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 270–230 cm^{-1}. The same is true for the spectra in the 200–150-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 340–320-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 $Ni(P(C_6H_5)_2C_2H_5)_2Br_2$ 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,
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Platinum- and Palladium–Tetrazole Complexes

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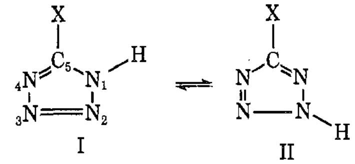
cis-Dichlorobis(triphenylphosphine)platinum(II) reacts with hydrazine and 5-phenyl-, 5-bromo-, or 5-chlorotetrazole to form *trans*-$Pt(H)(tetrazolato)(P(C_6H_5)_3)_2$. Proton nmr of solutions of these hydrides show that both the N_1- and N_2-bonded tetrazolato complexes are present. The zerovalent complexes $M(P(C_6H_5)_3)_4$ (M = Pd, Pt) react with some 5-substituted tetrazoles to form complexes of the type *cis*-$(P(C_6H_5)_3)_2M(tetrazolato)_2$. The proton nmr of the 5-methyltetrazolatopalladium complex seems to indicate the presence of four isomers in solution. Semiempirical one-electron molecular orbital calculations on model compounds indicate that the N_1- and N_2-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, acetylide 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, 5-halotetrazoles could potentially react with zerovalent palladium and platinum complexes by oxidative addition to form hydrido complexes (with either N_1- or N_2-bonded tetrazole or both). They could also possibly abstract halides to form halide or tetrazole halide complexes with N_1-, N_2-, or C-bonded tetrazole; furthermore, they could possibly react to form σ-bonded tetrazolato or π-bonded tetrazole complexes.



I II

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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nylphosphine)palladium(II)[13] were prepared according to literature procedures. All solvents were freed from water by standard procedures and stored over Linde 3A molecular sieves for at least 2 days prior to use. Infrared spectra were recorded on a Beckman IR-8 infrared spectrometer as KBr pellets and were calibrated with known frequency bands of polystyrene. Proton nmr spectra were obtained on the Varian Associates Model A-60 and HA-60-IL spectrometers in deuteriochloroform with tetramethylsilane as internal standard. Melting points or decomposition points were determined in air and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

II. Preparation of the Complexes. (A) ***cis*-Pt(P(C_6H_5)$_3$)$_2$(5-phenyltetrazolato)$_2$.**—A solution containing 82 mg (5.5×10^{-4} mol) of 5-phenyltetrazole in 3 ml of methanol was added to a solution of 166 mg (1.3×10^{-4} mol) of tetrakis(triphenylphosphine)platinum(0) in 25 ml of benzene. The originally yellow solution, which became colorless upon addition of the tetrazole, was flushed with nitrogen, stoppered, and stirred for 4 weeks at room temperature. The product was filtered, washed with 95% ethanol and 3 ml of benzene, and air dried; yield 143 mg (32%); colorless microcrystals; dec pt 275°. *Anal.* Calcd for $C_{50}H_{40}N_8P_2Pt$: C, 59.46; H, 3.99; N, 11.09; P, 6.13. Found: C, 59.15; H, 4.23; N, 11.12; P, 6.23.

Similarly, 5-cyclopropyltetrazole and tetrakis(triphenylphosphine)platinum(0) were allowed to react but no platinum-tetrazole complex was found after a period of 4 weeks.

(B) ***cis*-Pt(P(C_6H_5)$_3$)$_2$(5-cyclopropyltetrazolato)$_2$.**—To a slurry of 150 mg (1.9×10^{-4} mol) of *cis*-dichlorobis(triphenylphosphine)platinum(II) in 10 ml of absolute ethanol was added anhydrous (97%) hydrazine until the solution turned yellow and nearly all the platinum complex had dissolved. The solution was immediately filtered and an excess of 5-cyclopropyltetrazole was added to the filtrate. It was then heated to reflux for 5 min and allowed to cool to room temperature. The now nearly colorless solution was flushed with nitrogen, stoppered, and stirred magnetically for 6 hr. The precipitate, which formed upon reducing the solution to half-volume by aspiration at room temperature, was filtered, washed with 3 ml of 95% ethanol and 10 ml of ether, and dried under vacuum over P_4O_{10} at room temperature; yield 40 mg (24%); colorless microcrystals; dec pt 153°. *Anal.* Calcd for $C_{44}H_{40}N_8P_2Pt$: C, 56.35; H, 4.30; N, 11.95; P, 6.61. Found: C, 56.13; H, 4.49; N, 11.71; P, 6.57.

(C) ***trans*-(P(C_6H_5)$_3$)$_2$Pt(H)(5-substituted tetrazolato).**—Similarly, using 150 mg of *cis*-Cl_2Pt(P(C_6H_5)$_3$)$_2$ the following were prepared: (1) *trans*-(P(C_6H_5)$_3$)$_2$Pt(H)(5-phenyltetrazolato); yield 87 mg (53%); colorless microcrystals; dec pt 189–190°. *Anal.* Calcd for $C_{43}H_{36}N_4P_2Pt$: C, 59.65; H, 4.19; N, 6.47; P, 7.15. Found: C, 59.14; H, 4.37; N, 6.59; P, 7.24. (2) *trans*-(P(C_6H_5)$_3$)$_2$Pt(H) (5-chlorotetrazolato); yield 98 mg (62.3%); colorless microcrystals; dec pt 213–219°. *Anal.* Calcd for $C_{37}H_{31}N_4P_2ClPt$: C, 53.92; H, 3.79; N, 6.80; Cl, 4.30. Found: C, 53.99; H, 3.71; N, 6.73; Cl, 4.46. (3) *trans*-(P(C_6H_5)$_3$)$_2$Pt(H)(5-bromotetrazolato); yield 96 mg (58%); colorless microcrystals; dec pt 208–213°. *Anal.* Calcd for $C_{37}H_{31}N_4P_2BrPt$: C, 51.16; H, 3.60; N, 6.45; Br, 9.20. Found: C, 51.36; H, 3.60; N, 6.42; Br, 9.37.

(D) ***cis*-Pd(P(C_6H_5)$_3$)$_2$(5-phenyltetrazolato)$_2$ and *cis*-Pd(P(C_6H_5)$_3$)$_2$(5-cyclopropyltetrazolato)$_2$.**—An excess of the tetrazole was added to the reddish solution of 300 mg (2.51×10^{-4} mol) of tetrakis(triphenylphosphine)palladium(0) in 20 ml of a 1:1 mixture of methanol–dichloromethane. As the tetrazole was added, the solution became very faintly yellow-green. The solution volume was reduced to approximately 5 ml by aspiration at room temperature, flushed with nitrogen, stoppered, and stirred for 2 days at room temperature. The resultant colorless precipitate was filtered, washed with 5 ml of methanol, and recrystallized from dichloromethane–methanol: (1) *cis*-Pd(P(C_6H_5)$_3$)$_2$(5-phenyltetrazolato)$_2$; yield 206 mg (86%); colorless microcrystals; dec pt 151–153°. *Anal.* Calcd for $C_{50}H_{40}N_8P_2Pd$: C, 65.19; H, 4.38; N, 12.16; P, 6.72. Found: C, 65.02; H, 4.42; N, 12.09; P, 6.81. (2) *cis*-Pd(P(C_6H_5)$_3$)$_2$(5-cyclopropyltetrazolato)$_2$; yield 118 mg (64.5%); colorless microcrystals; dec pt 147–148°. *Anal.* Calcd for $C_{44}H_{40}N_8P_2Pd$: C, 62.23; H, 4.75; N, 13.20; P, 7.29. Found: C, 61.98; H, 4.73; N, 13.03; P, 7.16.

(E) ***cis*-Pd(P(C_6H_5)$_3$)$_2$(5-chlorotetrazolato)$_2$ and *cis*-Pd(P(C_6H_5)$_3$)$_2$(5-methyltetrazolato)$_2$.**—These two complexes were prepared from tetrakis(triphenylphosphine)palladium(0) prepared *in situ* by the following method.

trans-Pd(P(C_6H_5)$_3$)$_2$$Cl_2$, a 3 molar excess of triphenylphosphine, and a 3 molar excess of the tetrazole were suspended in 20 ml of a 6:1 molar ratio of absolute ethanol–anhydrous benzene and an excess of solid sodium borohydride was added slowly with stirring. Immediate effervescence occurred and the solution gradually changed color from lemon yellow to very faint yellow. The flask was stoppered after effervescence ceased and the stirring was continued for 12 hr. The solution was concentrated to half-volume by aspiration at room temperature and 10 ml of anhydrous ether was added. The product was filtered, washed with ether, and extracted with dichloromethane. The extract was concentrated, ether was added to incipient precipitation, and the product was filtered and recrystallized from dichloromethane–ether by aspiration at room temperature: (1) *cis*-Pd(P(C_6H_5)$_3$)$_2$(5-methyltetrazolato)$_2$; colorless microcrystals; 55% yield; dec pt 229–233°. *Anal.* Calcd for $C_{40}H_{36}N_8P_2Pd$: C, 60.27; H, 4.55; N, 14.06; P, 7.77. Found: C, 59.60; H, 4.58; N, 14.48; P, 8.48. Molecular weight: calcd, 797.13; found, 852 (osmometric in $CHCl_3$). (2) *cis*-Pd(P(C_6H_5)$_3$)$_2$(5-chlorotetrazolato)$_2$; colorless crystals; 62% yield; dec pt 241–244°. *Anal.* Calcd for $C_{38}H_{30}N_8P_2Pd$: C, 54.47; H, 3.61; N, 13.37; Cl, 8.46. Found: C, 53.86; H, 3.48; N, 12.98; Cl, 9.06. Molecular weight: calcd, 837.96; found, 901 (osmometric in $CHCl_3$).

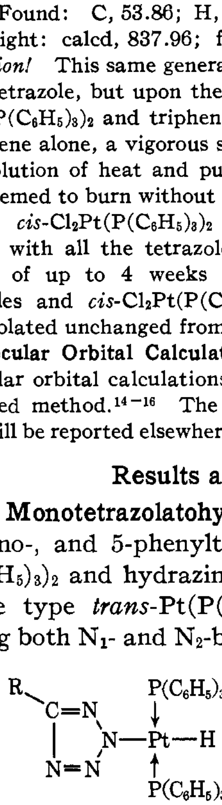
Caution! This same general procedure was attempted with 5-bromotetrazole, but upon the addition of the tetrazole to *trans*-Cl_2Pd(P(C_6H_5)$_3$)$_2$ and triphenylphosphine in benzene–ethanol or in benzene alone, a vigorous spontaneous reaction occurred with the evolution of heat and pungent white fumes and the whole mass seemed to burn without a visible flame.

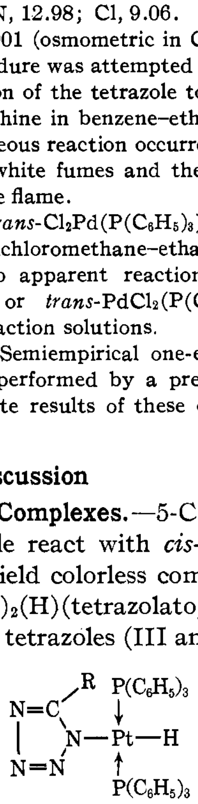
Both *cis*-Cl_2Pt(P(C_6H_5)$_3$)$_2$ and *trans*-Cl_2Pd(P(C_6H_5)$_3$)$_2$ were treated with all the tetrazoles in dichloromethane–ethanol for periods of up to 4 weeks with no apparent reaction. The tetrazoles and *cis*-Cl_2Pt(P(C_6H_5)$_3$)$_2$ or *trans*-PdCl_2(P(C_6H_5)$_3$)$_2$ were isolated unchanged from the reaction solutions.

Molecular Orbital Calculations.—Semiempirical one-electron molecular orbital calculations were performed by a previously described method.[14-16] The complete results of these calculations will be reported elsewhere.[17]

Results and Discussion

(a) **Monotetrazolatohydride Complexes.**—5-Chloro-, 5-bromo-, and 5-phenyltetrazole react with *cis*-Cl_2Pt(P(C_6H_5)$_3$)$_2$ and hydrazine to yield colorless complexes of the type *trans*-Pt(P(C_6H_5)$_3$)$_2$(H)(tetrazolato) containing both N_1- and N_2-bonded tetrazoles (III and IV).


III


IV

The geometry of the complexes was established from

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TABLE I

INFRARED AND NUCLEAR MAGNETIC RESONANCE DATA

Complex[a]	$\nu_{\text{Pt-H}}$, cm^{-1}	$\delta_{\text{Pt-H}}$, cm^{-1}	τ_{phenyl}	$\tau_{\text{Pt-H}}$	$J_{\text{Pt-H}}$, Hz	$J_{\text{P-H}}$, Hz	τ_{CH_3}
A	2222, 2212	881, 845	2.55	25.62, 26.13	964	13.2	...
B	2220, 2212	845, 840	2.55	25.62, 26.43	~916	12.5	...
C	2253, 2223	882, 850	2.56	25.66, 26.38	...	10.2	...
D	...	...	2.56	...	...	...	7.88, 8.12, 8.17, 8.49

[a] A, *trans*-Pt($P(C_6H_5)_3$)$_2$(H)(5-phenyltetrazolato); B, *trans*-Pt($P(C_6H_5)_3$)$_2$(H)(5-bromotetrazolato); C, *trans*-Pt($P(C_6H_5)_3$)$_2$(H)(5-chlorotetrazolato); D, *cis*-Pt($P(C_6H_5)_3$)$_2$(5-methyltetrazolato)$_2$.

the proton nmr spectra[18-20] (Table I). A representative spectrum is shown in Figure 1. The hydride spectra of the 5-phenyl- and 5-bromotetrazolato complexes possess a doublet of triplets (^{195}Pt satellite) to the low-field side of the central doublet of triplets with relative intensities of 1:4. The high-field satellite is obscured by the 2-kHz modulation side band (see Figure 1). Owing to the limited solubility the ^{195}Pt satellites were not observed for the 5-chlorotetrazolato complex. The magnitudes of $J_{\text{Pt-H}}$ and $J_{\text{P-H}}$ are in accord with those observed for other platinum hydrides.

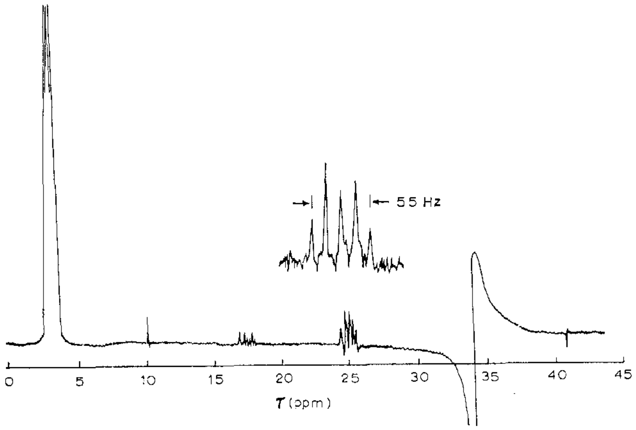

Figure 1.—HA-60-IL nmr spectrum of *trans*-Pt($P(C_6H_5)_3$)$_2$(H)-(5-phenyltetrazolato) in $CDCl_3$ at 30° with TMS internal standard: τ 2.7 (C_6H_5), 10 (TMS), 18.03 (^{195}Pt–H (platinum satellite)), 25.87 (Pt–H); 2-kHz modulation side band >30.

If these solutions consisted of only one of the two possible isomers III and IV, then the hydride nmr pattern would be expected to appear as nine lines. Coupling with the 33% natural abundance of ^{195}Pt ($I = {}^1/_2$) would give rise to an apparent triplet of relative intensities 1:4:1 with $J_{\text{Pt-H}} \approx 1000$ Hz.[18-20] These would be further split by the two equivalent cis ^{31}P atoms into a triplet of triplets with $J_{\text{P-H}} = 10$–20 Hz.[18-20]

If, on the other hand, both isomers were present in solution as in *trans*-(H)(SCN)Pt($P(C_2H_5)_3$)$_2$[18,20] and *trans*-(H)(NO_2)Pt($P(C_2H_5)_3$)$_2$,[18,20] this spectrum would be replicated with only slightly different chemical shifts to give rise to an 18-line spectrum. Thus, the existence of both isomers in solution is indicated by the presence of upfield and downfield multiplets of five lines with relative intensities of 4:1.

The hydride nmr pattern for these complexes is very similar to that found for the complex *trans*-Pt(H)(SCN)-($P(C_2H_5)_3$)$_2$ which exists as a 1:3 mixture of the thiocyanato–isothiocyanato complex in solution.[20] The relative intensities of the hydride resonances for the tetrazolato complexes show that the ratio of N_1-bonded to N_2-bonded complexes is approximately 1:1. As expected the τ values for the N_1-bonded and N_2-bonded complexes are very similar. The equimolar ratio of N_1- to N_2-bonded tetrazole suggests that the ligational abilities of these two nitrogen donors are essentially equivalent. Molecular orbital calculations[17] performed on the two isomers show that they have the same total energy and the same total overlap population. The two isomers should then theoretically be energetically equivalent. Furthermore, the calculated charge densities on the two hydridic hydrogens are very nearly the same with the N_2-bonded isomer possessing a slightly more hydridic hydrogen. The Löwdin hydridic hydrogen charge densities are as follows: N_2 bonded, −0.326; N_1 bonded, −0.322. The chemical shifts of the two hydridic hydrogens are thus predicted to be very similar in line with the experimental data. The calculated charge densities suggest that the more upfield resonance is due to the N_2-bonded isomer and the overlapping downfield resonance is due to the N_1-bonded isomer.

The infrared spectra of these complexes (Table I) show two medium-intensity bands in the 2212–2253-cm^{-1} range attributable to $\gamma_{\text{Pt-H}}$ and two weak bands in the 845–882-cm^{-1} range attributable to $\delta_{\text{Pt-H}}$.[18,19] The appearance of two distinct bands for $\gamma_{\text{Pt-H}}$ and $\delta_{\text{Pt-H}}$ in KBr supports the nmr data and suggests that both N_1- and N_2-bonded complexes are present in the solid state as well as in solution.

(b) **Bis-Tetrazolato Complexes.**—5-Cyclopropyltetrazole, on the other hand, reacted with *cis*-Cl_2Pt($P(C_6H_5)_3$)$_2$ and hydrazine to yield *cis*-($P(C_6H_5)_3$)$_2$Pt(5-cyclopropyltetrazolato)$_2$. This is similar to the reactions of the zerovalent complexes M($P(C_6H_5)_3$)$_4$ (M = Pd, Pt) which solely form complexes of the type M($P(C_6H_5)_3$)$_2$(5-substituted tetrazolato)$_2$.

Beck, *et al.*,[21] have prepared the trans complexes *trans*-Pd($P(C_6H_5)_3$)$_2$(5-R-tetrazolato)$_2$ (R = CH_3 or C_6H_5) from the reaction of *trans*-Pd($P(C_6H_5)_3$)$_2$(N_3)$_2$ with acetonitrile or benzonitrile, respectively. Their trans 5-CH_3 complex is dark yellow and decomposes at 205°; our cis complex is colorless and decomposes at 229–233°. Their trans 5-C_6H_5 complex is colorless and decomposes at 238°; our cis complex is colorless and decomposes at 151–153°. Their complexes are monomeric and possess low dipole moments in benzene; ours

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are monomeric in chloroform. All the $M(P(C_6H_5)_3)_2$-(tetrazolato)$_2$ complexes reported herein are colorless and soluble in nonpolar solvents such as CH_2Cl_2, $CHCl_3$, and benzene and insoluble in polar solvents such as ethanol, methanol, and water. Thus, the cis configuration is assigned to these complexes.[22]

The infrared spectra possess bands due to triphenylphosphine and to the tetrazole with the notable absence of any N-H stretching or bending frequencies. These complexes all have very similar spectra in the 1250-950-cm^{-1} region which is characteristic of the tetrazolate anion. The proton nmr spectra possess resonances due to triphenylphosphine and the 5 substituent (phenyl, methyl, or cyclopropyl) with the relative intensities supporting the analytical results. The spectra are devoid of any high-field resonances demonstrating the absence of any hydride species.

The methyl resonance for the complex *cis*-$(P(C_6H_5)_3)_2$-Pd(5-methyltetrazolato)$_2$ (Table I) appears as four distinct resonances with relative intensities of 2:2:1:1 from low to high field. Molecular models show that N_2-bonded tetrazole is free to rotate about the palladium-nitrogen bond, whereas N_1-bonded tetrazole is sterically hindered. The sterically most favored geometry has the tetrazole ring tilted with respect to the Pd-P-P plane resulting in four possible isomers for the cis complex. These are N_1-bonded (CH_3 up), N_1-bonded (CH_3 up); N_1-bonded (CH_3 up), N_1-bonded (CH_3 down); N_1-bonded, N_2-bonded; and N_2-bonded, N_2-bonded tetrazole. The observation of four distinct resonances for the methyl group in this complex suggests the possible presence of all four isomers in solution.[23] The cis isomer is recovered from this solution by addition of methanol.

The donor nitrogen atoms in the tetrazolate anion again are both N_1 and N_2 as for the hydride species above. Since the calculations show that the isomers are energetically equivalent, the 5-substituted tetrazoles may possibly behave as fluxional ligands[24] with the tetrazole undergoing a slow (on the nmr time scale) rearrangement at room temperature. Work is in progress to test this hypothesis.

(c) **Mechanisms.**—The final product in the hydrazine reduction of *cis*-$Cl_2Pt(P(C_6H_5)_3)_2$ is *trans*-Pt(H)-$Cl(P(C_6H_5)_3)_2$.[2a,25] It undergoes metathetical reactions with anionic donors that are better ligands than chloride;[18-20] many of the known platinum-phosphine-hydride complexes have been prepared by this method. This suggests that the reactive species in the hydrazine reduction reactions is *trans*-$Pt(H)Cl(P(C_6H_5)_3)_2$.

The reactions of the zerovalent complexes with the tetrazoles are in contrast to those which these complexes undergo with strong acids[5,26] (HX) and weak acids[4] (imides) where in both cases hydrides are formed. Since tetrazoles are intermediate in acid strength,[9] hydride complexes would also be expected from their reactions. It is likely that all the reactions of $M(P(C_6H_5)_3)_4$ involve either $M(P(C_6H_5)_3)_3$ or $M(P(C_6H_5)_3)_2$, both of which are formed in solution by dissociation.[8,27] The fact that the tetrazole-hydride complexes were prepared in the presence of excess tetrazole seems to suggest that no hydride intermediate is present in the reactions of $M(P(C_6H_5)_3)_4$ with tetrazoles. Thus, the mechanism of oxidative addition of the tetrazoles may differ from the mechanism of oxidative addition of either HX[26] or imides.[4]

Acknowledgments.—We thank Mr. Gordon Boudreaux for obtaining the A-60 nmr spectra. J. H. N. is grateful for the financial support afforded by Esso Research Laboratories, Humble Oil and Refining Co., Baton Rouge, La.

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