trans-chlorodinitrogenbis(triphenylphosphine)iridium(I), 21414-18-6; *trans*-bromocarbonylbis(methyldiphenylphosphine)iridium(I), 19354-07-5; trifluoroacetyl chloride, 354-32-5; difluoroacetyl chloride, 381-72-6; monofluoroacetyl chloride, 359-06-8; acetyl chloride, 75-36-5; trifluoromethyl iodide, 2314-97-8.

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Trans-Ligand Effects in the Insertion Reactions of Ethylene and Phenylmethylacetylene with Neutral and Cationic Hydridoplatinum(II) Complexes

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A series of cationic *trans*-$(PEt_3)_2PtHL^+PF_6^-$ (L = acetone, CO, PEt_3, $AsPh_3$, $P(OMe)_3$, $P(OPh)_3$) and neutral *trans*-$(PEt_3)_2PtHX$ ($X^- = Cl^-, NO_3^-, NO_2^-, CN^-$) complexes has been prepared and allowed to react with ethylene and phenylmethylacetylene. The reactivity to give inserted products is found to be a function of the trans group, L or X^-. Although the acetylene is the more reactive toward insertion, the same order of reactivity is found for both ethylene and phenylmethylacetylene. Reactivity of the cationic hydrides decreases in the order L = acetone >> CO > $AsPh_3$ > $P(OPh)_3$, $P(OMe)_3$, PEt_3 while the neutral hydrides follow the order $X^- = NO_3^- > Cl^-, NO_2^-, CN^-$. The mechanistic implications are considered and a general mechanism for insertion is proposed.

Chatt and Shaw's[1] initial demonstration of the insertion reaction 1 has provided a mechanistic foundation for many

$$\underset{\text{I}}{trans\text{-}(PEt_3)_2PtHCl} + C_2H_4 \xrightarrow[40\ \text{atm}]{90°} \underset{\text{II}}{trans\text{-}(PEt_3)_2PtC_2H_5Cl} \qquad (1)$$

discussions of homogeneous catalytic hydrogenation and isomerization.[2,3]

The intimate details of reaction 1 were initially assumed[4,5] to involve associative olefin coordination to give a five-coordinate hydridoolefin intermediate, followed by a migratory rearrangement and collapse to a square-planar insertion product. It has been pointed out that, in certain cases, an alternative mechanistic pathway not previously considered may apply.[6]

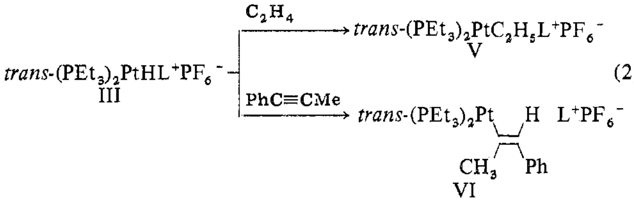
Thus, when the ligand trans to hydride is very weakly coordinating (e.g., as with acetone or NO_3^- [7]), a mechanism involving olefin coordination in the nascent site with displacement of the trans ligand to give a four-coordinate hydridoolefin complex is operative.

We recently presented evidence regarding this apparent mechanistic dichotomy[8] and discussed kinetic data which establish that in certain cases insertion proceeds by the latter mechanism.[9,10]

Some additional results reported herein indicate that the insertion of olefins and acetylenes into platinum–hydrogen bonds of square-planar Pt(II) complexes may be more profitably described in terms of a unified reaction scheme wherein the fate of the initially formed five-coordinate species is determined in large part by the ligand trans to hydride. Hence, the reaction may lead to insertion directly or to insertion via a pathway involving preliminary substitution.

Results

In an attempt to determine the mechanistic significance of the trans ligand we have investigated reactions 2 and 3 using a number of neutral (L) or anionic (X^-) groups.



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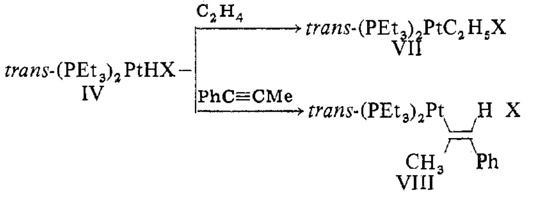


(3)

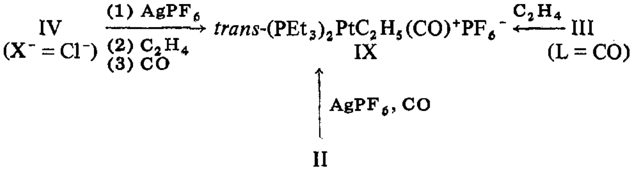
Reactions with Ethylene. Since the reaction of platinum(II) hydride complexes with nonterminal, fluorine- or cyano-substituted olefins is complicated by low yields of alkyl product[6] or competition from reactions other than insertion,[11,12] we have chosen ethylene as a model olefinic substrate. Samples containing the hydride complexes III or IV in acetone solution were prepared and sealed in NMR tubes with 1.5 equiv of ethylene. The tubes were placed in a thermostated bath at 35° and monitored by observing changes in the upfield NMR signal due to Pt–H. After 6 months the tubes were opened and the contents analyzed by examination of their infrared spectra.

Although reaction 3 has been shown to occur under forcing conditions[4] (100°, 100 atm) for IV ($X^- = Cl^-$, CN^-), both of these compounds as well as IV ($X^- = NO_2^-$)[13] were found to be inert toward reaction with ethylene under the conditions described in the Experimental Section. No changes were observed in the Pt–H NMR signal and infrared analysis of the total crude products shows a strong ν_{Pt-H} and no trace of the 1200-cm^{-1} band characteristic of the Pt–CH_2CH_3 moiety.[1]

In contrast, IV ($X^- = NO_3^-$) reacts very rapidly with ethylene in acetone[9] or methanol[7] according to eq 3 to give *trans*-$(PEt_3)_2PtC_2H_5NO_3$.

Reaction of ethylene with cationic platinum(II) hydride complexes containing a loosely bound solvent molecule trans to hydride (III, L = MeOH, acetone) has received considerable attention.[6,9,10] In general, a rapid, nearly quantitative insertion according to eq 2 occurs. It has been established that some neutral ligands, L, block insertion,[6] and we find, in agreement, that complexes III (L = PEt_3, $P(OMe)_3$, $P(OPh)_3$, $AsPh_3$) do not react with ethylene at 35° (1 atm).

Samples of III (L = CO) and ethylene in sealed tubes showed a slow consumption of hydride, which was complete after ca. 2–3 days at 35°. The product was identified as *trans*-$(PEt_3)_2PtC_2H_5(CO)^+PF_6^-$ which could also be obtained by CO quenching of the product from reaction of III (L = acetone) or by treatment of II with CO in the presence of $AgPF_6$.



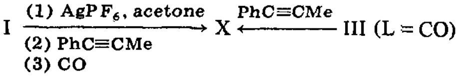
$$\underset{(X^- = Cl^-)}{\text{IV}} \xrightarrow[\substack{(2)\ C_2H_4\\ (3)\ CO}]{(1)\ AgPF_6} \underset{\substack{\text{IX}\\ \big\uparrow\ AgPF_6,\ CO\\ \text{II}}}{trans\text{-}(PEt_3)_2PtC_2H_5(CO)^+PF_6^-} \xleftarrow{C_2H_4} \underset{(L = CO)}{\text{III}}$$

It was critical to determine whether the formation of IX proceeded *via* a substitution route in which CO is displaced. Previous studies had shown that insertion results only if L is labile.[6] Repetition of the reaction with III (L = CO) and ethylene in a continuous-flow reactor designed to purge the system of carbon monoxide (see Experimental Section for details) gave the same product (IX). It is then certain that CO does not leave the coordination sphere during insertion.

Reactions with Phenylmethylacetylene. Previous studies have shown that nonterminal acetylenes bearing strong electron-withdrawing groups slowly insert into the Pt–C bond of $Q_2PtMeCl$[14] and that the reaction proceeds more readily with $Q_2PtCH_3(acetone)^+PF_6^-$ in nonnucleophilic media.[15] Simple olefins are, however, less reactive in this sense.[16]

In agreement with these results and with the greater reactivity anticipated for Pt–H vs. Pt–C,[15] we find that phenylmethylacetylene reacts readily with a number of neutral (III) and cationic (IV) hydrides. The neutral species IV where $X^- = Cl^-$, NO_3^-, but not IV where $X^- = CN^-$, reacted with PhC≡CMe in methanol according to eq 3 to give the appropriate vinyl derivatives. Reactions also occurred with the cationic hydrides III (L = $AsPh_3$, CO, acetone). The times of completion of the reactions (Table I), estimated by following the disappearance of the Pt–H NMR signal and/or the appearance of the product peaks of a solution containing ca. 0.3 *M* III or IV and 0.4 *M* PhC≡CMe, indicate that the relative ease of insertion is in the order of $X^- = NO_3^- > Cl^- >> CN^-$ for IV and L = acetone > CO > $AsPh_3$ > phosphites for III.

trans-$(PEt_3)_2Pt(C(CH_3){=}CHPh)CO^+PF_6^-$ (X) could also be obtained by CO quenching of the product from reaction of III (L = acetone) or III (L = CO) with PhC≡CMe in a nitrogen-purged flow reactor described above.



$$\text{I} \xrightarrow[\substack{(2)\ PhC\equiv CMe\\ (3)\ CO}]{(1)\ AgPF_6,\ acetone} \text{X} \xleftarrow{PhC\equiv CMe} \text{III}\ (L = CO)$$

Table I. Comparative Rates for the Insertion of Methylphenylacetylene

Complex	Solvent	Time of completion[a]
$(PEt_3)_2PtH(NO_3)$	Methanol-*d*	5 min
$(PEt_3)_2PtH(NO_3)$	Acetone-*d*	3 hr
$(PEt_3)_2PtHCl$	Methanol-*d*	40 hr
$(PEt_3)_2PtHCl$	Acetone-*d*	No observable reaction after 7 days
$(PEt_3)_2PtHCl$	Benzene-*d*	No observable reaction after 7 days
$(PEt_3)_2PtHCN$	Methanol	No observable reaction
$(PEt_3)_2PtH(acetone)^+PF_6^-$	Acetone-*d*	5 min
$(PEt_3)_2PtH(CO)^+PF_6^-$	Acetone-*d*	20 hr
$(PEt_3)_2PtH(AsPh_3)^+PF_6^-$	Acetone-*d*	8 days
$(PEt_3)_2PtHP(OPh)_3{}^+PF_6^-$	Methanol	No observable reaction[b]
$(PEt_3)_2PtHP(OMe)_3{}^+PF_6^-$	Methanol	No observable reaction[b]
$(PEt_3)_2PtH(PEt_3)^+PF_6^-$	Methanol	No observable reaction[b]

[a] For a reaction mixture containing 0.3 *M* complex and 0.4 *M* PhC≡CMe. [b] In a reaction time of at least 1 month.

Table II. PMR Parameters for the Platinum–Vinyl Complexes

	H[a]		CH_3[a]	
	δ, ppm	J_{Pt-H}, Hz	δ, ppm	J_{Pt-H}, Hz
trans-$(PEt_3)_2Pt$-$(C(CH_3){=}CHPh)NO_3$	6.65	91.8	2.23	56.5
trans-$(PEt_3)_2Pt$-$(C(CH_3){=}CHPh)Cl$	6.76	90.0	2.27	56.5
trans-$(PEt_3)_2Pt$-$(C(CH_3){=}CHPh)AsPh_3{}^+PF_6^-$	6.60	77.6	2.38	46.4
trans-$(PEt_3)_2Pt$-$(C(CH_3){=}CHPh)CO^+PF_6^-$	6.52	60.4	2.14	37.3

[a] All compounds measured in $CDCl_3$.

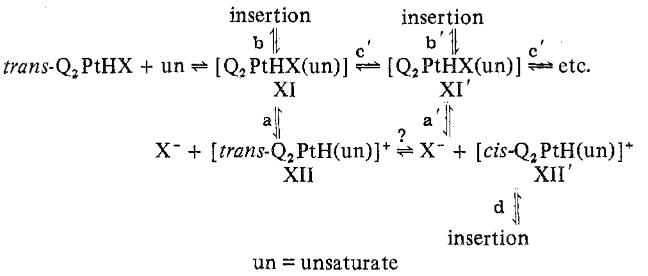
All the vinyl compounds VI and VIII have the cis geometry about the vinylic C═C bond in agreement with the expectation that insertion occurs via collapse of a four-center transition state. The stereochemistry in each case is evident from a consideration of their NMR spectra (Table II). Coupling between the vinyl proton and ^{195}Pt is in the range expected for a cis geometry[17,18] but decreases with increasing trans influence of L or X^-:[19] $NO_3^- > Cl^- > AsPh_3 > CO$. Coupling to the two equivalent cis PEt_3 groups is not observed but some small ^4J coupling to the methyl group is apparent ($^4J < 1$ Hz). Coupling of the vinyl CH_3 group to ^{195}Pt shows a similar trend relating to the trans influence of X^- or L.

Discussion

Previously we have demonstrated that the presence of substitution-labile ligands in the trans position, such as acetone and NO_3^- in III or IV, greatly facilitates the insertion of "un" into the Pt-H bond.[6,8-10] It has further been demonstrated that insertion proceeds via a four-coordinated intermediate, $Q_2PtH(un)^+$ (Q = tertiary phosphine), in these cases.[9,10] In contrast, evidence is here presented that in the reaction of III (L = CO) with ethylene and PhC≡CMe, CO does not leave the coordination sphere during insertion. It is therefore apparent that the mechanism of the insertion reactions of unsaturated organic compounds into Pt–H bonds depends on the trans ligands present in the complexes; insertion may occur via initial substitution ($X^- = Cl^-$, NO_3^- and L = acetone, methanol) or via a five-coordinated transition state ($X^- = SnCl_3^-$, L = CO, $AsPh_3$). These results can be accommodated in a generalized reaction mechanism presented in Scheme I.

Five-coordinate species XI, typical of those postulated for substitution reactions of square-planar Pt(II) complexes,[20] are initially formed by interaction with "un". These may be transition states with exceedingly short lifetimes (an associative interchange I_a process in the nomenclature of Langford and Gray[20]) or, with increasing stabilities, bona fide intermediates observable kinetically or spectroscopically (a nonconcerted

Scheme I



associative A substitution[20]). In suitable cases five-coordinate complexes of Pt(II) can be isolated in the absence of chelating ligands.[12,14,21,22] The enhanced stability observed in these cases is associated with the presence of strong π-acceptor ligands which give rise to the familiar kinetic trans effect.

Progress along the reaction coordinate according to Scheme I depends on the lifetimes and stabilities of XI, which, from the above discussion, are a function of the trans ligand L or X^-. With very weakly bound trans ligands ($X^- = NO_3^-$, L = acetone, MeOH) which do not assist in stabilizing five-coordinate intermediates, facile substitution occurs via an I_a mechanism

Scheme I, $\mathrm{XI} \xrightarrow{a} \mathrm{XII}' \xrightarrow{d}$ insertion product

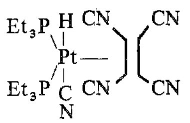
followed by insertion. The ease of formation of the charged intermediate XII and hence the rate of the reaction via this mechanism increase with a decrease in strength of Pt–X bond and an increase in polarity of the reaction medium. These are all borne out by the results shown in Table I (X = acetone > NO_3^- > Cl; MeOH > acetone > benzene as solvent).

The conditions for insertion via a five-coordinated intermediate

Scheme I, $\mathrm{XI} \xrightarrow{b}$ insertion product

are less certain. While it appears that a good π-acceptor capability for L or X is necessary (X = Cl, a poor π acceptor, no insertion in nonpolar solvent), it alone is insufficient to guarantee a facile direct associative insertion as is evidenced by the inertness of III (L = $P(OPh)_3$) and IV ($X^- = CN^-$) toward insertion. This behavior might be a simple reflection of the reluctance of CN^- and unsaturates to coordinate to the same metal.[23] Alternatively the ability of the group trans to hydride to facilitate direct associative insertion as with CO and $SnCl_3^-$ may be related to the intimate stereochemistry of the five-coordinate intermediate.[24] Although CO, $SnCl_3^-$, and CN^- are expected to extend the lifetime of five-coordinate intermediates, CO and $SnCl_3^-$ may provide accessible transition states leading to insertion whereas CN^- does not. This behavior may in turn be related to the strong equatorial site preference of some ligands[25] but not others.

In support of this we may note that a 1:1 adduct has been isolated from the reaction of TCNE and *trans*-$(PEt_3)_2PtHCN$.[12] Comparison of infrared spectra with that of the deuterated analog prepared from TCNE and *trans*-$(PEt_3)_2PtDCN$ revealed an increase in ν_{CN} for Pt–CN. Hence a strong coupling is indicated for ν_{Pt-H} and ν_{CN} suggesting a mutual trans geometry. Although crystallographic data are not available, it appears that the geometry is best described by XIII with axial H and CN.



XIII

Thus, in Scheme I, the initially formed five-coordinate species XI may have to acquire a different stereochemistry represented by XI etc. before facile insertion can occur. The nature of the trans ligand may well determine the ease of this stereochemical change and thus control the rate of insertion.

The case for L = $AsPh_3$ is not as clear but the expectation is that polar solvents will favor I_a or A substitution followed by insertion

Scheme I, $\xrightarrow{a}\xrightarrow{d}$

The steric requirements of the bulky $AsPh_3$ ligand favor dissociation and this is supported by the inertness of III (L = PEt_3). Apparently the phosphites (III, L = $P(OMe)_3$, $P(OPh)_3$) are not sufficiently good acceptors to give five-coordinate intermediates which can insert in a fashion similar to those containing CO and $SnCl_3^-$. Nor are they readily displaced so that insertion does not occur.

Experimental Section

Materials. Ethylene (CP grade, Mathesson) was used as received. Phenylmethylacetylene was purchased from Farchan Chemicals and was distilled before use.

The platinum hydrides IV ($X^- = CN^-, NO_2^-, NO_3^-$) were prepared from I[26] as described by Chatt and Shaw[1] and III (L = CO) and III (L = $AsPh_3$, PEt_3) using the procedures of Church and Mays[27] and Belluco et al.[28]

Preparation of *trans*-$(PEt_3)_2PtC_2H_5CO^+PF_6^-$. A. A solution of 100 mg of *trans*-$(PEt_3)_2PtHCO^+PF_6^-$ in 0.3 ml of acetone-d_6 was prepared in an NMR tube. Ethylene (1.5 equiv) was condensed in and the tube was sealed. After 3 days at 25° the tube was cooled to −78° and opened. Removal of solvent left a sticky yellow solid which was crystallized from CH_2Cl_2–Et_2O to give white needles, mp 118–119° (with gas evolution). Anal. Calcd for $C_{15}H_{35}P_3F_6OPt$: C, 28.43; H, 5.53. Found: C, 28.81; H, 5.65. Ir (KBr disk): 2079 (s) (C≡O), 1205 (m) ($\delta(Pt-CH_2CH_3)$), 840, 555 (s) (PF_6), and other bands at 1460 (ms), 1420 (ms), 1385 (m), 1250 (br, m), 1040 (s), 775, 765, 745 (m), 632 (m), 500 (ms), 455 (w), 425 (ms), 385 (w). PMR (acetone-d_6): δ 1.23 (q, $P-CH_2CH_3$), 2.25 (b, $P-CH_2CH_3$), ca. 0.8 (b, $Pt-CH_2CH_3$).

B. To 100 mg of *trans*-$(PEt_3)_2PtHCl$ in 2.0 ml of acetone was added 53.2 mg of $AgPF_6$. The thick white precipitate was separated and ethylene was bubbled through the supernatant for 0.5 hr. Then the flask was pressurized with CO and allowed to stand for 5 min. Removal of solvent gave an off-white solid which was recrystallized from CH_2Cl_2–Et_2O (57.4 mg); mp 119–120° (with gas evolution). The ir spectrum (KBr disk) showed it to be identical with that obtained in part A.

C. A solution of 108 mg of *trans*-$(PEt_3)_2PtHCO^+PF_6^-$ in 30 ml of acetone was supported on a medium-porosity sintered disk which was sealed in a 30-mm diameter tube and connected to a Hg-sealed vent through a water-cooled condenser. A slow stream of ethylene was passed through the disk. After 3 days the solvent was removed and the residue crystallized from CH_2Cl_2–Et_2O. Infrared analysis (KBr pellet) showed the product to be identical with that obtained in A and B.

D. *trans*-$(PEt_3)_2PtC_2H_5Cl$ (28.5 mg) was dissolved in 3 ml of acetone in a 25-ml round-bottom flask fitted with a serum cap. The flask was flushed with CO and then 14.6 mg of $AgPF_6$ in 3 ml of acetone was rapidly added via syringe. The resulting white precipitate was stirred for 5 min and separated. Removal of solvent left a yellow solid which was recrystallized from CH_2Cl_2–Et_2O to give white crystals (21 mg), mp 116–119° (decomposition with gas evolution). Infrared analysis showed the product to be identical with *trans*-$(PEt_3)_2PtC_2H_5CO^+PF_6^-$ obtained above.

Reaction of Phenylmethylacetylene with Platinum Hydrides. To a solution prepared by adding 60 mg of III (L = $P(OMe)_3$, $P(OPh)_3$) or IV ($X^- = CN^-$) to 5 ml of methanol was added 0.2 ml of PhC≡CMe. The reaction mixtures were held at 35° protected from light and monitored by observation of the ν_{Pt-H} band in the infrared spectra. After 1 month no change in the spectra was observed.

Preparation of *trans*-$(PEt_3)_2Pt(C(CH_3){=}CHPh)AsPh_3^+PF_6^-$. To a solution of 100 mg of *trans*-$(PEt_3)_2PtHAsPh_3^+PF_6^-$ in 5 ml of methanol was added 0.3 ml of PhC≡CMe. The flask was kept at 35° protected from light for 48 hr. Removal of solvent left a yellow oil. Trituration with ether gave a white solid (88 mg). The crude product was chromatographed through a small Florisil column eluting with $\mathrm{CH_2Cl_2}$. Crystallization from $\mathrm{CH_2Cl_2{-}Et_2O}$ gave white crystals, mp 144–145°. Anal. Calcd for $\mathrm{C_{39}H_{54}PtAsPF_6}$: C, 46.85; H, 5.44. Found: C, 46.78; H, 5.48. Ir (KBr disk): 1585 (br, m) (Pt–vinyl), 840 (s), 555 (s) ($\mathrm{PF_6}$), and other bands at 1480 (ms), 1450 (m), 1434 (s), 1415 (m), 1380 (mw), 1308 (w), 1350 (w), 1183 (w), 1158 (w), 1075 (m), 1035 (s), 998 (m), 760 (s), 738 (s), 695 (s), 530 (w), 485 (sh), 470 (w), 415 (w). PMR ($\mathrm{CDCl_3}$): δ 6.60 (t, $J_{\mathrm{Pt-H}}$ = 77.6 Hz, $\mathrm{PtC{=}CH}$), 2.38 (t, $J_{\mathrm{Pt-H}}$ = 46.4 Hz, $\mathrm{PtCCH_3}$), 1.50 (m, $\mathrm{P{-}C}H_2\mathrm{CH_3}$), 1.02 (q, $\mathrm{P{-}CH_2C}H_3$), 7.13, 7.60 (m) ($\mathrm{AsPh_3}$, $\mathrm{PtC{=}CPh}$).

Reaction of the Hydrides III and IV with Ethylene. A solution of 100 mg of the appropriate hydride was prepared in 0.3 ml of acetone-d_6 in an NMR tube; then ca. 1.5 equiv of ethylene was condensed in and the tube was sealed. Samples were placed in a 35° bath and monitored via observation of the PMR spectrum. No changes over a 6-month period were observed for III (L = $\mathrm{PEt_3}$, $\mathrm{AsPh_3}$, $\mathrm{P(OMe)_3}$, $\mathrm{P(OPh)_3}$) and IV ($\mathrm{X^-}$ = $\mathrm{Cl^-}$, $\mathrm{CN^-}$, $\mathrm{NO_2^-}$). The tubes were then cooled to −78° and opened. Infrared (KBr pellet) analysis of the tube contents showed strong bands for $\nu_{\mathrm{Pt-H}}$; the spectra were transparent at 1200 $\mathrm{cm^{-1}}$.

Preparation of *trans*-$\mathbf{(PEt_3)_2Pt(C(CH_3){=}CHPh)CO^+PF_6^-}$. A. To a solution prepared by adding 80 mg of *trans*-$\mathrm{(PEt_3)_2PtHCO^+PF_6^-}$ to 2 ml of methanol was added 0.2 ml of phenylmethylacetylene. After stirring of the mixture for 24 hr (35°) the solvent was removed and the residue taken up in $\mathrm{CH_2Cl_2}$. The crude product was purified by chromatography through a Florisil column eluting with $\mathrm{CH_2Cl_2}$. Crystallization from $\mathrm{CH_2Cl_2{-}Et_2O}$ gave white needles, mp 134–135° (64 mg). Anal. Calcd for $\mathrm{C_{22}H_{39}PtOPF_6}$: C, 36.62; H, 5.45. Found: C, 36.75; H, 5.38. Ir (KBr disk): 2115 (vs) (CO), 1580, 1565 (mw) (Pt–vinyl), 840 (vs), 555 (s) ($\mathrm{PF_6}$), and other bands at 1490 (mw), 1450 (m), 1422 (m), 1398 (m), 1260 (br, w), 1090 (w), 1040 (s), 1010 (mw), 910 (mw), 765 (s), 755 (sh), 745 (m), 700 (m), 513 (m), 458 (w), 410 (w). PMR ($\mathrm{CDCl_3}$): δ 7.35 (m, $\mathrm{PtC{=}CPh}$), 6.52 (t, $J_{\mathrm{Pt-H}}$ = 60.4 Hz, $\mathrm{PtC{=}CH}$), 2.14 (t, $J_{\mathrm{Pt-H}}$ = 37.3 Hz, $\mathrm{PtCCH_3}$), 2.11 (m, $\mathrm{P{-}C}H_2\mathrm{CH_3}$); 0.94 (q, $\mathrm{P{-}CH_2C}H_3$).

B. To 100 mg of *trans*-$\mathrm{(PEt_3)_2PtHCl}$ in 2 ml of acetone was added 53.2 mg of $\mathrm{AgPF_6}$ dissolved in acetone. The white precipitate was centrifuged and 49 mg of $\mathrm{PhC{\equiv}CCH_3}$ was syringed into the supernatant. After 15 min carbon monoxide was bubbled through for a period of 5 min. Removal of solvent left a colorless oil which was triturated with ether. The resulting white sticky solid was chromatographed through a small Florisil column eluted with $\mathrm{CH_2Cl_2}$ and crystallized from $\mathrm{CH_2Cl_2{-}Et_2O}$ to give 71 mg of white solid, mp 130–131°. Infrared analysis showed this material to be identical with that prepared in A.

C. A solution of 49 mg *trans*-$\mathrm{(PEt_3)_2PtHCl}$ in 5 ml of methanol was injected into the flow reactor described above. $\mathrm{PhC{\equiv}CMe}$ (0.15 ml) was injected and the reactor immersed in a 35° bath and continuously purged with a slow $\mathrm{N_2}$ stream. Infrared analysis of a 0.5-ml aliquot showed that reaction was complete after 48 hr. The spectrum was transparent at 2220 $\mathrm{cm^{-1}}$ and showed strong $\nu_{\mathrm{C\equiv O}}$ as described above.

Preparation of *trans*-$\mathbf{(PEt_3)_2Pt(C(CH_3){=}CHPh)(NO_3)}$. To a solution of 180 mg of *trans*-$\mathrm{(PEt_3)PtH(NO_3)}$ in 2 ml of MeOH was added 200 μl of $\mathrm{CH_3C{\equiv}CPh}$. After 1 hr the solution was evaporated to dryness under vacuum yielding a yellow oil which was eluted through a short Florisil column with ether. Hexane (15 ml) was introduced to the eluent. The solvent mixture was heated gently to evaporate away the ether. Large long white needles of *trans*-$\mathrm{(PEt_3)_2PtC(CH_3)CHPh(NO_3)}$ were formed on cooling; yield 165 mg (75%); mp 103–104°. Anal. Calcd for $\mathrm{PtC_{21}H_{39}P_2NO_3}$: C, 41.30; H, 6.39; N, 2.29. Found: C, 41.70; H, 6.55; N, 2.24. Ir (Nujol): 1590 (mw) (Pt–vinyl), 1465, 1279 (s) ($\mathrm{NO_3}$), and other bands at 1239 (w), 1173 (w), 1109 (w), 1083 (mw), 1067 (w), 1033 (s), 1006 (m), 991 (m), 920 (w), 839 (w), 805 (w), 769 (s), 753 (m), 731 (s), 708 (m), 670 (w), 513 (w), 410 (w). PMR ($\mathrm{CDCl_3}$): δ 7.40 (m, $\mathrm{PtC{=}CPh}$), 6.65 (t, $J_{\mathrm{Pt-H}}$ = 91.8 Hz, $\mathrm{PtC{=}CH}$), 223 (t, $J_{\mathrm{Pt-H}}$ = 56.5 Hz, $\mathrm{PtCCH_3}$), 1.80 (m, $\mathrm{P{-}C}H_2\mathrm{CH_3}$), 1.20 (q, $\mathrm{P{-}CH_2C}H_3$).

Preparation of *trans*-$\mathbf{(PEt_3)_2Pt(C(CH_3){=}CHPh)Cl}$. The method of preparation is similar to that of *trans*-$\mathrm{(PEt_3)_2Pt(C(CH_3){=}CHPh)(NO_3)}$. *trans*-$\mathrm{(PEt_3)_2PtHCl}$ was used and the mixture was allowed to react overnight; yield 60%; mp 104–105°. Anal. Calcd for $\mathrm{PtC_{21}H_{39}P_2Cl}$: C, 43.18; H, 6.68; Cl, 6.08. Found: C, 43.55; H, 6.60; Cl, 6.22. Ir (Nujol): 1590, 1588, 1568 (m) (Pt–vinyl), and other bands at 1490 (m), 1412 (m), 1252 (w), 1240 (w), 1151 (w), 1082 (m), 1068 (w), 1038 (s), 1015 (w), 911 (w), 832 (m), 809 (w), 769 (s), 753 (m), 731 (s), 708 (m), 570 (w), 530 (mw), 513 (w), 410 (w). PMR ($\mathrm{CDCl_3}$): δ 7.38 (m, $\mathrm{PtC{=}CPh}$), 6.76 (t, $J_{\mathrm{Pt-H}}$ = 90.0 Hz, $\mathrm{PtC{=}CH}$), 2.27 (t, $J_{\mathrm{Pt-H}}$ = 56.5 Hz, $\mathrm{PtCCH_3}$), 2.0 (m, $\mathrm{P{-}C}H_2\mathrm{CH_3}$), 1.2 (q, $\mathrm{P{-}CH_2C}H_3$).

Preparation of *trans*-$\mathbf{(PEt_3)_2PtEt(NO_3)}$. Ethylene was bubbled into a solution of 100 mg of *trans*-$\mathrm{(PEt_3)_2PtH(NO_3)}$ in 5 ml of MeOH for 1 hr at room temperature. The reaction mixture was then evaporated to dryness under vacuum. The resulting white solid residue was dissolved in ether and passed through a short Florisil column, and 3 ml of hexane was introduced. Evaporation of ether and cooling overnight at 0° gave white crystals of *trans*-$\mathrm{(PEt_3)_2PtEt(NO_3)}$; yield 90 mg (83%); mp 74–76°. Anal. Calcd for $\mathrm{C_{22}H_{35}PtP_2NO_3}$: C, 32.18; H, 6.70; N, 2.68. Found: C, 32.20; H, 6.95; N, 2.75. Ir (Nujol): 1457, 1284 (s) ($\mathrm{NO_3}$), and other bands at 1254 (w), 1200 (w), 1036 (s), 1015 (sh), 836 (w), 765 (s), 730 (s), 711 (sh). PMR: δ 1.80 (m, $\mathrm{P{-}C}H_2\mathrm{CH_3}$), 1.16 (q, $\mathrm{P{-}CH_2C}H_3$), ca. 0.92 (b, $\mathrm{Pt{-}CH_2C}H_3$).

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Registry No. *trans*-$\mathrm{(PEt_3)_2PtHCO^+PF_6^-}$, 54657-68-0; *trans*-$\mathrm{(PEt_3)_2PtHCl}$, 16842-17-4; *trans*-$\mathrm{(PEt_3)_2PtHAsPh_3{}^+PF_6^-}$, 54657-69-1; *trans*-$\mathrm{(PEt_3)_2PtH(NO_3)}$, 19582-28-6; *trans*-$\mathrm{(PEt_3)_2PtC_2H_5Co^+PF_6^-}$, 54657-71-5; *trans*-$\mathrm{(PEt_3)_2PtC_2H_5Cl}$, 54657-72-6; *trans*-$\mathrm{(PEt_3)_2PtEt(NO_3)}$, 54657-39-5; *trans*-$\mathrm{(PEt_3)_2PtH(acetone)^+PF_6^-}$, 51716-77-9; $\mathrm{C_2H_4}$, 74-85-1; $\mathrm{PhC{\equiv}CMe}$, 673-32-5; X, 54657-34-0; XI, 54657-35-1; XII, 54657-36-2; XIII, 54657-38-4.

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