

Chemistry of Heterocyclic Compounds. 18. Transition Metal Complexes of Selected 2-Pyridylacetylenes¹

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The synthesis of several 2-pyridyl-, di(2-pyridyl)-, and di(6-methyl-2-pyridyl)acetylene platinum complexes is described. Selected platinacycles derived from di(2-pyridyl)acetylenes were subsequently converted into metallabicycles which possess both a platinum-acetylene and metal-pyridine bond. The crystal and molecular structure of **9** has been determined by single-crystal X-ray diffraction. Ligand exchange reactions of **4** were studied by ¹H NMR spectroscopy.

Since the preparation of (Ar₃P)₂Pt(arylacetylene) complexes,² a wide variety of substituted acetylene transition metal complexes have been characterized.³ During the course of our studies associated with the synthesis of ion selective chelating ligands, several 2-pyridylacetylenes were prepared.⁴ In view of the substantial attention given to platinum-acetylene complexes, we sought to explore the unique dual coordinating properties of these heterocyclic acetylenes.

The 2-pyridyl moiety, although structurally similar to benzene, displays enhanced electron-withdrawing properties relative to benzene, somewhat analogous to the *p*-nitrophenyl substituent. Since nitrophenylacetylene complexes are known⁵ to form comparatively more stable complexes in the phosphine-platinum series, we had reason to expect that the 2-pyridylacetylene complexes could also be prepared. However, the more significant question which remained to be answered was: how will the dual functionality of the acetylene π bond and the nitrogen lone pair within the same molecule affect the mode of coordination? Platinum complexes with pyridine as one of the ligands are certainly profuse in the literature; however, no reports of platinacycles which possess the free 2-pyridyl function(s) are known to these authors.^{1b} Accordingly, we presently describe the unique dual functionality of these di(2-pyridyl)acetylenes to form initially heterocyclic platinacycles, then metallabicycles which possess both a platinum-acetylene and metal-pyridine bond. We also report the results of an X-ray crystallographic determination of one such platinum-cobalt metallabicyclic **9**.

Experimental Section⁶

Bis(triphenylphosphine)(diphenylacetylene)platinum was prepared according to the method of Greaves, Lock, and Maitlis,⁷ mp 161–165° dec (lit.⁷ mp 161–164°). Bis(diphenyl-4-tolylphosphine)(diphenylacetylene)platinum was similarly prepared: mp 161–165° dec; NMR (CDCl₃) δ 2.2 (ArCH₃, s, 6 H) and 6.8–7.3 (ArH, m, 38 H); ir (KBr) ν 1750 cm⁻¹ (>C=C<).

Anal. Calcd for C₅₂H₄₄P₂Pt: C, 67.51; H, 4.79. Found: C, 67.41; H, 4.85.

Bis(triphenylphosphine)[di(2-pyridyl)acetylene]platinum.
Method A. A solution of 709 mg (1 mmol) of tetrakis(triphenylphosphine)platinum⁸ in 20 ml of benzene was added to a benzene solution of di(2-pyridyl)acetylene⁴ (mp 69–71°, 360 mg, 2.2 mmol) under nitrogen. The mixture was stirred for 2 hr at room temperature, then the solvent was removed under reduced pressure. The residual yellow semisolid was extracted with 20 ml of hot petroleum ether (bp 35–45°), affording a yellow product, which was recrystallized from benzene-petroleum ether, then from ethanol, giving 420 mg of **7**: mp 192–193° (sealed tube); ir (KBr) ν 1764 (>C=C<), 1583 cm⁻¹ (Pyr); NMR (CDCl₃) δ 8.5 (6-Pyr-H, d, 2 H), 7–8 (Ar- and Pyr-H, m, 36 H).

Anal. Calcd for C₄₈H₄₀N₂P₂Pt: C, 64.07; H, 4.26; N, 3.11. Found: C, 64.17; H, 4.20; N, 3.07.

Method B. A suspension of *cis*-dichlorobis(triphenylphosphine)platinum⁹ (760 mg, 1 mmol) in 15 ml of 95% ethanol was treated with a solution of 2 ml of hydrazine hydrate in 5 ml of ethanol. The reaction mixture was stirred for 10 min under nitrogen at 40°, during which time the white suspension gave way to a pale yellow solution. The solution was filtered into a flask containing di(2-pyridyl)acetylene (750 mg, 4.6 mmol) dissolved in 10 ml of 95% ethanol. The mixture was warmed to 45°, and water was added dropwise until slightly turbid. The mixture was stored at 0° for 5 days, during which time the pale yellow complex slowly crystallized: 270 mg; mp 192–193°. The spectral data were superimposable with those of product obtained via method A.

Anal. Calcd for C₄₈H₃₈N₂P₂Pt: C, 64.07; H, 4.26; N, 3.11. Found: C, 63.81; H, 4.28; N, 2.92.

Bis(triphenylphosphine)[di(6-methyl-2-pyridyl)acetylene]platinum. A benzene solution of di(6-methyl-2-pyridyl)acetylene⁴ (mp 138–139°, 208 mg, 1 mmol) was added to a benzene solution of tetrakis(triphenylphosphine)platinum (1.2 g, 1 mmol). The solution was stirred for 15 min at room temperature under nitrogen, then the solvent was removed in vacuo. The residue was extracted with cyclohexane and filtered. The filtrate was allowed to evaporate slowly. The initially formed white, crystalline triphenylphosphine oxide (mp 151–153°) was discarded, and after approximately 4 days the desired orange crystalline complex was isolated: mp 189–195° (sealed tube); ir (KBr) ν 1760 cm⁻¹ (>C=C<); NMR (CDCl₃) δ 2.16 (6-Pyr-CH₃, s, 6 H) and 6.95–7.39 (Ar- and Pyr-H, m, 36 H).

Anal. Calcd for C₅₀H₄₂N₂P₂Pt: C, 64.72; H, 4.56; N, 3.02. Found: C, 64.63; H, 4.54; N, 3.02.

Bis(triphenylphosphine)[phenyl(2-pyridyl)acetylene]platinum was prepared by method B from phenyl(2-pyridyl)acetylene¹⁰ [bp 120–122° (0.3 mm)]. Upon cooling at 0° for 36 hr, the product crystallized from methanol as yellow needles: mp 170–175°; ir (KBr) ν 1747 (>C=C<), 1580 cm⁻¹ (Pyr); NMR (CDCl₃) δ 8.5 (6-Pyr-H, d, 1 H), 7–8 (Ar- and Pyr-H, m, 37 H).

Anal. Calcd for C₄₉H₃₉NP₂Pt: C, 60.52; H, 4.88; N, 1.22. Found: C, 60.53; H, 4.55; N, 1.47.

Bis[diphenyl(4-tolyl)phosphine][di(2-pyridyl)acetylene]platinum was prepared by method B from di(2-pyridyl)acetylene and *cis*-dichlorobis[diphenyl(4-tolyl)phosphine]platinum (mp 288–292°). After 4 days at 0°, the complex crystallized from aqueous ethanol as yellow cubes: mp 112–115° (sealed tube, dec); ir (Nujol) ν 1748 (>C=C<), 1578 cm⁻¹ (Pyr); NMR (CDCl₃) δ 2.2 (ArCH₃, s, 3 H), 8.5 (6-Pyr-H, d, 1 H), 6.9–7.2 (Ar- and Pyr-H, m, 38 H).

Anal. Calcd for C₅₀H₄₂N₂P₂Pt: C, 64.72; H, 4.56; N, 3.02. Found: C, 64.59; H, 4.38; N, 3.17.

Bis(tri-4-tolylphosphine)[phenyl(2-pyridyl)acetylene]platinum was prepared by method B from phenyl(2-pyridyl)acetylene and *cis*-dichlorobis(tri-4-tolylphosphine)platinum.¹¹ The complex was recrystallized from ethanol, affording yellow crystals: mp 209–211° (sealed tube, dec); ir (Nujol) ν 1780, 1750 (>C=C<), 1578 cm⁻¹ (Pyr); NMR (CDCl₃) δ 2.2 (ArCH₃, s, 18 H), 8.4 (6-Pyr-H, d, 1 H), 6.9–7.2 (Ar- and Pyr-H, m, 32 H).

Anal. Calcd for C₅₅H₅₁NP₂Pt: C, 67.20; H, 5.23; N, 1.42. Found: C, 67.20; H, 5.20; N, 1.39.

Bis(triphenylphosphine)[di(2-pyridyl)acetylene]platinum-dichlorocobalt(II). A benzene solution of 900 mg of bis(triphenylphosphine)di(2-pyridyl)acetyleneplatinum was warmed to 40°

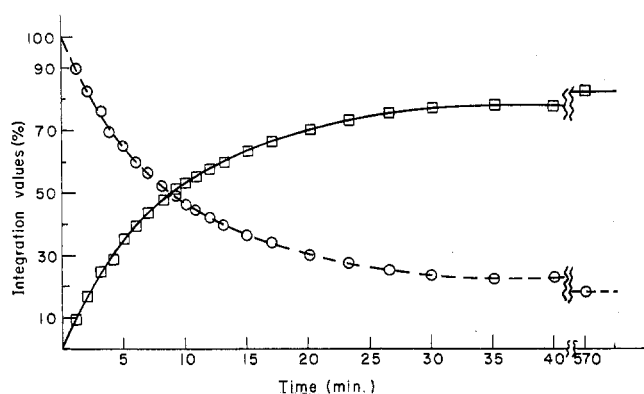


Figure 1. Plot of NMR integration values ($\pm 2\%$) of the 6-pyridylmethyl groups for 4 (---) vs. 12 (—) in benzene- d_6 at 37°.

and an ethanolic cobalt chloride solution (150 mg/20 ml) was added. The resulting green solution was evaporated in vacuo to dryness, and the residual solid was dissolved in benzene (ca. 70 ml). After filtration of undissolved solids, cyclohexane was added, and upon standing, the product formed as long, dark green needles: mp 270–280° (sealed tube, dec); ir (KBr) ν 1730 ($>C=C<$), 1597 (Pyr), 1120, 874, 770 cm^{-1} , uv-visible (EtOH) 610 nm (ϵ 246), 577 (182), 392 sh (3020).

Anal. Calcd for $C_{48}H_{38}N_2P_2Cl_2CoPt$: C, 59.09; H, 4.18; N, 2.55. Found: C, 59.13; H, 4.01; N, 2.49.

Bis(triphenylphosphine)[di(2-pyridyl)acetylene]platinumdichloropalladium(II). A benzene solution of bis(benzonitrile)dichloropalladium (960 mg, 0.25 mmol) was added dropwise under nitrogen to a stirred benzene solution of bis(triphenylphosphine)[di(2-pyridyl)acetylene]platinum at room temperature. Upon initial addition of a portion of palladium complex solution, a dark brown solid formed; then toward completion of this addition, a yellow solid precipitated, which was collected and copiously washed with cold benzene to remove benzonitrile: mp 250–260° (sealed tube, dec); ir (Nujol) ν 1707 ($>C=C<$), 1595 (Pyr), 1560 cm^{-1} .

Anal. Calcd for $C_{48}H_{38}N_2P_2Cl_2PdPt$: C, 53.47; H, 3.55; N, 2.60. Found: C, 53.56; H, 3.42; N, 2.51.

Attempted recrystallization of this solid from either dichloromethane-cyclohexane or ethanol-cyclohexane caused partial decomposition.

Attempted Preparation of Bis(triphenylphosphine)[di(2-pyridyl)acetylene]platinumdichloromercury(II). An ethanolic solution of 90 mg of bis(triphenylphosphine)[di(2-pyridyl)acetylene]platinum was stirred under nitrogen and an ethanolic mercuric chloride solution (28 mg/10 ml) was added. After cooling and filtering, the precipitate was dissolved in hot chloroform and filtered to remove the metallic mercury. Upon cooling and trituration with acetone or cyclohexane, $PtCl_2(PPh_3)_2$ was isolated: mp 305–308° (lit⁹ mp 310–312°); ir (CsBr-Nujol) ν 319 and 295 cm^{-1} .

The ethanol filtrate was concentrated to dryness and the residue chromatographed [thick layer, Brinkmann silica gel PF, 2 mm, ethyl acetate-cyclohexane (1:1)] affording 17 mg (94%) of di(2-pyridyl)acetylene, mp 69–71°.

NMR Study of Acetylene Exchange. Bis(diphenyl-4-tolylphosphine)(diphenylacetylene)platinum with Di(6-methyl-2-pyridyl)acetylene. Bis(diphenyl-4-tolylphosphine)(diphenylacetylene)platinum (93 mg, 0.1 mmol) dissolved in dry benzene- d_6 (500 μ l) was added to a NMR tube and thoroughly degassed with argon. At time zero, 21 mg (0.1 mmol) of di(6-methyl-2-pyridyl)acetylene in degassed benzene- d_6 (500 μ l) was added. The integration values for the free (δ 2.68) to complexed (δ 2.49) pyridylmethyl function vs. time (minutes) are plotted in Figure 1.

Crystal Data for Bis(triphenylphosphine)[di(2-pyridyl)acetylene]platinumdichlorocobalt(II). Bis(triphenylphosphine)[di(2-pyridyl)acetylene]platinumdichlorocobalt(II), $C_{48}H_{38}N_2P_2Cl_2CoPt$, dark green needles, mol wt 1030 $g\ mol^{-1}$, $a = 9.39$ (1), $b = 22.59$ (2), $c = 23.73$ (2) Å, $\beta = 101.4$ (1)°, $V = 4935$ Å³, space group $P2_1/c$, $Z = 4$, $D_c = 1.39$ $g\ cm^{-3}$. The 3306 independent observed reflections were measured with Zr filtered Mo K α radiation ($\lambda = 0.7107$ Å) by the $\theta/2\theta$ scan technique on an Enraf-Nonius PAD-3 diffractometer. All 56 nonhydrogen atoms were located by standard Patterson and Fourier techniques. Refinement is in progress, but the unweighted residual factor based on an isotropic, rigid group model stands at 0.125. No dispersion, absorp-

tion, or extinction corrections have yet been made, and all observed reflections have been included with unit weights.

Results and Discussion

Metallacycles. The platinum complexes of the pyridylacetylenes were prepared by the general methods previously described by Chatt et al.² or Maitlis et al.⁶ Addition of the acetylene to the hydrazine reduction product of *cis*-dichlorobis(triarylphosphine)platinum is the method of choice in these heterocyclic systems. The resultant complexes possess considerable stability as reflected by their inertness to air oxidation, diverse solvents, and thermal dissociation. The nitrogen lone pair also appears to be essentially inert to Pt(0) reactants under the reaction conditions. This inactivity sharply contrasts to behavior of these heterocyclic acetylenes with ether metal substrates, e.g., $Pd(PhCN)_2Cl_2$ or $Rh_2Cl_2(CO)_4$, from which polymeric metal-pyridyl complexes immediately precipitate. The absences of the initial, as well as expected reduced, acetylenic stretching frequencies in the infrared spectrum are indicative of such polymeric complexes.

Synthesis and recrystallization of 7 in hydrocarbon solvents led to the formation of transparent bright yellow prisms of a complex which analyzed consistently for $Pt_2(Ph_3P)_4(2-Pyr-C\equiv C-2-Pyr)_3$. However, recrystallization

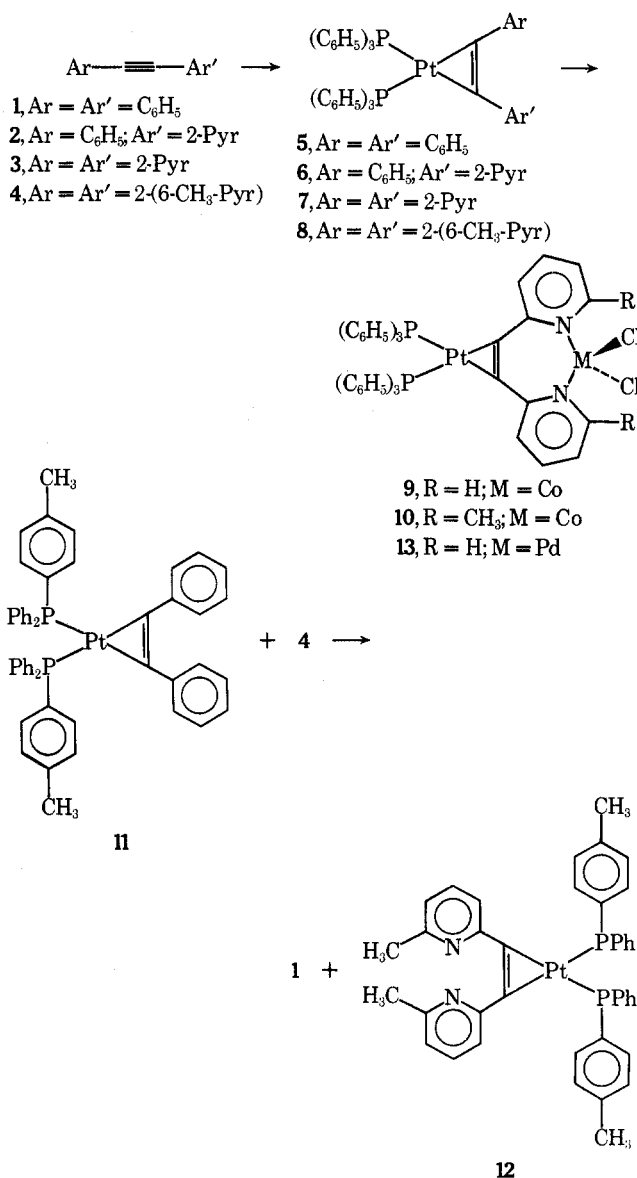


Table I
Selected Infrared Data

Ligand	ν_{\max} , cm^{-1}	Platina-cyclopropenes	ν_{\max}	Metallabicycles	ν_{\max}
1	2222 ^a	5	1768, 1740 ^b		
2	2227	6	1747		
3	2220 ^a	7	1764	9	1730
				13	1707
4	2215 ^a	8	1760	10	

^a Raman data. ^b From ref 7.

of this material from ethanol afforded the desired 1:1 complex. Since occlusion of the extra acetylene per two platinum 1:1 complexes is completely inhibited by recrystallization from donor solvents, the extra heterocyclic acetylene was probably loosely coordinated axially to the platinum complex plane.

The infrared spectra of these heterocyclic platinum complexes (6–8) display an observed reduced acetylene stretching frequency (ca. 450 cm^{-1} ; Table I), which is indicative of a strong acetylene to metal bonding and increased deviation of the acetylenic bond from linearity. This strikingly similar reduced acetylene stretching frequency of 6–8 to the metallabicycle 9, as well as 5,¹³ is suggestive of an approximate deviation of 40° from linearity.

Metallabicycles. Preparation of the metallabicycles exploits the *cis* orientation of the 2-pyridyl groups in 7. Addition of anhydrous cobalt chloride in ethanol to a benzene solution of 7 immediately produced a green solution, from which 9 can be isolated as green needles. The infrared spectrum of 9 shows a further lowering of the acetylenic stretching frequency (1730 cm^{-1}), and the visible absorption spectrum is similar to such tetrahedral cobalt complexes as $\text{Co}(\text{EtOH})_2\text{Cl}_2$ ¹⁴ and *o*-di(2-pyridyl)benzene- CoCl_2 .¹⁵

The cobalt bicycle, 9, is stable indefinitely in the solid state, but slowly dissociates in protic solvents. The half-life in ethanol is approximately 6 days at the initial concentration of 5×10^{-4} M. Although in complex 9 the cobalt is bound loosely in solution, the addition of a 6-methyl substituent on the pyridine rings prevents isolation of a stable crystalline complex (10); however, there is physical evidence that complexation does occur, albeit weakly. Slow dissociation of 9 may be, in part, the rationale for its unusually strong inhibitory properties in the electron transport chain of beef heart mitochondria. Preliminary studies¹⁶ indicated that 9 shows strong inhibition (89%) specifically for succinate-coenzyme Q reductase (complex II) at 10^{-6} M, whereas 7 showed little, if any, inhibition in these systems at 10^{-6} M.

Limited success has been realized in attempts to incorporate alternate transition metals into 7. Addition of a benzene solution of $\text{PdCl}_2(\text{PhCN})_2$ to 7 instantaneously gave an initial brown precipitate, which redissolved and gradually afforded a new semicrystalline solid. The infrared spectrum of this product included a band attributable to the reduced acetylenic stretch (1707 cm^{-1}). This further reduction of ca. 50 cm^{-1} over platinacycle 7 is consistent with the preparation of the palladium-containing bicycle 13. Dissolution of 13 in protic or "wet" solvents caused rapid decomposition; the resultant decomposition products were not investigated. All other attempts to add transition metal halides in ethanol to 7 failed to yield any fully characterizable products. The products isolated from attempted incorporations of FeCl_2 , CuCl_2 , NiCl_2 , PdCl_2 , ZnCl_2 , and RhCl_3 gave infrared spectra which showed no reduced acetylenic stretching frequency (1600–1800 cm^{-1}) region.

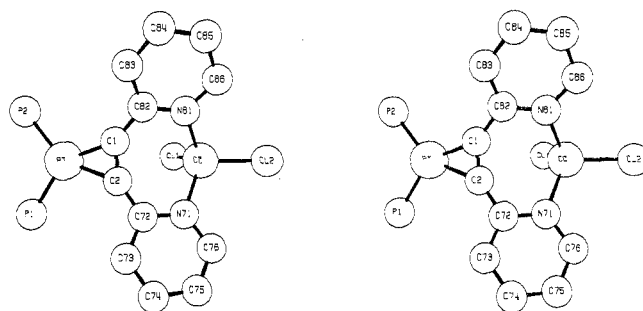
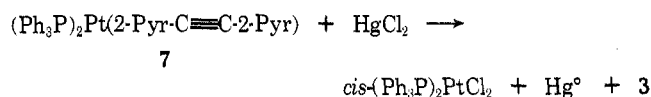


Figure 2. Stereopair diagram of the metallabicycle 9. Phenyl rings and hydrogen atoms have been omitted for clarity.

When 7 was subjected to ethanolic HgCl_2 , an immediate reaction occurred from which *cis*-dichlorobis(triphenylphosphine)platinum(II) and metallic mercury were isolated from the precipitate. The filtrate yielded a quantitative recovery of the starting acetylene 3. This spontaneous oxidation-reduction reaction can best be envisioned as two-electron oxidation of the ethylene dianion portion of the metallacycle 7 to 3 with simultaneous reduction of Hg^{II} to Hg^0 . The other platinacycles undergo a similar reaction with ethanolic HgCl_2 with an observable rapidity with increased electron-withdrawing acetylene substituents.



X-Ray Crystal Structure of Metallabicycle 9. Figure 2 is a stereopair diagram of the molecule with phenyl rings and hydrogen atoms omitted for clarity. The platinum(II) ion is bonded to two phosphorus atoms and the di(2-pyridyl)acetylene moiety in essentially planar coordination, though the $\text{C}_1\text{-C}_2$ axis is inclined at an angle of 5.8° to the mean platinum coordination plane. Upon coordination to the platinum, there occurs an effective reduction of the acetylene to an ethylene dianion, thus forming a platinacyclopropene ring. Rehybridization of the acetylenic carbon atoms causes the pyridine rings to bend back from the $\text{C}_1\text{-C}_2$ axis by 40°, identical with the angle found in bis(triphenylphosphine)diphenylacetyleneplatinum.¹³ The $\text{C}_1\text{-C}_2$ bond also apparently increases in length, from 1.20 Å in acetylene¹⁷ to 1.28 (8) Å. According to Pauling's formula,¹⁸ this is equivalent to a bond order of approximately 2.2. A similar lengthening, to 1.32 Å, was observed in bis(triphenylphosphine)diphenylacetyleneplatinum.¹³

Although there is a slight (15°) torsion of the pyridine rings about the $\text{C}_1\text{-C}_2$ axis, the ethylenic π -nodal plane is essentially coplanar with the platinum coordination plane. However, the pyridine rings are rotated out of the platinum coordination plane by 36°, which orientation must drastically reduce conjugation between the pyridine π system and the platinacyclopropene π system. Pyridine ring rotation allows the two nitrogen atoms to bond to the CoCl_2 moiety, thereby completing the tetrahedral coordination polyhedron about the cobalt(II) ion to give the molecule a puckered appearance. Indeed, the cobalt lies 1.88 Å below the platinum coordination plane, which plane makes a dihedral angle of 101° with the N-Co-N and Cl-Co-Cl planes are almost exactly perpendicular to one another. The awkward orientation of the two coordination polyhedra, and the Pt-Co distance of 4.614 (7) Å, precludes any direct metal-metal interaction.

Some further average molecular dimensions are as follows: $\text{Pt-P} = 2.269$ (9) Å, $\text{Pt-C} = 2.03$ (4) Å, $\text{P-phenyl C} =$

1.81 (1) Å, ethylenic C–pyridyl C = 1.40 (4) Å, Co–N = 2.05 (2) Å, Co–Cl = 2.19 (1) Å, P–Pt–P = 103.5 (5)°, N–Co–N = 106.1 (8)°, Cl–Co–Cl = 114.0 (7)°, Cl₁–Co–N = 112.1 (6)°, Cl₂–Co–N = 106.1 (6)°. All interatomic distances are consistent with previously reported¹⁹ values, though the Co–Cl distances may be slightly shorter than normal.

Ligand Exchange Reaction. Chatt originally noted^{2a} the ligand displacement reactions in complexes of the type Pt(Ar₃P)₂(Un), where Un represents either an olefin or acetylene. In general, acetylenic ligands bearing more electron-withdrawing substituents tend to displace from the complex the acetylene bearing less strongly electron-withdrawing substituents. Cook et al.²⁰ further explored the displacement reaction with respect to complexes of variously substituted phenylacetylenes and interpreted their results strictly in terms of a dissociative mechanism. Later Cook et al.^{5b} reported that an associative mechanism could also account for the observed kinetics. From a recent investigation, Halpern concluded that both mechanisms are involved and that the predominance of either is a function of the concentration of the exchanging ligands.²¹

The ligand substitution rates in these heterocyclic platinum complexes can be ascertained from ¹H NMR spectral data of the complexed vs. free acetylene ligands. Specifically, the chemical shifts of the methyl groups in 4 and 8 (δ 2.68 and 2.49, respectively) are separated sufficiently to permit accurate integration. One further convenience is to utilize diphenyl-4-tolylphosphine (δ 2.34 in the platinum complex) as an internal standard. Reaction of bis(diphenyl-4-tolylphosphine)(diphenylacetylene)platinum (11) with 4 was conducted in benzene-*d*₆ at 37°. The plot of integrated ¹H NMR signal intensities vs. time (Figure 1) indicated that 4 was 82% coordinated at equilibrium, and the reaction was 50% complete after 8.7 min. The initial rate of formation of complex 12 was 8.3 × 10⁻² mol/l. min⁻¹. Although we are not pursuing the kinetic aspects of this problem, the initial experiments indicate the electronic similarity between the 2-pyridyl and 4-nitrophenyl substituents in these acetylenic systems. The equilibrium constant (*K*_{eq} = 21) favors the displacement of diphenylacetylene from 11 to form the more stable heterocyclic complex. A comparable equilibrium constant was found for 4-nitrophenylacetylene and phenylacetylene complexes.^{5b}

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Registry No.—2, 13141-42-9; 3, 28790-65-0; 4, 42296-34-4; 5, 15308-61-9; 6, 51455-90-4; 7, 51455-89-1; 8, 51455-91-5; 9, 56783-88-1; 11, 56783-89-2; 12, 56783-90-5; 13, 56783-91-6; tetrakis(triphenylphosphine)platinum, 14221-02-4; *cis*-dichlorobis(triphenylphosphine)platinum, 15604-36-1; bis[diphenyl(4-tolyl)phosphine][di(2-pyridyl)acetylene]platinum, 56783-92-7; *cis*-dichlorobis[diphenyl(4-tolyl)phosphine]platinum, 56783-93-8; bis(tri-4-tolylphosphine)[phenyl(2-pyridyl)acetylene]platinum, 56783-94-9; *cis*-dichlorobis(tri-4-tolylphosphine)platinum, 31173-67-8; bis(benzonitrile)dichloropalladium, 14220-64-5.

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