

*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  $\text{PhLi-Vi}_4\text{Sn}$  reaction.

TABLE II  
STABILITY OF VINYLITHIUM IN ETHER SOLVENTS

Time <sup>a</sup>	Solvent	Yield (%) of $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	Yield (%) of $(\text{C}_6\text{H}_5)_4\text{Sn}$
0	$\text{Et}_2\text{O}$	65	75
6 min.	$\text{Et}_2\text{O}$	65	75
30 min.	$\text{Et}_2\text{O}$	74	97
2 hr.	$\text{Et}_2\text{O}$	73	
17 hr.	$\text{Et}_2\text{O}$	72	
7 days	$\text{Et}_2\text{O}$	65	
10 min.	THF	68	
22 hr.	THF	63	
7 days	THF	65	
2.5 hr. (at 65°)	THF	61	

<sup>a</sup> Time elapsed between formation of  $\text{CH}_2=\text{CHLi}$  and its reaction with tri-*n*-butyltin chloride.

**Attempted Preparation of Vinylithium 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 Gaj<sup>11</sup> by the reaction of bromobenzene with lithium wire at  $-60^\circ$ . 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.),  $n_D^{20}$  1.5169; lit.<sup>10</sup> b.p. 139° (0.6 mm.),  $n_D^{20}$  1.5155. The residue was distilled to obtain any higher boiling products, but only decomposition resulted.

**Reaction of Vinylithium with Tetraphenyltin in Tetrahydrofuran.**—Solid vinylithium was prepared by adding 0.1 mole of *n*-butyllithium in pentane to 0.05 mole of tetraphenyltin 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 vinylithium 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. 223–225°, 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. 10.5 g. in 600 ml. at room temperature. This supports the belief that in the previous experiment vinylithium and tetraphenyltin had reacted in an as yet unknown manner.

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[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

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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 coordination number of two, the properties of these complexes may indicate that these are linear polymers of the type  $\dots \text{BP-I}^+ \text{-BP-I}^+ \text{-BP-I}^+ \dots$  with an equivalent number of  $\text{IX}_2^-$  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  $\text{cm}^{-1}$  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 arranged in the *cis* configuration.<sup>2</sup> Since such an arrangement is obvi-

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 tribromide<sup>3</sup> and silver nitrate.<sup>4</sup> In both cases evidence is cited indicating that the two addition compounds are polymeric, with a

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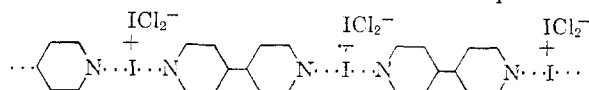
(3) P. Popov, *Zhur. Obshchei Khimii*, **19**, 47 (1947).

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



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



It should be remembered that compounds where positive iodine has a coordination 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.<sup>11</sup>

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.<sup>10,12-14</sup>

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 pyridine<sup>15</sup> 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

spectrum of a bipyridine would be particularly different from pyridine itself.<sup>16</sup> The assignment is summarized in Table I. The notation follows that of Corrsin, Fax and Lord.<sup>15</sup> The assignment of  $\nu_{8a}$  to the strong band at 1610  $cm^{-1}$  is different from that of Corrsin, Fax and Lord.<sup>15</sup> 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 I  
VIBRATIONAL ASSIGNMENTS OF PYRIDINE, 2,2'-BIPYRIDINE AND 4,4'-BIPYRIDINE

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)	1540(s)
19a	1490(s)	1458(vs)	1492(s)
19b	1447(vs)	1420(s)	1412(vs)
3	1220(w)	1250(s)	1222(s)
15	1149(w)	1140(w)	1131(w)
		1090(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)
			982(w)
			965(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)
			569(w)
			494(w)
16b	404(s)	402(s)	374(s)

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.<sup>17</sup> 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.*  $\nu_{8a}$  at 1610,  $\nu_{19a}$  at 1490,  $\nu_{19b}$

(11) H. Carlsohn, "Über 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).

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(15) L. Corrsin, B. J. Fax and R. C. Lord, *J. Chem. Phys.*, **21**, 1170 (1953). See, however, J. P. McCullough, D. R. Douslin, J. F. Messerly, I. A. Hossenlopp, T. C. Kincheloe and G. Waddington, *J. Am. Chem. Soc.*, **79**, 4289 (1957).

(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.

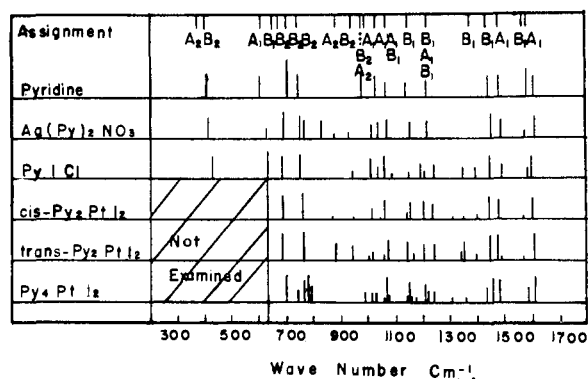


Fig. 1.—Line drawing representing the infrared spectra of pyridine and pyridine complexes. Line lengths are proportional to intensities. The assignment at the top is from Corrin, Fax and Lord (ref. 15). Classes  $A_1$ ,  $B_1$  and  $B_2$  are infrared-active in pyridine. Bands due to Nujol,  $\text{NO}_3^-$  and  $\text{ICl}$  are not shown.

at 1450,  $\nu_{15}$  at 1150,  $\nu_{18a,b}$  at 1070,  $\nu_{10b}$  at 750,  $\nu_{11}$  at 704,  $\nu_{6a}$  at 605 and  $\nu_{16b}$  at 404  $\text{cm}^{-1}$ ) all show frequency shifts of less than 10%. This is what might be expected for these rather weak  $\sigma$  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  $\text{N-X}$  force constant is large.

On the other hand there are regions of the spectrum which show considerable change. For example, the region around 1200  $\text{cm}^{-1}$  shows some new bands appearing in the complexes, as does the region around 1000  $\text{cm}^{-1}$  (whose complexities have been discussed by Zingaro and Tolberg<sup>10</sup>). However, we note that in both these regions the assignment provides for possible vibrations which are inactive in the pyridine itself. Thus, Corrin, Fax and Lord<sup>15</sup> assigned three vibrations to the region around 1220  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ .

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.*,  $\text{Py}^+$ ,  $\cdot$ -( $\text{ICl}$ ) $^-$ ) 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 coordinates 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

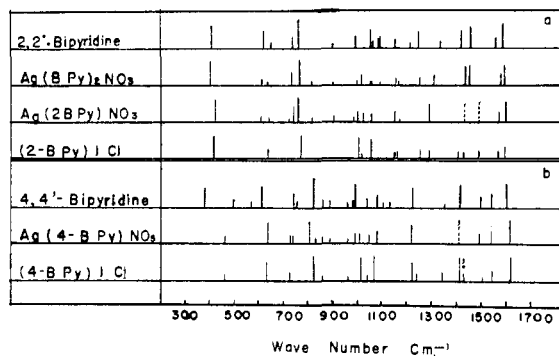


Fig. 2.—Line drawing representing the infrared spectra of (a) 2,2'-bipyridine and its complexes and (b) 4,4'-bipyridine and its complexes. Bands due to Nujol,  $\text{NO}_3^-$  and  $\text{ICl}$  are not shown.

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  $\nu_{16b}$  at 404  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  band to  $\nu_{16b}$  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  $\nu_{16b}$  does not seem to be very dependent on complex formation in the other compounds.

The upward shift of  $\nu_{6a}$  (at 605  $\text{cm}^{-1}$  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  $\nu_{19a}$ , the skeletal stretching made at 1420  $\text{cm}^{-1}$ , 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  $\text{cm}^{-1}$ .

Again, the bipyridines show quite large changes in the region around 1000  $\text{cm}^{-1}$  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  $\text{ICl}$  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 coordinates 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-2<sup>1</sup>

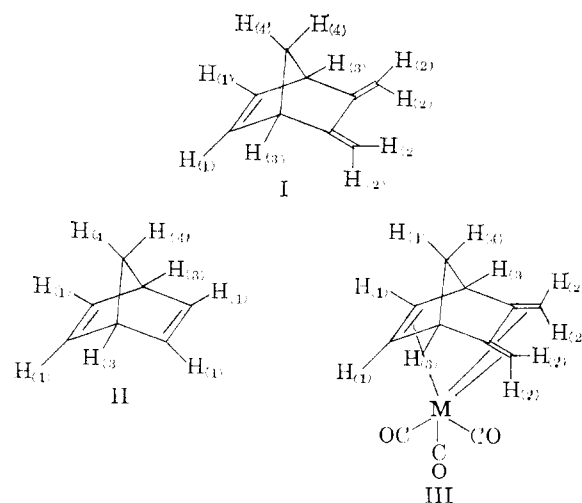
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The bicyclic triene 5,6-dimethylenebicyclo[2.2.1]heptene-2 (I) has been found to react with chromium, molybdenum and tungsten hexacarbonyls to produce volatile red-to-orange crystalline solids of composition  $C_9H_{10} \cdot M(CO)_3$  [ $M = Cr, Mo$  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  $\pi$ -complexes. Compounds of the type  $L \cdot M(CO)_3$  [ $M = Cr, Mo$  or  $W$ ] have been obtained from aromatic hydrocarbons,<sup>3</sup> and from cycloheptatriene or substituted cycloheptatrienes,<sup>4</sup> 1,3,5-cyclooctatriene<sup>5</sup> and perhaps even cyclononatetraene.<sup>3e</sup> In addition to complexes derived from conjugated trienes, metal complexes [ $L \cdot M(CO)_4$ ] involving the non-conjugated dienes 1,5-cyclooctadiene<sup>6</sup> and bicyclo[2.2.1]heptadiene (II)<sup>7</sup> have been reported, as well as compounds of composition  $L_2Mo(CO)_2$  derived from 1,3,6-cyclooctatriene<sup>8a</sup> and 1,3-cyclohexadiene.<sup>8</sup> 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-

bicyclo[2.2.1]heptene-2 ( $C_9H_{10}$ ) (I)<sup>9</sup> 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-



(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.

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(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. Wilkinson, *Chemistry & Industry*, 1592 (1958).

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

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.,  $C_9H_{10} \cdot Mo(CO)_3$ . However, if only two of the

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