Protonation of 9c with Triflic Acid. In the drybox, an NMR tube was charged with the cyclohexylphosphido complex **9c** (5 mg, 0.009 mmol) and ~0.5 mL of toluene. It was fitted with a gum rubber septum and removed from the box. Triflic acid (1.0 μL, 0.01 mmol, 1.1 equiv) was added all at once using a microliter syringe. As soon as the acid was added, a white precipitate formed. The tube was vigorously shaken and the solid collected on a glass frit. The white solid was washed with distilled water (~1 mL), and then ether (~1 mL) and allowed to air dry for 3 h. IR analysis (KBr) of the solid showed that the salt **11c** was the only carbonyl-containing compound.

Kinetic Studies on the Reaction of 1a with $CpW(CO)_3H$. Standard solutions of **1a** and $CpW(CO)_3H$ were prepared in THF in the drybox and stored in the dry box freezer and stored at −40 °C. For each run, 1 mL of the solution of **1a**, measured using a 1.0-mL volumetric pipet, was transferred to a 10-mL volumetric flask, and then an appropriate aliquot of the $CpW(CO)_3H$ solution was added using a volumetric pipet. The mixture was then diluted to 10 mL and shaken, a UV–vis cell equipped with a Kontes vacuum stopcock charged with the reaction mixture, and the stopcock sealed. The cell was removed from the drybox and placed into the temperature controlled cells. Spectra were taken at regular intervals after the solutions had been allowed to equilibrate in the cell holder. The temperature of the cell holder was calibrated using a thermocouple which had been previously calibrated using ice and boiling water.

The reactions were monitored by observing the increase in absorbance at 410 nm due to formation of the product $(CO)_3$(diars)$ReW(CO)_3Cp$. In all cases reactions were observed for at least 3 half-lives. Plots of absorbance vs time were fit to the increasing exponential function $y = A_1(1 - e(-A_2x)) + A_3$ using the IGOR Wavemetrics curve fitting program,[75] where y is the absorbance and x = time in seconds. The least-squares fit of the data gives the observed rate constant (k_{obs}) and the infinity point as $A_1 + A_3$. The linearity of the data was then checked by plotting ln $(A_\infty - A_t)$ vs time.

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Supplementary Material Available: ORTEP diagrams of **13b** and tables of positional parameters, anisotropic thermal parameters, and root-mean-amplitudes for **13b** (7 pages). Ordering information is given on any current masthead page.

OM920277A

(75) The Igor graphing and data analysis software is distributed by Wavemetrics, Lake Oswego, OR.

Reactions of Di- or Trialkynylphosphine and Di- or Trialkynylarsine Oxides with a Cationic Platinum–Hydride Complex: Mechanistic Features

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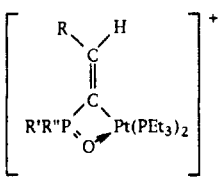
The reaction between a cationic Pt–H complex and $O{=}P(C{\equiv}CCMe_3)_3$ was followed by ^{31}P NMR at three temperatures. Addition of the Pt–H bond to an alkynyl substituent to give a Pt,P-μ-alkenylidene complex is observed with subsequent formation of the expected 1,2-dihydrophosphete product. A similar reaction with $O{=}AsPh(C{\equiv}CCMe_3)_2$ occurs with unexpected overall transfer of both alkynyl substituents from the As atom to the Pt ion, giving eventually a cationic $Pt^{II}(\eta^1$-alkynyl$)(\eta^1$-alkenyl) product. The X-ray structure of this latter complex has been determined: $P\bar{1}$; $Z = 2$; $a = 11.391$ (4) Å, $b = 16.040$ (4) Å, $c = 10.801$ (1) Å; $\alpha = 100.13$ (1)°, $\beta = 100.71$ (2)°, $\gamma = 80.23$ (2)°. A mechanism of formation of 1,2-dihydrophosphete or -arsete complexes involving Pt–H addition and subsequent alkynyl transmetalation is postulated.

Introduction

We have reported previously that cationic platinum–hydride reagents of the type $[trans\text{-}PtH(PEt_3)_2(solvent)]^+$ (**1**) react with alkynylphosphine or -arsine oxides by one of two routes, depending on the nature of the substituents within the *P*- or *As*-oxides. Monoalkynylphosphine oxides react with **1** to give Pt,P-μ-alkenylidene products **2** by regio- and stereoselective cis addition of the Pt–H bond across the alkynyl C–C triple bond.[1] Di- or trialkynylphosphine oxides containing propynyl- or phenylacetylide substituents also react with **1** to form addition products such as **2**.[2] However, di- or trialkynylphosphine oxides having *tert*-butylacetylide substituents react with **1** to afford complexes containing 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligands **3**.[1,2] The unexpected formation of the 1,2-dihydrophosphete ring system occurs presumably by an overall process of cis addition of the Pt–H bond



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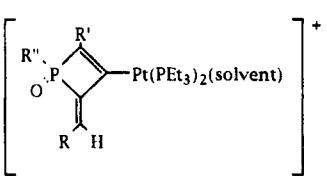

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(1) Lukehart, C. M.; McPhail, A. T.; McPhail, D. R.; Myers, J. B., Jr.; Soni, H. K. *Organometallics* **1989**, *8*, 1007–1014.

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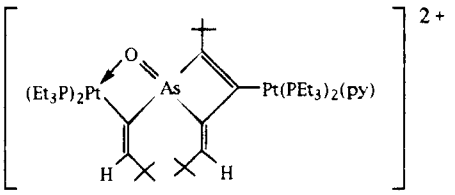
to one alkynyl substituent followed by an unusual insertion of a second alkynyl substituent into the Pt–alkenylidene bond formed from Pt–H addition. Reaction of 1 with di- or trialkynylphosphonium species containing *tert*-butylacetylide substituents gives similar results, although variation of the ancillary substituents at the phosphonium center affects the course of the reaction. Ancillary substituents of relatively large steric bulk favor heterocycle formation, those of lesser steric bulk favor μ-alkenylidene formation, and substituents of intermediate size give a mixture of the two types of products.[2]

Reaction of 1 with the arsine oxide $O{=}As(C{\equiv}CCMe_3)_3$ followed by addition of pyridine to the reaction solution affords the spirocyclic complex 4.[3] Formation of the ar-



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sacyclobutenyl ligand presumably occurs by a process similar to that which gives the 1,2-dihydrophosphete complexes 3. However, a second equivalent of 1 reacts with the remaining alkynyl substituent of the arsine oxide to form a Pt,As-μ-alkenylidene ligand, thereby generating a spirocyclic arsenic center.

Although little is known about the synthesis and chemistry of 1,2-dihydrophosphete heterocycles,[4] recent independent work by Mathey, Dotz, Doxsee, and Tumas has demonstrated formation of this ring system utilizing transition-metal organometallic reactants.[5] Only one example of a 1,2-dihydroarsete (ie., arsacyclobutene) has been reported prior to our preparation of compound 4.[5i] Because the transformation of dialkynyl phosphorus or arsenic compounds and 1 to the corresponding complexes containing unsaturated, four-membered heterocycles occurs so facilely and, presumably, involves an unusual organometallic rearrangement, we have attempted to elucidate mechanistic features of these reactions. We now report (1) the results of a kinetics study of the reaction of 1 with $O{=}P(C{\equiv}CCMe_3)_3$ and (2) the results of the reaction of 1 with the arsenic oxide $O{=}AsPh(C{\equiv}CCMe_3)_2$. Spectroscopic evidence strongly indicates that the first major step in the reaction of 1 with $O{=}P(C{\equiv}CCMe_3)_3$ is the expected formation of a Pt,P-μ-alkenylidene complex. This intermediate then undergoes rearrangement to form the heterocyclic product. Reaction of 1 with $O{=}AsPh(C{\equiv}CCMe_3)_2$ gives an unexpected elimination of $[PhAsO]_n$ and formation of a cationic platinum complex containing both of the alkynyl substituents of the arsenic oxide reagent. A mechanism involving migration of an alkynyl substituent from the main-group atom to the platinum center is proposed for these reactions.

Experimental Section

Materials and Methods. All manipulations were performed under an atmosphere of dry, prepurified nitrogen and at room temperature unless otherwise indicated. Solvents were dried and distilled before use according to standard methods.[1]

^1H NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz) or on an IBM NR-300 spectrometer (300 MHz) using the ^2H signal of the solvent as an internal lock frequency. Chemical shifts (in δ) were measured with respect to the residual solvent peak as an internal reference. ^{31}P NMR spectra were recorded on an IBM NR-200 spectrometer operating at a frequency of 81 MHz. Chemical shifts (in δ) were measured with respect to the external reference of 85% H_3PO_4. Microanalyses were performed by the Department of Chemistry, Vanderbilt University, Nashville, TN, or by Galbraith Laboratories, Inc., Knoxville, TN.

The cationic platinum–hydride salts [*trans*-$Pt(H)(PEt_3)_2$(solvent)][SbF_6], where the solvent ligand is either THF or acetone-d_6, were prepared from the neutral chloro complex by reaction with $AgSbF_6$ in the appropriate solvent as described previously.[1-3,6] The phosphine oxide $O{=}P(C{\equiv}CCMe_3)_3$[1] and the arsine $AsPhCl_2$[7] were prepared according to published procedures.

Preparation of $AsPh(C{\equiv}CCMe_3)_2$. To a solution of 24.4 mmol of $Me_3CC{\equiv}CH$ in 15 mL of THF at −78 °C was added 24.4 mmol of *n*-butyllithium solution. The reaction solution was warmed to 25 °C for 3 h and was then cooled to −78 °C. To this solution was added 12.2 mmol of $AsPhCl_2$ with stirring, and then the solution was warmed to 25 °C for 12 h. The solvent was removed at reduced pressure to give a white solid. The reaction residue was extracted with pentane. The extractant was filtered through Celite, and the solvent was removed from the filtrate to give the product as a white solid in 90% yield: mp 95–96 °C; ^1H NMR ($CDCl_3$) δ 1.25 (s, 18, CMe_3), 7.35–7.44 (m, 3, Ph), 7.62–7.70 (m, 2, Ph).

Preparation of $O{=}AsPh(C{\equiv}CCMe_3)_2$ (11). To a solution of 3.5 mmol of $AsPh(C{\equiv}CCMe_3)_2$ in 15 mL of pentane was added 4.5 mmol of *t*-BuOOH as a 3.0 M solution in 2,2,4-trimethylpentane. The reaction mixture was stirred for 30 min, and then the solvent was removed at reduced pressure. The reaction residue was extracted with pentane, and the product was obtained as white crystals upon cooling this solution to −20 °C in 56% yield: mp 111–112 °C; ^1H NMR ($CDCl_3$) δ 1.23 (s, 18, CMe_3). 7.36–7.42 (m, 3, Ph), 7.62–7.68 (m, 2, Ph). Anal. Calcd for $C_{18}H_{23}AsO$: C, 65.45; H, 7.02. Found: C, 65.36; H, 7.32.

Preparation of {*trans*-$Pt[C{\equiv}C(CMe_3)][(C_5H_5N)C{=}C(CMe_3)(H)](PEt_3)_2$}[$SbF_6$] (12). To a solution of 0.50 mmol of [*trans*-$Pt(H)(PEt_3)_2(THF)$][SbF_6] in CH_2Cl_2 at −78 °C was added 0.164 g (0.50 mmol) of 11. After 2 h, the reaction solution was warmed to 25 °C and was stirred for 18 h. Pyridine (0.10 mL) was then added to the reaction solution. After an additional reaction time of 3 h, the solvent was removed at reduced pressure. The reaction was extracted with diethyl ether. After this solution was filtered, the solvent was removed at reduced pressure. The product was crystallized from a CH_2Cl_2/THF/Et_2O solvent mixture at −20 °C to give 0.065 g (15%) of 12 as yellow prisms: mp 159–161 °C; ^1H NMR ($CDCl_3$) δ 1.05–1.19 (m, 18, PCH_2CH_3), 1.19 (s, 9, CMe_3), 1.33 (s, 9, CMe_3), 1.98–2.22 (m, 12, PCH_2CH_3), 6.60 (s, 1, $C{=}CHCMe_3$, $^3J_{PtH}$ = 60 Hz), 8.14 (t, 2, C_5H_5N, $^3J_{HH}$ = 7.0 Hz), 8.52 (t, 1, C_5H_5N, $^3J_{HH}$ = 7.0 Hz), 9.37 (d, 2, C_5H_5N, $^3J_{HH}$ = 6.4 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 0.47 (s, 2 PEt_3, $^1J_{PtP}$ = 2428 Hz). Anal. Calcd for $C_{29}H_{54}F_6HP_2PtSb$: C, 38.29; H, 5.98. Found: C, 38.22; H, 5.86.

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Table I. Summary of Crystallographic Data for Complex 12

mol formula	$C_{29}H_{54}F_6NP_2PtSb$
mol wt	984.45
cryst color, habit	yellow, platelet
cryst syst	triclinic
space group (No.)	$P\bar{1}$ (2)
cell dimens	
a, Å	11.391 (4)
b, Å	16.040 (4)
c, Å	10.801 (1)
α, deg	100.13 (1)
β, deg	100.71 (2)
γ, deg	80.23 (2)
no. of orientation rflns; 2θ range, deg	23; 34.4–35.0
V, Å^3	1890 (2)
Z	2
D_{calcd}, g/cm^3	1.730
μ(Mo Kα), cm^{-1}	54.54
radiation: λ, Å	0.71069
temp, °C	23
cryst dimens, mm	1.45 × 1.13 × 0.40
scan technique	ω–2θ
scan speed, deg/min	8.0
scan width, deg	1.78 + 0.30 tan θ
$2\theta_{max}$, deg	50.2
total no. of rflns ($+h,\pm k,\pm l$)	7049
no. of rflns, $I > 3.0\sigma(I)$	5234
no. of variables	356
extinctn cor	3.17 × 10^{-7}
R (R_w)	0.066 (0.081)
GOF	3.28

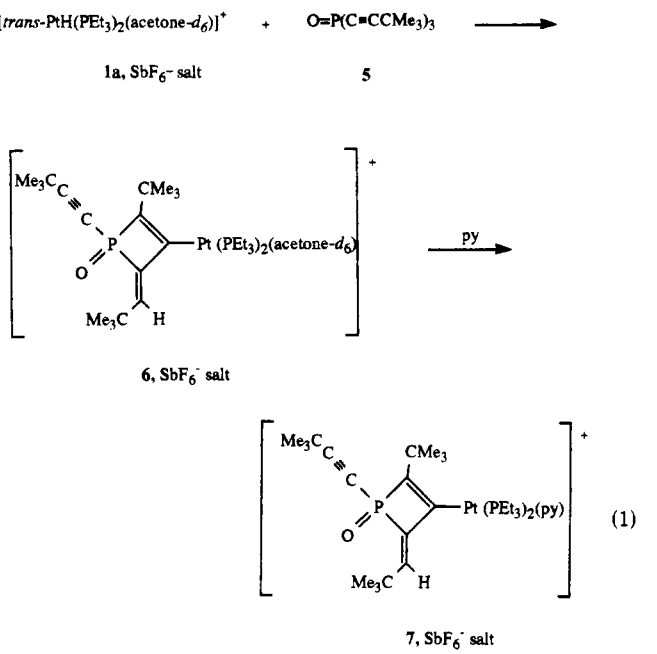
Kinetics Study of the Reaction of [*trans*-Pt(H)(PEt$_3$)$_2$(acetone-d_6)][SbF$_6$] and O=P(C≡CCMe$_3$)$_3$. A kinetics study of the reaction between [*trans*-Pt(H)(PEt$_3$)$_2$(acetone-d_6)][SbF$_6$] and O=P(C≡CCMe$_3$)$_3$ was carried out in acetone-d_6 solution at 273, 278, and 298 K. The relative mole ratio of reactants was 1:1, and the reactant concentrations were either 1.86 × 10^{-4} or 1.40 × 10^{-4} M depending on the temperature of the reaction. The reaction was followed by ^{31}P NMR, with spectra being recorded on an IBM NR-200 spectrometer operating at a frequency of 81 MHz. Chemical shifts (in δ) were measured with respect to the external reference of 85% H_3PO_4. A variable-temperature unit was used to control the reaction temperature throughout the reaction. The reaction was followed for at least 3 half-lives, and the change in concentration of observed species (as determined from the ratio of the area of the PEt$_3$ resonances of each species relative to the total area of the PEt$_3$ phosphorus resonances) was measured as a function of time. Spectral data were acquired over a 5-min period beginning immediately after mixing the reactants at intervals of 10–15 min, depending on the reaction temperature.

The change in concentration of each species as a function of time was modeled via several mechanistic schemes, as discussed in the text. Integrated rate expressions were obtained using Laplace transformations according to standard methods.[8] An iterative process of fitting calculated concentrations to observed concentrations by changing the numerical values of the relevant rate constants were performed using experimental initial rates as starting values for the appropriate rate constants. The best fit of calculated and experimental data gave the preferred mechanism and the values of the rate constants at each temperature. Activation parameters were calculated from the standard Eyring equation for reactions performed in solution.[9]

X-ray Crystal Structure Analysis of Complex 12. Single crystals of complex **12** were obtained as described above. A large crystal (1.45 × 1.13 × 0.40 mm) was chosen for data collection. Crystal data, data collection specifications, and refinement parameters for this analysis are provided in Table I. Orientation reflections used for space group and unit cell determination and intensity data were recorded on a Rigaku AFC6S diffractometer (23 orientation reflections; Mo Kα radiation, λ = 0.71069 Å; graphite monochromator; ω–2θ scans; 7049 nonequivalent reflections, $+h,\pm k,\pm l$, corrected for absorption). The triclinic cell was confirmed by application of TRACER-II software. The reflection intensities were corrected for the usual Lorentz and polarization effects, and an analytical absorption correction was applied. Redundant data were not used. An extinction correction was applied to the data, but the extinction parameter was not refined. The crystal structure was solved by direct methods and was refined by standard procedures using the TEXSAN software package developed by Molecular Structure Corp., Woodlands, TX. All non-hydrogen atoms were located from difference electron density maps. Full-matrix least-squares refinement of atomic parameters (anisotropic for all non-hydrogen atoms, except for atom C(34), which was refined isotropically due to disorder, including fixed-H contributions) converged at R = 0.066 (R_w = 0.081) using 5234 reflections with $I > 3.00\sigma(I)$. The F atoms were refined anisotropically, but some thermal parameters were large due to disorder of the anion. The maximum peaks in the final electron difference map had intensities of 3.6, 3.3, and 1.6 e/Å^3 and were located respectively at distances of 1.12, 0.97, and 1.30 Å from the Pt atom.

Results and Discussion

Kinetics Study of the Reaction between a Cationic Platinum Hydride Complex and O=P(C≡CCMe$_3$)$_3$. The reaction between [*trans*-Pt(H)(PEt$_3$)$_2$(acetone-d_6)][SbF$_6$] (**1a**) or analogous cationic platinum–hydride complexes containing other solvents as ligands and O=P(C≡CCMe$_3$)$_3$ (**5**) is known to give 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide complexes, such as **6**. These compounds are easily converted to the known pyridine complex **7**, as shown in eq 1.[1]



To obtain more mechanistic information concerning the reaction of cationic platinum–hydride complexes with compounds containing dialkynylelementa fragments, we followed the reaction of **1a** and **5** in acetone-d_6 solution by ^{31}P NMR. ^{31}P NMR spectral data for these compounds are particularly useful, because resonances of PEt$_3$ ligands have good intensity, have a relatively wide chemical shift range, and reveal stereochemical features at both the Pt center and ligand sites. For example, the resonances of the trans PEt$_3$ ligands of complexes containing these 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligands appear as AB quartets due to the dissymmetric center located at the P atom.[1,2]

When complex **1a** is mixed with **5** in acetone-d_6 solution at −30 °C, a reaction occurs within 5 min upon mixing the

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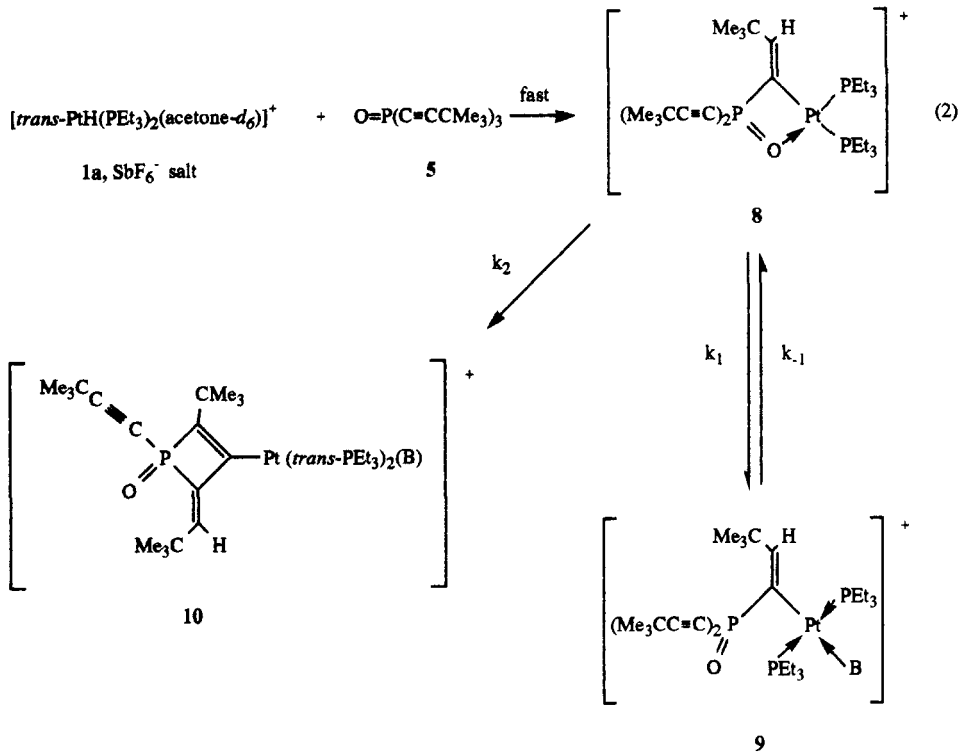
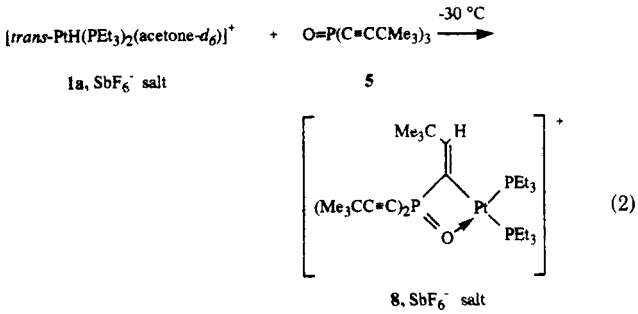
Scheme I



reagents to give quantitative formation of the Pt,P-μ-alkenylidene complex 8, as shown in eq 2. Complex 8 is



characterized adequately from ^{31}P NMR spectral data. Resonances for the two nonequivalent, cis PEt_3 ligands appear as doublets of doublets at δ 11.5 and 17.6 with respective $^1J_{PtP}$ coupling constants of 4046 and 2281 Hz, $^3J_{PP(O)}$ coupling constants of 8.6 and 18.3 Hz, and a $^2J_{PP}$ coupling constant of 18.5 Hz. The phosphorus resonance of the P=O group appears at δ 16.6 and exhibits $^2J_{PtP}$ coupling of 267 Hz. For the known analogous complex in which the *tert*-butyl groups of 8 are replaced by methyl substituents, the corresponding ^{31}P NMR spectrum shows resonances for the two PEt_3 ligands at δ 8.1 and 15.7 with $^1J_{PtP}$ coupling constants of 4089 and 2296 Hz, $^3J_{PP(O)}$ coupling constants of 8 and 27 Hz, respectively, and a $^2J_{PP}$ coupling constant of 16 Hz. The phosphorus resonance of the P=O group of this latter complex appears at δ 24.6 with a $^2J_{PtP}$ coupling constant of 286 Hz.[2] We assume that the P=O group of 8 is coordinated to the Pt atom in analogy to structures found in related compounds.[1,2]

When solutions of complex 8 are warmed to 273, 278, or 298 K, a subsequent chemical reaction occurs at a rate conveniently followed by ^{31}P NMR. Although these spectra are complex, a kinetics analysis of the change in the areas of the most intense resonances of each observed species as a function of time has been accomplished. These data reveal (1) a smooth and complete disappearance of species 8, (2) the concomitant appearance of three species, each having an AB quartet resonance (these resonances are centered at δ 14.4, 16.2, and 18.9 with $^1J_{PtP}$ coupling of 2653, 2647, and 2701 Hz and $^2J_{PP}$ coupling of 388, 340, and 356 Hz, respectively), and (3) the smooth appearance and subsequent disappearance of another species which has a phosphorus resonance centered at δ 0.62. Plots of the change in relative molar concentration of each type of species as a function of time are shown in Figure 1, as taken from data acquired in triplicate at each temperature.

Upon completion of the reaction, the three species exhibiting AB quartet resonances can be converted quantitatively to the known 1,2-dihydrophosphete complex 7 via the addition of pyridine. These species are clearly assigned to 1,2-dihydrophosphete complexes, such as 6, in which endogenous Lewis bases occupy the solvent coordination site at the Pt center. These very labile ligands are readily displaced by pyridine to form 7. The identity of the intermediate species exhibiting a resonance at δ 0.62 remains uncertain due to its relatively low concentration. The resonance of this species also appears to be an AB quartet with $^1J_{PtP}$ coupling of 4207 Hz. We assign this species to a Pt,P-μ-alkenylidene complex having trans PEt_3 ligands that are magnetically nonequivalent because of restricted rotation of the bulky phosphine oxide group.

A proposed mechanism to explain these observations is shown in Scheme I. The platinum–hydride cation **1a** undergoes rapid regio- and stereoselective addition to one of the alkynyl substituents of 5 to give the *cis*-Pt,P-μ-alkenylidene complex 8. Complex 8 undergoes geometrical isomerization to its trans isomer 9, in which an endogenous Lewis base (B) probably coordinates to the Pt center. Species 8 and 9 attempt to attain equilibrium; however, species 8 undergoes a competitive unimolecular rearrangement to form the 1,2-dihydrophosphete complex 10. The mechanism of this rearrangement is unknown, but ring formation probably occurs through an overall insertion mechanism that is most likely to occur at a *cis*-$Pt(PEt_3)_2$ center.

The mechanism proposed in Scheme I was tested mathematically by integrating the appropriate rate ex-

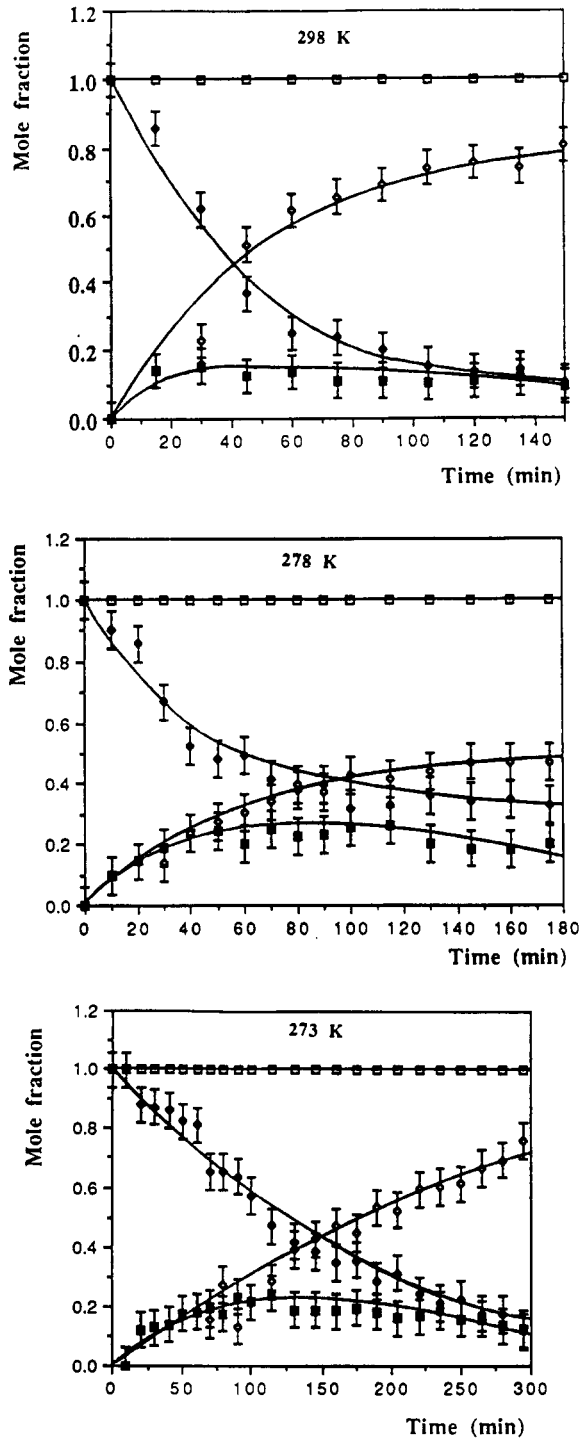
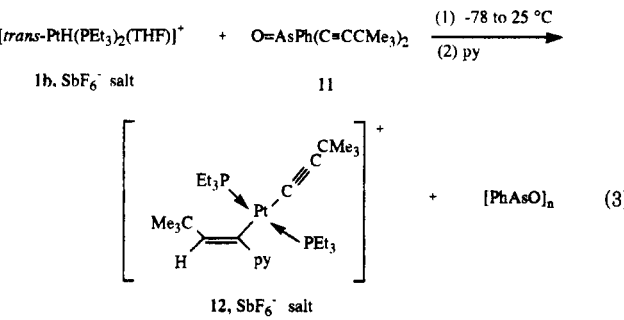


Figure 1. Plots of the mole fraction of each species, 8, 9, and 10, as a function of time at 273, 278, and 298 K, where the symbols have the following meaning: filled diamond, 8; open diamond, 10; filled square, 9; open square, total mole fraction of all species. The brackets represent the range of values observed for three data sets.

pressions; then, by using initial reaction rates as a starting point, the values of the three rate constants were adjusted iteratively to provide the best match of calculated species concentrations to those observed experimentally. Four other kinetics models were also tested in a similar fashion. These models included (1) an equilibrium between 8 and 9 with 9 being the intermediate to 10, (2) a unidirectional conversion of 8 to 9 to 10, (3) the same mechanism as shown in Scheme I but with unidirectional conversion of 9 to 10, and (4) mechanism 3 with unidirectional conversion of 8 to 9 (i.e. $k_{-1} = 0$). A good fit of calculated to observed relative concentration values could not be obtained with either mechanism placing 9 as a sole intermediate to 10. Satisfactory agreement is obtained with either the mechanism shown in Scheme I or with similar mechanisms incorporating a unidirectional conversion of 9 to 10. We propose the simpler mechanism in Scheme I on the basis of our assumption that insertion arrangements would occur preferably at a *cis*-$Pt(PEt_3)_2$ center.

The evaluated rate constants at 298 K are as follows: $k_1 = 1.67 \times 10^{-4}$ s^{-1}, $k_{-1} = 4.27 \times 10^{-4}$ s^{-1}, and $k_2 = 2.72 \times 10^{-4}$ s^{-1}. The activation parameters at 298 K calculated from the values of k_2 representing the overall cyclization step are $\Delta H^{\ddagger} = 27 \pm 3$ kJ/mol and $\Delta S^{\ddagger} = -51 \pm 3$ eu. The large negative value for $\Delta S^{\ddagger}$ is consistent with an overall cyclization reaction.

Reaction between a Cationic Platinum Hydride Complex and O=AsPh(C≡CCMe$_3$)$_2$. We anticipated that reaction of [*trans*-Pt(H)$(PEt_3)_2$(THF)][SbF_6] (**1b**) with O=AsPh(C≡CCMe$_3$)$_2$ (**11**) would give a 2-alkylidene-1,2-dihydroarsete *As*-oxide complex, in direct analogy to the reaction of **1b** with O=PPh(C≡CCMe$_3$)$_2$, in which the expected 2-alkylidene-1,2-dihydrophosphete *P*-oxide is formed.[2] However, the only product of this reaction containing Pt is the unusual Pt(alkenyl)(alkynyl) complex **12**, as shown in eq 3. The other isolated product is the



known $[PhAsO]_n$ oligomer, which was identified by its melting point and ^{1}H NMR.[10] Although **12** and the phenylarsine oxide oligomer are obtained in low yield (14%), these are the only observed products of this reaction. These products are separated by careful fractional crystallization, which accounts for the low isolated yield of the pure products.

Complex **12** has been characterized by microanalysis, NMR, and X-ray crystallography. In the ^{1}H NMR spectrum of **12**, the *tert*-butyl resonances appear as singlets at δ 1.19 and 1.33, a singlet alkenyl resonance appears at δ 6.60 with $^3J_{PtH}$ coupling of 60 Hz, and the expected resonances for the PEt_3 and pyridine groups are also evident. The ^{31}P NMR spectrum of **12** consists of a singlet resonance at δ 0.47 for the PEt_3 ligands with $^1J_{PtP}$ coupling of 2428 Hz, which is consistent with a *trans*-$Pt(PEt_3)_2$ fragment.

The molecular structure of **12** has been determined by X-ray crystallography. A summary of the crystallographic data is provided in Table I, values of selected interatomic bond distances and angles are listed in Table II, and a listing of atomic positional coordinates is provided in Table III. An ORTEP view of **12** showing the atomic numbering scheme is presented in Figure 2. The cationic portion of **12** contains a typical square-planar, Pt(II) coordination complex. The two PEt_3 ligands have a trans relative orientation about the Pt center with a P1–Pt–P2 angle of 170.7 (1)°. Alkynyl and alkenyl ligands occupy the re-

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Scheme II

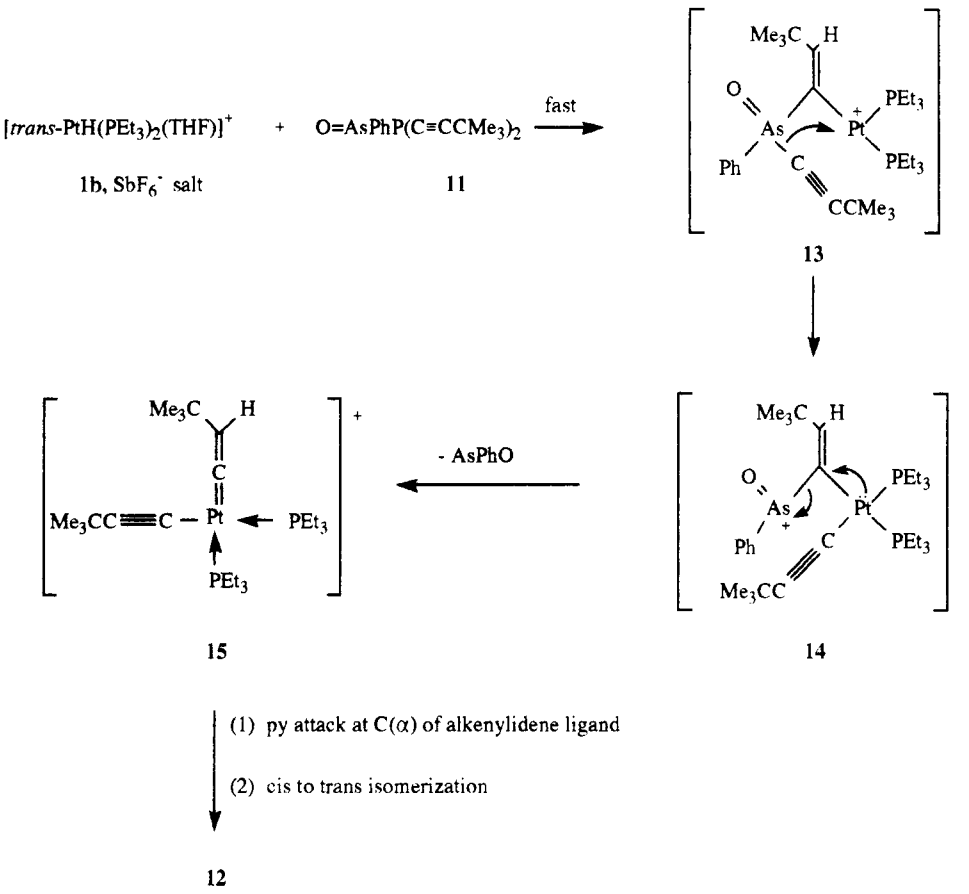

Table II. Selected Bond Distances (Å) and Bond Angles (deg) for Complex 12[a]

	Bond Distances		
Pt1–P1	2.311 (4)	C1–C2	1.33 (2)
Pt1–P2	2.295 (4)	C1–N1	1.50 (2)
Pt1–C1	2.08 (1)	C30–C31	1.20 (2)
Pt1–C30	2.00 (1)		
	Bond Angles		
P1–Pt1–P2	170.7 (1)	Pt1–C1–C2	119 (1)
P1–Pt1–C1	94.6 (4)	Pt1–C1–N1	113.7 (1)
P1–Pt1–C30	85.6 (4)	Pt1–C30–C31	176 (1)
P2–Pt1–C1	94.5 (4)	N1–C1–C2	112 (1)
P2–Pt1–C30	85.3 (4)	C7–N7–C11	119 (1)
C1–Pt1–C30	179.8 (5)	C30–C31–C32	178 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

maining two coordination sites with Pt1–C1 and Pt1–C30 distances of 2.08 (1) and 2.00 (1) Å, respectively, which are typical of Pt(II)–C_{sp^2} and Pt(II)–C_{sp} σ bonds.[11] The C1–C2 and C30–C31 distances of 1.33 (2) and 1.20 (2) Å, respectively, are also typical of C–C double and triple bonds in such compounds. The corresponding C–C double- and triple-bond distances in the complex [*trans*-$Pt(PPh_3)_2$-$(C{\equiv}CPh)(CPh{=}CH_2)$] are 1.26 (4) and 1.18 (2) Å, respectively.[12]

The alkynyl ligand is bonded to the Pt(II) atom in a terminal, linear coordination mode with a Pt1–C30–C31 angle of 176 (1)°. The Pt1–C1–C2 angle of 119 (1)° indicates near-sp^2 hybridization about C1, as expected for the donor atom of a η^1-alkenyl ligand. The Pt1 and alkenyl protons occupy trans positions about the C1–C2 double bond. An unusual feature of the alkenyl ligand is that a pyridine molecule is bonded as a substituent on the donor atom, C1. The C1–N1 distance of 1.50 (2) Å is consistent with a C–N σ bond, and the Pt1–C1–C2, N1–C1–C2, and Pt1–C1–N1 angles of 119 (1), 112 (1), and 113.7 (1)°, respectively, confirm nearly planar hybridization about C1. The dihedral angle between the plane of the pyridine substituent and that of the principal coordination plane is 96.8°. The positive charge of the complex resides formally on N1.

The formation of **12** requires the transfer of both *tert*-butylalkynyl substituents of **11** to the cationic Pt(II) ion of complex **1b**. A mechanism that is consistent with this observation and invokes an expected Pt–H addition reaction is suggested in Scheme II. Regio- and stereoselective addition of the Pt–H bond of **1a** to one of the alkynyl substituents of **11** would give the Pt,As-μ-alkenylidene intermediate **13**. Transmetalation of the remaining alkynyl substituent from the As atom to the cationic Pt(II) center would give intermediate **14**. Alkynyl migration is probably favored by the high reactivity of As–C(alkynyl) bonds and the electrophilicity of the metal ion. This reaction is also expected from the known chemistry of phosphirane oxides.[13] Elimination of PhAsO occurs next to give intermediate **15**. This elimination is facilitated by the known stability of PhAsO oligomers and by the tendency of Pt to stabilize α-carbocations.[11] Intermediate **15** contains terminal alkynyl and alkenylidene ligands in a cationic complex. Nucleophilic addition of pyridine at C(α) of the terminal alkenylidene ligand would form the unusual alkenyl ligand observed in **12**. At some

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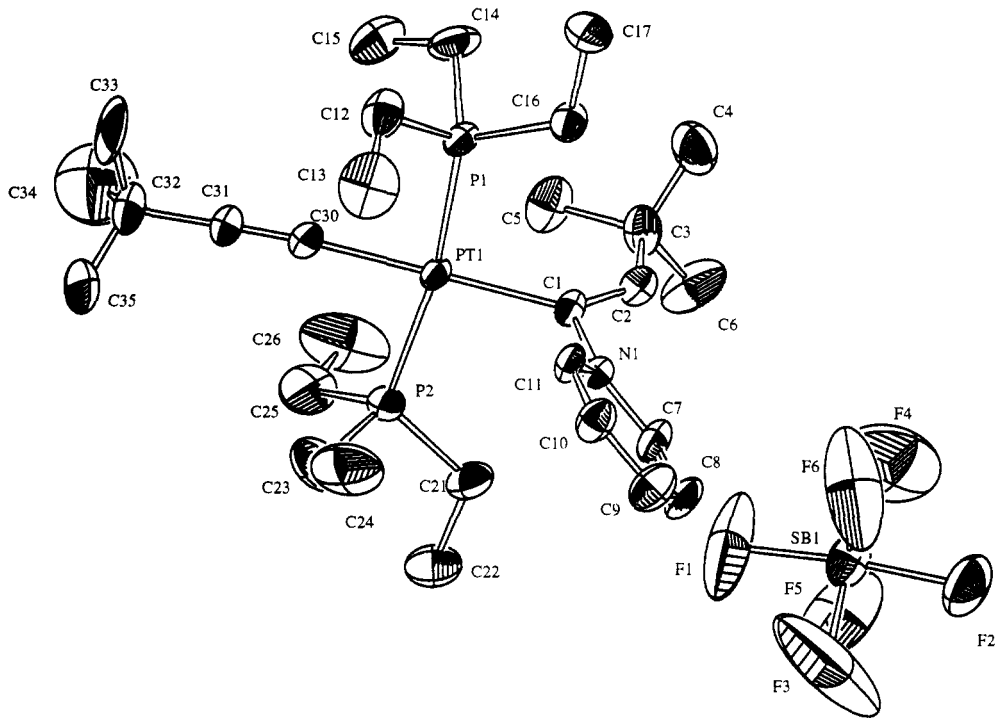
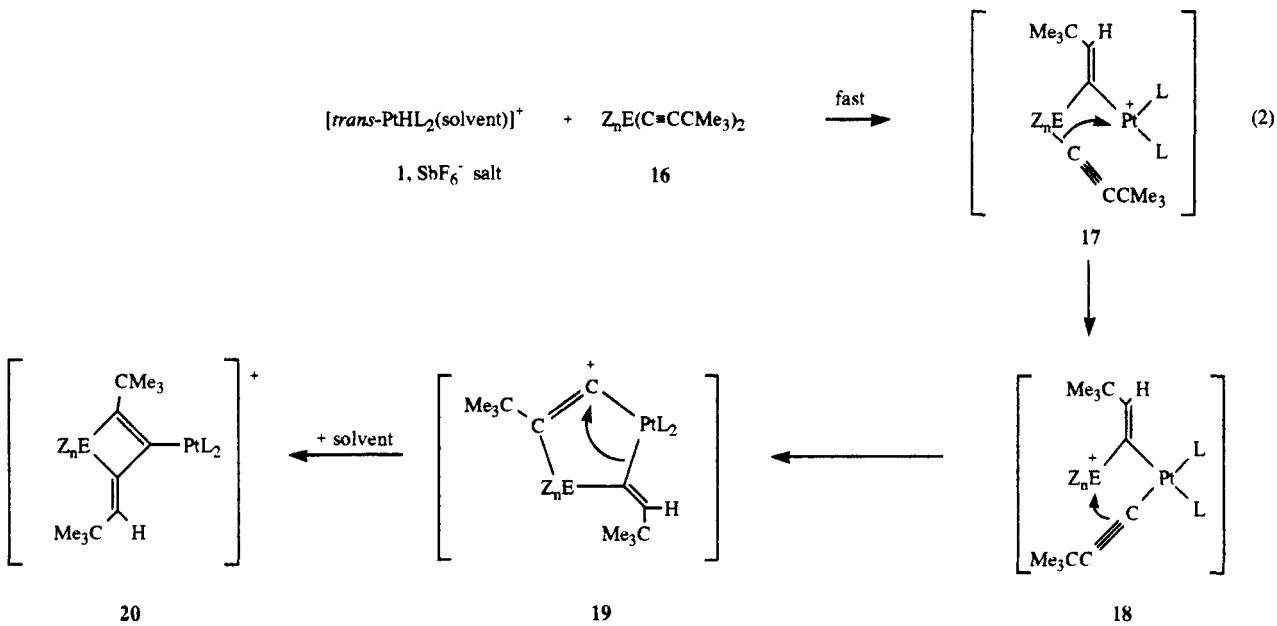


Figure 2. ORTEP view of complex **12** showing the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

Scheme III



point in the mechanism, the two phosphine ligands isomerize to a trans orientation. The observed stereochemistry of the alkenyl ligand presumably results from the preferred path of approach of the pyridine ligand. The stereoselectivity provided by the initial Pt–H addition is lost upon formation of the terminal alkenylidene ligand.

Conclusions

Suggested Mechanism for 1,2-Dihydrophosphete or -arsete Oxide Formation. We suggest that the results discussed above might provide some insight into the mechanism of heterocycle formation in the reaction of di- or trialkynylphosphine or di- or trialkynylarsine oxides with cationic platinum–hydride complexes. The kinetics study demonstrates that Pt–H addition to an alkynyl substituent is a rapid process that is followed by a slower rearrangement to give a 2-alkylidene-1,2-dihydrophosphete *P*-oxide complex. Reaction of **1b** and **11** follows a different pathway at some point in the overall mechanism, but the structure of the product **12**, indicates successful Pt–H addition to an alkynyl substituent and alkynyl transfer from the As atom to the Pt atom.

To the extent that these observations can be related to the mechanism of heterocycle formation, we suggest that the 1,2-dihydrophosphete or -arsete oxide complexes isolated from these reactions are formed by a mechanism similar to that postulated in Scheme III. This mechanism would presumably also apply to di- or trialkynylphosphonium reactants.[2] Reaction of a Pt–H species such as **1** with the appropriate phosphorus or arsenic reactant

Table III. Non-Hydrogen Atom Fractional Coordinates for Complex 12 with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
Pt(1)	0.45053 (5)	0.29644 (3)	0.24611 (5)
Sb(1)	0.0610 (1)	0.1487 (1)	0.6859 (1)
P(1)	0.3539 (3)	0.3507 (2)	0.0901 (3)
P(2)	0.5732 (4)	0.1861 (3)	0.3845 (4)
F(1)	0.209 (1)	0.147 (2)	0.651 (2)
F(2)	−0.088 (1)	0.136 (1)	0.712 (2)
F(3)	0.100 (2)	0.039 (1)	0.683 (5)
F(4)	0.008 (3)	0.260 (1)	0.714 (3)
F(5)	0.131 (2)	0.154 (2)	0.853 (1)
F(6)	−0.004 (2)	0.161 (2)	0.523 (1)
N(1)	0.246 (1)	0.1769 (6)	0.265 (1)
C(1)	0.293 (1)	0.2611 (8)	0.312 (1)
C(2)	0.223 (1)	0.3136 (9)	0.386 (1)
C(3)	0.236 (1)	0.399 (1)	0.461 (1)
C(4)	0.141 (2)	0.465 (1)	0.408 (2)
C(5)	0.361 (2)	0.426 (1)	0.467 (2)
C(6)	0.215 (3)	0.394 (1)	0.597 (2)
C(7)	0.202 (1)	0.138 (1)	0.343 (1)
C(8)	0.154 (1)	0.063 (1)	0.299 (2)
C(9)	0.155 (2)	0.026 (1)	0.173 (2)
C(10)	0.202 (1)	0.065 (1)	0.100 (1)
C(11)	0.245 (1)	0.1411 (8)	0.145 (1)
C(12)	0.410 (2)	0.320 (1)	−0.058 (1)
C(13)	0.420 (2)	0.226 (2)	−0.107 (2)
C(14)	0.367 (2)	0.465 (1)	0.130 (2)
C(15)	0.489 (2)	0.488 (1)	0.187 (2)
C(16)	0.191 (1)	0.354 (1)	0.044 (1)
C(17)	0.127 (2)	0.409 (1)	−0.054 (2)
C(21)	0.505 (2)	0.154 (1)	0.503 (2)
C(22)	0.592 (2)	0.101 (1)	0.598 (2)
C(23)	0.642 (3)	0.088 (2)	0.294 (3)
C(24)	0.570 (3)	0.044 (1)	0.189 (3)
C(25)	0.705 (2)	0.232 (2)	0.473 (3)
C(26)	0.680 (3)	0.316 (2)	0.565 (3)
C(30)	0.602 (1)	0.2773 (8)	0.184 (1)
C(31)	0.695 (1)	0.277 (1)	0.146 (2)
C(32)	0.808 (2)	0.274 (1)	0.096 (2)
C(33)	0.787 (3)	0.311 (3)	−0.021 (5)
C(34)	0.882 (5)	0.337 (3)	0.198 (5)
C(35)	0.879 (3)	0.191 (2)	0.092 (5)

(16) would give the expected addition product **17**. Transmetalation of the alkynyl substituent from the main-group element (E) to the Pt atom would form intermediate **18**. If elimination of a main-group fragment does not occur, then electrophilic attack by the cationic main-group atom on the alkynyl ligand would give intermediate **19**. Species **19** is partially stabilized by the Pt atom, and subsequent internal nucleophilic attack at this α carbocation would give formation of the four-membered ring **20**, as shown. Intermediates **18** and **19** are not detected by NMR in the course of these reactions due to their presumed high reactivity. A similar mechanism of alkynyl transfer has been invoked recently in the organoboration of tetraalkynylstannanes to give stannacyclopentadienes.[14] However, the extent to which the mechanism proposed above applies to the formation of four-membered heterocycles from reaction of platinum–hydride complexes such as **1** with dialkynylsilanes, sulfones, or ketones is uncertain.[6,15] Further study of these reaction mechanisms is needed.

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Supplementary Material Available: A summary of the chemical kinetics study and tables of atomic positional parameters and equivalent isotropic thermal parameters, anisotropic temperature factor parameters, interatomic distances and angles, torsion angles, and selected least-squares-plane data for **12** (15 pages). Ordering information is given on any current masthead page.

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