anisotropic thermal parameters for all except 23 non-hydrogen atoms, due to the limitations of SHELXTL. The 23 atoms left as isotropic were normal carbon atoms. Hydrogen atoms were included at calculated positions by using a riding model, with C–H of 0.96 Å and $U_H = 1.2U^*_C$. The largest shift in the final cycle of refinement was 0.005 for y of C(57). There are no exceptionally short intermolecular contacts in the structure.

The final difference map has 50 peaks with heights between 1.0 and 2.7 e Å^{-3}. Four of the largest fifteen appear to be hydride ligands. These were not well-behaved upon refinement, but contour maps drawn through and parallel to the $Ir_2CuCl_2(CO)_2$ plane reveal that these electron densities have radial symmetry and central maxima. Their presence can also be inferred from the vacant coordination sites at Ir.

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Supplementary Material Available: Complete tables of bond distances and angles, hydrogen atom positions, and anisotropic thermal parameters (7 pages); a listing of structure factor amplitudes (70 pages). Ordering information is given on any current masthead page.

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(20) The absorption correction is made by using Program XABS, B. Moezzi, Ph.D. Dissertation, University of California, Davis. The program obtains an absorption tensor from $F_o - F_c$ difference.

Transformation of a Trialkynylphosphine Oxide to a 2-Alkylidene-1,2-dihydro-3-phosphete *P*-Oxide Ligand by Pt–H Addition and Rearrangement Reactions. Activation of Molecular Hydrogen by a Platinum(II) Complex

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Addition of the Pt—H bond of $[trans\text{-}Pt(H)(PEt_3)_2(THF)]^+$ to the C$\equiv$C triple bond of the alkynyl substituent of $O{=}PPh_2(C{\equiv}CPh)$ occurs regioselectively to give a Pt,P μ-alkenylidene complex. Similar addition of a Pt—H bond to the trialkynylphosphine oxide $O{=}P(C{\equiv}CCMe_3)_3$ presumably occurs also, but a facile insertion rearrangement takes place to form a novel 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligand. Complexes containing this heterocyclic alkenyl ligand react with molecular hydrogen at −78 °C and at atmospheric pressure to give neutral monohydride complexes. The X-ray structure of one such complex has been determined: $\{trans\text{-}Pt[C{=}C(CMe_3)P(OBF_3)(C{\equiv}CCMe_3)C{=}C(CMe_3)(H)][P(n\text{-}Pr)_3]_2(H)\}$; monoclinic; $P2_1/c$; $Z = 4$; $a = 11.006$ (4) Å, $b = 21.435$ (5) Å, $c = 19.518$ (5) Å; $\beta = 100.72$ (3)°. Other reaction chemistry and a discussion of proposed mechanisms for the formation of these unusual complexes are reported.

Introduction

We have reported previously that the Pt—H or Pt—R bond of the reagents $[trans\text{-}Pt(R)(PEt_3)_2(acetone)]^+$ adds regioselectively across the C$\equiv$C triple bond of terminal alkynyl ligands of mononuclear organometallic compounds to give homo- or heterodinuclear complexes containing μ-alkenylidene ligands.[2a,b] These platinum reagents also add Pt—H or Pt—R bonds regioselectively across M$\equiv$C triple bonds of terminal alkylidyne ligands of mononuclear organometallic compounds to afford heterodinuclear complexes containing μ-alkylidene ligands.[2c–e] The regiochemistry observed for these Pt–H addition reactions is precisely that expected for having initial coordination of the C–C or M–C multiple bond to the coordinatively unsaturated complex $[HPt(PEt_3)_2]^+$ followed by 1,2-addition of the Pt–H bond across the unsaturated bond such that the H ligand adds to the site normally preferred by electrophilic reagents. This mechanism is proposed by analogy to the mechanism deduced by Clark and co-workers for the addition of this platinum hydride species to alkynes.[3]

We have undertaken a study of the addition of Pt–H reagents to *main-group* alkynyl compounds to obtain new heterocyclic compounds containing bridging alkenylidene functional groups. We now report our initial results of Pt–H additions to phosphine oxides that contain one or more alkynyl substituents. The cationic Pt—H reagent $[trans\text{-}Pt(H)(PEt_3)_2(THF)]^+$ adds regioselectively to the C$\equiv$C triple bond of the alkynyl substituent of $O{=}PPh_2(C{\equiv}CPh)$ to give a Pt,P μ-alkenylidene compound where

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the phosphine oxide group coordinates to the platinum atom affording a Pt—C—P—O four-membered ring. However, when the trialkynylphosphine oxide $O{=}P(C{\equiv}CCMe_3)_3$ reacts with such cationic Pt—H reagents, the μ-alkenylidene species formed by regioselective addition of the Pt—H bond to one of the alkynyl ligands undergoes further reaction with a second alkynyl substituent to give a novel 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligand. The formation of this new type of phosphetene ring is an unexpected result of an apparently very facile intramolecular rearrangement. Two Pt(II) complexes containing 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligands can be converted to cationic, three-coordinate Pt(II) species that will react with molecular hydrogen at −78 °C and at atmospheric pressure to give neutral, four-coordinate Pt(II) monohydride products. This latter reaction represents an unusually facile, formal heterolytic cleavage of molecular hydrogen by a Pt(II) complex. These results and other related chemistry are discussed below.

Experimental Section

Materials and Methods. All manipulations were performed under an atmosphere of dry, prepurified nitrogen and at room temperature unless otherwise indicated. Diethyl ether, hexane, pentane, and tetrahydrofuran (THF) were dried over Na/K alloy with benzophenone having been added to the diethyl ether and THF. Methylene chloride was dried over CaH_2, and acetone was dried over $CaSO_4$. All solvents were distilled under nitrogen prior to use.

Infrared (IR) spectra were recorded on a Perkin-Elmer 727 spectrophotometer as solutions in a 0.10-mm sodium chloride cavity cell using the solvent as a reference, and a polystyrene film was used as the calibration standard. Solid-state IR spectra were recorded on the same instrument as KBr pellets. ^1H NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz) or 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 were measured with respect to the external reference of 85% H_3PO_4. Microanalyses were performed by Mic Anal, Tucson, AZ, and by Galbraith Laboratories, Inc., Knoxville, TN.

The known phosphine oxides $O{=}P(Ph)_2(C{\equiv}CPh)$ (**1**) and $O{=}P(C{\equiv}CCMe_3)_3$ (**4**) were prepared according to standard synthetic procedures.[4] The cationic platinum hydride reagents **2**, **5**, and **6** were prepared from the neutral chloride derivatives by reaction with the appropriate silver salt as described previously.[2,3]

Preparation of {*cis*-Pt[OP(Ph)$_2$-(*E*)-C═C(Ph)(H)](PEt$_3$)$_2$}[SbF$_6$] (3). To a THF solution of $O{=}P(Ph)_2(C{\equiv}CPh)$ (**1**) (0.191 g, 0.631 mmol) was added $[Pt(H)(PEt_3)_2(THF)][SbF_6]$ (**2**) (0.571 mmol). After the reaction was stirred for 7.25 h, the solvent was removed under vacuum. The reaction residue was crystallized from ethanol to give 0.264 g (48%) of **3** as a white solid: mp 168–170 °C; ^1H NMR ($CDCl_3$) δ 1.05–1.35 (m, 18, PCH_2CH_3), 1.80–1.96 (m, 6, PCH_2CH_3), 1.96–2.20 (m, 6, PCH_2CH_3), 6.66–6.84 (m, 5, C_6H_5), 7.81 (d of d, 1, C═C*H*Ph, $^3J_{P(O)H}$ = 56.7 Hz, $^4J_{PH}$ = 10.3 Hz, $^3J_{PtH}$ = 72 Hz); $^{31}P\{H\}$ NMR ($CDCl_3$) δ 8.15 (d of d, PEt_3, $^2J_{PP}$ = 17.3 Hz, $^3J_{P(O)P}$ = 6.6 Hz, $^1J_{PtP}$ = 4013 Hz), 16.60 ("t", PEt_3, $^2J_{PP}$ = 17.2 Hz, $^3J_{P(O)P}$ = 17.1 Hz, $^1J_{PtP}$ = 2207 Hz), 84.51 (d of d, P═O, $^2J_{P(O)Pt}$ = 282 Hz, $^3J_{P(O)P}$ = 17.1 Hz, $^3J_{P(O)P}$ = 6.6 Hz); IR (KBr, cm^{-1}) ν(C═C) 1596 (m), 1583 (m), 1569 (m), ν(PO) 1112 (vs). Anal. Calcd for $C_{32}H_{46}F_6OP_3PtSb$: C, 39.60; H, 4.78. Found: C, 39.86; H, 4.88.

Preparation of {*trans*-Pt[C═C(CMe$_3$)P(O)(C≡CCMe$_3$)-C═C(CMe$_3$)(H)](PEt$_3$)$_2$(H$_2$O)}[SbF$_6$]·H$_2$O (7). To an acetone solution of **4** (0.154 g, 0.531 mmol) was added 0.530 mmol of **2**. After the solution was stirred for 19 h, the solvent was removed under vacuum. The reaction residue was crystallized from an acetone/diethyl ether solution at −20 °C to give 0.295 g (56%) of **7** as a white solid: mp 225–230 °C dec; ^1H NMR ($CDCl_3$) δ 1.00–1.32 (m, 18, PCH_2CH_3), 1.20 (s, 9, CMe_3), 1.28 (s, 9, CMe_3), 1.44 (s, 9, CMe_3), 1.65–2.20 (m, 12, PCH_2CH_3), 5.68 (br s, 4, H_2O), 6.12 (d, 1, C═C*H*CMe$_3$, $^3J_{P(O)H}$ = 48.6 Hz). Anal.. Calcd for $C_{30}H_{62}F_6O_3P_3PtSb$: C, 36.23; H, 6.28. Found: C, 36.25; H, 6.08 (1.34 molar equiv of water as determined by the Karl Fischer method).

Preparation of {*trans*-Pt[C═C(CMe$_3$)P(O)(C≡CCMe$_3$)-C═C(CMe$_3$)(H)](PEt$_3$)$_2$(H$_2$O)}[BF$_4$] (8). To a THF solution of **4** (0.200 g, 0.690 mmol) was added 0.690 mmol of $[Pt(H)(PEt_3)_2(THF)][BF_4]$ (**5**). A white solid precipitated from solution after 30–40 min. After the reaction was stirred for an additional 3.5 h, the supernatant solution was removed by syringe. The white solid was washed twice with 5 mL of THF and three times with 10 mL of diethyl ether and then dried under vacuum. Diethyl ether (50 mL) was added to the combined supernatant and washings to precipitate more of **8** to give a combined yield of 0.425 g (74%). Compound **8** can be crystallized from THF/acetone solution at −20 °C; mp 235–238 °C dec; ^1H NMR ($CDCl_3$) δ 1.0–1.30 (m, 18, PCH_2CH_3), 1.21 (s, 9, CMe_3), 1.23 (s, 9, CMe_3), 1.40 (s, 9, CMe_3), 1.70–1.85 (m, 12, PCH_2CH_3), 5.24 (br s, 2, H_2O), 6.04 (d, 1, C═C*H*CMe$_3$, $^3J_{P(O)H}$ = 47.4 Hz, $^4J_{PtH}$ = 9.0 Hz); $^{31}P\{H\}$ NMR ($CDCl_3$) δ 3.29 (br s, P(O), $^3J_{PtP(O)}$ = 711 Hz), 14.61, 16.75 (AB q, PEt_3, $^2J_{P(A)P(B)}$ = 363 Hz, $^1J_{PtP(A)} \approx {}^1J_{PtP(B)} \approx$ 2672 Hz); IR (KBr, cm^{-1}) ν(C≡C) 2160 (m), ν(PO) 1172 (vs). Anal. Calcd for $C_{30}H_{60}BF_4O_2P_3Pt$: C, 43.54; H, 7.31. Found: C, 43.47; H, 7.41.

Preparation of {*trans*-Pt[C═C(CMe$_3$)P(O)(C≡CCMe$_3$)-C═C(CMe$_3$)(H)][P(*n*-Pr)$_3$]$_2$(H$_2$O)}[BF$_4$] (9). The same procedure used to prepare **8** was used for the preparation of **9**. Due to the greater solubility of **9** compared to that of **8**, a precipitate was not observed during the reaction. Complex **9** was crystallized from THF/pentane solution at −20 °C to give 0.295 g (47%) of **9** as a white solid: mp 175–178 °C dec; ^1H NMR ($CDCl_3$) δ 0.97–1.07 (m, 18, $PCH_2CH_2CH_3$), 1.206 (s, 9, CMe_3), 1.214 (s, 9, CMe_3), 1.36 (s, 9, CMe_3), 1.45–1.80 (m, 24, $PCH_2CH_2CH_3$), 5.02 (br s, 2, H_2O), 5.96 (d, 1, C═C*H*CMe$_3$, $^3J_{P(O)H}$ = 46 Hz, $^4J_{PtH}$ = 7 Hz); $^{31}P\{H\}$ NMR ($CDCl_3$) δ 0.08 (br s, P(O), $^3J_{PtP(O)}$ = 738 Hz, 3.63, 5.03 (AB q, PR_3, $^2J_{P(A)P(B)}$ = 343 Hz, $^1J_{PtP(A)} \approx {}^1J_{PtP(B)} \approx$ 2647 Hz); IR (KBr, cm^{-1}) ν(C≡C) 2160 (m), ν(PO) 1150 (s). Anal. Calcd for $C_{36}H_{72}BF_4O_2P_3Pt$: C, 47.42; H, 7.96. Found: C, 47.36; H, 8.43.

Preparation of {*trans*-Pt[C═C(CMe$_3$)P(O)(C≡CCMe$_3$)-C═C(CMe$_3$)(H)](PEt$_3$)$_2$(C$_5$H$_5$N)}[BF$_4$] (10). To a solution of 0.104 g (0.125 mmol) of **8** in CH_2Cl_2 was added 0.157 g (1.98 mmol) of pyridine. The reaction solution was stirred for 45 min, and then the volume of solution was reduced by ca. 50% under reduced pressure. Hexane was added to the solution to induce crystallization of **10** upon cooling the solution to −20 °C. Complex **10** was isolated as a white solid (0.074 g, 66%): mp 112–116 °C dec; ^1H NMR ($CDCl_3$) δ 0.95–1.15 (m, 18, PCH_2CH_3), 1.21 (s, 9, CMe_3), 1.23 (s, 9, CMe_3), 1.43 (s, 9, CMe_3), 1.45–1.75 (m, 12, PCH_2CH_3), 6.12 (d, 1, C═C*H*CMe$_3$, $^3J_{P(O)H}$ = 48.1 Hz, $^4J_{PtH}$ = 7.9 Hz), 7.74 (t, 1, C_5H_5N, $^2J_{HH}$ = 9.4 Hz), 7.90 (t, 1, C_5H_5N, $^2J_{HH}$ = 8 Hz), 8.04 (t, 1, C_5H_5N, $^2J_{HH}$ = 9.4 Hz), 8.65 (d of d, 2, C_5H_5N, $^2J_{HH}$ = 5.2, 13.6 Hz); $^{31}P\{H\}$ NMR ($CDCl_3$) δ 5.14 (br s, P(O), $^3J_{PtP(O)}$ = 571 Hz), 7.96, 8.36 (AB q, PEt_3, $^2J_{P(A)P(B)}$ = 353 Hz, $^1J_{PtP(A)} \approx {}^1J_{PtP(B)} \approx$ 2600 Hz); IR (KBr, cm^{-1}) ν(C≡C) 2155 (m), ν(PO) 1180 vs; FAB spectrum, parent peak at *m/e* 801. Anal. Calcd for $C_{35}H_{63}BF_4NOP_3Pt$: C, 47.30; H, 7.14. Found: C, 47.01; H, 6.93.

Preparation of {*trans*-Pt[C═C(CMe$_3$)P(OMe)(C≡CCMe$_3$)C═C(CMe$_3$)(H)](PEt$_3$)$_2$(I)]}[BF$_4$] (11). To a solution of 0.139 g (0.158 mmol) of **8** in CH_2Cl_2 was added 0.05 mL (0.803 mmol) of methyl iodide. The reaction solution was stirred for 6 h, and then the solvent was removed under reduced pressure. The reaction residue was crystallized from a CH_2Cl_2/diethyl ether solution at −20 °C to give 0.063 g (42%) of **11** as a white solid: mp 137–138 °C; ^1H NMR ($CDCl_3$) δ 1.04–1.38 (m, 18, PCH_2CH_3), 1.20 (s, 9, CMe_3), 1.38 (s, 9, CMe_3), 1.41 (s, 9, CMe_3), 1.95–2.30 (m, 12, PCH_2CH_3), 4.16 (d, 3, P(O)Me, $^3J_{P(O)H}$ = 14.7 Hz), 6.63 (d, 1, C═C*H*CMe$_3$, $^3J_{P(O)H}$ = 55.6 Hz, $^4J_{PtH}$ = 8.1 Hz); $^{31}P\{H\}$ NMR ($CDCl_3$) δ −0.59, 0.53 (AB q, PEt_3, $^2J_{P(A)P(B)}$ = 365 Hz, $^1J_{PtP(A)}$ =

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2411 Hz, ${}^1J_{\mathrm{PtP(B)}}$ = 2443 Hz), 35.69 (s, P(O), ${}^3J_{\mathrm{PtP(O)}}$ = 830 Hz). Anal. Calcd for $C_{31}H_{61}BF_4IOP_3Pt$: C, 39.13; H, 6.46. Found: C, 38.94; H, 6.59.

Preparation of {*trans*-Pt[C═C(CMe$_3$)P(OBF$_3$)(C≡CCMe$_3$)C═C(CMe$_3$)(H)](PEt$_3$)$_2$(H)} (12). A large molar excess of powdered CaH_2 was added to a CH_2Cl_2 solution of 0.165 g (0.199 mmol) of 8, and the reaction mixture was stirred for 2 h. The reaction mixture was then filtered, and the filtrate was collected in flame-dried glassware. A slow stream of H_2 gas was passed through the filtrate solution for 2.5 h at −78 °C. After removal of the solvent under reduced pressure, the reaction residue was extracted twice with 15-mL portions of hexane followed by extraction with two 15-mL portions of diethyl ether. The ether extracts were collected, and the solvent was removed under pressure to give a white solid. The crude solid was crystallized from CH_2Cl_2/hexane solution at −20 °C to give 0.088 g (55%) of **12** as a white, hygroscopic solid: mp 178–179 °C; ^{1}H NMR ($CDCl_3$) δ −7.11 (d of "t", 1, PtH, ${}^2J_{\mathrm{PH}}$ = 18.3 Hz, ${}^4J_{\mathrm{P(O)H}}$ = 28.3 Hz, ${}^1J_{\mathrm{PtH}}$ = 655 Hz), 1.0–1.2 (m, 18, PCH_2CH_3), 1.2–2.1 (m, 12, PCH_2CH_3), 1.22 (s, 9, CMe_3), 1.32 (s, 9, CMe_3), 1.44 (s, 9, CMe_3), 4.62 (br s, 2, H_2O), 6.17 (d, 1, C═CHCMe$_3$, ${}^3J_{\mathrm{P(O)H}}$ = 56.4 Hz, ${}^4J_{\mathrm{PtH}}$ = 6.5 Hz); ^{31}P{H} NMR ($CDCl_3$) δ 15.52, 17.30 (d of AB q, PEt$_3$, ${}^2J_{\mathrm{P(A)P(B)}}$ = 358 Hz, ${}^4J_{\mathrm{P(O)P(A)}}$ = 4.0 Hz, ${}^4J_{\mathrm{P(O)P(B)}}$ = 4.1 Hz, ${}^1J_{\mathrm{PtP(A)}}$ = 2671 Hz, ${}^1J_{\mathrm{PtP(B)}}$ = 2704 Hz), 24.4 (br s, P(O)BF$_3$, ${}^3J_{\mathrm{PtP(O)}}$ = 453 Hz); IR (KBr, cm^{-1}) ν(C≡C) 2160 (w), ν(PtH) 1960 (s), ν(PO) 1113 (vs). Anal. Calcd for **12**·H$_2$O, $C_{30}H_{61}BF_3O_2P_3Pt$: C, 44.50; H, 7.60; P, 11.48. Found: C, 44.32; H, 7.77; P, 11.71.

Preparation of {*trans*-Pt{[C═C(CMe$_3$)P(OBF$_3$)(C≡CCMe$_3$)C═C(CMe$_3$)(H)][P(*n*-Pr)$_3$]$_2$(H)} (13). The same procedure provided above for the preparation of 12 was used to prepare 13. From 0.159 g (0.174 mmol) of 9 was obtained 0.065 g (42%) of 13 as a hygroscopic white solid: mp 124–128 °C dec; ^{1}H NMR ($CDCl_3$) δ −7.24 (d of "t", 1, PtH, ${}^2J_{\mathrm{PH}}$ = 18.7 Hz, ${}^4J_{\mathrm{P(O)H}}$ = 28.0 Hz, ${}^1J_{\mathrm{PtH}}$ = 679 Hz), 0.95–1.12 (m, 18, $PCH_2CH_2CH_3$), 1.20 (s, 9, CMe_3), 1.30 (s, 9, CMe_3), 1.35 (s, 9, CMe_3), 1.33–1.95 (m, 24, $PCH_2CH_2CH_3$), 4.65 (br s, 2, H_2O), 6.14 (d, 1, C═CHCMe$_3$, ${}^3J_{\mathrm{P(O)H}}$ = 57 Hz, ${}^4J_{\mathrm{PtH}}$ = 7.8 Hz); ^{31}P{H} NMR ($CDCl_3$) δ 6.3, 8.2 (d of AB q, PR$_3$, ${}^2J_{\mathrm{P(A)P(B)}} \approx$ 360 Hz, ${}^4J_{\mathrm{P(O)P(A)}}$ = 4.9 Hz, ${}^4J_{\mathrm{P(O)P(B)}}$ = 4.4 Hz, ${}^1J_{\mathrm{PtP(A)}} \approx {}^1J_{\mathrm{PtP(B)}} \approx$ 2649 Hz), 25.39 (br s, P(O)BF$_3$, ${}^3J_{\mathrm{PtP(O)}}$ = 455 Hz); IR (KBr, cm^{-1}) ν(C≡C) 2160 (w), ν(PtH) 2000 (m), ν(PO) 1110 (vs). Anal. Calcd for **13**·H$_2$O, $C_{36}H_{73}BF_3O_2P_3Pt$: C, 48.38; H, 8.23. Found: C, 48.62; H, 7.99.

Preparation of {*trans*-Pt[C═C(CMe$_3$)P(O)(C≡CCMe$_3$)-C═C(CMe$_3$)(H)](PEt$_3$)$_2$(H)} (14). An NMR sample solution of 12 was titrated quantitatively to 14 upon adding portions of pyridine to the sample solution up to a total amount of added pyridine equal to one equivalent. (This reaction was monitored by observing changes in the Pt–H resonances.) On a synthetic scale, complex 14 was isolated as colorless crystals in 18% yield as a co-product from the preparation of 12 by concentrating the hexane extract solutions to a volume necessary to induce crystallization of 14 at −20 °C: mp 171–172 °C; ^{1}H NMR ($CDCl_3$) δ −6.74 (d of "t", 1, PtH, ${}^2J_{\mathrm{PH}}$ = 18.9 Hz, ${}^4J_{\mathrm{P(O)H}}$ = 23.9 Hz, ${}^1J_{\mathrm{PtH}}$ = 652 Hz), 1.00–1.13 (m, 18, PCH_2CH_3), 1.18 (s, 9, CMe_3), 1.25 (s, 9, CMe_3), 1.30 (s, 9, CMe_3), 1.70–1.95 (m, 12, PCH_2CH_3), 5.88 (d, 1, C═CHCMe$_3$, ${}^3J_{\mathrm{P(O)H}}$ = 49.3 Hz, ${}^4J_{\mathrm{PtH}}$ = 7.0 Hz); ^{31}P{H} NMR ($CDCl_3$) δ 12.63 (br s, P(O), ${}^3J_{\mathrm{PtP(O)}}$ = 374 Hz), 17.33, 18.35 (d of AB q, PEt$_3$, ${}^2J_{\mathrm{P(A)P(B)}}$ = 367 Hz, ${}^4J_{\mathrm{P(O)P(A)}} \approx {}^4J_{\mathrm{P(O)P(B)}} \approx$ 3.5 Hz, ${}^1J_{\mathrm{PtP(A)}} \approx {}^1J_{\mathrm{PtP(B)}} \approx$ 2738 Hz); IR (KBr, cm^{-1}) ν(C≡C) 2163 (s), ν(PtH) 1917 (s), ν(PO) 1177 (vs). Anal. Calcd for $C_{30}H_{59}OP_3Pt$: C, 49.78; H, 8.22. Found: C, 49.82; H, 8.43.

X-ray Crystal Structure Analysis of Complex 13. Complex 13, prepared as described above, was recrystallized from CH_2Cl_2/hexane solution at −20 °C in the form of colorless prisms.

Crystal data: $C_{36}H_{71}BF_3OP_3Pt$, M = 875.79, monoclinic, a = 11.006 (4) Å, b = 21.435 (5) Å, c = 19.518 (5) Å, β = 100.72 (3)° (from 25 orientation reflections; 30° < θ < 49°), V = 4524.2 Å^3, Z = 4, d_{calcd} = 1.286 g cm^{-3}, μ(Cu Kα radiation, λ = 1.5418 Å) = 71.7 cm^{-1}. Space group $P2_1/c$ (C_{2h}^5) uniquely from the systematic absences: $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$. Crystal dimensions: 0.30 × 0.30 × 0.30 mm.

Preliminary unit-cell parameters and space group information were derived from oscillation and Weissenberg photographs. Intensity data ($+h,+k,\pm l,\theta_{\max}$ = 67°, 8464 reflections) were recorded at 25 °C on an Enraf-Nonius CAD-4 diffractometer [Cu Kα radiation, incident-beam graphite monochromator; ω–2θ scans, scan width (1.20 + 0.14 tan θ)°]. Lorentz, polarization, and empirical absorption ($T_{\max}$:$T_{\min}$ = 1.00:0.78) corrections were applied to the data, and equivalent reflections were then averaged (R_{merge} = 0.019 on $|F_o|$) to yield a total of 8021 unique reflections out of which those 5526 with $I > 3.0\sigma(I)$ were retained for the analysis.

Table I. Non-Hydrogen Atom Fractional Coordinates (×10^4) for Complex 13 with Estimated Standard Deviations in Parentheses

atom	x	y	z
Pt	3076.0 (3)	4811.5 (1)	2666.3 (1)
P(1)	3928 (2)	2863.0 (8)	2361 (1)
P(2)	4742 (2)	5210.9 (9)	2280 (1)
P(3)	1192 (2)	4622.3 (9)	2953 (1)
C(2)	3114 (5)	3500 (3)	1921 (3)
C(3)	3502 (6)	3872 (3)	2567 (3)
C(4)	4114 (6)	3437 (3)	3013 (3)
C(5)	2475 (6)	3673 (3)	1306 (4)
C(6)	2148 (8)	3305 (4)	631 (4)
C(7)	761 (11)	3329 (7)	387 (7)
C(8)	2593 (11)	2633 (5)	693 (6)
C(9)	2746 (13)	3628 (7)	68 (5)
C(10)	4839 (7)	3439 (4)	3749 (4)
C(11)	4655 (9)	4051 (5)	4123 (5)
C(12)	6202 (8)	3363 (6)	3748 (5)
C(13)	4374 (10)	2910 (6)	4150 (5)
C(14)	5304 (7)	2680 (4)	2063 (4)
C(15)	6244 (6)	2562 (4)	1880 (4)
C(16)	7409 (7)	2430 (4)	1661 (4)
C(17)	8181 (10)	3007 (6)	1697 (8)
C(18)	8113 (8)	1969 (6)	2146 (8)
C(19)	7162 (11)	2164 (9)	945 (7)
C(21)	5327 (9)	4702 (4)	1661 (5)
C(22)	6205 (13)	4938 (7)	1281 (7)
C(23)	6419 (14)	4490 (8)	709 (6)
C(24)	6085 (7)	5382 (4)	2943 (5)
C(25)	5834 (10)	5809 (5)	3545 (5)
C(26)	6962 (13)	5879 (7)	4116 (6)
C(27)	4387 (8)	5947 (4)	1803 (4)
C(28)	3283 (9)	5901 (5)	1215 (5)
C(29)	2918 (12)	6511 (6)	836 (7)
C(31)	672 (8)	5211 (4)	3511 (5)
C(32)	1515 (11)	5272 (5)	4198 (5)
C(33)	976 (12)	5739 (6)	4672 (6)
C(34)	−38 (8)	4608 (5)	2161 (5)
C(35)	30 (13)	5106 (7)	1658 (8)
C(36)	−215 (19)	5546 (10)	1497 (13)
C(37)	1020 (6)	3876 (3)	3368 (4)
C(38)	−203 (7)	3732 (4)	3587 (5)
C(39)	−154 (8)	3123 (5)	3982 (5)
O	3349 (4)	2222 (2)	2441 (3)
B	2083 (9)	2038 (5)	2589 (6)
F(1)	1460 (5)	2481 (3)	2674 (5)
F(2)	1606 (6)	1620 (4)	2177 (4)
F(3)	2365 (8)	1744 (5)	3211 (5)

The crystal structure was solved by the heavy-atom method.[5] Initial Pt atom coordinates where derived from a Patterson map. The remaining non-hydrogen atoms were located in a series of F_o and difference Fourier syntheses. Non-hydrogen atom positional and anisotropic temperature factor parameters were refined by full-matrix least-squares calculations during which $\sum w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized. Hydrogen atoms, except for those on C(36) which had a large temperature factor (B_{eq} = 31.2 Å^2), were included in the structure-factor calculations at idealized positions. A secondary extinction correction, included as a variable in the later least-squares iterations, refined to 1.7 × 10^{-7}. The least-squares refinement converged at R = 0.047 (R_w = 0.064)[6] with the largest shift-to-error ratio <0.03 for all parameters save those of C(36) which tended to oscillate in alternate cycles and for which the corresponding values for positional and temperature factor parameters were 0.11 and 0.72, respectively, in the final cycle. The largest peak in the final difference Fourier

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(5) Crystallographic calculations were performed on PDP11/44 and MicroVAX II computers by use of the Enraf-Nonius Structure Determination Package.

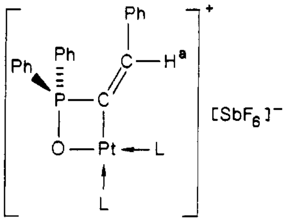
(6) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

synthesis (0.90 e Å^{-3}) was located 1.47 Å from Pt. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 7. Final non-hydrogen atom positional parameters are listed in Table I. Anisotropic temperature factor parameters, hydrogen atom positional and isotropic thermal parameters, and a listing of observed and calculated structure amplitudes are provided as supplementary material.[8]

Results

When the alkynylphosphine oxide **1** is treated with the cationic platinum hydride complex **2**, the Pt—H bond adds regioselectively across the alkynyl C≡C triple bond to give the Pt,P μ-alkenylidene complex **3**, as shown in eq 1. This addition reaction parallels the known addition of Pt—H bonds across a C≡C triple bond of alkynyl ligands in mononuclear compounds to give cationic, homo- or heterodinuclear complexes containing μ-alkenylidene ligands.[2a,b]

$$\underset{\mathbf{1}}{O{=}PPh_2(C{\equiv}CPh)} + \underset{\mathbf{2}}{[Pt(H)(PEt_3)_2(THF)]^+[SbF_6]^-} \xrightarrow{THF}$$



(1)

3, L = PEt$_3$

Spectroscopic data support the structural representation shown in **3**. The P═O stretching band frequency of the free molecule **1** appears at 1190 cm^{-1}. In complex **3**, this band appears at 1112 cm^{-1}, and a shift of 78 cm^{-1} to lower frequency is consistent with coordination of the phosphine oxide group to the Pt(II) atom.[9] The ^{1}H NMR resonance of the alkenylidene proton H^a provides diagnostic confirmation of the structure of **3** and of the regioselectivity of the Pt–H addition reaction based on NMR data reported for known μ-alkenylidene ligands[2a,b] and Pt(II)–alkenyl complexes.[10] The chemical shift for the proton H^a of δ 7.81 appears nearly 2.5 ppm to lower field than that expected for Pt(II)–alkenyl complexes but within the expected chemical shift range for μ-alkenylidene proton resonances.[2a,b] Proton H^a couples to the P(O) phosphorus nucleus with a $^3J_{P(O)H}$ coupling constant of 56.7 Hz and to the Pt nucleus with a $^3J_{PtH}$ coupling constant of 72 Hz. The value of $^3J_{P(O)H}$ is consistent with a trans orientation of the P(O) and H^a groups as found in phospholene oxides,[11] and the value of $^3J_{PtH}$ is a diagnostic indication of a cis disposition of Pt(II) and H^a atoms in an alkenyl ligand.[10] Proton H^a is also coupled to the trans PEt$_3$ phosphorus nucleus with a $^4J_{PH}$ coupling constant of 10.3 Hz. Coupling between H^a and the phosphorus nucleus of the cis PEt$_3$ ligand is not resolved, and such coupling is not observed in known Pt(II)–alkenyl complexes.[10]

The ^{31}P NMR data of **3** are also consistent with the structure shown above. The resonance of the phosphine oxide group appears at low field (δ 84.5) compared to the chemical shift values of free triorganophosphine oxides. This chemical shift reflects the phosphonium ion character of a phosphorus atom in a phosphine oxide group that is coordinated to a metal atom.[12] The relatively small value for $^2J_{P(O)Pt}$ of 281.5 Hz is expected because of the structural effect of the highly strained four-membered chelate ring. The multiplicity of the Pt satellites of this resonance is consistent with the monomeric structure shown for **3**. The P(O) phosphorus nucleus also couples differently to the two nonequivalent PEt$_3$ phosphorus nuclei, as expected, with $^3J_{P(O)P}$ coupling constants of 17.1 and 6.6 Hz. The two phosphorus nuclei of the PEt$_3$ ligands couple to each other with a $^2J_{PP}$ value of 17.2 Hz, and these nuclei couple to the Pt nucleus with $^1J_{PtP}$ coupling constants of 2207 and 4013 Hz. The values of these coupling constants are consistent with the cis orientation of the two PEt$_3$ ligands and the nonequivalent donor properties of the ligands trans to these phosphine ligands.[13]

When the trialkynylphosphine oxide **4** is treated with the cationic platinum hydride reagents **2**, **5**, and **6**, an unusual sequence of addition and insertion reactions takes place to give the new heterocyclic compounds **7**–**9** (as shown in Scheme I). Compounds **7**–**9** are cationic, four-coordinate Pt(II) complexes containing either trans PEt$_3$ (**7** and **8**) or trans P(n-Pr)$_3$ (**9**) ligands, an aquo ligand, and the same 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligand. These complexes differ only in the identity of the anionic counterion and the amount of water of crystallization. The water molecules are extracted apparently from exogenous sources. Complex **7** is particularly hygroscopic. Microanalysis of **7** is consistent with the presence of two water molecules (of which 1.34 water molecules per molecule of **7** have been determined by the Karl Fischer method).

Complex **8** reacts with pyridine to give displacement of the aquo ligand and formation of the analogous pyridine complex **10**. Complex **10** is not strongly hygroscopic, and a FAB spectrum of **10** contains a parent peak for the cationic platinum complex at 801 amu. A FAB spectrum of complex **8** contains a peak at 722 amu which is assigned to the parent ion of the cationic platinum complex minus the aquo ligand. Complex **8** also reacts with excess methyl iodide to give the phosphine oxide alkylation product **11** rather than a Pt(IV) oxidative addition product.

Complexes **8** and **9** react with CaH$_2$ followed by hydrogen gas at −78 °C and at atmospheric pressure to give the neutral Pt(II) monohydride complexes **12** and **13**, respectively. NMR control experiments demonstrate that Pt hydride formation occurs only after reaction with molecular hydrogen. This synthetic method follows that used by Crabtree et al. for the reaction of an iridium–aquo complex with molecular hydrogen.[14] Complexes **12** and **13** are hygroscopic solids presumably due to the presence of the BF$_3$ adduct to the phosphine oxide group of the 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligand. Complex **12** reacts with pyridine in essentially quantitative yield to give the adduct-free derivative **14**. Complex **14** is not strongly hygroscopic. Complexes **12** and **13** slowly

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(7) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(8) See the paragraph at the end of this paper regarding supplementary material.

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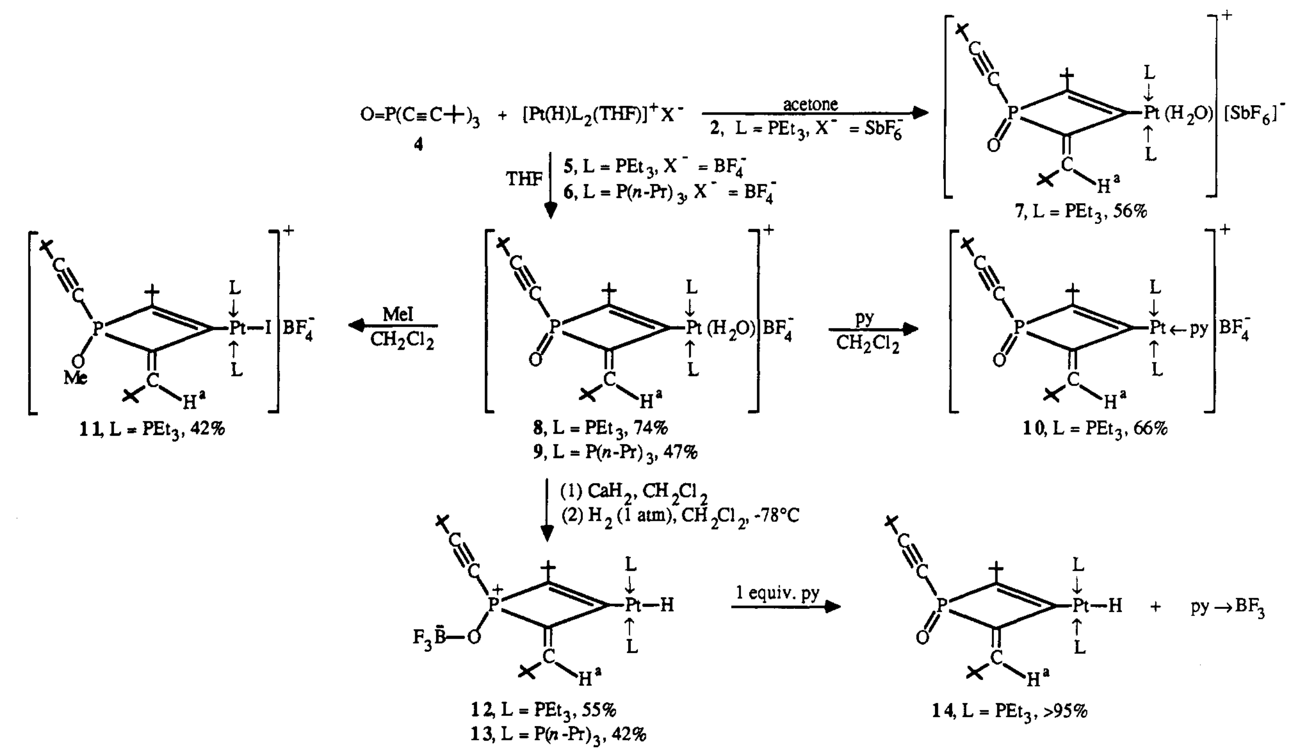
Scheme I



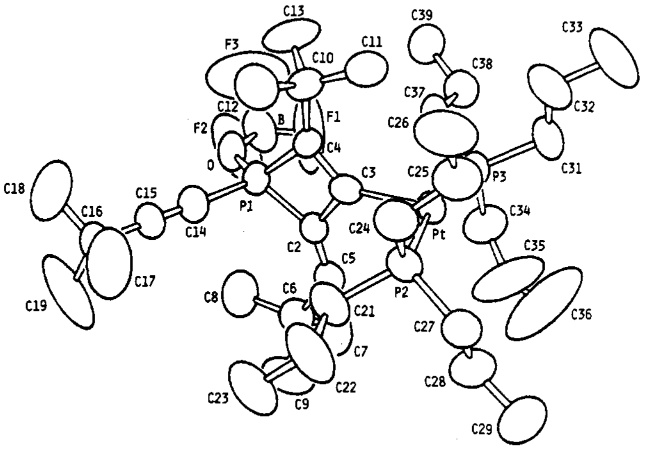


Figure 1. An ORTEP plot of complex **13**, with thermal ellipsoids at the 33% probability level. Hydrogen atoms have been omitted for clarity.

convert to adduct-free species upon repeated manipulations due, presumably, to reaction of the BF_3 adduct with exogenous sources of water.

The importance of the reactions of **8** and **9** with molecular hydrogen made it highly desirable to have an X-ray structural characterization of a representative hydride complex. Moreover, an unambiguous determination of the structure of the unusual 2-alkylidene-1,2-dihydro-3-phosphete ligand (which contains a previously unknown heterocyclic system) was necessary to permit the proper interpretation of NMR spectral data for complexes **7–14**. Thus, an X-ray crystal structure analysis of complex **13** was performed. A view of the structure is presented in Figure 1. Non-hydrogen atom positional parameters are listed in Table I. Crystals of **13** contain discrete molecules of the complex separated by normal van der Waals distances. Selected intramolecular distances and angles are provided in Table II.

Table II. Selected Distances (Å) and Angles (deg) in Complex 13 with Estimated Standard Deviations in Parentheses

(a) Bond Lengths

Pt–C(3)	2.085 (6)	P(1)–O	1.535 (5)
Pt–P(2)	2.275 (2)	C(2)–C(3)	1.486 (8)
Pt–P(3)	2.282 (2)	C(2)–C(5)	1.326 (9)
P(1)–C(2)	1.766 (6)	C(3)–C(4)	1.365 (8)
P(1)–C(4)	1.754 (6)	C(14)–C(15)	1.183 (11)
P(1)–C(14)	1.764 (9)	O–B	1.527 (12)

(b) Bond Angles

P(2)–Pt–P(3)	166.64 (7)	P(1)–C(2)–C(3)	87.9 (4)
P(2)–Pt–C(3)	97.1 (2)	P(1)–C(2)–C(5)	142.4 (5)
P(3)–Pt–C(3)	94.7 (2)	C(3)–C(2)–C(5)	129.7 (6)
C(2)–P(1)–C(4)	77.9 (3)	C(2)–C(3)–C(4)	101.8 (8)
C(2)–P(1)–C(14)	113.6 (3)	C(2)–C(3)–Pt	124.3 (4)
C(2)–P(1)–O	124.0 (3)	C(4)–C(3)–Pt	133.9 (4)
C(4)–P(1)–C(14)	113.8 (4)	P(1)–C(4)–C(10)	131.5 (5)
C(4)–P(1)–O	123.3 (3)	C(3)–C(4)–C(10)	135.8 (6)
C(14)–P(1)–O	103.4 (3)	P(1)–C(4)–C(3)	92.3 (4)

(c) Torsion Angles

C(4)–P(1)–C(2)–C(3)	2.8 (4)	C(2)–C(3)–C(4)–P(1)	3.6 (5)
C(2)–P(1)–C(4)–C(3)	–3.0 (4)	Pt–C(3)–C(4)–C(10)	–5.9 (13)
P(1)–C(2)–C(3)–C(4)	–3.5 (5)	C(2)–C(3)–Pt–P(2)	–88.1 (5)
C(5)–C(2)–C(3)–Pt	1.2 (10)	C(2)–C(3)–Pt–P(3)	85.5 (5)
P(1)–C(2)–C(5)–C(6)	0.7 (13)		

The Pt(II) atom has a typical "square-planar" coordination geometry with two trans $P(n\text{-}Pr)_3$ ligands and with the heterocyclic ligand located trans to the hydride ligand (which was not located in the structural determination). The values of the Pt–P(2) and Pt–P(3) distances are normal, and the value of the P(2)–Pt–P(3) angle is 166.64 (7)°. The Pt–C(3) distance of 2.085 (6) Å represents a normal Pt(II)–C(alkenyl) bond length. A survey of Pt(II)–(η^1-alkenyl) structures reveals Pt(II)–C(alkenyl) distances in the range of 2.022 (8)–2.08 (2) Å.[15] The Pt–C(3) distance of **13** falls in the upper part of this range possibly due to steric interaction between the heterocyclic ligand

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[15] Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, pp 471–762.

and the phosphine ligands. This interligand repulsion might also account for the slight distortion of the P(2)–Pt–P(3) angle from linearity.

The 2-alkylidene-1,2-dihydro-3-phosphete ring, with a mean endocyclic dihedral angle of 3.2° about the ring bonds, is approximately planar. The directly bonded atoms C(5), Pt, and C(10) all lie fairly close ($\Delta = 0.011, 0.086, 0.055$ Å, respectively) to the least-squares plane through the ring atoms, and the dihedral angle between this plane and that through Pt, P(2), P(3), and C(3) ($\Delta_{\max} = 0.079$ Å) is 89.7°. The P(1)–C(2) and P(1)–C(4) distances at 1.766 (6) and 1.754 (6) Å, respectively, are considerably shorter than the corresponding values of 1.83 (1) and 1.93 (1) Å in a (2-oxo-1,2-dihydrophosphete)W(CO)$_5$ complex,[16a] and their mean (1.760 Å) is only slightly longer than P–C distances [1.733 (3)–1.746 (5) Å][17,18] in phosphorin rings, indicating that a significant amount of P–C d_π–p_π bonding must be present in the 1,2-dihydrophosphete ring of complex **13**. The endocyclic C–P–C angle at 77.9 (3)° in **13** is greatly enlarged over that of 71.9 (5)° in the above tungsten complex,[16a] and it is slightly smaller than those of 80.0–85.9° in phosphetane rings which are all puckered to varying extents depending on their substitution patterns.[19,20] The endocyclic C(2)–C(3) and C(3)–C(4) C–C single and double bond distances of 1.486 (8) and 1.365 (8) Å, respectively, compare well to the corresponding distances of 1.48 (1) and 1.36 (1) Å, respectively, in the 2-oxo-1,2-dihydrophosphete ligand of the tungsten complex mentioned above.[16a] The exocyclic alkylidene C(2)–C(5) distance of 1.326 (9) Å and the alkynyl C(14)–C(15) distance of 1.183 (11) Å represent, respectively, bonafide C–C double and triple bond lengths. Other bond lengths and angles are in accord with expectations when the effects of intramolecular nonbonded interactions are taken into consideration. Thus, for example, distortions from a regular square-planar geometry at Pt [C(3)–Pt–P(2) = 97.1 (2)°, C(3)–Pt–P(3) = 94.7 (2)°] are necessary to gain relief from interactions between the bulky P(n-Pr)$_3$ ligands and the 1,2-dihydrophosphete ring.

The IR and ^{1}H and ^{31}P NMR data for complexes **7**–**14** confirm the presence of a 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligand in these compounds. The solid-state IR spectrum of the free phosphine oxide **4** shows P=O and C≡C stretching bands at 1205 and 2160 cm^{-1}, respectively. For complexes **8**–**10** and **14**, and alkynyl C≡C stretching band is observed at 2155–2163 cm^{-1}, as expected, and the P=O stretching band for the phosphine oxide groups appears in the range of 1150–1180 cm^{-1}. For complexes **12** and **13**, an alkynyl C≡C stretching band is also observed at 2160 cm^{-1}, while the stretching band for the phosphine oxide groups that are now coordinated to a BF$_3$ moiety have shifted significantly to lower frequency (1113 and 1110 cm^{-1}, respectively). These frequencies compare well to the P–O frequency of 1112 cm^{-1} for compound **3** in which the phosphine oxide group is coordinated to the platinum atom. Complexes **12**–**14** also have Pt–H stretching bands that appear in the range of 1917–2000 cm^{-1}.

The ^{1}H NMR spectral data of compounds **7**–**14** support the structure and dissymmetry imposed by the presence of the 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligands. The three *tert*-butyl groups within each complex are nonequivalent, as expected, and the *tert*-butyl resonances appear as singlets at the average chemical shift values of δ 1.39, 1.28, and 1.21 ppm. In each complex, the resonance of the alkylidene proton, H^a, appears as a doublet in the range δ 5.88–6.04 ppm. This chemical shift range is that expected for *alkenyl* proton environments and is nearly 2 ppm to higher field than that expected for the resonances of protons in μ-alkenylidene proton environments (as observed for H^a in compound **3**). Decoupling experiments verify that the doublet resonance is due to P–H coupling, presumably between H^a and the phosphorus nucleus of the P(O) group. The average value of the $^3J_{\mathrm{P(O)H}}$ coupling constants of complexes **7**–**14** is 51 Hz (cf. the corresponding value of $^3J_{\mathrm{P(O)H}}$ for complex **3** is 56.7 Hz). The H^a resonances of complexes **8**–**14** also show satellites due to $^4J_{\mathrm{PtH^a}}$ coupling (the spectrum of **7** was not of sufficiently high resolution to reveal this coupling). The average value of this $^4J_{\mathrm{PtH^a}}$ coupling constant is 7.6 Hz (cf. the corresponding value of $^3J_{\mathrm{PtH^a}}$ observed in complex **3** is 72.0 Hz). Observation of this $^4J_{\mathrm{PtH^a}}$ coupling is a diagnostic confirmation of the unusual insertion reaction that forms the phosphetenyl skeleton. For the hygroscopic compounds, a resonance due to coordinated water appears in the range of δ 4.62–5.88 ppm (see Experimental Section). The presence of a P(O)Me group in complex **11** is confirmed by the appearance of a doublet resonance for these methyl protons at δ 4.16 ppm with a value of 14.7 Hz for the $^3J_{\mathrm{PH}}$ coupling constant.

For the platinum hydride complexes **12**–**14**, the hydride resonances appear as a doublet of pseudo triplets. In the BF$_3$ adducts **12** and **13**, these resonances are centered, respectively, at δ −7.11 and −7.24 ppm. In the free phosphine oxide complex **14**, the hydride resonance appears at δ −6.74 ppm (the corresponding derivative of **13** has a hydride resonance at δ −6.93 ppm). Decoupling experiments verify that the splitting of the hydride resonance arises solely from Pt–H and P–H coupling. The average values of these coupling constants are as follows: $^2J_{\mathrm{PH}}$, 18.6 Hz; $^4J_{\mathrm{P(O)H}}$, 26.7 Hz; and $^1J_{\mathrm{PtH}}$, 662 Hz. The value of $^2J_{\mathrm{PH}}$ is that expected for a structure having two PEt$_3$ ligands cis to a hydride ligand,[13] and the value of $^1J_{\mathrm{PtH}}$ is that expected for a *trans*-PtL$_2$R(H) complex where R possesses a carbon donor atom [e.g. the value of $^1J_{\mathrm{PtH}}$ in the complex *trans*-Pt(PPh$_3$)$_2$(CH$_2$CH$_2$CH$_2$CN)(H) is 636 Hz[21]]. Although the average value of the $^4J_{\mathrm{P(O)H}}$ coupling of 26.7 Hz is considerably larger than the $^4J_{\mathrm{PH}}$ coupling constant of 0–10 Hz observed in phosphorinane systems,[22] the $^4J_{\mathrm{P(O)H}}$ coupling constant observed in compounds **12**–**14** is less than half the value of the $^3J_{\mathrm{P(O)H^a}}$ coupling constant observed in compound **3**. The effect of the strained geometry of the 1,2-dihydrophosphete ring and of the presence of an intervening Pt atom on the magnitude of this $^4J_{\mathrm{P(O)H}}$ coupling to the hydride ligand is not known.

The ^{31}P NMR spectra have been recorded for compounds **8**–**14**. The chemical shifts of the resonances of the phosphorus nuclei of the phosphine oxide moieties can be grouped into two classes based on the chemical structure of the phosphetenyl ligand. For compounds **8**–**10** and **14**, the phosphine oxide groups are not coordinated to a Lewis acid. These phosphorus resonances appear in the region of δ 0.08–12.63 ppm. Complexes **11**–**13** have phosphine oxide moieties coordinated either to BF$_3$ (**12** and **13**) or to CH$_3$$^+$ (**11**) (through direct alkylation). The resonances of

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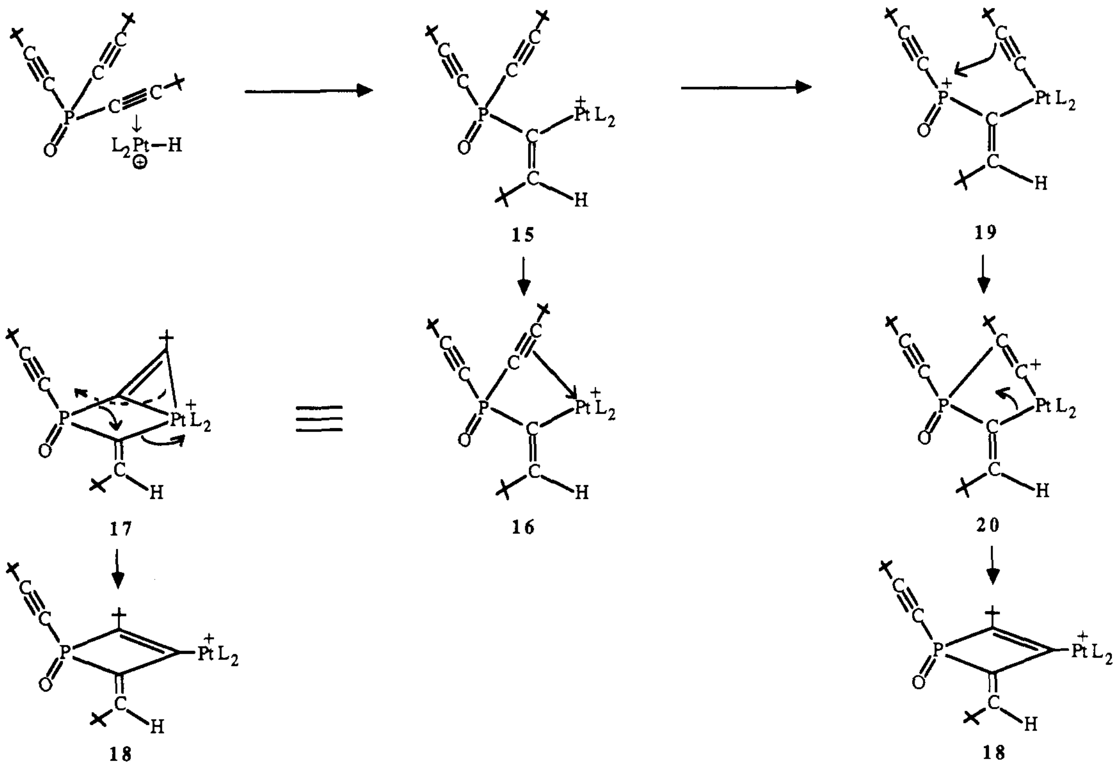
(22) Bentrude, W. G.; Setzer, W. N. ref 8, pp 365–389.

Scheme II



the P(O) group in these complexes occur to lower field in the range of δ 24.4–35.69 ppm. The values of ${}^3J_{\text{PtP(O)}}$ for these resonances are found in the range of 374 Hz (14) to 830 Hz (11).

A diagnostic indication that the unusual 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligand is present in these compounds is the observation of AB coupling patterns for the two nonequivalent phosphorus nuclei of the PR_3 ligands. Even though the two PR_3 are oriented at trans coordination sites about the Pt(II) atom, the molecular dissymmetry generated by the heterocyclic ligand is revealed in the nonequivalence of the ${}^{31}P$ resonances of the PR_3 ligands. The ${}^{31}P$ chemical shifts for the two PR_3 ligands occur in the expected region (these values range from –0.59 to +18.35 ppm), and the average value for the degree of anisochronism between the AB pairs of PR_3 ligands is 1.39 ppm. The average value for ${}^2J_{\text{P(A)P(B)}}$ of 358 Hz is determined by analysis of the spectral AB multiplets. This value is consistent with ${}^2J_{\text{PP}}$ values for other platinum complexes having trans phosphine ligands.[13d] For example, the value of ${}^2J_{\text{PP}}$ in the complex *trans*-$Pt(PEt_3)_2Cl_2$ is 436 Hz (while ${}^2J_{\text{PP}}$ in *cis*-$Pt(PMe_3)_2Cl_2$ is only 18.9 Hz), and the value of ${}^2J_{\text{PP}}$ in the dinuclear complex *trans,trans*-$(MeCN)(Me_2EtP)_2PtPt(NCMe)_2(PMe_2Et)$ is 358 Hz.[13a] The values of ${}^1J_{\text{PtP(A)}}$ and ${}^1J_{\text{PtP(B)}}$ are very similar (average value is 2632 Hz) and appear to be in the range expected for *trans*-$Pt(PEt_3)_2(Me)(X)$ complexes where X is CN or an electronegative group.[13d] The value of ${}^1J_{\text{PtP}}$ observed for platinum hydride compounds, such as *trans*-$Pt(PPh_3)_2(CH_2CH_2CH_2CN)(H)$, is 3160 Hz; the average value of ${}^1J_{\text{PtP}}$ for the hydride complexes 12–14 is 2692 Hz. The AB multiplets for the trans PR_3 ligands of the hydride complexes 12–14 appear as doublets of AB "quartets". This additional splitting is assigned to long-range coupling between the PR_3 and P(O) phosphorus nuclei to give ${}^4J_{\text{P(O)P(A)}}$ and ${}^4J_{\text{P(O)P(B)}}$ coupling constants in the range of 3.5–4.9 Hz. Values for four-bond P—P coupling constants of 2.6 and 2.9 Hz have been observed in a pentaphosphane.[23]

Discussion

Addition of the Pt–H bond of **2** across the C≡C triple bond of the alkynylphosphine oxide **1** to give **3** occurs with the regioselectivity observed for similar additions to alkynyl ligands in organometallic compounds. Both types of alkynyl substrates give μ-alkenylidene products from these Pt–H addition reactions.

However, the addition of cationic Pt–H reagents, like **2**, **5**, and **6** to a C≡C triple bond of the trialkynylphosphine oxide **4** leads, serendipitiously, to a facile insertion–rearrangement to give complexes **7–9** which have an unusual 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligand. These complexes are the only known examples of such heterocyclic systems to our knowledge. Mathey et al. have prepared two 2-oxo-1,2-dihydrophosphete *P*-oxides and their reduced alcohol derivatives which represent the only other known examples of phosphetene heterocycles. These authors have questioned the earlier report of a 1,2-dihydrophosphete molecule by Russian chemists.[16a,24] Mathey et al. have reported recently that the insertion reaction used to prepare the first examples of a 2-oxo-1,2-dihydrophosphete may not be a highly favored reaction.[25]

We propose two possible mechanisms for the formation of the 1,2-dihydrophosphete ligand in our system (see Scheme II). Both mechanisms begin with the regioselective addition of the Pt–H bond of the cationic platinum hydride reagent to one of the alkynyl substituents of **4** to give the three-coordinate Pt,P μ-alkenylidene complex **15** (which might be stabilized by P(O) coordination or by coordination of a solvent molecule). The isolation of compound **3** supports the postulation of this addition reaction being the first step of the mechanism. One possible

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[23] Hahn, J. ref 8, pp 331–364.

[24] Nurtdinov, S. Kh.; Ismagilova, N. M.; Fakhrutdinova, R. A.; Zykova, J. V. *Zh. Obshch. Khim.* **1983**, *53*, 1045–1049.

[25] Svara, J.; Marinetti, A.; Mathey, F. *Organometallics* **1986**, *5*, 1161–1167.

mechanism involves the coordination of another alkynyl substituent of the phosphine oxide to the cationic Pt(II) atom as an η^2-alkyne ligand, **16**. This coordination is promoted by the thermodynamic chelate effect. Complex **16** can be represented in the σ-bonded formulation shown as **17**. Intramolecular rearrangement of σ-bonding electron pairs as indicated would give **18**. A driving force for this rearrangement might be the reduction of internal ring strain in going from a formal bicyclic structure, like **17**, to the four-membered heterocyclic ring in **18**.

Another postulated mechanistic route invokes heterolytic cleavage of a phosphorus–alkynyl bond in **15** to transfer an alkynyl ligand to the cationic Pt(II) atom affording intermediate **19**. Electrophilic attack by the very electron-deficient R_2PO^+ center on the alkynyl π-system would give the Pt-stabilized carbonium ion shown in **20**. Internal nucleophilic addition to the carbonium center by a Pt–C σ-bonding pair of electrons would convert **20** to **18**. This mechanistic alternative is supported by the known cleavage of the phosphorus–alkynyl bond of $Ph_2(Me_3CC{\equiv}C)P{=}O$ by $Ru_3(CO)_{12}$ or $Fe_2(CO)_9$ to give di- or trinuclear complexes containing separated μ-alkynyl and μ-$Ph_2P{=}O$ ligands.[26]

The cationic complexes **18** could react with exogenous water to give products **7**–**9**. The conversion of **8** to **10** is a simple ligand substitution reaction. Complex **8** reacts with excess methyl iodide to give alkylation of the phosphine oxide group and coordination of iodide ion to the Pt(II) atom. Oxidative addition of methyl iodide to **8** or **11** to give a Pt(IV) species does not occur rapidly under the conditions used in this reaction. Platinum(II)–alkenyl complexes, such as *trans*-$[Pt(X)(CH{=}CH_2)(PEt_2Ph)_2]$, react slowly with neat methyl iodide at room temperature.[10]

The reaction of complexes **8** and **9** (as anhydrous species) with molecular hydrogen at −78 °C and at atmospheric pressure to give the monohydride products **12** and **13** is analogous to the known reaction of *cis*-$PtCl_2(PEt_3)_2$ with molecular hydrogen to give *trans*-$Pt(H)Cl(PEt_3)_2$ and HCl.[27] The overall reaction appears to be the heterolytic cleavage of H_2 to give a platinum monohydride complex and HX. In the conversion of **8** and **9** to **12** and **13**, the BF_4^- ion presumably coordinates to the anhydrous, three-coordinate, cationic Pt(II) species and reaction with H_2 gives HF (which is not detected) and BF_3 (which forms an adduct with the phosphine oxide group). The mechanism of reaction between these cationic Pt(II) species and H_2 is not known; however, these Pt(II) intermediates might be very electrophilic reagents. A reductive addition of hydrogen might occur also based on the low reactivity of **8** toward oxidative addition of methyl iodide. Complex **10** does not react with molecular hydrogen under these conditions presumably due to the strong coordination of the pyridine ligand and the weak electrophilicity of the platinum atom in this complex. Conversion of the BF_3 adduct **12** to the free phosphine oxide **14** by titration with pyridine is an expected reaction based on the relative Lewis base strengths of phosphine oxide groups and pyridine.

Conclusions

Addition of cationic platinum hydride complexes to a trialkynylphosphine oxide occurs rapidly to give an unusual 1,2-dihydrophosphete heterocyclic ligand. These cationic product complexes react with molecular hydrogen to afford analogous neutral, platinum monohydride compounds. This synthetic method might be useful for the formation of strained cyclic or heterocyclic compounds of other elements, and the intramolecular rearrangement observed in these reactions might be generally applicable to a variety of reactive substituents. We intend to determine the general scope of this synthetic method and the conditions required to obtain the heterocyclic ligand as a free molecule. Studies of the possible catalytic formation of these 1,2-dihydrophosphete *P*-oxides and of the electrophilic reaction chemistry of the anhydrous intermediate complexes are also intended.

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Registry No. **1**, 7608-18-6; **2**, 119455-71-9; **3**, 119455-73-1; **4**, 22752-38-1; **5**, 119455-74-2; **6**, 119455-76-4; **7**, 119455-78-6; **8**, 119455-79-7; **9**, 119455-81-1; **10**, 119455-83-3; **11**, 119455-88-8; **12**, 119455-84-4; **13**, 119455-85-5; **14**, 119455-86-6.

Supplementary Material Available: Tables of anisotropic temperature factor parameters, hydrogen atom positional and isotropic thermal parameters, interatomic distances and angles, and displacements of atoms from least-squares planes for **13** (10 pages); a listing of observed and calculated structure amplitudes for **13** (37 pages). Ordering information is given on any current masthead page.

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[26] Fogg, D. E.; Taylor, N. J.; Meyer, A.; Carty, A. J. *Organometallics* **1987**, *6*, 2252–2254.

[27] James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, pp 285–369.