water. The bands of $HFe(CO)_4^-$ appeared in the infrared spectrum of this solution within 5 min after addition of the water. Pyrrolidine carbamate was prepared by bubbling CO_2 through a solution of pyrrolidine and water in ether according to the method of Faurholt, *et al.*[14] It was possible to identify the infrared bands of the carbamate with those in solutions of species II described above, paralleling the identification in the piperidine case.[3] No attempt was made to isolate pyrrolidine carbamate from solutions of II.

Preparation and Stoichiometry of Solid Species I. Pyrrolidine Case. Pyrrolidine (10 ml) was frozen at liquid nitrogen temperatures in a tube sealed with a serum stopple. $Fe(CO)_5$ (3 ml) was added to the tube and frozen in another layer above the amine. The tube was then allowed to warm slowly to room temperature. As melting occurred, crystals formed in the tube, first at the interface, then throughout the sample. After about 1 hr the sample was almost completely crystalline, with only a small amount of excess liquid remaining. The reaction product was filtered under N_2. Although samples of the pale yellow-white crystals were stored in sealed tubes under N_2 and protected from light, after about 24 hr discoloration indicative of decomposition began to be apparent. The crystals could be easily purified immediately prior to use by vacuum sublimation. The stoichiometry of this solid was determined spectrophotometrically, making use of the fact that it dissociates completely to $Fe(CO)_5$ and pyrrolidine when dissolved in an inert solvent such as cyclohexane. The amounts of these two components in the compound were determined by comparing the intensities of the 1960-cm^{-1} band of $Fe(CO)_5$ and the 784-cm^{-1} band of pyrrolidine in a cyclohexane solution of the compound with those of solutions containing known amounts of the individual reagents in the same solvent. The molar ratio of pyrrolidine to $Fe(CO)_5$ in I was thus determined to be 2.2:1.[6]

Spectra of Solid I in Various Solvents. Solid I (0.2 g) was dissolved in 1 ml of *n*-heptane, in THF, and in DMSO. The spectrum of the *n*-heptane solution showed only the bands of $Fe(CO)_5$ in the 5-μ region, in THF the bands of I and of free $Fe(CO)_5$ were present, and in DMSO only the bands of I could be seen in the 5-μ region (see Figure 3).

Conductance Measurements. The conductance measurements were carried out using the instrument described in ref 3. To measure the concentration dependence of the conductance, 18 ml of pyrrolidine was placed in the cell, which had been previously flushed with N_2 and sealed with serum stopples. $Fe(CO)_5$ was added in small portions using Hamilton microliter syringes. In a typical pyrrolidine experiment (Figure 3) the amount of $Fe(CO)_5$ was increased from 0.001 to 0.20 ml.

Dielectric Constant of Pyrrolidine. The dielectric constant of pyrrolidine was measured using a Model DM01 Dipolmeter manufactured by the Kahl Scientific Instrument Co.[15] An MFL 1 cell was used, and gave a cell reading of 2702.6, which corresponded to a dielectric constant of 6.34.

Preparation of Pyrrolidine Hydrochloride. Pyrrolidine hydrochloride was prepared by slowly adding 12 *M* HCl to an aqueous solution of pyrrolidine in water. The water was then removed under vacuum, yielding the white, crystalline, hydroscopic amine hydrochloride.

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[14] C. Faurholt and A. Jensen, *Acta Chem. Scand.*, **6**, 1073 (1952).

[15] We thank Dr. M. Cefola for the use of this instrument.

Molecular Asymmetry in the Coordination of Olefins to Transition Metals. IV. *cis*-Dichloro(olefin)(amine)platinum(II) Complexes

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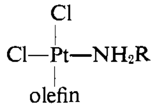
Contribution from the Istituto Chimico, Università di Napoli, Sez. VII del Centro Nazionale di Chimica Macromolecolare del CNR, Naples, Italy.

Received May 20, 1966

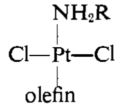
Abstract: Studies were extended on the molecular asymmetry that arises from the coordination of an olefin possessing symmetry differing from C_{2v} or D_{2h} to a transition metal. The stereochemical behavior of the Pt(II) complexes with an asymmetric amine *cis* coordinated to the olefinic ligand was examined. In this paper polarimetric behavior, preparation, and characterization are reported for complexes of this type with the olefins ethylene, propene, *cis-* and *trans*-butene, *t*-butylethylene, styrene, ethyl α-chloroacrylate, *trans*-3-hexene, *trans*-1,4-dichloro-2-butene, and *trans*-cyclooctene.

Continuing our investigations concerning the molecular asymmetry of the complexes of the transition metals with olefins possessing symmetry differing from C_{2v} or D_{2h},[1] we have studied the diastereoisomeric compounds *cis*-dichloro(olefin)-(*S*)-(α-phenethylamine)platinum(II) (I). Some preliminary data concerning these compounds has already been reported in previous brief communications.[2] For *cis* compounds, we observed a notable departure from the unity value of the



$$\begin{array}{c} \text{Cl} \\ | \\ \text{Cl—Pt—NH}_2\text{R} \\ | \\ \text{olefin} \end{array}$$

I



$$\begin{array}{c} \text{NH}_2\text{R} \\ | \\ \text{Cl—Pt—Cl} \\ | \\ \text{olefin} \end{array}$$

II

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[1] (a) G. Paiaro, P. Corradini, R. Palumbo, and A. Panunzi, *Makromol. Chem.*, 71, 184 (1964); (b) G. Paiaro and A. Panunzi, *J. Am. Chem. Soc.*, **86**, 5148 (1964).

[2] (a) G. Paiaro and A. Panunzi, *Tetrahedron Letters*, **8**, 4411 (1965): (b) P. Corradini, S. F. Mason, G. Paiaro, A. Panunzi, and G. H. Searle, *J. Am. Chem. Soc.*, **88**, 2863 (1966).