

methanol, giving *trans*-PdCl(COCH₃)[P(CH₃)₂C₆H₅]₂ (0.104 g, 40%), mp 129–130° dec. $\nu(\text{C}=\text{O})$ 1675 (s), 1654 cm⁻¹ (sh). Nmr in CHCl₃: $\delta(\text{CH}_3\text{P})$ -1.73 ppm, $^2J + ^4J(\text{PH}) = 7.3$ Hz; $\delta(\text{CH}_3\text{CO})$ -1.78 ppm. *Anal.* Calcd for C₁₈H₂₆ClOP₂Pd: C, 46.9; H, 5.5. Found: C, 46.7; H, 5.85. The compound blackened slowly on storage.

(b) *trans*-PtClCH₃[P(CH₃)₂C₆H₅]₂ (0.102 g) in methanol (3 ml) was heated with CO (5 atm) at 80° for 4 hr in a sealed tube. The solvent was evaporated and the product was recrystallized from methanol giving *trans*-PtCl(COCH₃)[P(CH₃)₂C₆H₅]₂ (0.073

g, 68%), mp 153–157° dec. $\nu(\text{C}=\text{O})$ 1632 cm⁻¹ (s). Nmr in CHCl₃: $\delta(\text{CH}_3\text{P})$ -1.44 ppm; $^2J + ^4J(\text{PH}) = 7.5$ Hz, $^3J(\text{PtH}) = 37$ Hz; $\delta(\text{CH}_3\text{CO})$ -1.73 ppm, $^3J(\text{PtH}) = 13.5$ Hz. *Anal.* Calcd for C₁₈H₂₆ClOP₂Pt: C, 39.3; H, 4.6. Found: C, 39.4; H, 4.8.

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CONTRIBUTION FROM THE CHEMISTRY DIVISION,
ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS, AND
TODD WEHR CHEMISTRY BUILDING, MARQUETTE UNIVERSITY, MILWAUKEE, WISCONSIN

Low-Frequency Infrared Spectra of Planar and Tetrahedral Nickel Bromide Complexes of Diphenylalkylphosphines^{1a}

BY JIN TSAI WANG,^{1b} CARL UDOVICH, K. NAKAMOTO, A. QUATTROCHI, AND J. R. FERRARO*

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The Ni–Br and Ni–P stretching bands characteristic of the planar and tetrahedral forms have been established for a series of compounds of the type Ni(P(C₆H₅)₂R)₂Br₂ where R is an alkyl group. The results of metal isotope studies showed that the Ni–Br and Ni–P stretching frequencies are located at *ca.* 330 and 260 cm⁻¹, respectively, for the planar form, and *ca.* 270–230 and 200–160 cm⁻¹, respectively, for the tetrahedral form.

Introduction

Complexes of the type Ni(P(C₆H₅)₂R)₂Br₂ (R, alkyl) exist in two isomeric forms: tetrahedral (green) and *trans* planar (brown).² Hayter and Humic³ have isolated a number of pairs of these isomeric forms and determined their structures by electronic spectra, magnetic moments, and X-ray powder patterns. However, no systematic far-infrared studies have yet been made to distinguish these two forms. The purpose of this work was to prepare several pairs of these isomers and to assign the bands characteristic of each form. It is anticipated that the main spectral differences between the two forms will occur for the skeletal vibrations such as the Ni–P and Ni–Br stretching modes. In a previous communication,⁴ it was demonstrated that the use of metal isotopes provided a clear-cut band assignment for these metal–ligand vibrations. This technique was therefore applied to several typical complexes of the aforementioned type. Spectral differences between the two isomers are not only useful for identification pur-

poses, but are also of theoretical interest since these isomers differ only in the configuration around the central metal.

Experimental Section

Preparation of Compounds. Ligands.—The diphenylalkylphosphines were prepared by the method of Davies and Jones,⁵ from chlorodiphenylphosphine and alkylmagnesium bromide.

Complexes.—The tetrahedral (green) complexes were prepared by the addition of the phosphine to a concentrated solution of nickel bromide in ethanol.³ The *trans*-planar (brown) forms were obtained by recrystallization of the corresponding green forms from the solvents listed in Table I.

The *trans*-planar Ni(P(C₆H₅)₂C₂H₅)₂Br₂ complex could not be obtained by recrystallization from CS₂ solution at room temperature. It was prepared by the process of lyophilization. First, the tetrahedral isomer was dissolved in CS₂ by the gradual addition of CS₂ to a steam-heated flask. The green color changed to brown-purple and the flask was then immediately cooled in liquid nitrogen. The frozen sample was transferred to a Dry Ice–isopropyl alcohol slush bath and the solvent was removed with a high-vacuum system.

The solvents used for recrystallization of the products, magnetic moments, and microanalysis are tabulated in Table I.

Complexes containing metal isotopes were prepared on a milligram scale by the methods used for the preparation of the natural abundance species. The ⁶⁸Ni (99.98% pure) and ⁶²Ni (99.02% pure) isotopes were purchased from Oak Ridge National Laboratory. The purity of each complex was checked by comparing the spectrum with that of the corresponding complex containing the metal of natural abundance.

Magnetic Moment Measurements.—The magnetic moments were determined by using the Faraday technique.⁶ Ferrous ammonium sulfate was used as the standard.

(5) W. C. Davies and J. W. Jones, *J. Chem. Soc.*, 33 (1929).

(6) H. Selig, F. A. Cafasso, D. M. Gruen, and J. G. Malm, *J. Chem. Phys.*, **36**, 3440 (1962).

* To whom correspondence should be addressed at Argonne National Laboratory.

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(2) This terminology will be used throughout this paper and follows the terminology used by previous workers. It is understood that the angles around the nickel atom are ~109° in the tetrahedral form, while they are ~90° in the *trans*-planar form.

(3) R. G. Hayter and F. S. Humic, *Inorg. Chem.*, **4**, 1701 (1965).

(4) K. Nakamoto, K. Shobatake, and B. Hutchinson, *Chem. Commun.*, 1451 (1969).

TABLE I
Ni(P(C₆H₅)₂R)₂Br₂

R	$\mu(25^\circ)$, BM	Color	Solvent	Microanalysis, %							
				Calcd			Found				
				C	H	X	C	H	X	M	
Ethyl	3.18	Green	Ethanol	51.98	4.67	24.70	51.66	4.73	...	8.93 ^a	
	...	Brown	CS ₂				52.53	4.77	26.28		
<i>n</i> -Propyl	3.17	Green	Ethanol	53.38	5.08	23.67	53.01	5.11	24.01		
	0	Brown	CH ₂ Cl ₂ -ether				52.96	4.88	24.94		
Isopropyl	3.12	Green	Ethanol	53.38	5.08	23.67	53.09	5.20	23.32		
	0	Brown	C ₆ H ₆ - <i>n</i> -hexane				52.60	5.01	24.62		
Isobutyl	3.20	Green	Ethanol	54.81	5.45	22.73	54.81	5.36	...		
	0	Brown	CS ₂				54.95	5.23	...		

^a Calcd for Ni, 9.07%.TABLE II
LOW-FREQUENCY INFRARED SPECTRA (400–150 cm⁻¹) OF PLANAR AND TETRAHEDRAL
Ni(P(C₆H₅)₂R)₂Br₂ TYPE COMPOUNDS

	Structure	Ni-Br str		Ni-P str		Ligand vibration ^c			
		ν	$\Delta\nu^b$	ν	$\Delta\nu^b$				
⁵⁸ Ni(P(C ₆ H ₅) ₃) ₂ Br ₂ ^c	Trans planar	337.8 ^d	10.5	265.0	4.7	374.0	327.8	190.4	155.1
⁵⁸ Ni(P(C ₆ H ₅) ₃) ₂ Br ₂	Tetrahedral	266.5	5.2	196.8	1.1				
		234.1	2.3	189.5	2.0	399.0	...	220.4	150.0
⁵⁸ Ni(P(C ₆ H ₅) ₂ C ₂ H ₅) ₂ Br ₂	Trans planar	323.0	6.5	243.0	5.0	354.0	301.0	220.0	160.0
	Tetrahedral	259.0	5.5	194.5	1.7	333.2	302.8	220.0	165.0
		249.2	6.8	182.0	3.0				
		239.0	3.8						
Ni(P(C ₆ H ₅) ₂ (<i>n</i> -C ₃ H ₇)) ₂ Br ₂	Trans planar	335	...	260	...	280	245	222	195, 123
	Tetrahedral	260	...	178	...	280	240	220	196
		240	...	162	...				
Ni(P(C ₆ H ₅) ₂ (<i>i</i> -C ₃ H ₇)) ₂ Br ₂	Trans planar	337	...	273	...	298, 265	238	220	155, 125
	Tetrahedral	262	...	195	...	296	235	216	160
		255	...	170	...				
Ni(P(C ₆ H ₅) ₂ (<i>i</i> -C ₄ H ₉)) ₂ Br ₂	Trans planar	330	...	261	239	221	190
	Tetrahedral	265	...	190	230	...	190
		175	...				

^a These ligand vibrations show very small or zero shifts (below 1 cm⁻¹) by the metal isotope substitution technique. ^b Isotopic shifts, $\nu(^{58}\text{Ni}) - \nu(^{62}\text{Ni})$. ^c K. Shobatake and K. Nakamoto, *J. Amer. Chem. Soc.*, **92**, 3332 (1970). ^d Average values obtained for multiple runs of the spectra.

Spectral Measurements.—The spectra of the stable tetrahedral forms were obtained by using the Nujol mull technique. However, the spectra of the unstable planar forms could not be obtained in a Nujol mull, because they are readily converted into the corresponding green form as soon as they are ground in a mortar. Thus, their spectra were measured in a diamond cell combined with a beam condenser.⁷ The instruments used were the Beckman IR-12 (4000–250 cm⁻¹), the Beckman IR-11 (800–33 cm⁻¹), the Perkin-Elmer Hitachi FIS-3 (400–33 cm⁻¹), and the Perkin-Elmer Model 301 (650–80 cm⁻¹). Instrument calibrations were made by means of polystyrene film, solid mercury oxide, and water vapor.

The spectra were run with a scanning speed of 1–2 cm⁻¹/min. Reproducibility of the spectra was checked by running the spectra three to five times. The average error in frequency reading was 0.5 cm⁻¹.

Results and Discussion

Tetrahedral Complexes.—Complexes of the type Ni(P(C₆H₅)₃)₂X₂ (X is a halogen) are known to be tetrahedral.^{8,9} Far-infrared spectra of these compounds have been assigned recently by Boorman and Carty⁸ and by Bradbury, *et al.*⁹ For Ni(P(C₆H₅)₃)₂Br₂, the former investigators assigned the Ni-Br stretching bands at 265 and 232 cm⁻¹ and the Ni-P stretching bands at

193 and 184 cm⁻¹. However, the latter investigators assigned the Ni-Br stretchings at 267, 258 (sh), and 218 cm⁻¹ and the Ni-P stretching bands at 190 and 148 cm⁻¹. In order to examine these previous assignments, the pair of isotopic species ⁵⁸Ni(P(C₆H₅)₃)₂Br₂ and its ⁶²Ni analog have been prepared and their spectra measured to observe the isotopic shifts due to the metal isotopes.

Theoretically, two Ni-Br stretching and two Ni-P stretching vibrations are infrared active under the C_{2v} symmetry of the tetrahedral Ni(P(C₆H₅)₃)₂Br₂ molecule. Furthermore, these four vibrations should be shifted to lower frequencies when ⁵⁸Ni is substituted by ⁶²Ni. In agreement with this prediction, Table II shows that four bands at 266.5, 234.1, 196.8, and 189.5 cm⁻¹ of the ⁵⁸Ni species are metal isotope sensitive. The former two bands are assigned to the Ni-Br stretching bands, since they are completely missing in the corresponding chloro and iodo complexes. The latter two bands are assigned to the Ni-P stretching bands since they are halogen insensitive. These assignments are in good agreement with those of Boorman and Carty⁸ but are different from those of Bradbury, *et al.*,⁹ for several bands. The bands at 218 and 148 cm⁻¹ reported by Bradbury, *et al.*, were found to be insensitive to metal isotope substitution and probably arise from ligand vibrations.

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(8) P. M. Boorman and A. J. Carty, *ibid.*, **4**, 101 (1968).

(9) J. Bradbury, K. P. Forest, R. H. Nuttall, and D. W. Sharp, *Spectrochim. Acta, Part A*, **23**, 270 (1967).

It is anticipated that the Ni-Br and Ni-P stretching frequencies of tetrahedral $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{R})_2\text{Br}_2$ type compounds are similar to those established above for tetrahedral $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Br}_2$, since the substitution of a phenyl group by an alkyl group does not cause marked shifts in these frequencies. In fact, Figure 1 and Table

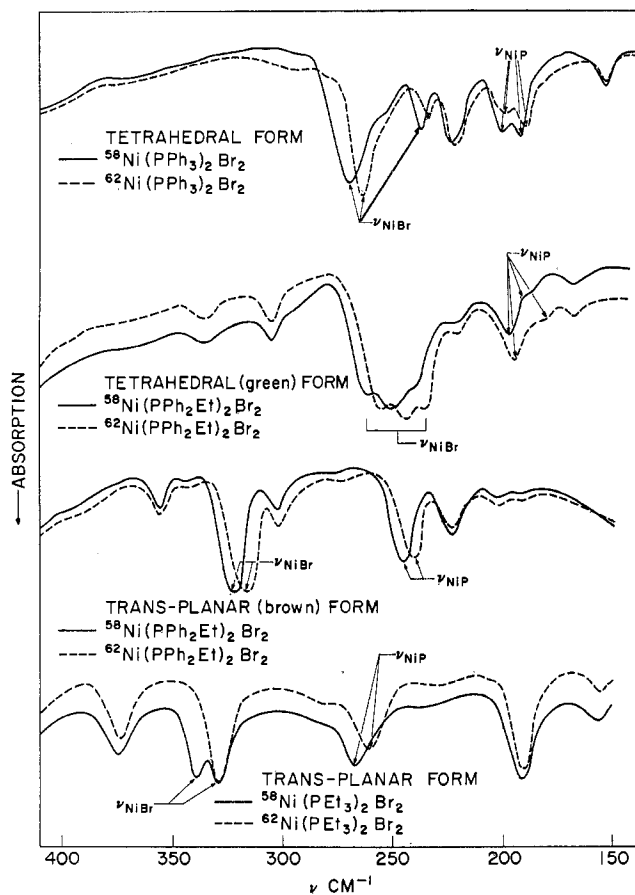


Figure 1.—Infrared spectra from 400 to 150 cm^{-1} of several $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{R})_2\text{Br}_2$ and $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5)_2\text{Br}_2$ complexes—tetrahedral and trans-planar forms.

II show that the spectrum of tetrahedral $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5)_2\text{Br}_2$ is very similar to that of $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Br}_2$. In order to assign the spectrum of the former, we have compared the far-infrared spectra of $^{58}\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5)_2\text{Br}_2$ and its ^{62}Ni analog. As is seen in Figure 1, three bands at 259.0, 249.2, and 239.0 cm^{-1} and two bands at 194.5 and 182.0 cm^{-1} of the ^{58}Ni species are metal isotope sensitive. From the comparison of these frequencies with those of $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Br}_2$, it is readily seen that the former three bands are due to the Ni-Br stretching, whereas the latter two bands are due to the Ni-P stretching modes. It was found that a benzene solution (green) of this compound (natural abundance Ni) exhibits two bands at 268.5 and 237.5 cm^{-1} . It is possible that the three bands appearing in the solid state may be caused by correlation field effects. The present assignments are essentially similar to those reported by Boorman and Carty,⁸ who have assigned the 260- and 238- cm^{-1} bands as the Ni-Br stretching and the 194- and 168- cm^{-1} bands to the Ni-P stretching modes.

As is seen in Table II, the far-infrared spectra of the other tetrahedral complexes, $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{R})_2\text{Br}_2$, where R is *n*- C_3H_7 , *i*- C_3H_7 , or *i*- C_4H_9 , are essentially similar to those of $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Br}_2$ and $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5)_2\text{Br}_2$ (green form) discussed above.

Planar Complexes.—Complexes of the type $\text{Ni}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{X}_2$, are known to be trans planar.^{8,10} The far-infrared spectra of $\text{Ni}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Cl}_2$ and $\text{Ni}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Br}_2$ have recently been assigned by Shobatake and Nakamoto¹¹ using the metal isotope method. Theoretically, one Ni-X vibration and one Ni-P stretching vibration are infrared active under the C_{2h} symmetry of the trans-planar $\text{Ni}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{X}_2$ type molecule. Furthermore, they are shifted to lower frequencies when ^{58}Ni is substituted by ^{62}Ni . In agreement with this prediction, it was found that two bands at 337.8 and 265.0 cm^{-1} of *trans*- $^{58}\text{Ni}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Br}_2$ are shifted by 10.5 and 4.7 cm^{-1} , respectively, to lower frequencies by the ^{58}Ni - ^{62}Ni substitution. The former band was assigned to the Ni-Br stretching mode, since the corresponding chloro complex does not show any absorption in this region. The latter band was assigned to the Ni-P stretching mode, since the chloro complex also exhibits a similar metal isotope sensitive band at 273.4 cm^{-1} . Table II lists the observed frequencies, isotopic shifts, and band assignments, and Figure 1 illustrates the spectra of *trans*- $\text{Ni}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Br}_2$ (^{58}Ni and ^{62}Ni).

It is anticipated that the Ni-Br and Ni-P stretching vibrations of the trans-planar $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{R})_2\text{Br}_2$ type compounds are essentially similar to that of *trans*- $\text{Ni}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Br}_2$, discussed above. In fact, Figure 1 and Table II show that trans-planar $^{58}\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5)_2\text{Br}_2$ exhibits the Ni-Br and Ni-P stretching bands at 323.0 and 243.0 cm^{-1} , respectively. As is shown in Table II, the spectra of the other planar complexes $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{R})_2\text{Br}_2$, where R is *n*- C_3H_7 , *i*- C_3H_7 , or *i*- C_4H_9 , are essentially similar to those of *trans*- $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5)_2\text{Br}_2$ and *trans*- $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5)_2\text{Br}_2$ discussed above.

Comparison of the Spectra between Tetrahedral and Planar Forms.—As started above, the green tetrahedral form exhibits two (or three) Ni-Br stretching bands near 250 cm^{-1} and two Ni-P stretching bands between 200 and 160 cm^{-1} , whereas the brown trans-planar form exhibits one Ni-Br stretching band near 330 cm^{-1} and one Ni-P stretching band near 260 cm^{-1} . In a series of complexes of the type $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{R})_2\text{Br}_2$, the distinction of the two forms can readily be made by the presence or absence of a relatively strong band near 330 cm^{-1} . In the case of tetrahedral complexes, this band is absent although a weak ligand vibration may appear in the same region.

As stated previously, the unstable planar form (brown) is easily converted to the tetrahedral form (green) by heating or dissolving it in solvents such as ethanol. This conversion is easily detected by the change in the far-infrared region; the strong Ni-Br

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stretching band near 330 cm^{-1} of the planar form is weakened as the conversion proceeds. However, the spectra near 250 cm^{-1} are not as useful as the spectra near 330 cm^{-1} , since both forms absorb in the region $270\text{--}230\text{ cm}^{-1}$. The same is true for the spectra in the $200\text{--}150\text{ cm}^{-1}$ region since the appearance of ligand vibration complicates the spectra.

It should be noted that the purity of the tetrahedral form is rather difficult to determine from its visual color (green) and uv spectra, because the presence of a small amount of the planar form in the tetrahedral form does not cause marked changes in these physical properties. In this respect, a study of the far-infrared spectra in the

$340\text{--}320\text{ cm}^{-1}$ region is highly significant as discussed above.

The spectra of the two forms are also different in the region above 400 cm^{-1} . For example, the tetrahedral $\text{Ni}(\text{P}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5)_2\text{Br}_2$ exhibits two bands at 479 (stronger) and 461 (weaker) cm^{-1} , whereas its planar isomer absorbs at 489 and 478 cm^{-1} with almost the same intensity. Since these vibrations originate in the phosphine ligand, spectral differences between two forms are characteristic of the phosphine ligand involved. Thus, it is not possible to discuss the spectra systematically for a series of complexes containing different phosphines.

CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORIES,
TULANE UNIVERSITY, NEW ORLEANS, LOUISIANA 70118,
AND THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT, NAVAL WEAPONS CENTER, CHINA LAKE, CALIFORNIA 93555

Platinum- and Palladium-Tetrazole Complexes

BY JOHN H. NELSON,^{1a} DONALD L. SCHMITT,^{1a} RONALD A. HENRY,^{1b}
DONALD W. MOORE,^{1b} AND HANS B. JONASSEN*,^{1a}

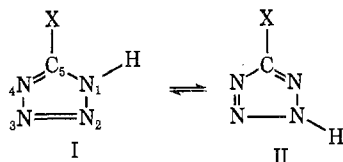
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cis-Dichlorobis(triphenylphosphine)platinum(II) reacts with hydrazine and 5-phenyl-, 5-bromo-, or 5-chlorotetrazole to form *trans*-Pt(H)(tetrazolato)(P(C₆H₅)₃)₂. Proton nmr of solutions of these hydrides show that both the N₁- and N₂-bonded tetrazolato complexes are present. The zerovalent complexes M(P(C₆H₅)₃)₄ (M = Pd, Pt) react with some 5-substituted tetrazoles to form complexes of the type *cis*-(P(C₆H₅)₃)₂M(tetrazolato)₂. The proton nmr of the 5-methyltetrazolopalladium complex seems to indicate the presence of four isomers in solution. Semiempirical one-electron molecular orbital calculations on model compounds indicate that the N₁- and N₂-bonded tetrazoles are energetically equivalent and support the conclusions derived from the nmr data.

Introduction

Zerovalent palladium and platinum complexes undergo a wide variety of oxidative addition reactions.²⁻⁸ With acids they yield hydrides; with olefins and acetylenes, olefin and acetylene complexes; with vinyl halides, vinyl complexes; with α -haloacetylenes, acetylidene complexes; with β -haloacetylenes, allene complexes; and with halocarbons, halide complexes.

5-Substituted tetrazoles exist in two tautomeric forms (I and II) and behave as weak acids.⁹ Thus,



* To whom correspondence should be addressed.

- (1) (a) Tulane University. (b) Naval Weapons Center.
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5-halotetrazoles could potentially react with zerovalent palladium and platinum complexes by oxidative addition to form hydrido complexes (with either N₁- or N₂-bonded tetrazole or both). They could also possibly abstract halides to form halide or tetrazole halide complexes with N₁-, N₂-, or C-bonded tetrazole; furthermore, they could possibly react to form σ -bonded tetrazolato or π -bonded tetrazole complexes.

The reactions of 5-chloro-, 5-bromo-, 5-methyl-, 5-phenyl-, and 5-cyclopropyltetrazole with tetrakis(triphenylphosphine)platinum(0), tetrakis(triphenylphosphine)palladium(0), *cis*-dichlorobis(triphenylphosphine)platinum(II), and *trans*-dichlorobis(triphenylphosphine)palladium(II) were studied. It was also hoped that this study would give information about which nitrogen(s) in the tetrazole ring acts as the donor atom(s) in the tetrazole complexes.⁹

Experimental Section

I. Reagents and Physical Measurements.—The tetrazoles were prepared in the Chemistry Division, Naval Weapons Center, China Lake, Calif. Tetrakis(triphenylphosphine)platinum(0),¹⁰ tetrakis(triphenylphosphine)palladium(0),¹¹ *cis*-dichlorobis(triphenylphosphine)palladium(II),¹² and *trans*-dichlorobis(triphe-

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