Studies on the Reaction of Bis(triphenylphosphine)platinum–Acetylene Complexes with Protonic Acids[1] and the Characterization of Platinum Complexes with 2,4-Hexadiyne and 1-Phenyl-1-butyn-3-one

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Abstract: The reaction of $(PPh_3)_2Pt$(butyne-2) with HCl, HBr, HCO_2H, CF_3CO_2H, CH_3COSH, C_6H_5COSH, and picric acid has been studied, the product being $(PPh_3)_2PtX_2$ and an isomeric mixture of *cis*- and *trans*-butene-2. The yield of olefin is quantitative, with no gas chromatographic evidence for butane formation or free butyne-2. The reaction yields predominantly *cis*-butene-2, although the ratio of the trans isomer is larger with the sulfur acids. The reduction of alkynes to alkenes is unaffected by the presence in the solution of thiophene, allyl methyl sulfide, or aniline hydrochloride, which act as inhibitors for heterogeneously catalyzed hydrogenation reactions. The mechanism of the reaction is discussed and is considered to proceed *via* Pt(II) and Pt(IV) hydrides in addition to the isolable vinyl complex. Complexes of $(PPh_3)_2Pt$ with 2,4-hexadiyne and 1-phenyl-1-butyn-3-one have been prepared and their structures determined by ir and nmr spectroscopy. The complex between $(PPh_3)_3RhCl$ and 1-phenyl-1-butyn-3-one is also described.

The reaction between the complexes $(PPh_3)_2Pt$(acetylene) and protonic acids HX has been found to yield complexes of general formula $(PPh_3)_2PtX_2$ and the corresponding olefin.[1a,3,4] In the current study we wished to consider the scope and limitations of this reaction as a means of reducing acetylenes to olefins. In addition, it was of interest from the viewpoint of the mechanism of the reaction to be able to determine the isomer distribution of the olefin formed, and so a study has been made of the reaction of $(PPh_3)_2Pt$(butyne-2) with protonic acids because of the ready availability of gas chromatography for the separation and identification of the isomers of butene. At room temperature the elution of butene-1 from the column is complete before any butene-2 starts to come off (which is also well separated into the cis and trans isomers), so each isomer can be estimated separately. Although some isomer ratios of butene-2 are reported for the reaction of aqueous acids with $(PPh_3)_2Pt$(butyne-2), these data are probably somewhat inaccurate compared to those of the gaseous or solid acids because of the subsequent addition of the acid to butene-2. When aqueous HCl or HBr is used, extra peaks are obtained on the gas chromatogram which increase in size when the solution of butene-2 in the reaction medium is allowed to stand for a short while. Since these peaks increase in size at the expense of those due to *cis*- and *trans*-butene-2, it is apparent that these new peaks are due to a subsequent reaction or isomerization. In view of this the reaction with anhydrous acids is much more applicable and we have not studied further the nature of these other products. Since the rates of the reactions of aqueous hydrohalic acid with the cis and trans isomers may not be equal, an accurate estimate of the initial isomer ratio formed cannot be obtained in the case of aqueous hydrohalic acids. Although the reaction is somewhat limited in that aqueous acids cannot be used as a method for reduction of acetylenes to olefins, it does have the advantage that in no case did we observe any significant (<1%) amount of butane formation.

The results obtained from the gas chromatographic analysis of butene-2 are summarized in Table I, where the relative amounts of the cis and trans isomers obtained for a range of protonic acids and solvents are shown. The range of solvents should preferably be wider, but certain restrictions eliminate several possibilities: solvents such as ethanol, ether, and hexane cannot be used because of the insolubility of $(PPh_3)_2Pt$(butyne-2) in these liquids; solvents such as acetone, DMF, and DMSO are also unavailable because they

Table I. Per Cent Trans Isomer Obtained in the Reaction of $(PPh_3)_2Pt$(butyne-2) with Protonic Acids[a]

	$CHCl_3$	Aromatic solvents[b]
HCl(g)	20[c]	8[d]
HCl (concd)	26	9
CH_3CO_2H	22	14
CF_3CO_2H	42	14
$C_6H_2(NO_3)_3OH$		10
CH_3COSH	34	53
C_6H_5COSH	30	44

[a] In the preliminary communication the isomers were reversed in error. In a typical run 100 mg of complex was dissolved in 1 ml of solvent and the acid added at room temperature. [b] Isomer ratios measured in benzene, toluene, or xylene solution were found to be the same. [c] An isomer ratio of 23% trans was obtained when the initial $CHCl_3$ solution of $(PPh_3)_2Pt$(butyne-2) was saturated with aniline hydrochloride. When the initial solution contained 20% allyl methyl sulfide, 30% *trans*-butene-2 was obtained. [d] When the benzene contained 5% thiophene the mixture of butenes contained 9% of the trans isomer.

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[1] (a) For a preliminary communication, see P. B. Tripathy and D. M. Roundhill, *J. Amer. Chem. Soc.*, **92**, 3825 (1970); (b) presented in part at the Second North American Meeting of the Catalysis Society, Houston, Texas, Feb 1971.

[2] NSF Undergraduate Summer Research Trainee.

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react readily with protonic acid. Certain acids also cannot be used; with imides and HCN we are unable to obtain olefins, and in the case of HBr, although butene-2 was obtained, the rate of addition of even anhydrous HBr to yield bromobutane was too rapid to allow meaningful measurement of the ratio of butenes formed.[5]

The reaction proceeds very rapidly, and upon introduction of acid to a solution of $(PPh_3)_2Pt$(butyne-2) a quantitative yield of *cis*-$(PPh_3)_2PtX_2$ is almost immediately precipitated, which makes the reaction rather difficult to study by conventional kinetics. Gas chromatographic analysis shows no evidence for the formation of butane, and the lack of any remaining butyne-2 shows that the reaction has gone to completion; in addition there is no evidence for isomerization leading to the formation of butene-1. The absence of the further hydrogenation of butenes to butane is probably due to the difference in stability of acetylene and olefin complexes of $(PPh_3)_2Pt$; the greater stability to dissociation of the acetylene complex over the olefin complex allows the intermediate hydride formed to transfer to the coordinated acetylene to yield the vinyl complex. Since the olefin complex is much more labile,[6] it is probable that dissociation occurs either prior to hydride formation or before transfer can occur. This explanation is reinforced by the fact that in the case of $(PPh_3)_2Pt(C_2F_4)$, where the olefin is more firmly bonded, the product of the reaction with acids is the fluoroalkyl complex.[3]

The mechanism of the reaction has been considered previously and has been found to proceed *via* the isolable vinyl intermediate, which is then further converted by HX to the olefin and *cis*-$(PPh_3)_2PtX_2$. We believe that the mechanism of the reaction is the one shown in Figure 1 which involves the intermediate formation of two platinum hydrides and can be described as pseudocatalytic since the acetylene complex can readily be prepared from the dihalo complex.

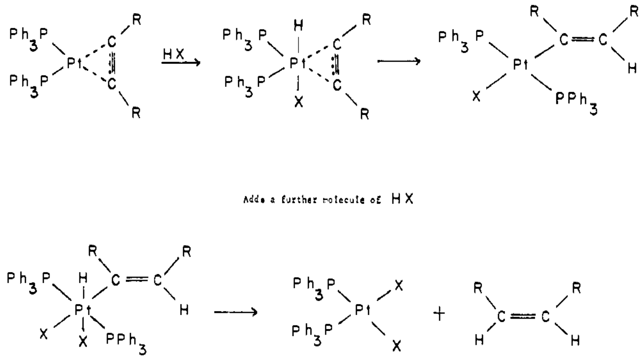

Figure 1. Mechanism of the reaction of complexes of the type $(PPh_3)_2Pt$(acetylene) with protonic acids.

We have not isolated either of the intermediate hydrides, but they represent reasonable structures since hydrides of both platinum(II)[7,8] and platinum(IV)[9] have been isolated and characterized in similar systems. The mechanism shown in Figure 1 is essentially that discussed in the preliminary communication[1a] except that the vinyl intermediate is shown with a cis stereochemistry about the double bond. This communication was primarily concerned with the mechanism of the reaction, and there was no way of determining the stereochemistry about this double bond; the trans stereochemistry was suggested in order to explain the conversion of a coordinated *cis*-diphenylacetylene[10] to *trans*-stilbene (mp 122°, τ 3.01). Since the publication of this work, however, it has been shown that the vinyl complexes obtained by the addition of 1 mol of acid are to be regarded as cis about the double bond.[11] Since stilbene is obtained from the reaction exclusively in the trans form, the two possible places where isomerization occurs are the transfer of the hydrogen in the platinum(IV) hydride complex from the metal to the olefin and formation of the somewhat unstable *cis*-stilbene followed by its subsequent isomerization to the trans isomer. Since *cis*-stilbene is isomerized to the trans isomer by HBr,[12] this latter explanation seems quite plausible, although in the protonation of an iridium–vinyl complex with HCl a good yield of the cis isomer has been obtained, with only a small amount of the trans isomer being produced.[13] From the results of this work it must be concluded that *cis*-stilbene is stable in the reaction medium, and hence it appears that retention of configuration is not observed in the conversion of the platinum–vinyl complex into the free olefin.

The range of solvents which can be used in the conversion of butyne-2 to butene-2 is somewhat limited because of the reasons mentioned earlier; this means that it is rather difficult to make a full study of the factors which may influence the isomer ratio of butene-2 obtained. The results, however, are shown in Table I, and a few comments can be made in relation to the mechanism of the reaction and its scope as a preparative reduction method. In the latter respect it can be seen from Table I that the method can be used with a variety of acids, including weak ones such as acetic acid. We have found that the cis isomer predominates, but that there is quite a large variation in the isomer ratio indicating that there can be extensive change in configuration in the final step of the reaction. With the exception of the sulfur acids, there seems to be a significant increase in the amount of trans isomer when the polarity of the solvent is increased; CH_2Cl_2 gives very similar results to $CHCl_3$, but extensive work was not carried out with this solvent because its high volatility caused it to be more rapidly eluted from the column than was convenient. The sulfur acids are quite anomalous, giving a high proportion of the trans isomer even when the nonpolar aromatic solvents were used. This effect cannot be correlated with the trans influence of the anion, or the proportion of *trans*-butene-2 in benzene would be larger with HCl than with CF_3COOH. It is possible, however, that the effect may be due to the ability of the conjugate base to act as a ligand, which has been found[14] to be important in determining the stabil-

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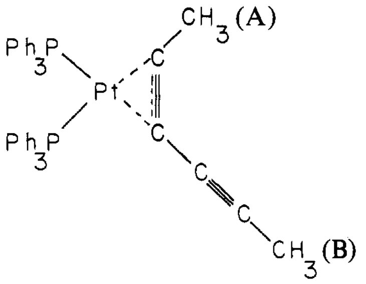

Figure 2. Structure of the complex bis(triphenylphosphine)-platinum–2,4-hexadiyne.

ity of platinum hydrides. From this previous study it appeared that the isolation of platinum hydrides by the oxidative addition of protonic acids was favored when the conjugate base is a good ligand for platinum. It may be possible to extend this argument to the present work, since it is reasonable to assume that isomerization of the cis vinyl complex to a trans olefin occurs because the trans isomer is the thermodynamically more stable isomer. If the sulfur ligand forms a more stable hydride, it might be expected that the transfer step would occur more slowly, thereby allowing more complete isomerization to the trans isomer.

In Table I the results are shown for reactions carried out in the presence of several substances which have poisoning effects on heterogeneous catalysts in hydrogenation reactions. In this reaction the hydrogenation still occurs readily in the presence of these substances and the isomer ratio of butene-2 formed is little affected. In addition, the formation of butene-2 in the presence of allyl methyl sulfide shows that not only is the reaction unaffected by sulfur compounds, but that other olefins in the reaction mixture do not affect the reduction of acetylenes.

Although we have been unable to obtain reliable quantitative results, it is of interest to note that butene-2 can be obtained from the reaction of $(PPh_3)_2Pt$(butyne-2) with HBF_4. Since fluoroborate is a very poor ligand for platinum, this observation implies that a three-coordinate ionic vinyl intermediate will be formed, but we have been unable to isolate this complex pure. Recently we have found, however, that aqueous HF,[15] unlike the anhydrous[16] acid, will react with $(PPh_3)_4Pt$ to form a hydride. Since HBF_4 in aqueous solution readily dissociates to HF, it now seems more likely that it is HF which is responsible for the reaction, the intermediate being the fluoroplatinum–vinyl complex.

Since this method of reduction is specific for an acetylenic bond, it appears likely that this reaction can be used to reduce an acetylene to an olefin without affecting other functional groups such as double bonds and carbonyl groups. In view of this we have studied the complexes of $(PPh_3)_2Pt$ with 2,4-hexadiyne and 1-phenyl-1-butyn-3-one. Although we have not confirmed the possibility of selective reduction, the ligands have given several novel complexes which are now reported.

2,4-Hexadiyne. The reaction of *cis*-$(PPh_3)_2PtCl_2$ and hydrazine with 2,4-hexadiyne leads to the formation of the acetylene complex shown in Figure 2, where only one of the triple bonds is coordinated ($\nu_{C\equiv C}$ 1760 cm^{-1}), with the other one free ($\nu_{C\equiv C}$ 2205 cm^{-1}). This represents a lowering of 400 cm^{-1} from the absorption of the free ligand (the ν_8 band assigned to the triple bond stretch is at 2160 cm^{-1}) for the coordinated triple bond and an increase of 45 cm^{-1} for the free one.[17] The coordination of only one of the triple bonds is further confirmed by the ^{1}H nmr spectrum of the complex. The B methyl protons appear at τ 8.2, which is the same as in the free ligand, but the A methyl protons appear as a doublet at τ 8.0 ($J_{P(trans)-CH_3}$ = 6 Hz) flanked by satellites due to ^{195}Pt ($J_{^{195}Pt-CH_3}$ = 40 Hz);[18] integration of the methyl against the phenyl protons further confirms the stoichiometry. The lability of the complex follows the expected trend,[19] since addition of diphenylacetylene to the solution of the complex causes the ^{1}H nmr spectrum to collapse to a single line at τ 8.2, indicating displacement of the diyne and formation of $(PPh_3)_2Pt$(diphenylacetylene).

We have been unable to prepare the complex with both triple bonds coordinated to the metal, although complexes have been isolated where each triple bond of a diyne is coordinated.[20] Methods which have been attempted include carrying out the reaction with a deficit of 2,4-hexadiyne (which resulted in a lower yield of the above complex) and reaction of $(PPh_3)_2Pt$(2,4-hexadiyne) with $(PPh_3)_2PtCl_2$ and hydrazine, which was equally unsuccessful. It appears unlikely that steric factors can be responsible, and it seems more probable that this effect may be due to the coordination of one of the triple bonds causing a change in reactivity of the other in conjugation with it.

1-Phenyl-1-butyn-3-one. The reactions of this keto-acetylene with complexes of both platinum and rhodium have been studied. The reactions with $(PPh_3)_2Pt$(butyne-2) and $(PPh_3)_3PhCl$ proceed readily, yielding complexes where the triple bond of 1-phenyl-1-butyn-3-one is coordinated, and butyne-2 and triphenylphosphine are respectively replaced. Both complexes show bands due to a coordinated acetylene, at 1720 cm^{-1} for the platinum complex and at 1860 cm^{-1} for the rhodium complex. These positions are close to those expected for such complexes; the free ligand shows a band at 2220 cm^{-1}, and as in the corresponding complexes with hexafluorobutyne-2, the lowering of $\nu_{C\equiv C}$ is much greater with the $(PPh_3)_2Pt$ complex than with the $(PPh_3)_2RhCl$ complex.[21,22] In addition there are bands due to $\nu_{C=O}$ which are of slightly greater intensity than the coordinated triple bond, these being at 1635 cm^{-1} for the platinum complex and 1625 cm^{-1} for the rhodium complex (the free ligand shows a band due to $\nu_{C=O}$ at 1670 cm^{-1}). In addition to the ir spectra the ^{1}H nmr spectra are closely similar, with the integrated phenyl:methyl ratio confirming the stoichiometry. The methyl resonance appears at τ 8.37 with the platinum complex and at τ 8.57 with the rhodium

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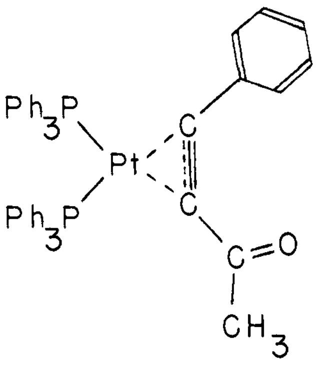

Figure 3. Structure of the complex bis(triphenylphosphine)-platinum–1-phenyl-1-butyn-3-one.

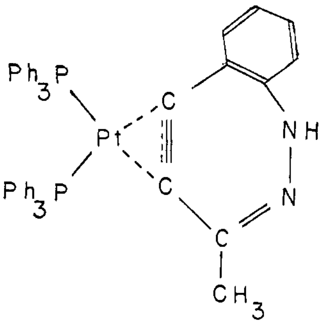

Figure 4. Structure of the complex bis(triphenylphosphine)-platinum–7-methylbenzo[3,4]-1,2-diazepine.

complex, the line appearing as a singlet (the free ligand shows this band at τ 7.67). The structure of the platinum complex is shown in Figure 3; the rhodium complex will be similar. The rhodium complex reacts in a comparable manner to other acetylene or olefin complexes of $(PPh_3)_2RhCl$ in that 1-phenyl-1-butyn-3-one is readily displaced by CO to give $(PPh_3)_2RhCOCl$, which was identified by its ir spectrum.

The usual method for the preparation of acetylene complexes of $(PPh_3)_2Pt$, however, is to reduce *cis*-$(PPh_3)_2PtCl_2$ with hydrazine in the presence of excess acetylene. When this method is used with 1-phenyl-1-butyn-3-one, a new complex is obtained which is pale cream in color rather than the bright yellow of the complex formed in the reaction with $(PPh_3)_2Pt$(butyne-2). This new complex shows a strong band in the ir spectrum at 1730 cm^{-1} but only a weak band in the 1600–1700-cm^{-1} region, indicating loss of the keto group. The ^{1}H nmr spectrum shows resonances at τ 2.95 (35, phenyl) and 8.34 (3, methyl), the integration showing that the ratio of ligand:$(PPh_3)_2Pt$ is 1:1. Since the microanalytical data show that nitrogen is present in the complex, it is apparent that the keto group must have been lost by condensation with hydrazine (or, more correctly, with the platinum–hydrazine intermediate[9] initially formed in the reaction). This reaction would be expected to lead to the formation of a hydrazone complex. However, such compounds are extremely difficult to isolate and could not be obtained in the presence of excess ketoacetylene. The reason that hydrazones are difficult to isolate is that they react with a second molecule of the ketone to form an azine; it is possible that such a complex could be formed in this reaction, but since there is no band in the ir spectrum in the 2200-cm^{-1} region the second triple bond must also be coordinated to $(PPh_3)_2Pt$. This would give a complex containing only about 1.6% nitrogen, and since the observed molecular weight is 830, with no evidence of dissociation in the nmr spectrum, it seems unlikely that such a structure can satisfactorily explain the analytical and spectral data found for the complex.

The most reasonable structure which can explain the data is the one shown in Figure 4 with a coordinated 7-methylbenzo[3,4]-1,2-diazepine group. This structure is quite feasible, since coordination of a triple bond to a metal causes a large deviation from linearity in this group, the bending being in a cis manner away from the metal. The resultant geometry about the triple bond closely resembles that of an olefin,[10] thereby allowing small-ring[23] compounds to be isolable which could not be obtained if the triple bond were free and linear. Although the complex shows no band due to the carbonyl, the ir spectrum shows a weak band at 1655 cm^{-1} which can be assigned to $\nu_{C=N}$ (this stretching mode is usually weak, especially in conjugated systems, and is not very useful for structure diagnosis[24]) and a second weak band at 3380 cm^{-1} which is probably due to ν_{NH}. Although there is extensive conjugation in the ring system, it is not aromatic; however, it is significant to note that when a model is made of the structure using Lapine–Leybold models with an olefin in place of a coordinated acetylene, the structure readily forms as a strain-free slightly puckered ring.

A plausible rationalization for the reactivity of the ortho hydrogen on the phenyl ring can be made by comparison of the effect with that of phenylphosphines. In several cases it has been found that with a coordinated phenylphosphine the ortho hydrogen on the ring is reactive and is replaced by the transition metal.[25,26] The reaction we now describe seems to represent a similar case where coordination of the triple bond has allowed the ortho hydrogen to become reactive.

Experimental Section

Infrared spectra were obtained as Nujol mulls on Perkin-Elmer Model 700 or Beckman IR8 spectrometers. Nuclear magnetic resonance spectra were obtained on Varian A-60 and T-60 spectrometers as solutions in $CDCl_3$ using tetramethylsilane as internal reference. Gas chromatography, for the analysis of butenes, was carried out at room temperature on a Varian Aerograph Model 600 instrument equipped with a Leeds and Northrup Speedomax H recorder, using helium as carrier gas. The column used was 30 ft long and packed with an adsorbent consisting of 25% Ucon on Chromosorb. Identification of the isomers was carried out by comparison of their retention times with those obtained by the sodium ethoxide elimination reaction of 2-bromobutane,[27] the areas of the peaks being measured both by a Disc integrator and by a compensating planimeter. Retention times are not given because of their extreme sensitivity to temperature fluctuations; each of the experimental runs was followed by injection of the above

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standard in order that the identity of the cis and trans isomers could be verified. A check of the isomer ratio of butene-2 after completion of the reaction showed that the proportion of cis and trans isomers was not changed even after several hours in contact with the reaction medium, indicating that there is no isomerization of the butenes following their initial formation. Typical solutions used for the measurement of the isomer ratio of butene-2 obtained contained 100 mg of $(PPh_3)_2Pt$(butyne-2) in approximately 1 ml of solvent; to this solution was added excess acid; from the resulting suspension, between 1 and 5 μl was taken and injected into the column. The solvents used were Baker Analyzed grade and the acids were commercial samples. Butyne-2, 1-phenyl-1-butyn-3-one, and 2,4-hexadiyne were obtained from Farchan Research Chemicals, Willoughby, Ohio. The first two were used without purification, but the diyne was purified by sublimation *in vacuo* immediately prior to use. Hexafluorobutyne-2 was obtained from Peninsular ChemResearch, and potassium tetrachloroplatinite from Engelhard Industries, Inc. Microanalyses were carried out by Chemalytics Inc., Tempe, Ariz., and Schwarzkopf Microanalytical Laboratories, Woodside N. Y. The preparations of $(PPh_3)_2$-Pt(butyne-2) and $(PPh_3)_2$Pt(diphenylacetylene) were carried out by the method described previously.[19] All preparations were carried out under nitrogen.

Preparation of Vinyl Complexes from $(PPh_3)_2$Pt(diphenylacetylene) and Protonic Acids. In the preparation of the chloro complex, $(PPh_3)_2Pt(PhC{\equiv}CPh)$ (1.0 g) was dissolved in the minimum volume of benzene (~3 ml) and 0.08 ml of concentrated HCl was added. The solution was stirred at room temperature for 1 hr and the very pale yellow microcrystalline precipitate was filtered to give the complex in quantitative yield, $\nu_{C=C}$ 1590 cm^{-1} (m). *Anal.* Calcd for $C_{50}H_{41}ClP_2Pt$: C, 64.2; H, 4.38; Cl, 3.78. Found: C, 64.1; H, 4.29; Cl, 4.01.

Similarly, using equimolar proportions of the diphenylacetylene–platinum complex and picric acid, the picrate-substituted vinyl complex $(PPh_3)_2$Pt(picrate)(CPh=CHPh) was obtained. In this case, however, the initial product may separate as an oil and recrystallization from ethanol is necessary to obtain the pure complex. *Anal.* Calcd for $C_{56}H_{43}N_3O_7P_2Pt$: C, 59.7; H, 3.85; N, 3.73; P, 5.50. Found: C, 59.7; H, 3.99; N, 3.74; P, 5.53.

The same method was used further to prepare the 1-2-diphenylvinyl complex using *p*-toluenesulfonic acid: $\nu_{C=C}$ 1510, ν_{SO_3H} 1200 cm^{-1}; τ 3.0 (45, phenyl), 7.92 (3, methyl). *Anal.* Calcd for $C_{57}H_{48}O_3P_2PtS$: C, 64.0; H, 4.52; P, 5.78. Found: C, 63.7; H, 4.56; P, 5.68.

Bis(triphenylphosphine)platinum–2,4-Hexadiyne. Hydrazine was added to a suspension of *cis*-$(PPh_3)_2PtCl_2$ (0.53 g) in ethanol until a yellow solution was obtained. Excess 2,4-hexadiyne was then added and the solution was stirred. The colorless compound which precipitated was filtered, washed with ethanol, and dried *in vacuo* to yield the complex: mp 145–147° (the complex begins to decompose at 130°); yield 0.40 g (75%); $\nu_{C\equiv C}$ (Nujol mull and solution in $CHCl_3$) 2205, 1760 cm^{-1}; τ 2.8 (30, phenyl), 8.0 (3), and 8.2 (3, methyl, ($J_{P(trans)-CH_3} = 6$ Hz, $J_{Pt-CH_3} = 40$ Hz). *Anal.* Calcd for $C_{42}H_{36}P_2Pt$: C, 63.2; H, 4.56. Found: C, 63.5, 63.3; H, 4.46, 4.31.

Bis(triphenylphosphine)platinum–1-Phenyl-1-butyn-3-one. To a solution of $(PPh_3)_2$Pt(butyne-2) (310 mg) in benzene was added excess 1-phenyl-1-butyn-3-one. After allowing the solution to stand for about 10 min, nitrogen was blown through the solution, to remove butyne-2, until only a small quantity of solvent remained. Ethanol was added to this solution when bright yellow crystals of the complex were obtained. These crystals were filtered and dried *in vacuo*: mp 172° (with decomposition to a red liquid); yield 255 mg (74%); $\nu_{C\equiv C}$ 1720, $\nu_{C=O}$ 1635 cm^{-1}; τ 2.95 (35, phenyl), 8.37 (3, methyl). *Anal.* Calcd for $C_{46}H_{38}OP_2Pt$: C, 64.0; H, 4.43; P, 7.17. Found: C, 63.6; H, 4.25; P, 7.23.

Bis(triphenylphosphine)platinum–7-Methylbenzo[3,4]-1,2-diazepine. To a suspension of *cis*-$(PPh_3)_2PtCl_2$ (750 mg) in ethanol (9 ml) hydrazine hydrate was added dropwise (1 ml in 1 ml of ethanol) until the *cis*-$(PPh_3)_2PtCl_2$ was *almost* completely dissolved. The yellow solution was filtered and excess 1-phenyl-1-butyn-3-one added. The solution was heated to reflux under nitrogen and then allowed to cool to room temperature or −10°, when the crude complex was obtained; yield 432 mg (51%). The complex was recrystallized by dissolving it in benzene, filtering the solution (a white solid is removed which is probably hydrazine hydrochloride), adding ethanol, and allowing the solution to stand at −10°. The pale, cream-colored crystals were filtered and dried *in vacuo* for 48 hr. The complex starts to turn brown at 137° and finally melts to a red liquid at 151°: $\nu_{C\equiv C}$ 1730, $\nu_{C=N}$ 1655 (w), ν_{NH} 3380 (w) cm^{-1}; τ 2.95 (35, phenyl), 8.34 (3, methyl, $J_{Pt-CH_3} =$ 4 Hz). *Anal.* Calcd for $C_{46}H_{38}N_2P_2Pt$: C, 63.0; H, 4.37; N, 3.21; P, 7.06; mol wt, 876. Found: C, 62.7, 63.1; H, 4.38, 4.66; N, 3.23, 3.15; P, 7.05; mol wt, 830 ($CHCl_3$). (The N analysis was carried out on separate samples by two different analysts.)

Chlorobis(triphenylphosphine)rhodium–1-Phenyl-1-butyn-3-one. To a burgundy-colored solution of $(PPh_3)_3RhCl$ (220 mg) in benzene (~15 ml) was added excess 1-phenyl-1-butyn-3-one, and the solution was stirred. After about 2 hr a bright yellow precipitate was obtained (in some of the reaction runs it was necessary to add ethanol to cause the precipitation) which was filtered and dried *in vacuo* to give the complex: mp 147° (with decomposition); yield 140 mg (73%); $\nu_{C\equiv C}$ 1860, $\nu_{C=O}$ 1625 cm^{-1}; τ 2.70 (35, phenyl), 8.57 (3, methyl). *Anal.* Calcd for $C_{46}H_{38}ClOP_2Rh$: C, 68.5; H, 4.75. Found: C, 69.6; H, 4.97.

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