

tation on the preparation and subsequent reaction of the phosphonium ylide.

In the present study, we wish to report a novel method for the preparation of a phosphonium ylide from the corresponding phosphonium halide without using a strong base. A few studies have been published on the behavior of phosphonium salts in electrolytic reduction.<sup>1,2</sup> Although polarographic studies indicate one-electron reduction of the phosphonium salt, little is known about the detailed reaction mechanism and no attempt has been made to trap the reduction intermediate by an appropriate reactant. Recently, the electrolytic reduction of a series of  $\omega$ -cyanoalkyltriphenylphosphonium salts in the presence of styrene with a mercuric cathode has been reported, and a homolytic cleavage of the carbon-phosphorus bond has been observed.<sup>3</sup> In our preliminary study, we found that in the electrolysis of an aqueous solution of (carbomethoxymethyl)triphenylphosphonium chloride with a carbon electrode, the corresponding ylide immediately separated on the electrode. Furthermore, the appearance of the characteristic color of the ylide at the surface of the cathode was observed in the electrolysis of a solution of methyl- or ethyltriphenylphosphonium iodide in dimethylformamide. These observations strongly suggest the formation of the phosphonium ylide at the surface of the carbon cathode.

Thus, in the present study, the electrolysis of a series of phosphonium halides in the presence of a carbonyl compound, such as benzaldehyde, butyraldehyde, or cyclohexanone, was investigated to demonstrate the formation of the phosphonium ylide. The electrolysis was carried out with a carbon electrode at 15–50 V, and the carbonyl compound was used as solvent. A fine glass filter was used between the anodic and cathodic chambers. The yields of the olefinic products are shown in the Table I. The results clearly indicate that

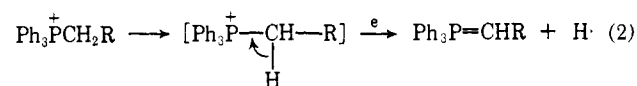
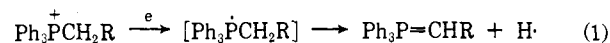
Table I. Yields of the Olefinic Products (%)<sup>a</sup>

R	Ph <sub>3</sub> PRX	X	Carbonyl compound		
			Benzaldehyde	Butyraldehyde	Cyclohexanone
CH <sub>3</sub>		I	84	40 <sup>b</sup>	
C <sub>2</sub> H <sub>5</sub>		I	95		15
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>		Br	72	95	95
CH <sub>2</sub> COOCH <sub>3</sub>		Cl	75	50	

<sup>a</sup> Yields were determined by vpc. <sup>b</sup> The yield may be better than that shown since the product is highly volatile.

the electrolytic method of generating phosphonium ylides from the corresponding salts is a unique and useful way of preparing the ylide without using a strong base. This method may allow the preparation of new ylides which could not be prepared by the usual technique.

Although sufficient experimental evidence is not available yet, two routes are conceivable for the formation of the ylide. Route 1 is the usual one-electron reduction of the phosphonium ion and route 2 is proton abstraction from the  $\alpha$  methylene by the cathode. The formation of a small amount of benzene observed in the electrolysis of methyltriphenylphosphonium



iodide might suggest a preference for route 1. Further study of the reaction and an attempt to generate sulfonium ylides by electrolysis are currently in progress.

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### The Use of Far-Infrared Spectroscopy in Characterizing Metal-Thiocyanate Bonding in Palladium(II) Complexes

Sir:

Metal-NCS or metal-SCN bonding in thiocyanate complexes has been most commonly determined<sup>1–5</sup> by infrared spectroscopy in the mid-infrared region.<sup>6</sup> The infrared spectra of palladium(II) thiocyanate complexes in this region are characterized by three absorption bands: the C–N stretching frequency which occurs below 2100 cm<sup>-1</sup> for Pd–NCS and above 2100 cm<sup>-1</sup> for Pd–SCN with some overlap,<sup>2,4</sup> the C–S stretching frequency at 860–780 cm<sup>-1</sup> for Pd–NCS and 720–690 cm<sup>-1</sup> for Pd–SCN,<sup>3</sup> and the N–C–S bending mode which has a single peak at 480–460 cm<sup>-1</sup> for Pd–NCS and several peaks in the region 500–400 cm<sup>-1</sup> with the most intense near 420 cm<sup>-1</sup> for Pd–SCN.<sup>7</sup> The difficulties inherent in determining bond type based on any of these three absorptions have been pointed out by a number of authors.<sup>1</sup> Correlations based on the C–N stretching frequency are difficult because the variation of peak position with bond type is very small and overlap often occurs. Correlations based on the C–S stretching frequency can be uncertain because the peaks are often weak and sometimes obscured by peaks due to other ligands in the complex; also, as was pointed out by Sabatini and Bertini,<sup>1</sup> a peak assigned to C–S stretching in a Pd–NCS complex may actually be an overtone of the N–C–S bending mode in a Pd–SCN complex. For example, on the basis of a C–S stretching frequency of 865 cm<sup>-1</sup>, the compound [Pd(py)<sub>2</sub>(thiocyanate)<sub>2</sub>] was thought<sup>8</sup> to contain N-bonded thiocyanates; however, as was later shown,<sup>1</sup> this peak is actually an overtone of the N–C–S bending frequency at 424 cm<sup>-1</sup>, and the compound is in fact [Pd(py)<sub>2</sub>(SCN)<sub>2</sub>] (see Table I). Correlations based on the N–C–S bending frequencies are perhaps best, although often the peaks are weak and are sometimes obscured by absorptions due to other ligands.

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**Table I.** Vibration Frequencies ( $\text{cm}^{-1}$ ) in Substituted Palladium(II) Thiocyanate Complexes<sup>a</sup>

Complex	Sulfur bonded			
	C-N str	C-S str	-SCN bend	Pd-S str
[Pd(Ph <sub>3</sub> As) <sub>2</sub> (SCN) <sub>2</sub> ]	2120 <sup>b</sup>	<i>d</i>	418 <sup>b</sup>	311
[Pd(bipy)(SCN) <sub>2</sub> ]	2117 <sup>c</sup>	700 <sup>c</sup>	<i>d</i>	319
[Pd(Et <sub>4</sub> dien)(SCN)]SCN	2103	710 <sup>e</sup>	435	295
[Pd(py) <sub>2</sub> (SCN) <sub>2</sub> ]	2112 <sup>b</sup>	<i>d</i>	424 <sup>b</sup>	305
[Pd(Ph <sub>3</sub> Sb) <sub>2</sub> (SCN) <sub>2</sub> ]	2119 <sup>c</sup>	<i>d</i>	440	290
[Pd(phen)(SCN) <sub>2</sub> ]	2116 <sup>b</sup>	697 <sup>b</sup>	418 <sup>b</sup>	305

Complex	Nitrogen bonded			
	C-N str	C-S str	-NCS bend	Pd-N str
[Pd(Ph <sub>3</sub> As) <sub>2</sub> (NCS) <sub>2</sub> ]	2085 <sup>b</sup>	854 <sup>b</sup>	<i>d</i>	265
[Pd(bipy)(NCS) <sub>2</sub> ]	2100 <sup>b</sup>	845 <sup>b</sup>	458 <sup>b</sup>	261
[Pd(Et <sub>4</sub> dien)(NCS)]SCN	2080	832 <sup>e</sup>	472	268
[Pd(Ph <sub>3</sub> P) <sub>2</sub> (NCS) <sub>2</sub> ]	2095 <sup>b</sup>	853 <sup>b</sup>	<i>d</i>	270
[Pd( <i>n</i> -Bu <sub>3</sub> P) <sub>2</sub> (NCS) <sub>2</sub> ]	2100 <sup>b</sup>	846 <sup>b</sup>	448 <sup>b</sup>	<i>d</i>

<sup>a</sup> Abbreviations: Ph, phenyl; bipy, 2,2'-bipyridine; py, pyridine; phen, 1,10-phenanthroline; *n*-Bu, *n*-butyl; Et<sub>4</sub>dien, 1,1,7,7-tetraethyldiethylenetriamine. <sup>b</sup> Frequencies taken from ref 1. <sup>c</sup> Frequencies taken from ref 8. <sup>d</sup> Band masked by absorption due to the organic ligands. <sup>e</sup> Frequencies taken from ref 11.

The Pd-N and Pd-S stretching frequencies should occur in still a fourth (lower frequency) region of the infrared spectrum, and we have accordingly investigated several palladium(II) complexes in this region. Forster and Goodgame<sup>9</sup> and Sabatini and Bertini<sup>7</sup> have reported stretching frequencies for various transition metal thiocyanate complexes and found values in the neighborhood of 300  $\text{cm}^{-1}$  for Pd-SCN complexes. Kharitonov, Tsintsadze, and Porai-Koshits<sup>10</sup> have calculated that peaks due to Pd-NCS stretching should be about 45  $\text{cm}^{-1}$  lower than those for Pd-SCN, if the M-N and M-S force constants are approximately the same.

Three pairs of palladium(II) thiocyanate linkage isomers, recently prepared by Burmeister and Basolo<sup>8</sup> and Baddley and Basolo,<sup>11</sup> seemed especially appropriate for use in arriving at assignments for the Pd-ligand atom vibration frequencies. The sulfur-bonded forms of these linkage isomers (*i.e.*, [Pd(Ph<sub>3</sub>As)<sub>2</sub>(SCN)<sub>2</sub>] and [Pd(Ph<sub>3</sub>As)<sub>2</sub>(NCS)<sub>2</sub>], [Pd(bipy)(SCN)<sub>2</sub>] and [Pd(bipy)(NCS)<sub>2</sub>], [Pd(Et<sub>4</sub>dien)(SCN)]SCN and [Pd(Et<sub>4</sub>dien)(NCS)]SCN) are prepared from K<sub>2</sub>[Pd(SCN)<sub>4</sub>] by the replacement of two or three thiocyanate groups by other ligands. Inasmuch as this starting compound possesses Pd-S bonds,<sup>7</sup> the complexes as initially obtained also have this structure. Each of these S-bonded compounds is converted to the N-bonded isomer on standing or with increase of temperature. Each pair of these linkage isomeric compounds thus provides a unique opportunity to examine the Pd-S and Pd-N stretching frequencies in the presence of identical ligand atmospheres. Spectra of these complexes as well as those of several other Pd-NCS and Pd-SCN compounds were obtained and assignments made in all cases by comparison with the spectra of the analogous chloro complexes. The results are given in Table I.

The results agree with the two previously reported Pd-SCN stretching frequencies of 298 and 300  $\text{cm}^{-1}$  for

(9) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715 (1965).

(10) Y. Y. Kharitonov, G. V. Tsintsadze, and M. A. Porai-Koshits, *Zh. Neorgan. Khim.*, **10**, 792 (1965).

(11) W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2944 (1966).

((CH<sub>3</sub>)<sub>4</sub>N)<sub>2</sub>[Pd(SCN)<sub>4</sub>]<sup>9</sup> and K<sub>2</sub>[Pd(SCN)<sub>4</sub>],<sup>7</sup> respectively, confirm the calculations of Kharitonov and coworkers,<sup>10</sup> and indicate that the M-N and M-S force constants are about the same. There appears to be a definite correlation of absorption peak positions in the region 320–260  $\text{cm}^{-1}$  with sulfur- or nitrogen-bonded complexes. All substituted Pd-SCN complexes exhibit a peak in the region 320–290  $\text{cm}^{-1}$ , and all Pd-NCS complexes a peak in the region 270–260  $\text{cm}^{-1}$ .

Perhaps a word of caution is in order for anyone considering using the far-infrared method on these or similar compounds. Spectra of a number of these complexes were obtained by both the CsI pellet and Nujol mull techniques. In every case which involved the pellet technique, exchange of thiocyanate ligands by iodide from the CsI matrix appeared to have taken place.

The complexes were prepared by the procedures of Burmeister and Basolo<sup>8</sup> and Baddley and Basolo.<sup>11</sup> Infrared spectra (700–200  $\text{cm}^{-1}$ ) were obtained by F. S. Bonomo of the Denver Research Institute and recorded on a Beckman Model IR-7 spectrophotometer using Nujol mulls on polyethylene plates. Spectra in the sodium chloride region were obtained on a Beckman Model IR-8 spectrophotometer using Nujol mulls. The sulfur-bonded forms of the linkage isomers were stored in Dry Ice up to the time their spectra were obtained.

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## The Stereochemistry of Jervine and Related Alkaloids<sup>1, 2</sup>

Sir:

Evidence is advanced herewith for revision of the configuration at C-17 in the formulation of jervine (I).<sup>3,4</sup> The argument also provides a firm basis for assignment of complete relative and absolute configurations to jervine (I), veratrobazine (II), 11-deoxojervine (III), veratramine (IV), and verarine (V).<sup>5</sup>

A recent X-ray diffraction study of veratrobazine revealed that the alkaloid possesses the structure and *relative* configuration II.<sup>6</sup> Although the structural resemblance to jervine was noted, the authors commented: "It remains to be shown whether the stereochemistry of the two molecules is identical at corresponding asymmetric centers." The similarity of the physical properties of veratrobazine<sup>7</sup> to those reported for jervin-11 $\beta$ -ol<sup>8</sup> suggested the possible identity of the two materials. The hypothesis was tested by direct

(1) Veratrum Alkaloids. LIV.

(2) This investigation was supported by Public Health Service Research Grant No. HE-02275 from the National Heart Institute.

(3) The 17 $\alpha$ -oxide and 20 $\alpha$ -methyl configurations for jervine were originally suggested solely on the basis of biogenetic analogy to normal steroids; see, *e.g.*, O. Wintersteiner, *et al.*, *J. Am. Chem. Soc.*, **76**, 5609 (1954); **78**, 6193 (1956).

(4) A chemical argument in support of assignment of the 17 $\alpha$ -oxide configuration has recently been advanced by T. Masamune, M. Takasugi, A. Murai, and K. Kobayashi, *ibid.*, **89**, 4521 (1967).

(5) For a recent review of the chemistry and stereochemistry of the jerveratrum alkaloids, see S. M. Kupchan and A. W. By, *Alkaloids*, **10**, 193 (1968).

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