n-butyllithium-tetravinyltin reaction in pentane, in this solvent. The results are shown in Table II. The tetraphenyltin noted in the last column is that produced in the PhLi-Vi₄Sn reaction.

Table II

STABILITY OF VINY	LLITHIUM	IN ETHER SOL	VENTS
Time	Solvent	Yield (%) of (C4H9): SnCH=CH2	Yield (%) of (C6H6)4Sn
0	Et_2O	65	75
6 min.	Et_2O	65	75
30 min.	Et ₂ O	74	97
2 hr.	Et ₂ O	73	
17 hr.	Et_2O	72	
7 days	Et ₂ O	65	
10 min.	THF	68	
22 hr.	THF	63	
7 days	THF	65	
2.5 hr. (at 65°)	THF	61	

^a Time elapsed between formation of CH₂==CHLi and its reaction with tri-*n*-butyltin chloride.

Attempted Preparation of Vinyllithium in Tetrahydrofuran.—To 22.6 g. (0.06 mole) of triphenylvinyltin in tetrahydrofuran was added 75 ml. of 0.8 M phenyllithium in tetrahydrofuran (0.06 mole). The latter solution was prepared using the method of Gilman and Gaj¹¹ by the reaction of bromobenzene with lithium wire at -60° . The dark red mixture was stirred for two hr. at room temperature; some solid precipitated during this time. Tri-*n*-butyltin chloride (18.5 g., 0.057 mole) was added, and the mixture was stirred for 5 hr. and then hydrolyzed with 5% HCl. Tetraphenyltin (8 g., m.p. 223-225°) was filtered, and the organic layer of the filtrate was distilled to remove solvent. Ether was added to the residue, and the solution was shaken with 35 g. of potassium hydroxide in 150 ml. of water. The ether layer was separated, the solvent removed and an additional 1.5 g. of tetraphenyltin was filtered (total yield 39%). Distillation of the filtrate gave no tri-*n*-butylvinyltin. Crude tri-*n*-butylphenyltin was distilled between 115–130° (0.25–0.45 mm.). This was redistilled to give 6.8 g. (33%) of tri-*n*-butylphenyltin, b.p. 116–118° (0.25 mm.), n^{20} D 1.5169; lit.¹⁹ b.p. 139°(0.6 mm.), n^{20} D 1.5155. The residue was distilled to obtain any higher boiling products, but only decomposition resulted.

Reaction of Vinyllithium with Tetraphenyltin in Tetrahydrofuran.—Solid vinyllithium was prepared by adding 0.1 mole of *n*-butyllithium in pentane to 0.05 mole of tetravinyltin and was dissolved in tetrahydrofuran. Tetraphenyltin (21.3 g., 0.05 mole) was dissolved in 500 ml. of hot tetrahydrofuran, and this solution was cooled to room temperature. A large amount of tetraphenyltin precipitated on cooling. To this mixture was added 100 ml. of the yellow vinyllithium solution (determined to be 0.5 *M*) in tetrahydrofuran. The precipitated tetraphenyltin immediately dissolved. After 10 min., the color of the solution changed to red, the color characteristic of phenyllithium in tetrahydrofuran. Addition of 150 ml. of water caused precipitation of 9 g. of tetraphenyltin, m.p. 223-223, which was filtered off. Separation of the organic layer and removal of the solvent gave another 1.3 g. of tetraphenyltin (total recovery 49%). Attempted distillation of the liquid residue was not successful.

In another experiment, 17.3 g. of tetraphenyltin was dissolved in 600 ml. of hot tetrahydrofuran (the total volume of solvent present in the previous experiment), and on cooling to room temperature, 6.7 g. precipitated. Thus the solubility of tetraphenyltin in dry tetrahydrofuran is ca. 10.5g. in 600 ml. at room temperature. This supports the beliet that in the previous experiment vinyllithium and tetraphenyltin had reacted in an as yet unknown manner.

Acknowledgments.—The authors are grateful for support of this work by the Chemistry Branch, Office of Naval Research (1957–1958), and by the National Science Foundation (1959–1960) through Grant G 7325. M.A.W. is indebted to the National Institutes of Health for a Predoctoral Fellowship.

(19) H. Gilman and S. D. Rosenberg, J. Am. Chem. Soc., 75 2507 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF IOWA, IOWA CITY, IOWA]

Studies on the Chemistry of Halogens and of Polyhalides. XXI. Halogen Complexes of 4,4'-Bipyridine and the Infrared Spectra of Pyridine Complexes

BY ALEXANDER I. POPOV,¹ JOHN C. MARSHALL, FRANCIS B. STUTE AND WILLIS B. PERSON Received February 4, 1961

The preparation of solid 1:2 addition compounds of 4,4'-bipyridine with iodine halides is described. These compounds, in contrast with the analogous 2,2'-bipyridine complexes, are insoluble in common organic solvents, polar as well as non-polar. This precludes the possibility of studying them in solutions. Since unipositive iodine can have a coördination number of two, the properties of these complexes may indicate that these are linear polymers of the type ... BP-I⁺-BP-I⁺-BP-I⁺... with an equivalent number of IX_2^- ions attached electrostatically to the chain. Infrared spectra of these complexes as well as those of pyridine and 2,2'-bipyridine with iodine monochloride and with silver ion were observed in the 300-4000 cm.⁻¹ spectral region. In view of the complexity of these spectra only qualitative comparisons are given.

Introduction

While numerous halogen complexes of simple heterocyclic amines have been studied in the past, very little attention has been paid to the complexes of polynuclear heterocycles. A recent study of the 2,2'-bipyridine-iodine halide complexes gave some indications that the positive iodine may be coordinated to two nitrogen atoms of the bipyridine with the molecule being arraigned in the *cis* configuration.² Since such an arrangement is obvi-

(2) A. I. Popov and R. T. Pflaum, J. Am. Chem. Soc., 79, 570 (1957).

ously impossible in the case of 4,4'-bipyridine, it was of interest to study the properties of the corresponding halogen complexes. A comparison was made between infrared spectra of the halogen and of the silver complexes.

References to complexes of 4,4'-bipyridine are not plentiful in the literature. The two most pertinent reports describe the formation of complexes with arsenic tribromide³ and silver nitrate.⁴ In both cases evidence is cited indicating that the two addition compounds are polymeric, with a

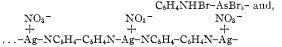
⁽¹⁾ Department of Chemistry. Northern Illinois University. DeKalb, Illinois.

⁽³⁾ P. Popov, Zhur. Obshchei Khimii. 19, 47 (1947).

⁽⁴⁾ W. J. Peard and R. T. Pflaum, J. Am. Chem. Soc., 80, 1593 (1958).

possible structure being

 \dots BrHNC₅H₅-C₅H₄NHBr-AsBr₃-BrHNC₆H₄-



It seemed interesting to compare the properties of the halogen and the silver pyridine complexes, and consequently, a number of silver complexes was prepared and studied.

Experimental Part

Eastman Kodak spectrograde pyridine was used without further purification since the infrared spectra showed the absence of picolines which are the most likely contaminants. The 2,2'-bipyridine was obtained from G. F. Smith Chemical Co. and purified as described earlier.² The preparation of iodine monochloride, of pyridine–ICl complex and of 2,2'bipyridine-2ICl complex has likewise been described in earlier publications.^{2,5}

Reagents.—The 4,4'-bipyridine was prepared by treating pyridine with acetic anhydride in the presence of zinc, then deacetylating, as was described by Dimroth and co-workers.⁶ It was found that the heating period prior to the removal of zinc and zinc acetate in the first step of the synthesis is quite critical and essentially no product was obtained when the mixture was heated for 1 hr. as recommended.⁶ When the heating time was cut down to 20–25 min., a 15% yield of 4,4'-bipyridine was obtained as the end result. The product was purified by recrystallization from slightly basic aqueous solutions and dried at 75°. The white needle-like crystals melted sharply at 111.8– 112.0° which is identical to the literature value. Elemental analysis gave 76.78% C, and 5.10% H, calcd., 76.90% C and 5.15% H.

Iodine monochloride and iodine bromide were prepared by previously outlined techniques.⁷ All other chemicals were of reagent grade quality.

Halogen Complexes of 4,4'-Bipyridine.—Iodine monochloride complex of 4,4'-Bipyridine was prepared by slowly mixing equimolar solutions of the two components in carbon tetrachloride. The procedure is similar to that used for the preparation of the 2,2'-bipyridine complex.² The addition compound was obtained in the form of yellow powder which subsequently was filtered and washed. Because of its insolubility in ordinary solvents (see below), it could not be recrystallized. The yield was quantitative. The compound does not show a definite melting point but starts to decompose at ~230°. It dissolves with decomposition in aqueous hydrochloric acid. Analysis gave 24.86% C, 1.86% H, iodometric equivalent 120.1, calcd. for BP-2ICl, 24.97% C, 1.68% H, iodometric equivalent 120.2. Total halogen was determined by fusing the substance in a Parr bomb and precipitating halide ions with silver. Total halogen found, 67.53%; calcd. 67.76%.

21Cl, 24.97% C, 1.68% H, iodometric equivalent 120.2. Total halogen was determined by fusing the substance in a Parr bomb and precipitating halide ions with silver. Total halogen found, 67.53%; calcd. 67.76%. The analogous 4,4'-bipyridine-2IBr complex was prepared in a similar manner. It was obtained in the form of an orange-yellow powder which melted with decomposition at 260-265°. Analysis gave 21.34% C, 1.33% H, 72.67% total halogen and iodometric equivalent of 143.4, calcd. for BP-2IBr, 21.08% C, 1.42% H, 72.59% total halogen and iodometric equivalent of 142.5. The yield was of the order of 98%.

This compound is very similar in properties to the ICl analog. It is stable in air, does not undergo hydrolysis with atmospheric moisture and is insoluble in water and in common organic solvents.

If the reaction of iodine monochloride with 4,4'-bipyridine is carried out in chloroform acidified with hydrochloric acid, the reaction product which precipitates out as yellow micro-crystalline powder is not BP·2ICl but BP·2HICl₂. The analysis gave 22.25% C, 1.90% H, 71.34% halogen and iodometric equivalent of 139.2; calcd. 21.66% C, 1.44% H, 71.48% halogen, iodometric equivalent of 138.0. The

(6) O. Dimroth and R. Heene, Ber., 54, 2937 (1921); O. Dimroth and F. Frister, *ibid.*, 55, 3963 (1922).

(7) A. I. Popov, D. H. Geske and N. C. Baenziger, *J. Am. Chem. Soc.*, **78**, 1793 (1956); A. I. Popov and W. A. Deskin, *ibid.*, **80**, 2976 (1958).

complex melted with decomposition at $191-194^{\circ}$. Attempts were made to prepare BP·2HIBr₂, BP·2I₂ and BP·2Br₂ complexes by the same technique. Yellow-orange precipitates were obtained, but in all cases the analysis showed that the amount of halogen was 5-10% lower than the theoretical amount. It is quite possible, however, that these compounds can be prepared in reasonable states of purity by some modification of the experimental technique. This work will be continued.

work will be continued. **Pyridine-Silver Nitrate Complex.**—This was prepared by the addition of 2 g. of reagent grade silver nitrate to 10 ml. of spectro-grade pyridine. After the dissolution of the silver salt, 40 ml. of acetonitrile was added and the resulting mixture was evaporated to dryness under reduced pressure at room temperature. The residue, in the form of white micro-crystalline powder, was recrystallized three times from water and air-dried. The m.p. was 80-84° as compared with the literature value of 87°⁸ and 79-84°.⁶ **2.2'**-Bipyridinosilver(I) Nitrate.—About 0.5 g. of 2.2'bipyridine was dissolved in 50 ml. of hot absolute alcohol and mixed with 50 ml of hot saturated solution of cilver

2.2'-Bipyridinosilver(I) Nitrate.—About 0.5 g. of 2.2'bipyridine was dissolved in 50 ml. of hot absolute alcohol and mixed with 50 ml. of hot saturated solution of silver nitrate in the same solvent. The solution was allowed to cool slowly to room temperature and white needles of 2,2'bipyridinosilver(I) nitrate separated out. This compound is quite unstable especially in the presence of moisture but it can be carefully recrystallized from absolute alcohol. The crystals begin to decompose at around 120° and form the "bis" compound. Analysis gave 35.56% C, 2.31% H, and 12.64% N. Calcd.36.84% C, 2.65% H and 12.89% N. It is interesting to note that although a 1:1 compound of pyridine with silver nitrate previously has been identified in solution,⁹ it has not been prepared in the solid state.

field in solution,⁹ it has not been prepared in the solid state. Bis-2,2'-bipyridinosilver(I) Nitrate.—A simple way of preparing this compound seems to be by the recrystallization from water-alcohol mixture of the 1:1 compound described above. The product, in the form of light yellow crystals, had a m.p. of 136-137° which compared favorably with the literature value of 135°.

4,4'-Bipyridinosilver(I) Nitrate.—This compound was prepared as described in the literature, but it was found that the reaction in acetonitrile solutions gave a purer product than the reaction in alcohol. The product was recrystallized from water. The m.p. was above 300°. Analysis gave 37.03% C, 2.65% H and 13.07% N. Calcd. 36.83% C, 2.47% H and 12.89% N.

Spectral Measurements.—Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrometer in the sodium chloride region and with a modified Perkin-Elmer Model 12c spectrometer, used in double pass, in the potassium bromide and cesium bromide regions.

The spectrum of pyridine was obtained with a thin liquid sample between KBr or CsBr windows and the spectra of 2,2'-bipyridine and 4,4'-bipyridine were in KBr or CsBr pellets. The question of sampling the other compounds was somewhat more complicated. The Py-ICI, 2,2'-BP·2ICl, $(2,2'-BP)_2AgNO_3$ and $2,2'-BP\cdotAgNO_3$ complexes in KBr pellets decomposed in the pellet press and had to be dispersed in Nujol; PyAgNO₃ was quite unstable either in pellets or in Nujol mulls between alkali halide windows, and its spectrum was obtained by placing the Nujol mull between silver chloride or polyethylene windows. It is interesting to note that the silver and the iodine monochloride complexes of 4,4'-bipyridine were found to be stable in KBr pellets and gave good spectra.

The instability of these complexes in KBr pellets does not seem to have been considered in the earlier studies of the infrared spectra of pyridine complexes.^{4,10} It appears that this effect is especially important in the study of the 2,2'-bipyridine complex with silver; this explains the difference between the spectra obtained in this study for this compound and that in the literature.⁴

Results and Discussion

Halogen complexes of 4,4'-bipyridine were found to be insoluble in water and in all common organic solvents, both polar and non-polar. They did dissolve to a slight extent in dimethylformamide but

(9) K. Sone, P. Krumholz and M. Stammreich, J. Am. Chem. Soc., 77, 777 (1955).

⁽⁵⁾ A. I. Popov and R. H. Rygg, J. Am. Chem. Soc., 79, 4622 (1957).

⁽⁸⁾ S. M. Jorgensen, J. prakt. Chem., 33, 501 (1886).

this dissolution was accompanied by decomposition. Consequently, solution spectra of these compounds in the ultraviolet-visible spectral regions could not be obtained, nor could any other convenient physico-chemical studies be made in order to elucidate their structures. In view of the fact that it was impossible to recrystallize the powder obtained in their preparations, suitable crystals could not be obtained for the single crystal X-ray work on the structure of the solids.

It seems that this insolubility can be an indication of the polymeric structure of these complexes. By analogy with the arsenic tribromide-4,4'-bipyridine complex one may write the following structure for the iodine monochloride complex

$$\begin{array}{c} \operatorname{ICl}_2^- & \operatorname{ICl}_2^- & \operatorname{ICl}_2^- \\ + & & - \\ \operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \end{array} \right) \xrightarrow{+} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{I} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \cdots \operatorname{N} \right) \xrightarrow{-} \\ \left(\operatorname{N} \cdots \operatorname{N$$

It should be remembered that compounds where positive iodine has a coördination number of two are well known in the literature. Some of the examples are $(C_5H_5N)_2INO_3$, $(C_5H_5N)_2IClO_4$, etc.¹¹

If the 4,4'-bipyridine-2ICl complex is polymeric, one would expect it to be somewhat less prone to decomposition than the monomer. In this respect, we have seen that the above complex melts with decomposition starting at 230° while the melting point of 2,2'-BP-2ICl complex is 139° and is sharp and reversible; also the Py-ICl and 2,2'-BP-2ICl complexes are decomposed in the KBr pellet press, while the 4,4'-BP-2ICl gave excellent pellets, indicating a higher stability for the latter compound.

Discussion of the Infrared Spectra

The infrared studies were undertaken in the hope that they might yield some information about the structure of the complexes, particularly that of the 4,4'-bipyridine–ICl complex. Infrared spectra of pyridine, 2,2'-bipyridine and 4,4'-bipyridine were obtained in the region from 300 to 4000 cm.⁻¹. These were compared with the spectra of the complexes with iodine monochloride and with silver ion in the same spectral range. The comparisons showed the usual remarkable changes in the appearance of the spectra of pyridines which would be expected from the earlier studies in pyridine complexes.^{10,12-14}

The objective of this study was to find which bands changed the most in the spectrum of the amine when complexing occurred and then to use the accepted assignment for pyridine¹⁵ in order to understand why these should be particularly sensitive. In order to do this, it was necessary to assign the strong infrared absorptions in the spectrum of the two bipyridines, since this had not been done before. This was not particularly difficult since it was not expected that the major features of the

(11) H. Carlsohn, "Uber eine neue Klasse von Verbindungen des positiv einwertigen Jods," Verlag von S. Hirzel, Leipzig, 1932.

(12) N. S. Ham, A. Rees and A. Walsh, Nature, 169, 110 (1952).

(13) D. L. Glusker, H. W. Thompson and R. S. Mulliken, J. Chem. Phys., 21, 1407 (1953).

(14) D. L. Glusker and H. W. Thompson, J. Chem. Soc., 471 (1955).
(15) L. Corrsin, B. J. Fax and R. C. Lord, J. Chem. Phys., 21, 1170 (1953).
See, however, J. P. McCullough, D. R. Doustin, J. F. Messerly, I. A. Hossenlopp, T. C. Kincheloe and G. Waddington, J. Am. Chem. Soc., 79, 4289 (1957).

spectrum of a bipyridine would be particularly different from pyridine itself.¹⁶ The assignment is summarized in Table I. The notation follows that of Corrsin, Fax and Lord.¹⁵ The assignment of ν_{8a} to the strong band at 1610 cm.⁻¹ is different from that of Corrsin, Fax and Lord.¹⁶ We believe the persistence of the band at 1610 cm.⁻¹ in the complexes is more likely to be characteristic of a fundamental than of a combination band.

	TABLE	c I	
VIBRATIONAL ASS	IGNMENTS OF	Pyridine,	2,2'-BIPYRIDINE
	AND 4,4'-BI	YRIDINE	
Freq. no.	Pyridine	2,2'-bip	4,4'-bip
2, 7a, 7b, 13	3050(s)	3070(s)	3050(s)
8a	1610(s)	1589(vs)	1600(vs)
8b	1589(vs)	1582(s)	1 54 0(s)
19a	1490(s)	1458(vs)	1492(s)
19Ъ	1447(v s)	1420(s)	1412(vs)
3	1220(w)	1250(s)	1222(s)
15	1149(w)	1140(w)	1131(w)
		10 90(s)	1102(w)
18a,b	1070(s)	1085(s)	1078(s)
12	1033(s)	1040(s)	1042(w)
1	993(s)	992(w)	994(s)
			98 2(w)
			9 65(w)
10a	885(vw)	896(w)	882(w)
			852(w)
			748(w)
10b	749(vs)	742(w)	735(s)
11	704(vs)	756(vs)	808(vs)

 6a	605(s)	619(s)	605(s)
0a	000(0)	010(0)	569(w)
			494(w)
1 6 b	404(s)	402(s)	374(s)
1		. 1 41 - 1 -	

The next step was to study the changes in spectra as the complexes were formed. These changes in appearance proved to be extremely complicated, and it was not possible to reach many general conclusions about structure from them. This situation certainly was to be expected for the bipyridine complexes, since so little is understood about the changes in pyridine itself.

Pyridine Complexes.—In order to try to visualize these changes in pyridine spectra, we have resorted to the simplified 'line drawing'' method of presentation shown in Fig. 1. Unpublished studies on pyridine-platinum complexes prepared by Prof. J. R. Doyle of this Laboratory are included for comparison.¹⁷ While this method of presenting data may be somewhat of an oversimplification, it does permit us to draw some tentative conclusions regarding spectral changes for pyridine complexes. These spectra as well as those illustrated in Figs. 2a and 2b, do not include bands attributed to Nujol, nitrate or iodine monochloride.

In the first place there is apparently a remarkable consistency in *frequency* for most of the vibrations in pyridine. Thus, the bands in pyridine which can be followed (cf. ν_{8a} at 1610, ν_{19a} at 1490, ν_{19b}

(16) See R. N. Jones and C. Sandorfy, "Chemical Applications of Spectroscopy," Vol. IX, of "Technique of Organic Chemistry" (A. Weissberger, Ed.), Interscience Publishers, Ltd., New York, N. Y., 1956, Chapter 4.

 $(17)\,$ We are very grateful to Professor J. R. Doyle, for making these available to us in a private communication.

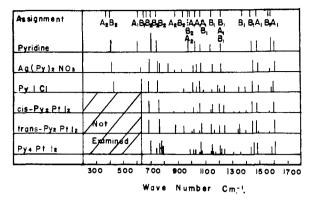


Fig. 1.—Line drawing representing the infrared spectra of pyridine and pyridine complexes. Line lengths are proportional to intensities. The assignment at the top is from Corrsin, Fax and Lord (ref. 15). Classes A_1 , B_1 and B_2 are infrared-active in pyridine. Bands due to Nujol, NO₃⁻ and ICl are not shown.

at 1450, ν_{15} at 1150, $\nu_{18a,b}$ at 1070, ν_{10b} at 750, ν_{11} at 704, ν_{6a} at 605 and ν_{16b} at 404 cm.⁻¹) all show frequency shifts of less than 10%. This is what might be expected for these rather weak σ complexes involving the lone pair electrons of the nitrogen atom. The presence of the silver ion or of the iodine atom will disturb the frequencies appreciably only if the N-X force constant is large.

On the other hand there are regions of the spectrum which show considerable change. For example, the region around 1200 cm.⁻¹ shows some new bands appearing in the complexes, as does the region around 1000 cm.⁻¹ (whose complexities have been discussed by Zingaro and Tolberg¹⁰). However, we note that in both these regions the assignment provides for possible vibrations which are inactive in the pyridine itself. Thus, Corrsin, Fax and Lord¹⁵ assigned three vibrations to the region around 1220 cm.⁻¹ where only one absorption band is observed in pyridine. It is not surprising that this region of the spectrum might become more complicated upon formation of a strong complex. The same is true of the region around 1000 cm.⁻¹.

In conclusion, it seems that the major changes occurring in the spectrum of pyridine as it forms complexes are probably to be interpreted, for the most part, as changes in intensity alone. Small frequency shifts may occur, but these do not appear to exceed 10%. However, the redistribution of charge which results on complexing (*i.e.*, Py^+ , .-(ICl)⁻) is not symmetrical over the pyridine molecule. Thus, vibrations with no resulting dipole moment change in pyridine suddenly appear with rather large moment changes in pyridine complexes. This gives rise to the very great changes in the appearance of the spectrum. A more complete knowledge of the normal coördinates of the vibrations of the pyridine molecule might well enable us to learn something about how this positive charge is redistributed.

Bipyridine Complexes.—With this survey of the pyridine spectrum in mind, let us now consider the spectra of the bipyridines and their complexes. Figure 2a shows the same simplified line drawing

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4, 4'- Bipyridine		4		ւնս	1		1.]_	ь
Ag (4-8 Py) NOs	1	. 1.	الحا	11	1	1	i 1	

Fig. 2.—Line drawing representing the infrared spectra of (a) 2,2'-bipyridine and its complexes and (b) 4,4'-bipyridine and its complexes. Bands due to Nujol, NO, and I Clarenot shown.

for the 2,2'-bipyridine complexes used earlier to represent the spectra of the pyridine complexes. Figure 2b gives the representation of the spectra of the 4,4'-bipyridine complexes. Again we see many examples of the rather drastic changes in intensity, and rather small frequency shifts, that characterized the spectra of the pyridine complexes. Since the bipyridines are more complicated molecules than pyridine, the spectra are much more complicated and the changes on complexing are even harder to interpret. There are, however, some rather surprising changes in the spectra of the bipyridines which deserve some discussion.

First of all, consider the changes in ν_{16b} at 404 cm.⁻¹ in pyridine. This out-of-plane skeletal bending vibration shows a characteristic shift to higher frequencies in pyridine and in 2,2'-bipyridine complexes. However, in 4,4'-bipyridine the logical assignment of the 374 cm.⁻¹ band to ν_{16b} presents us with a problem in the complexes. Apparently this band just disappears without trace in the complexes. This behavior is quite difficult to understand, since the intensity of ν_{16b} does not seem to be very dependent on complex formation in the other compounds.

The upward shift of ν_{6a} (at 605 cm.⁻¹ in pyridine) on complex formation appears to be similar in pyridine and 4,4'-bipyridine but anomalous in the 2,2'-bipyridine complexes. The possibility of chelate formation in complexes with the latter amine results in some differences in its behavior. The other band which seems to indicate such a difference is ν_{19a} , the skeletal stretching made at 1420 cm.⁻¹, in 2,2'-bipyridine. The analogous frequencies in the other amines seem to remain relatively constant as complexing occurs; in the 2,2'-bipyridine, this band apparently moves upward some 50 cm.⁻¹.

Again, the bipyridines show quite large changes in the region around 1000 cm.⁻¹ as complexing occurs. This is to be expected in view of the complexity of this region. There does not appear to be any simple interpretation of these changes, except that they very likely are due to intensity changes resulting from the charge redistribution on complex formation. The marked simplification of the spectrum of 4,4'-bipyridine in ICl complex is notable, even if it is not understood. The study of the infrared spectra of complexes of the bipyridines was not very helpful in understanding the nature of these complexes. However, this study does provide some further empirical information about the nature of spectral changes to be expected on complex formation. The pyridine complexes provide the best information on this question. It would appear that the changes in spectra, while profoundly affecting the appearance of the spectrum, result mostly from changes in the relative *intensities* of vibrations. The changes in *frequency* appear to be of the order of 5% for larger observed changes; changes of this small magnitude are to be expected only if the formation of the complex does not radically change the chemical bonding in the donor molecule. The spectra of the bipyridines support these general conclusions. However, the consequence of the relative smallness of the effects in the infrared spectra is that little information on structure of these complexes can be gained until reliable normal coördinates are available so that the *intensity* changes can be understood.

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Chemistry of the Metal Carbonyls. XI. Metal Complexes of 5,6-Dimethylenebicyclo [2.2.1]heptene-2¹

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The bicyclic triene 5,6-dimethylenebicyclo[2.2.1]heptene-2 (I) has been found to react with chromium, molybdenum and tungsten hexacarbonyls to produce volatile red-to-orange crystalline solids of composition C_9H_{10} ·M(CO)₃ [M = Cr, Mo or W]. The spectral properties of these new compounds are discussed, as well as the reactions of some related polyenes with metal carbonyls.

Recently a variety of polyolefins and aromatic hydrocarbons have been shown to react with carbonyls of Group VI metals to afford π -complexes. Compounds of the type $L \cdot M(CO)_3$ [M = Cr, Mo or W] have been obtained from aromatic hydrocarbons,³ and from cycloheptatriene or substituted cycloheptatrienes,⁴ 1,3,5-cycloöctatriene⁵ and perhaps even cyclononatetraene.3e In addition to complexes derived from conjugated trienes, metal complexes $[L \cdot M(CO)_4]$ involving the nonconjugated dienes 1,5-cycloöctadiene⁶ and bicyclo-[2.2.1]heptadiene $(II)^7$ have been reported, as well as compounds of composition $L_2Mo(CO)_2$ derived from 1,3,6-cycloöctatriene^{ba} and 1,3-cyclohexa-diene.⁸ In view of the existence of these various Group VI metal complexes having a variety of trienes and dienes as ligands, it seemed worthwhile to investigate reactions between 5,6-dimethylene-

(1) Previous paper in this series, P. M. Treichel, E. Pitcher, R. B. King and F. G. A. Stone, J. Am. Chem. Soc., 83, 2593 (1961).

(2) National Science Foundation Predoctoral Research Fellow. 1958-1961.

(3) (a) B. Nicholls and M. C. Whiting, J. Chem. Soc., 551 (1959);
(b) E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen and W. Semmlinger, Ber., 91, 2763 (1958); (c) G. Natta, R. Ercoli and F. Calderazzo, Chem. e Ind. Milano, 40, 287 (1958); (d) E. O. Fischer, N. Kriebitzsch and R. D. Fischer, Ber., 92, 3214 (1959);
(e) R. B. King and F. G. A. Stone, J. Am. Chem. Soc., 82, 4557 (1960).
(4) (a) E. W. Abel, M. A. Bennett, R. Burton and G. Wilkinson, J. Chem. Soc., 4559 (1958); (b) T. A. Manuel and F. G. A. Stone, Chemistry & Industry, 231 (1960).

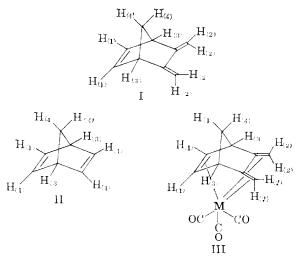
(5) (a) E. O. Fischer, C. Palm and H. P. Fritz, Ber., 92, 2645 (1959);
(b) E. O. Fischer and C. Palm, Z. Naturforschg., 14b, 598 (1959).

(6) (a) T. A. Manuel and F. G. A. Stone, Chemistry & Industry, 1349
(1959); (b) E. O. Fischer and W. Fröhlich, Ber., 92, 2995 (1959);
(c) M. A. Bennett and G. Wilkinson, Chemistry & Industry, 1516
(1959).

(7) (a) R. Pettit, J. Am. Chem. Soc., **81**, 1266 (1959); (b) R. Burton, M. L. H. Green, E. W. Abel and G. Wikinson, Chemistry & Industry, 1592 (1958).

(8) E. O. Fischer and W. Fröhlich, Z. Naturforschg., 15b, 266 (1960).

bicyclo[2.2.1]heptene-2 (C_9H_{10}) (I)⁹ and the carbonyls of chromium, molybdenum and tungsten, in order to determine the role Compound I would play as a ligand to a Group VI metal. In Com-



pound I the isolated double bond and the two conjugated double bonds are in a similar relationship to one another as the two double bonds of bicycloheptadiene (II). It seemed quite probable, therefore, that when Compound I was heated with a Group VI metal carbonyl, such as molybdenum hexacarbonyl, all three double bonds of the triene, because of their favorable steric disposition, would displace carbonyl groups from the hexacarbonyl to form a tricarbonyl complex, *e.g.*, C_9H_{10} ·Mo(CO)₃. However, if only two of the

(9) (a) K. Alder, S. Hartung and O. Netz, Ber., 90, 1 (1957); (b)
 M. A. P. Bowe, R. G. J. Miller, J. B. Rose and D. G. M. Wood, J. Chem. Soc., 1541 (1960).